HANDBOOK OF FREE RADICAL INITIATORS

HANDBOOK OF FREE RADICAL INITIATORS

E.T. DENISOV
T.G. DENISOVA
T.S. POKIDOVA

Institute of Problems of Chemical Physics
Russian Academy of Sciences
Moscow

WILEY-
INTERSCIENCE

A JOHN WILEY & SONS, INC., PUBLICATION

Copyright © 2003 by John Wiley & Sons, Inc. All rights reserved.

Published by John Wiley & Sons, Inc., Hoboken, New Jersey.
Published simultaneously in Canada.

No part of this publication may be reproduced, stored in a retrieval system, or transmitted in any form or by any means, electronic, mechanical, photocopying, recording, scanning, or otherwise, except as permitted under Section 107 or 108 of the 1976 United States Copyright Act, without either the prior written permission of the Publisher, or authorization through payment of the appropriate per-copy fee to the Copyright Clearance Center, Inc., 222 Rosewood Drive, Danvers, MA 01923, 978-750-8400, fax 978-750-4470, or on the web at www.copyright.com. Requests to the Publisher for permission should be addressed to the Permissions Department, John Wiley & Sons, Inc., 111 River Street, Hoboken, NJ 07030, (201) 748-6011, fax (201) 748-6008, e-mail: permreq@wiley.com.

Limit of Liability/Disclaimer of Warranty: While the publisher and author have used their best efforts in preparing this book, they make no representations or warranties with respect to the accuracy or completeness of the contents of this book and specifically disclaim any implied warranties of merchantability or fitness for a particular purpose. No warranty may be created or extended by sales representatives or written sales materials. The advice and strategies contained herein may not be suitable for your situation. You should consult with a professional where appropriate. Neither the publisher nor author shall be liable for any loss of profit or any other commercial damages, including but not limited to special, incidental, consequential, or other damages.

For general information on our other products and services please contact our Customer Care Department within the U.S. at 877-762-2974, outside the U.S. at 317-572-3993 or fax 317-572-4002.

Wiley also publishes its books in a variety of electronic formats. Some content that appears in print, however, may not be available in electronic format.

Library of Congress Cataloging-in-Publication Data:

Denisov, E. T. (Evgeny Timofeevich)
Handbook of free radical initiators / E.T. Denisov, T.G. Denisova,
T.S. Pokidova.
p. cm.
Includes bibliographical references and index.
ISBN 0-471-20753-5 (cloth : acid-free paper)
1. Radicals (Chemistry)—Handbooks, manuals, etc. 2. Free radicals
(Chemistry)—Handbooks, manuals, etc. 3. Free radicals
(Chemistry)—Mechanism of action—Handbooks, manuals, etc. I. Denisova,
Taisa G. II. Pokidova, T. S. (Tamara S.) III. Title.
QD471 .D47 2003
541.2′24—dc21 2002009951

Printed in the United States of America

10 9 8 7 6 5 4 3 2 1

To the memory of Grigorii Alekseevich Razuvaev
a great scientist, teacher, and person
of extraordinary fate

CONTENTS

PREFACE

The aim of this Handbook is to present an up-to-date account of the physicochemical data on radical initiators and radical generation reactions. Initiators are used in technological processes, for example, polymerization, oligomerization, network formation, and modification of polymers. They are widely used in organic synthesis to initiate chain reactions. Initiators are one of the important elements of the mechanistic study of different chain reactions. In addition to initiators, we offer comprehensive information about bimolecular reactions of free radical generation. The chemistry of initiators and reactions of radical generation were intensively studied during the last 40 years and are very complex. A few mechanisms of homolytic splitting of molecules into free radicals were found. Researchers were faced with the simultaneous occurrence of unimolecular and chain reaction mechanisms of initiator decay. Both homolytic and heterolytic decomposition of some initiators exist. Homolytic decay of an initiator is accompanied by the cage effect in solvents and polymers. All data concerning the peculiarities of initiator decay were collected and discussed in this Handbook. We attempted to write a comprehensive physicochemical encyclopedia on initiators and their initiating reactions. Comprehensive information concerning initiators was collected. Readers will find the data and bibliography on the synthesis, structure, and thermochemistry of initiators, as well as detailed information on the rate constants and activation energies of the decomposition of initiators and bimolecular reactions of free radical generation.

This Handbook is divided into three parts.

Part I is devoted to initiators of free radicals and contains eight chapters. In Chapter 7, the different mechanisms of initiator decomposition are discussed. Chapter 2 is devoted to the cage effect that accompanies the decomposition of initiators in liquids and solid polymers. Chapter 3 presents a short description of the methods of study of initiator decomposition. Chapters 4–8 include complex scientific information about initiators: peroxides, polyoxides, azo compounds, polyphenylbutanes, phenylhydrazins, nitrites, nitro compounds, and so on.

Part II is devoted to bimolecular reactions of free radical generation. A wide variety of such reactions was observed. The reader will find the data on free radical generation by reactions of retrodisproportionation, reactions of paraffins and olefins with haloid molecules (F_2, Cl_2, etc.), bimolecular and trimolecular reactions of RH with O_2, reactions of ozone and NO_2, bimolecular reactions of hydroperoxides, reactions of thermal chain initiation in polymerization, and reactions of transition metal ions.

In Part III the data on the rate constants of reactions of free radicals formed from initiators are collected: decay and isomerization of free radicals, reactions of radicals with solvents and monomers, recombination, and disproportionation of free radicals. It is anticipated that the majority of the users of this Handbook will be researchers and technologists, as well as undergraduate students, postgraduate students, and professors who will find it a unique and helpful reference book.

Symbols and units used in this Handbook are in accordance with UPAC recommendations as written in the manual "Quantities, Units and Symbols in Physical Chemistry", Blackwell Scientific Publications, London, 1988.

We are grateful to Elena Batova for attentive English editing of this book and to Ludmila Pilipetskaya and Lidiya Abramova for rapid and accurate typing of the manuscript.

All comments, critical notes, and suggestions are welcomed by the authors. Address comments to E. T. Denisov, T. G. Denisova, and T. S. Pokidova, Institute of Problems of Chemical Physics, Chernogolovka, Moscow Region, 142432, Russia. Email: EDENISOV@ICP.AC.RU

Chernogolovka, Moscow Region
June 19, 2002

EVGENY T. DENISOV
TAISA G. DENISOVA
TAMARA S. POKIDOVA

SYMBOLS AND ABBREVIATIONS

PHYSICOCHEMICAL SYMBOLS

Symbol	*Meaning*	*Unit*
A	Preexponential factor in Arrhenius equation of reaction rate constant $k = A \times \exp(-E/RT)$	s^{-1} (unimolecular reaction), $L\,mol^{-1}\,s^{-1}$ (bimolecular), $L^2\,mol^{-2}\,s^{-2}$ (trimolecular)
A_0	Preexponential factor of reaction rate constant per attacked atom among bonds with equireactivity	s^{-1} (unimolecular reaction), $L\,mol^{-1}\,s^{-1}$ (bimolecular), $L^2\,mol^{-2}\,s^{-2}$ (trimolecular)
b	$2b^2$ is the force constant of chemical bond	$kJ^{1/2}\,mol^{-1/2}\,m^{-1}$
D	Diffusion coefficient	$m^2\,s^{-1}$
D_{Y-X}	Dissociation energy of Y–X bond	$kJ\,mol^{-1}$
e	Probability of formed free radical pair to escape the cage of solvent or polymer	
e	Base of natural logarithms	2.7183

E	Activation energy for the reaction of the Arrhenius equation for reaction rate constant	kJ mol^{-1}
E_e	Activation energy for the reaction of the parabolic model of the bimolecular reaction; $E_\mathrm{e} = E + 0.5hLv - 0.5\ RT$	kJ mol^{-1}
f	Stoichiometric coefficient for free radical acceptance by an acceptor of free radicals	
ΔG^0	Gibbs energy of a reaction under standard conditions (298 K, 1 atm)	kJ mol^{-1}
ΔH^0	Enthalpy of reaction (298 K, 1 atm)	kJ mol^{-1}
$\Delta H^{\neq}$	Enthalpy of transition state	kJ mol^{-1}
ΔH_e	Enthalpy of reaction that includes the difference of zero vibrational energies for reacting bonds	kJ mol^{-1}
ΔH_f^0	Enthalpy of a molecule formation under standard conditions (298 K, 1 atm)	kJ mol^{-1}
ΔH_v^0	Enthalpy of a molecule evaporation under standard conditions (298 K, 1 atm)	kJ mol^{-1}
h	Planck constant, $h = 6.626075 \times 10^{-34}$	J s
K_C	Equilibrium constant, $RT \ln K_\mathrm{C} = -\Delta G^0$	(mol/l)$^{\Delta \mathrm{n}}$
k	Reaction rate constant	s^{-1} (unimolecular reaction), L mol^{-1} s^{-1} (bimolecular), L^2 mol^{-2} s^{-2} (trimolecular)
k_a	Rate constant for an acceptor reaction with free radicals	L mol^{-1} s^{-1}
k_d	Rate constant for decomposition of an initiator to free radicals	s^{-1}
k_D	Rate constant for a diffusion controlled reaction	L mol^{-1} s^{-1}
k_i	Rate constant for an initiation (free radicals formation)	s^{-1} (unimolecular reaction), L mol^{-1} s^{-1} (bimolecular)
k_ind	Rate constant for the induced decomposition of initiator	L$^{1/2}$ mol$^{-1/2}$ s^{-1}

k_{is}	Rate constant for the initiator isomerization	s^{-1}
k_l	Reaction rate constant in the liquid phase	s^{-1} or $L\,mol^{-1}\,s^{-1}$
k_m	Rate constant for the initiator decomposition to molecular products	s^{-1}
k_p	Rate constant for chain propagation	$L\,mol^{-1}\,s^{-1}$
k_{rot}	Rate constant for free radical rotation in the cage	$2\pi\ s^{-1}$
k_s	Reaction rate constant in the solid phase	s^{-1} or $L\,mol^{-1}\,s^{-1}$
k_{sc}	Rate constant for the scrambling reaction in the cage	s^{-1}
k_t	Rate constant for the chain termination	$L\,mol^{-1}\,s^{-1}$
L	Avogadro's number, $L = 6.0221367 \times 10^{23}$	mol^{-1}
n_D	Refractive index	
Δn	Mol change in a reaction	
p	Pressure	Pa
R	Gas constant, $R = 8.314510$	$J\,mol^{-1}\,K^{-1}$
r_R	Radius of radical R	m
$S^0(RH)$	Entropy of formation for RH in the gas phase under standard conditions	$J\,mol^{-1}\,K^{-1}$
$\Delta S^{\neq}$	Entropy of activation	$J\,mol^{-1}\,K^{-1}$
t	Time	s
T	Absolute temperature	K
Q (RH)	Molecular partition function of RH	
$Q^{\neq}$	Molecular partition function of transition state	
v	Reaction rate	$mol\,L^{-1}\,s^{-1}$
v_i	Rate for the initiation reaction	$mol\,L^{-1}\,s^{-1}$
v_{i0}	Rate for the thermal initiation reaction	$mol\,L^{-1}\,s^{-1}$
v_{ind}	Rate for the induced decomposition of the initiator	$mol\,L^{-1}\,s^{-1}$
$\Delta V^{\neq}$	Change of molecular volume due to formation of the transition state, $\Delta V^{\neq} = V^{\neq}$ (transition state) $- V$ (reactants)	$cm^3\,mol^{-1}$

α	Ratio b_i/b_f for the attacked (b_i) and forming (b_f) bonds	
γ	Degree of stretching of a polymer film	
ε	Molar absorption coefficient	$L\,mol^{-1}\,cm^{-1}$
η	Viscosity	Pa s
η	Quantum yield of chemiluminescence	
κ	Ionic strength, $\kappa = 0.5\Sigma c_i z_i^2$, c_i and z_i are concentration and charge of ith ion in solution	$mol\,L^{-1}$
λ	Length of light wave	m
μ	Dipole moment of molecule	D
ν_i	Frequency of valence vibration for the reacting bond	s^{-1}
ν_f	Frequency of valence vibration for the forming bond	s^{-1}
ν_R	Frequency of free radical R$^\bullet$ rotation	$2\pi\ s^{-1}$
π	Ratio of circumference to diameter of a circle, $\pi = 3.141592$	
ρ	Density	$kg\,m^{-3}$
τ	Induction period	s
ϕ	Photochemical yield	

SYMBOLS DESIGNATING PHYSICOCHEMICAL METHODS

AFR	Acceptors of free radicals method
BEBO	Bond energy–bond order
BEBL	Bond energy–bond length
bp	Boiling point, K
CL	Chemiluminescence method
DNP	Dynamic nuclear polarization
EG	Electronography
EPR	Electron paramagnetic resonance
GLC	Gas–liquid chromatography
IPM	Intersecting parabola model of reaction
IR	Infrared spectroscopy
KDI	Kinetics of decay of initiator
KPF	Kinetics of end product formation

KIR	Kinetics of chain reaction in the presence of decomposing initiator
mp	Melting point, K
MS	Mass spectrometry
MW	Molecular weight, g mol^{-1}
NMR	Nuclear magnetic resonance spectroscopy
QCH	Quantum chemical calculation
RRKM	Rice–Ramsperger–Kassel–Marcus theory of unimolecular reactions
RSA	Rentgen structural analysis
UV	Ultraviolet

CHEMICAL SYMBOLS AND ABBREVIATIONS

acac	Acetylacetonate
AIBN	Azoisobutyronitrile
$AmO^•$	Nitroxyl radical
ArOH	Phenol
Ar_2OH	Sterically hindered phenol
$Ar_2O^•$	Sterically hindered phenoxyl radical
BDE	Bond dissociation energy
DBPO	Di-*tert*-butyl peroxalate
DBP	Peroxide, bis(1,1-dimethylethyl)-
DCP	Peroxide, bis(1-methyl-1-phenylethyl)-
EDTA	Ethylenediaminetetraacetic acid
I	Initiator
InH	Acceptor reacting with alkoxyl and peroxyl radicals
PE	Polyethylene
$P^•$	Macroradical
PH	Polymer
$PO_2^•$	Peroxyl macroradical
PP	Polypropylene
Q	Acceptor reacting with alkyl radicals
RH	Organic substance reacting with its C—H bond
R^1H	Aliphatic or alicyclic hydrocarbon
R^2H	Olefin hydrocarbon

R^3H	Alkylaromatic hydrocarbon
RN_2R	Azo compound
RO_xH	Hydroperoxide ($x = 2$), hydrotrioxide ($x = 3$)
RO_xR	Peroxide ($x = 2$), trioxide ($x = 3$), tetroxide ($x = 4$)
$RO^\bullet$	Alkoxyl radical
$RO_2^\bullet$	Peroxyl radical
$RS^\bullet$	Thiyl radical
TMS	Tetramethyl silane

Handbook of Free Radical Initiators. E.T. Denisov, T.G. Denisova, T.S. Pokidova
Copyright © 2003 John Wiley & Sons, Inc.
ISBN: 0-471-20753-5

PART I

INITIATORS

Handbook of Free Radical Initiators. E.T. Denisov, T.G. Denisova, T.S. Pokidova
Copyright © 2003 John Wiley & Sons, Inc.
ISBN: 0-471-20753-5

1

MECHANISMS OF DECOMPOSITION OF INITIATORS

1.1 INTRODUCTION

A lot of organic molecules, dealing with technique, technological processes, and organic synthesis, are stable at moderate (~300–400 K) and elevated (>400 K) temperatures. Atoms of these compounds are connected by sufficiently strong chemical bonds with bond dissociation energy (BDE) ~350–500 kJ mol^{-1}. Radical initiators are molecules bearing one or several weak bonds with BDE ~100–200 kJ mol^{-1}. When the temperature of the reaction is sufficiently high, the initiator decomposes with homolysis of the weakest bond and produces free radicals. These free radicals initiate a chain or nonchain free radical reaction.

What are the factors that influence the BDE of any chemical bond? First, there are atoms forming the bond. Here are a few examples of the types of bonds in various compounds:[1,2]

Compound	CH_4	Et	$MeNH_2$	MeOH	MeI	MeOOMe
Bond	C–H	C–C	C–N	C–O	C–I	O–O
D (kJ mol^{-1})	440	378	358	388	240	161

The following bonds have sufficiently low values of BDE:

Compound	MeOOMe	MeONO	$HONO_2$	Me_3CNO_2	MeNO	$PrN_2CH_2CH{=}CH_2$
Bond	O–O	O–N	O–N	C–N	C–N	N–C
D (kJ mol^{-1})	157	175	207	245	167	141

Organometallic compounds have weak metal–carbon bonds:[2]

Compound	$SnMe_4$	$SbMe_5$	$HgMe_2$	$PbMe_4$	$BiMe_4$	$TiMe_4$
Bond	Sn–C	Sb–C	Hg–C	Pb–C	Bi–C	Ti–C
D (kJ mol^{-1})	294	255	255	239	218	167

Atoms surrounding the atom with the bond being split also influence the BDE. Here are a few examples:[2–4]

Peroxide[3]	MeOOMe	EtOOEt	$(Me_3CO)_2$	$(MeC(O)O)_2$	$(PhC(O)O)_2$
D_{O-O} (kJ mol^{-1})	158.1	153.1	166.5	131.2	124.4

Hydrazine[2]	H_2NNH_2	H_2NNHMe	H_2NNMe_2	H_2NNHPh	Ph_2N-NPh_2
D_{N-N} (kJ mol^{-1})	275.3	268.2	246.9	218.8	125.0

Polysulfide[4]	EtSSEt	PhSSPh	EtS-SSH	PhS-SSH	EtSS–SSEt
D_{S-S} (kJ mol^{-1})	285.0	223.0	213.0	182.0	142.0

A π-bond in the α-position has a strong influence on the dissociating bond. This influence is clearly seen for several alkylaromatic hydrocarbons:[1,3]

Hydrocarbon	Et–Et	$Et-CH_2Ph$	$PhPr_2C-CPr_2Ph$	$Ph_2MeC-CMePh_2$
D_{C-C} (kJ mol^{-1})	364	318	150.6	125.5

This dependence is the result of stabilization of the formed radical due to the interaction of an unpaired electron with π-electrons of the benzene ring.

Different mechanisms of free radicals formation as a result of initiator decomposition are known. Most initiators decompose with dissociation of the weakest bond, for example,

$$R^1O-OR^2 \rightarrow R^1O^\bullet + R^2O^\bullet$$

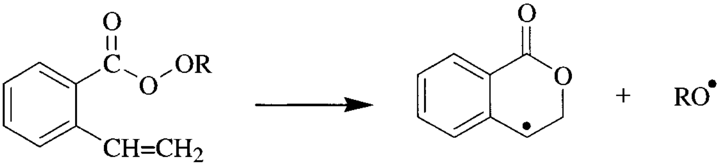
Initiators that decompose with simultaneous dissociation of two or more bonds are known, for example,[5,6]

$$R-N=N-R \rightarrow R^\bullet + N_2 + R^\bullet$$

$$RC(O)O-OR^1 \rightarrow R^\bullet + CO_2 + R^1O^\bullet$$

This decay is known as concerted fragmentation (see Section 1.3).

Some ortho-substituted benzoyl peroxides decompose with formation of unstable intermediates. These intermediates are the result of formation of an additional bond between the oxygen atom of the benzoyloxy radical and ortho substituent, for example,[5,6]



This decay was called anchimerically assisted peroxide cleavage (see Section 1.4).

The decomposition of initiators very often proceeds homolytically with dissociation of the molecule to free radicals only. However, there are compounds that decay simultaneously to free radicals and molecular products. For example, peresters decay to free radicals with dissociation on the O—O bond and their isomerization to aryloxyester proceeds in parallel:[6]

$$\mathrm{PhMe_2COOC(O)Ph \rightarrow PhMe_2CO^{\bullet} + PhC(O)O^{\bullet}}$$

$$\mathrm{PhMe_2COOC(O)Ph \rightarrow PhOCMe_2OC(O)Ph}$$

Free radicals formed from the initiator react with the reactant or recombine. Free radicals formed from the initiator or reactant also can react with the initiator.[6] If this reaction proceeds intensely, the initiator is decomposed by free radicals, and this decreases its effectiveness as an initiator (see Section 1.5).

1.2 NONCONCERTED UNIMOLECULAR DECOMPOSITION

Before decomposition, a molecule of the initiator (I) should be activated. Its activation is the result of collisions of the initiator molecule with other molecules M in the gas or liquid phase. The energized molecule may undergo deenergization by collision with a normal molecule, or it may undergo a unimolecular reaction to form products. These three processes are quite distinct and the situation may be represented as:

$$\mathrm{I + M \rightarrow I^* + M}$$

$$\mathrm{I^* + M \rightarrow I + M^*}$$

$$\mathrm{I^* \rightarrow I^{\#} \rightarrow R_1^{\bullet} + R_2^{\bullet}}$$

where I^* is the activated molecule and $I^{\#}$ is the activated complex. The activated molecule I^* passes through the top of the activation barrier. The energized molecule I^* has acquired all the energy it needs to become the activated molecule $I^{\#}$. The full description of the activation process and reaction is given by the Rice–Ramsperger–Kassel–Marcus (RRKM) theory of unimolecular reactions.[7–12] This theory describes the dependence of the rate constant for unimolecular decay of molecules on gas pressure. When the pressure is growing, the rate constant of decomposition $k_d \rightarrow k_\infty$, and

$$k_\infty = k^\# e^{-E/RT} \tag{1.1}$$

where $k^\#$ is the rate constant of $I^\#$ decay. The expression for initiator decay in solution, where the frequency of molecular collisions is extremely great, is the same. According to transition state theory, the rate constant of unimolecular reactions at high pressure is the following:[11]

$$k_d = k_\infty = e\frac{RT}{Lh}e^{\Delta S^\#/R}e^{-E/RT} \tag{1.2}$$

When a polyatomic molecule, for example, peroxide ROOR, decomposes to two free radicals RO$^\bullet$, the following changes in the energy distribution are observed:[13]

1. One stretching vibration along the O—O bond disappears,
2. One inner rotation of the O—O bond disappears,
3. Two C—O—O angles vibrations disappear.

As a result, the activation entropy of unimolecular decomposition $\Delta S^\# > 0$ and the preexponential factor $[A = eRT(Lh)^{-1}\exp(\Delta S^\#/R)]$ is sufficiently higher than $eRT(Lh)^{-1} \approx 10^{13}$ s^{-1}. For many unimolecular reactions $\Delta S^\# \approx 20$–80 J mol^{-1} K^{-1}.[13]

Due to the elongation of the dissociating bond (e.g. O—O in peroxide), the volume of the transition state $I^\# > I$. As a result, the difference in the volumes $V(I^\#) - V(I) = \Delta V^\#$ is positive. The study of decomposition of initiators with one bond dissociation under pressure gives evidence that $\Delta V^\#$ is positive and helps us to evaluate $\Delta V^\#$ according to the following dependence of k on pressure p:[3,14]

$$\ln k = \ln k_0 - \frac{\Delta V^\#}{RT}\frac{p}{1+bp} \tag{1.3}$$

where $k_0 = k$ at $p = 0$ and $b = 9.2 \times 10^{-9}$ Pa^{-1}. The value of $\Delta V^\#$ depends on the pressure p:

$$\Delta V^{\neq} = \Delta V_0^{\neq}(1 + bp)^{-2} \tag{1.4}$$

1.3 CONCERTED FRAGMENTATION OF INITIATORS

Peroxides have the weak O—O bond and usually decompose with dissociation of this bond. The rate constants of this decomposition of ROOR into RO$^\bullet$ radicals demonstrates a low successibility of the BDE of the O—O bond to the structure of the R fragment (see Chapter 4). Bartlett and Hiat[15] studied the decay of many peresters and found that rate constants of their decomposition covered a range $>10^5\ s^{-1}$. The following mechanism of decomposition was proposed:[5]

$$RC(O)OOR^1 \rightarrow R^{\bullet} + CO_2 + R^1O^{\bullet}$$

parallel with a simple dissociation of one O–O bond. This decay of the molecule to fragments was named concerted fragmentation. The energy needed for the activation of the molecule is concentrated simultaneously on the two bonds: R–C(O) and O–O. Among other products, CO_2 is formed as the result of perester fragmentation. The formation of the π bond of formed carbon dioxide partially compensates for the energy of dissociation of the C–C and O–O bonds of perester. The decay of perester into four fragments is known:[16]

$$Me_3COOCMe_2C(O)OOCMe_3 \rightarrow 2Me_3CO^{\bullet} + MeCOMe + CO_2$$

The following peculiarities characterize the concerted fragmentation in comparison to the decay of a molecule with dissociation of one bond:[5,6]

Decay with Dissociation of One Bond	**Concerted Fragmentation**
1. Activation energy is equal to the dissociation energy of the weakest bond. ($E \approx D \approx$ 140–160 kJ mol^{-1} for peresters.)	Activation energy of decay is sufficiently lower than the BDE of the weakest bond. ($E \approx$ 90–125 kJ mol^{-1}for peresters.)
2. Entropy of activation $\Delta S^{\#} > 0$, $\Delta S^{\neq} \approx 20\text{–}80\ J\,mol^{-1}\ K^{-1}$ for peroxide decomposition.	Entropy of activation is low; for perester decomposition, $\Delta S^{\neq} \approx -10\text{–}10\ J\,mol^{-1}\,K^{-1}$.
3. The dissociation of one bond leads to an increase in the volume of the molecule; $\Delta V^{\#} \approx 10 \pm 3\ cm^3\ mol^{-1}$ (see Table 1.1).	Concerted decomposition occurs through the compact transition state and $\Delta V^{\#}$ is close to zero; $\Delta V^{\neq} \approx -5\text{–}5\ cm^3\,mol^{-1}$ (see Table 1.1).
4. Rate constant of decay of symmetric RN=NR and nonsymmetric RN=NR^1 molecules are close due to a low difference in BDE of the R–N bonds in these two molecules (see Chapter 4).	The rate constants of decay of RN=NR and RN=NR^1 azo compounds are very different due to their simultaneous dissociation (see Chapter 4).

The model for interacting oscillators was developed to describe the concerted decomposition of a molecule.[33] The decomposing molecule is treated as a collection of oscillators. The reaction of concerted decomposition is described as the transition of the system of oscillators from the thermal vibration with amplitude

TABLE 1.1 Values of $\Delta V^{\#}$ of Unimolecular Nonconcerted and Concerted Decomposition of Initiators (Eq. 1.3)

Initiator	Solvent	T (K)	$\Delta V^{\#}$ ($cm^3\ mol^{-1}$)	Reference
	Dissociation of One Bond			
$Me_3COOCMe_3$	Benzene	393	12.6	17
$Me_3COOCMe_3$	Carbon tetrachloride	393	13.3	17
$Me_3COOCMe_3$	Cyclohexane	393	6.7	17
$Me_3COOCMe_3$	Toluene	393	5.4	17
$Me_3COOCMe_3$	Heptane	398	13.4	18
$Me_3COOCMe_3$	Heptane	428	9.8	18
$PhC(O)OOC(O)Ph$	Carbon tetrachloride	333	9.6	19
$PhC(O)OOC(O)Ph$	Carbon tetrachloride	343	8.6	19
$PhC(O)OOC(O)Ph$	Styrene	303	10	20
$PhC(O)OOC(O)Ph$	Allyl acetate	353	4.7	21
$PhC(O)OOC(O)Ph$	Acetophenone	353	4.8	21
$CH_3C(O)OOCMe_3$	Acetophenone	403	5.0	22
$PhC(O)OOCMe_3$	Cumene	352.6	10.2	23
$PhC(O)OOCMe_3$	Chlorobenzene	352.6	12.7	23
$PhC(O)OOCMe_3$	Chlorobenzene	403	8.0	22
$(E)\text{-}EtCH{=}CPrC(O)OOCMe_3$	Cumene	373	6.8	24
$(Z)\text{-}EtCH{=}CPrC(O)OOCMe_3$	Cumene	373	9.0	24
Ph_3CCHPh_2	Toluene	343	13.1	25
	Simultaneous Dissociation of Two Bonds			
$[Me_2CHC(O)O]_2$	Isooctane	323	−5.1	26
$PhCH_2C(O)OOCMe_3$	Cumene	352.6	1.0	27
$PhCH_2C(O)OOCMe_3$	Cumene	243.6	0.4	28
$PhCH_2C(O)OOCMe_3$	Cumene	403	1.7	22
$PhCH_2C(O)OOCMe_3$	Chlorobenzene	352.6	1.5	27
$3\text{-}ClC_6H_4CH_2C(O)OOCMe_3$	Cumene	352.6	1.6	28
$4\text{-}ClC_6H_4CH_2C(O)OOCMe_3$	Cumene	352.6	1.2	28
$4\text{-}MeC_6H_4CH_2C(O)OOCMe_3$	Cumene	352.6	0.2	28
$4\text{-}MeOC_6H_4CH_2C(O)OOCMe_3$	Cumene	333	0.2	28
$4\text{-}MeOC_6H_4CH_2C(O)OOCMe_3$	Cumene	403	3.1	22
$[MeOC(O)(CH_2)_3C(O)O]_2$	Benzene	343	0.0	29
$[MeOC(O)(CH_2)_3C(O)O]_2$	Toluene	343	0.0	29
$Me_2CHC(O)OOCMe_3$	Different solvents	403	1.6	30
$Me_2CHC(O)OOCMe_3$	Cumene	338	0.3÷1.9	30
$Me_2CHC(O)OOCMe_3$	Cumene	338	1.6÷3.2	30
cyclo-$C_6H_{11}C(O)OOCMe_3$	Cumene	352.6	1.6÷3.9	23
$(CN)Me_2CN{=}NCMe_2(CN)$	Toluene	335.5	3.8	31
$(CN)Me_2CN{=}NCMe_2(CN)$	Toluene	335.3	3.4÷2.5	32
$PhMe_2CN{=}NCMe_2Ph$	Cumene	328	5.0	24
$PhMe_2CN{=}NCMe_2Ph$	Chlorobenzene	328	4.3	24
$[4\text{-}CH_3C_6H_4CMe_2]_2N_2$	Cumene	328	4.6	24
$Me_3CON{=}NOCMe_3$	Octane	328	4.3	25

d to the vibration with critical amplitude d^*. If n bonds participate in concerted decomposition and the activated energy is equal to E_n the rate constant of concerted decomposition k_n depends on n and E_n according to Eq. (1.5):

$$k_n = A_0 \frac{n}{2n-1} \left(\frac{nRT}{\pi E_n} \right)^{n-1/2} \exp \frac{-E_n}{RT} \qquad (1.5)$$

where $A_0 = A$ at $n = 1$. When $n = 2$,

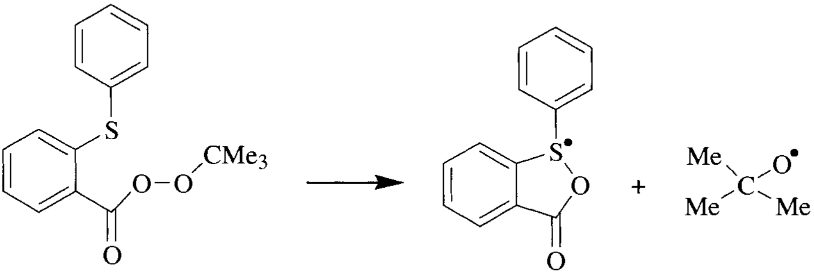
$$k_2 = A_0 \sqrt{\frac{2RT}{\pi E_2}} \exp \frac{-E_2}{RT} \qquad (1.6)$$

1.4 ANCHIMERICALLY ASSISTED DECOMPOSITION OF PEROXIDES

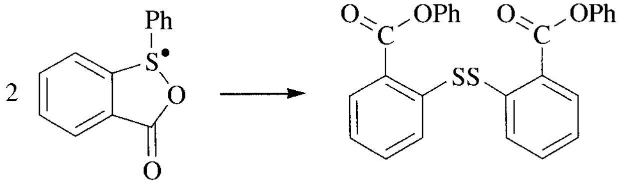
There is experimental evidence that some ortho substituents in 1,1-dimethylethylbenzoyl peresters strongly accelerate the decomposition of peresters.[5] Ortho substituents in 1,1-dimethylethylbenzoyl peresters and values illustrating the ratio of rate constants k_d(ortho substituted)/k_d(H) at 333 K are written below:[5]

o-CH=CHPh$_2$	*o*-SCH$_3$	*o*-SPh
67	140.000	250.000

We see a very strong influence of the ortho substituent containing sulfur. The following mechanism was proposed:[5]



Accelerating action of ortho substituents with p- or π-electrons is due to the formation of an intermediate bond of the type O$^\bullet \cdots$S or O$^\bullet \cdots$C=C in the transition state.



Disulfide was found to be the main product (yield 52.5%) of this perester decomposition. This bond formation compensates (partially) for the activation energy for dissociation of the O—O bond in perester. The empirical peculiarities of anchimeric assistance decomposition are the following:

1. Activation energy of this decomposition is lower than the BDE for the O—O bond, and the rate constant is much higher than the typical k_d for compounds of this class.
2. Solvent changes the rate constants of this decomposition dramatically.
3. Products of the recombination of radical pairs in the cage differ from the parent compounds.

1.5 DECAY OF INITIATORS TO FREE RADICALS AND MOLECULAR PRODUCTS

Peroxides split easily into free radicals because they have a weak O—O bond. In addition to homolytic reactions, peroxides can participate in heterolytic reactions as well, for example, they can undergo hydrolysis under the catalytic action of acids. Both reactions, homolytic and heterolytic, can occur simultaneously. For example, perbenzoates decompose to free radicals and simultaneously isomerize to esters.[34] The kinetic characteristics of both reactions are given in Table 1.1. It is seen that the para substituent slightly influences the rate constants of the homolytic splitting of the perester. The rate constant of heterolytic isomerization, by contrast, strongly depends on the nature of the para substituent. Polar solvent accelerates the heterolytic isomerization. Reaction of isomerization was proposed to proceed through the cyclic transition state.[35]

Parallel reactions of homolytic splitting and heterolytic isomerization was evidence for triphenylcumylperoxylsilane (anisole, $T = 433\text{–}463$ K):[34]

$$\mathrm{Ph_3SiOOCMe_2Ph} \rightarrow \mathrm{Ph_3SiO^{\bullet}} + \mathrm{PhMe_2CO^{\bullet}} \qquad (k_d)$$

$$\mathrm{Ph_3SiOOCMe_2Ph} \rightarrow \mathrm{PhOSiPh_2OCMe_2Ph} \qquad (k_{is})$$

The rate constants k_d and k_{is} were estimated and found to be the $\log[k_d(\mathrm{s}^{-1})] = 15.5 - 167/RT$ and $\log[k_{is}(\mathrm{s}^{-1})] = 8.2 - 104/RT$, $\Delta S_d^{\#} = 39.7\ \mathrm{J\,mol^{-1}\,K^{-1}}$ and $\Delta S_{is}^{\#} = -39.7\ \mathrm{J\,mol^{-1}\,K^{-1}}$. It is seen that $E_d > E_{is}$, however, $\Delta S_d^{\#} > 0$

and $\Delta S^{\#}_{\text{is}} < 0$. The cyclic transition state was assumed for the isomerization reaction.[34] Isomerization of this kind was not observed in the case of aliphatic silane peroxides. Polyarylperoxysilanes take part in isomerization of this type:[35]

$$Ph_2Si(OOCMe_3)_2 \rightarrow Ph(PhO)Si(OOCMe_3)(OCMe_3)$$

Alkylperoxyphosphates undergo heterolytic isomerization simultaneously with homolytic splitting:[36]

$$Me_3COOP(O)Et_2 \rightarrow MeOMe_2COP(O)Et_2 \qquad (k_{\text{is}})$$

$$Me_3COOP(O)Et_2 \rightarrow Me_3CO^{\bullet} + Et_2P(O)O^{\bullet} \qquad (k_{\text{d}})$$

The rate constants of these reactions were found to be very close: $k_d = 2.0 \times 10^{-5}\ s^{-1}$ and $k_{is} = 2.2 \times 10^{-5}\ s^{-1}$ (*n*-nonane, 403 K). Competition between homolytic and heterolytic reactions influences the effectiveness of initiation. When the heterolytic isomerization of initiator occurs, its effectiveness on initiation is $e = k_i\ (2k_d + 2k_{is})^{-1}$. It can be increased by changing the solvent and temperature.

TABLE 1.2 Kinetic Parameters of Heterolytic Isomerization and Homolytic Decomposition of Peresters[a]

Para Substituent	Conditions	$k \times 10^4$ (s^{-1})	E (kJ mol^{-1})	log(A) (s^{-1})
p-$XC_6H_4Me_2COOC(O)Ph \rightarrow p$-$XC_6H_4OCMe_2OC(O)Ph$ (373 K)				
H	313–393 K	5.8	115	12.94
Cl		1.92	121	13.28
Br	Chlorobenzene	2.68	119	13.19
NO_2		0.0945	129	14.09
p-$XC_6H_4C(O)OOCMe_2Ph \rightarrow p$-$XC_6H_4C(O)OC(OPh)Me_2$ (298 K)				
NO_2	283–323 K	282	84	13.15
Br		70	87	14.05
H	Methanol	26	90	14.14
CH_3		19	83	12.80
p-$XC_6H_4C(O)OOCMe_3 \rightarrow p$-$XC_6H_4C(O)O^{\bullet} + Me_3CO^{\bullet}$ (383 K)				
H	373–403 K	0.28	156	16.85
CH_3		0.32	151	16.11
Cl	Phenoxybenzene	0.16	164	17.66
NO_2		0.16	172	18.22

[a] See Refs. 34 and 35.

1.6 CHAIN DECOMPOSITION OF INITIATORS

Initiators are introduced into the reactant, as a rule, in very small amounts. Initiators produce free radicals and most react with reactant or solvent, or recombine with other free radicals. Radicals formed from the initiator or reactant react only negligibly with the initiator. However, we know systems (initiator-reactant) where free radicals induce the chain decomposition of initiators.[6,37,38] Bartlett and Nozaki were the first to recognize the induced decomposition of benzoyl peroxide in different solvents.[39,40] They found that the empirical rate constant of benzoyl peroxide decomposition increases with an increase in the peroxide concentration in a solution. The dependence of the rate of peroxide decomposition on its concentration was found to be

$$v = k_d[\mathrm{PhC(O)OOC(O)Ph}] + k_{ind}[\mathrm{PhC(O)OOC(O)Ph}]^{3/2} \tag{1.7}$$

This dependence is the result of common proceeding of homolytic decay of peroxide with the rate constant k_d and chain decomposition of peroxide due to reactions with the radical formed from the solvent RH according to the following kinetic scheme:

$$\begin{aligned}
\mathrm{PhC(O)OOC(O)Ph} &\rightarrow [\mathrm{PhCO_2^{\bullet} + PhCO_2^{\bullet}}] \rightarrow 2\mathrm{PhCO_2^{\bullet}} && (k_i)\\
[\mathrm{PhCO_2^{\bullet} + PhCO_2^{\bullet}}] &\rightarrow [\mathrm{PhCO_2^{\bullet} + Ph^{\bullet}}] + \mathrm{CO_2} &&\\
[\mathrm{PhCO_2^{\bullet} + Ph^{\bullet}}] &\rightarrow \mathrm{PhCO_2^{\bullet} + Ph^{\bullet}} &&\\
[\mathrm{PhCO_2^{\bullet} + Ph^{\bullet}}] &\rightarrow \mathrm{PhC(O)OPh} &&\\
\mathrm{PhCO_2^{\bullet} + RH} &\rightarrow \mathrm{PhCOOH + R^{\bullet}} &&\\
\mathrm{Ph^{\bullet} + RH} &\rightarrow \mathrm{PhH + R^{\bullet}} &&\\
\mathrm{R^{\bullet} + PhC(O)OOC(O)Ph} &\rightarrow \mathrm{PhC(O)OR + PhCO_2^{\bullet}} && (k_p)\\
\mathrm{R^{\bullet} + R^{\bullet}} &\rightarrow \mathrm{RR\ or\ RH + R'H} && (2k_t)
\end{aligned}$$

Empirical $k_{ind} = k_i^{1/2}k_p(2k_t)^{-1/2}$ and $k_i = 2ek_d$. The chain length depends on the ratio $k_p(2k_t)^{-1/2}$: the faster the reaction of the radical $\mathrm{R^{\bullet}}$ with peroxide, the longer the chain length. Intensive chain decay of peroxide was observed at a sufficiently high peroxide concentration. For example, $k_d = 6.36 \times 10^{-5}\ \mathrm{s^{-1}}$ and $k_{ind} = 3.35 \times 10^{-4}\ (\mathrm{L/mol})^{1/2}\ \mathrm{s^{-1}}$ for dibenzoyl peroxide decomposition in cyclohexane at 353 K;[39,40] and $k_d[\mathrm{I}] = k_{ind}[\mathrm{I}]^{3/2}$ at $[\mathrm{PhC(O)OOC(O)Ph}] = 3.6 \times 10^{-2}\ \mathrm{s^{-1}}$. When peroxide is used as an initiator of the free radical polymerization reaction of the macroradical with peroxide, the molecular weight of the forming polymer is lower.[41] For the rate constants of these reactions, see Chapter 18.

The very intensive chain decomposition of benzoyl peroxide was found in alcoholic solutions.[39,42,43] This is the result of the very high reductive activity of ketyl radicals formed from alcohol. They cause the chain decomposition of peroxide by the following mechanism:

$$\mathrm{PhC(O)OOC(O)Ph} \rightarrow 2e\mathrm{PhCO_2^{\bullet}} \qquad (k_d)$$

$$\mathrm{PhCO_2^{\bullet} + R^1R^2CHOH \rightarrow PhCOOH + R_1R_2C^{\bullet}OH}$$

$$\mathrm{R^1R^2C^{\bullet}OH + PhC(O)OOC(O)Ph \rightarrow R^1R^2C(O) + PhCOOH + PhCO_2^{\bullet}} \qquad (k_p)$$

$$\mathrm{2R^1R^2C^{\bullet}OH \rightarrow R^1R^2C(O) + R^1R^2CHOH} \qquad (2k_t)$$

The kinetics of peroxide decomposition are described by Eq. (1.7). However, the values of $k_{\mathrm{ind}} = k_p k_i^{1/2} (2k_t)^{-1/2}$ are sufficiently higher. For the rate constants k_p and $2k_t$, see Chapters 18 and 20.

An exotic chain mechanism was found for the 1,1-dimethylethyl hydroperoxide chain decomposition. This hydroperoxide decomposes at elevated temperatures (370 K and higher). Introduction of initiator (I) into the solution with this hydroperoxide induces its decay with the rate $\nu = \text{const} \times [\mathrm{I}]$. The initiators used were found to decompose more rapidly with the hydroperoxide. The following chain mechanism was proved:[44–46]

$$\mathrm{I \rightarrow r^{\bullet}} \qquad (k_i)$$

$$\mathrm{r^{\bullet} + ROOH \rightarrow rH + RO_2^{\bullet}}$$

$$\mathrm{RO_2^{\bullet} + RO_2^{\bullet} \rightarrow 2RO^{\bullet} + O_2} \qquad (k_p)$$

$$\mathrm{RO_2^{\bullet} + RO_2^{\bullet} \rightarrow ROOR + O_2} \qquad (k_t)$$

The peculiarity of this mechanism is the unusual reaction of chain propagation, namely, $\mathrm{2RO_2^{\bullet} \rightarrow 2RO^{\bullet} + O_2}$. As a result, the rate of chain propagation is independent of the reactant (ROOH) concentration. The ratio $k_p/k_t = 4.1 \times 10^4 \exp(-22/RT)$ for 1,1-dimethylethylperoxyl in a benzene solution.[47]

Secondary hydroperoxides are easily attacked at the α-C—H bond. As a result, peroxide $\mathrm{R^1OOH}$ can react by its O—O bond with the alkyl radical formed from the solvent RH:

$$\mathrm{R^1OOH + R^{\bullet} \rightarrow R^1O^{\bullet} + ROH} \qquad (k_{p1})$$

and its α-C—H bond:

$$\mathrm{R^1R^2CHOOH + R^{\bullet} \rightarrow RH + R^1R^2C(O) + HO^{\bullet}} \qquad (k_{p2})$$

The kinetics of hydroperoxide decomposition obeys Eq. (1.8):[6]

$$\ln \frac{[\mathrm{ROOH}]_0}{[\mathrm{ROOH}]} + \ln \frac{[\mathrm{ROOH}]^{1/2} + k_d/(k_{p1} + k_{p2})}{[\mathrm{ROOH}]_0^{1/2} + k_d/(k_{p1} + k_{p2})} = k_d t \qquad (1.8)$$

For the values of rate constants, see Chapters 4 and 18.

Chain decomposition of secondary hydroperoxides proceeds in an oxidized reactant ($R^1R^2CH_2$) in the reaction with peroxyl radicals:[6]

$$R^1R^2CHOOH + RO_2^{\bullet} \rightarrow ROOH + HO^{\bullet} + R^1R^2C(O) \qquad (k_{p2})$$

This reaction plays an important role in the liquid-phase oxidation of hydrocarbons.[48]

REFERENCES

1. W. Tsang, in *Energetics of Free Radicals*, A. Greenberg and J. Liebman (Eds.), Blackie Academic and Professional, New York, 1996, p. 22.
2. *Handbook of Chemistry and Physics*, D. R. Lide (Ed.), CRC Press, Boca Raton, FL, 1991–1992.
3. E. T. Denisov, *Liquid-Phase Reaction Rate Constants*, IFI/Plenum, New York, 1974.
4. C. Chatgilialoglu and M. Guerra, in *The Chemistry of Sulfur-Containing Functional Groups*, S. Patia and Z. Rappoport (Eds.), Wiley, Chichester (1993).
5. T. Koenig, in *Free Radicals*, J. K. Kochi (Ed.), John Wiley & Sons, Inc., New York, 1973, Vol. 1, p. 113.
6. E. T. Denisov, *Mechanisms of homolytics decomposition of molecules in the liquid phase, in Itogi Nauki i Tekhniki, Ser. Kinetika i Kataliz* (Russian), VINITI, Moscow, 1981.
7. P. J. Robinson and K. A. Holbrook, *Unimolecular Reactions*, John Wiley & Sons, Inc., London, 1972.
8. W. Forst, *Theory of Unimolecular Reactions*, Academic, New York, 1973.
9. V. N. Kondratiev and E. E. Nikitin, *Gas-Phase Reactions*, Springer-Valley, Berlin, 1981.
10. H. O. Pritchard, *The Quantum Theory of Unimolecular Reactions*, Cambridge University Press, 1984.
11. K. J. Laidler, *Chemical Kinetics*, Harper and Row, New York, 1987.
12. R. P. Wayne, in *Comprehensive Chemical Kinetics*, C. H. Bamford and C. F. H. Tipper (Eds.), Elsevier, Amsterdam, The Netherlands, 1969, Vol. 2, p. 189.
13. S. Benson, *Thermochemical Kinetics*, John Wiley & Sons, Inc., New York, 1968.
14. M. G. Gonikberg, *Chemical Equilibrium and Reaction Rate under High Pressures* (Russian), Khimiya, Moscow, 1969.
15. P. D. Bartlett and R. R. Hiatt, *J. Am. Chem. Soc.* **80**, 1398 (1958).
16. W. H. Richardson and W. C. Koskinen, *J. Org. Chem.* **41**, 3182 (1976).
17. C. Walling and G. Metzger. *J. Am. Chem. Soc.* **81**, 5365 (1959).
18. A. S. Okunevich, S. A. Samoilov, and V. N. Monastyrskiy, *Zh. Fiz. Khim.* **43**, 2265 (1969).
19. A. E. Nicholson and R. G. W. Norrish. *Discuss Faraday Soc.* **22**, 97 (1956).
20. A. E. Nicholson and R. G. W. Norrish. *Discuss Faraday Soc.* **22**, 104 (1956).
21. C. Walling and J. Pellon, *J. Am. Chem. Soc.* **79**, 4782, 4786 (1957).
22. J. Owens and T. Koenig, *J. Org. Chem.* **39**, 3153 (1974).

23. R. C. Neuman and J. V. Behar. *J. Am. Chem. Soc.* **91**, 6024 (1969).
24. R. C. Neuman and G. D. Holmes. *J. Am. Chem. Soc.* **93**, 4242 (1971).
25. R. C. Neuman and R. J. Bussey. *J. Am. Chem. Soc.* **92**, 2440 (1970).
26. R. C. Lamb, J. G. Pacifici, and P. W. Ayers, *J. Am. Chem. Soc.* **87**, 3928 (1965).
27. R. C. Neuman and J. V. Behar, *J. Am. Chem. Soc.* **89**, 4549 (1967).
28. R. C. Neuman and J. V. Behar, *J. Org. Chem.* **36**, 654 (1971).
29. V. M. Zhulin, E. K. Starostin, S. I. Moryasheva, and G. I. Nikishin, *Izv. AN SSSR, Ser. Khim.* 1237 (1979).
30. R. C. Neuman and R. P. Pankratz, *J. Am. Chem. Soc.* **95**, 8372 (1973).
31. A. H. Ewald and R. G. W. Norrish, *Discuss Faraday Soc.* **22**, 138 (1956).
32. M. Ya. Botnikov, V. M. Zhulin, L. G. Bubnova, and G. A. Stashina, *Izv. AN SSSR, Ser. Khim.* 229 (1977).
33. I. V. Aleksandrov, *Teor. Experim. Khimiya*, **12**, 299 (1976).
34. V. A. Yablokov, *Isomerisation of Organic and Elementorganic Peroxides of IV Group Elements*, Doctor Diss. Thesis (Russian), Leningrad Technological Institute, Leningrad, 1976.
35. Yu. A. Aleksandrov, *Liquid-Phase Autooxidation of Elementorganic Compounds* (Russian), Nauka, Moscow, 1978.
36. V. P. Maslennikov, *Organic Peroxides of Elements of II-V Groups of Periodic System*, Doctor Diss. Thesis (Russian), Moscow State University, Moscow, 1976.
37. K. U. Ingold and B. P. Roberts, *Free-Radical Substitution Reaction*, Wiley-Interscience, New York, 1971.
38. M. L. Poutsma, in *Free Radicals*, J. K. Kochi (Ed.), John Wiley & Sons, Inc., New York, 1973, Vol. 2, p. 113.
39. K. Nozaki and P. D. Bartlett, *J. Am. Chem. Soc.* **68**, 1686 (1946).
40. K. Nozaki and P. D. Bartlett, *J. Am. Chem. Soc.* **68**, 2377 (1946).
41. G. C. Eastmond, in *Comprehensive Chemical Kinetics*, C. H. Bamford and C. F. H. Tipper (Eds.), Elsevier, Amsterdam, The Netherlands, 1976 Vol. 14A, p. 1.
42. P. D. Bartlett and K. Nozaki, *J. Am. Chem. Soc.* **69**, 2299 (1947).
43. P. D. Bartlett and W. E. Vaughan, *J. Phys. Chem.* **51**, 942 (1947).
44. J. A. Howard, *Adv. Free Radical Chem.* **4**, 49 (1972).
45. T. Mill and D. G. Hendry, in *Comprehensive Chemical Kinetics*, C. H. Bamford and C. F. H. Tipper (Eds.), Elsevier, Amsterdam, The Netherlands, 1980, Vol. 16, p. 1.
46. J. A. Howard and K. U. Ingold, *Can. J. Chem.* **47**, 3797 (1969).
47. J. R. Thomas, *J. Am. Chem. Soc.* **87**, 3935 (1965).
48. N. M. Emanuel, E. T. Denisov, and Z. K. Maizus, *Liquid-Phase Oxidation of Hydrocarbons*, Plenum Press, New York, 1967.

Handbook of Free Radical Initiators. E.T. Denisov, T.G. Denisova, T.S. Pokidova
Copyright © 2003 John Wiley & Sons, Inc.
ISBN: 0-471-20753-5

2

CAGE EFFECT

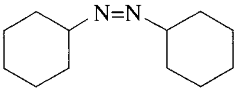
2.1 INTRODUCTION

Upon decomposition of a molecule of initiator in the gas phase, the formed radicals immediately fly apart in different directions. The decomposition of a molecule in the liquid phase leads to the formation of two radicals that exist side by side for a certain time, surrounded by solvent molecules. The solvent molecules due to intermolecular forces create a "cage" around a pair of formed radicals, which is called the cage effect.[1-4] The cage effect was discovered by Frank and Rabinowitch.[5] Some experimental evidence was found for the existence of the cage effect. The cage effect is very important for understanding the chemistry and kinetics of initiator decomposition in various solvents and solid polymers. The rate constant for the interaction of two radicals is very high. As a result, some radicals react with each other before they are formed from the initiator pair of radicals. In the 1960s and 1970s, widespread experimental evidence was obtained concerning the cage effect in liquids.

2.2 EXPERIMENTAL EVIDENCE FOR THE CAGE EFFECT

2.2.1 Quantum Yield

According to Einstein's law the quantum yield ϕ for molecule photodissociation in the gas phase is equal to unity. Frank and Rabinowitch[5] predicted the reduction of the quantum yield in a solution due to the cage effect. The quantum yield $\phi < 1$ was evidenced in the photodissociation of I_2, Br_2, and RN_2R.

Molecule	Solvent	λ (nm)	T (K)	ϕ	Reference
I_2	CCl_4	440	298	0.14	6
Br_2	CCl_4	440	298	0.22	7
	CCl_4		298	0.24	8

2.2.2 Products of Radical Pair Combination

Free radicals formed from an initiator in the gas phase take part in other reactions and recombine with very low probability (0.1–2%). Decomposition of the initiator in the liquid phase leads to the formation of radical pairs, where a probability of recombination of the formed radicals is high. For example, photolysis of azomethane in the gas phase in the presence of propane (RH) gives the ratio $[C_2H_6]/[N_2] = 0.015$.[9] This ratio is low due to the fast reaction of formed methyl radicals with propane:

$$CH_3N{=}NCH_3 + h\nu \rightarrow C^{\bullet}H_3 + N_2 + C^{\bullet}H_3$$

$$C^{\bullet}H_3 + (CH_3)_2CH_2 \rightarrow CH_4 + (CH_3)_2C^{\bullet}H$$

$$2(CH_3)_2C^{\bullet}H \rightarrow (CH_3)_2CHCH(CH_3)_2 \quad \text{or} \quad (CH_3)_2CH_2 + CH_3CH{=}CH_2$$

In the liquid phase, this ratio was 0.65 due to the recombination of the methyl radical pair in the cage:

$$CH_3N{=}NCH_3 + h\nu \rightarrow [C^{\bullet}H_3 + C^{\bullet}H_3] + N_2$$

$$[C^{\bullet}H_3 + C^{\bullet}H_3] \rightarrow C_2H_6$$

$$[C^{\bullet}H_3 + C^{\bullet}H_3] \rightarrow 2C^{\bullet}H_3$$

When molecules of a solvent are stable toward free radicals formed from the initiator, a scavenger of radicals is added to consume all free radicals that escaped the recombination in the cage. The yield of the product of primary formed radicals illustrates the probability of cage radical pair recombination. For example, thermolysis of azoisobutyronitrile (AIBN) in CCl_4 gives tetramethylsuccinonitrile a 80% yield; this yield falls to a value of 19% in the presence of *n*-butanethiol as a free radical acceptor.[10] The last value, 19%, characterizes the recombination of radicals in the cage. Formed from the initiator, free radicals start free radical polymerization in the presence of monomers and are incorporated into macromolecules, for example,

$$RN{=}NR \rightarrow [R^{\bullet} + R^{\bullet}] + N_2$$

$$[R^{\bullet} + R^{\bullet}] \rightarrow R{-}R$$

$$[R^\bullet + R^\bullet] \rightarrow 2R^\bullet$$

$$R^\bullet + CH_2{=}CHPh \rightarrow RCH_2C^\bullet HPh, \text{etc.}$$

The fraction of R fragments incorporated into the polymer increases as the concentration of the monomer increases, reaching a limiting value of 70% at a styrene concentration $>2\ \mathrm{mol\,L^{-1}}$. The remaining 30% can be attributed to the reactions of the geminate pairs.[11]

2.2.3 Crossover Experiments

When a mixture of perdeuterio and protio azomethane in 1 : 1 ratio was photolyzed in the gas phase, the isolated ethane was found to be a statistical mixture of three possible dimers: $C_2H_6/C_2H_3D_3/C_2D_6 = 1:2:1$.[12,13] The reactions are:

$$CH_3N{=}NCH_3 + h\nu \rightarrow 2C^\bullet H_3 + N_2$$

$$CD_3N{=}NCD_3 + h\nu \rightarrow 2C^\bullet D_3 + N_2$$

$$C^\bullet H_3 + C^\bullet H_3 \rightarrow C_2H_6$$

$$C^\bullet H_3 + C^\bullet D_3 \rightarrow CH_3CD_3$$

$$C^\bullet D_3 + C^\bullet D_3 \rightarrow C_2D_6$$

In an isooctane solution, 75% of C_2H_6 and C_2D_6 were formed, which was the result for pair $C^\bullet H_3$ and $C^\bullet D_3$ recombination in the cage:[12]

$$CH_3N{=}NCH_3 + h\nu \rightarrow [C^\bullet H_3 + C^\bullet H_3] + N_2$$

$$[C^\bullet H_3 + C^\bullet H_3] \rightarrow C_2H_6$$

$$CD_3N{=}NCD_3 + h\nu \rightarrow [C^\bullet D_3 + C^\bullet D_3] + N_2$$

$$[C^\bullet D_3 + C^\bullet D_3] \rightarrow C_2D_6$$

This difference in the yields of symmetrical dimers in the liquid (75%) and gas (25%) phases ($75 - 50 = 25\%$) is the result of geminate recombination in the cage of the liquid. Similar results were reported for the ethane and methyl acetate isolated from thermolysis of a mixture of protio and perdeuterio acetyl peroxide.[14,15] The following reactions occur in the cage:

$$CH_3C(O)OOC(O)CH_3 \rightarrow [CH_3C(O)O^\bullet + CH_3C(O)O^\bullet]$$

$$[CH_3C(O)O^\bullet + CH_3C(O)O^\bullet] \rightarrow [C^\bullet H_3 + CH_3C(O)O^\bullet] + CO_2$$

$$[C^\bullet H_3 + CH_3C(O)O^\bullet] \rightarrow C^\bullet H_3 + CH_3C(O)O^\bullet$$

$$[C^\bullet H_3 + CH_3C(O)O^\bullet] \rightarrow CH_3C(O)OCH_3$$

$$[C^\bullet H_3 + CH_3C(O)O^\bullet] \rightarrow [C^\bullet H_3 + C^\bullet H_3] + CO_2$$

$$[C^{\bullet}H_3 + C^{\bullet}H_3] \rightarrow C^{\bullet}H_3 + C^{\bullet}H_3$$

$$[C^{\bullet}H_3 + C^{\bullet}H_3] \rightarrow C_2H_6$$

The same was observed for the decomposition of $CD_3C(O)OC(O)CD_3$.

2.2.4 Oxygen-18 Scrambling and Racemization

The back recombination for the pair of acetoxy radicals with the formation of parent diacetyl peroxide was seen in special experiments on the decomposition of acetyl peroxide labeled by the ^{18}O isotope on the carbonyl group.[16] The reaction of acetyl peroxide with NaOMe produces methyl acetate and all ^{18}O isotopes are contained in the carbonyl group. The transition of ^{18}O atoms from the carbonyl to the peroxide groups of acetyl peroxide were detected by hydrolysis of peroxide to hydrogen peroxide and conversion of the resulting hydrogen peroxide to dioxygen by permanganate oxidation. The amount of ^{18}O in the formed O_2 was analyzed by mass spectrometry (MS). It was found that the scrambling of ^{18}O occurred during the decomposition of peroxide. After some decomposition time period, the residue of peroxide was found to contain peroxide with the ^{18}O isotope in the carbonyl, as well as in the peroxide groups. This scrambling of ^{18}O isotopes proves the cage recombination of acetoxy radicals:

$$MeC(^{18}O)OOC(^{18}O)Me \rightarrow [MeC(^{18}O)O^{\bullet} + MeC(^{18}O)O^{\bullet}]$$

$$[MeC(^{18}O)O^{\bullet} + MeC(^{18}O)O^{\bullet}] \rightarrow MeC(O)^{18}O^{18}OC(O)Me \qquad (k_{sc})$$

The proportion of peroxide with ^{18}O in the carbonyl group was found to decrease at the time of decomposition, and the proportion of ^{18}O in the peroxide group was found to increase (isooctane, 353 K, $[MeCOOCOMe]_0 = 0.05$ mol L^{-1}):[16]

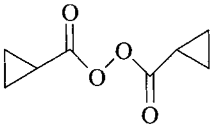
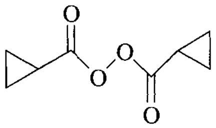
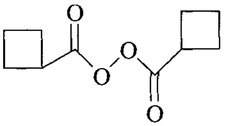
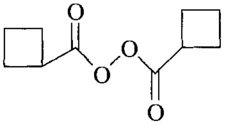
t(s)	0	870	17,400
$^{18}O_2/^{16}O_2$	0.00428	0.01451	0.02228
$C(^{18}O)/C(^{16}O)$	1.000	0.712	0.499

The rate constant for the scrambling k_s was found to increase with increasing viscosity of the solvent:[16]

Solvent	Isooctane	Dodecane	Octadecane	Mineral oil
$k_{sc} \times 10^5 (s^{-1})$	4.00	4.68	5.25	6.37

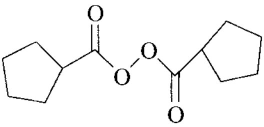
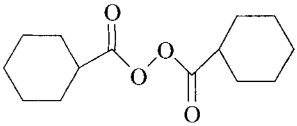
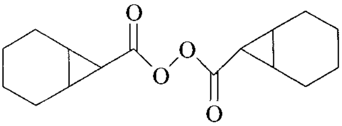
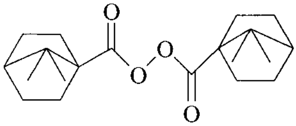
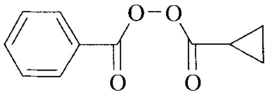
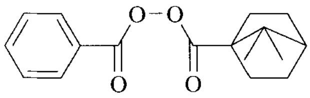
The higher the viscosity of the solvent, the longer the period of time for radical pair existence in the cage and the higher the observed value for the scrambling rate constant (see Table 2.1).The same phenomena was observed at photolysis of benzoyl peroxide and 1,1-dimethylethyl perbenzoate.[1]

TABLE 2.1 The Percentage of Radical Pairs (f_r x 100) that Recombine with the Formation of the Parent Molecule and Rate Constants of Radical Pairs Combination (k_s) According to the Data on ^{18}O Scrambling

Peroxide	Solvent	T (K)	$f_r \times 100$	k_{sc} (s^{-1})	Reference
Diacetyl-, MeC(O)OOC(O)Me	Isooctane	353	35	4.40×10^{-5}	17
Diacetyl-, MeC(O)OOC(O)Me	Dodecane	353	43	4.68×10^{-5}	17
Diacetyl-, MeC(O)OOC(O)Me	Octadecane	353	50	5.25×10^{-5}	17
Acetylpropionyl-, MeC(O)OOC(O)Et	Isooctane	353	17	1.66×10^{-5}	1
Dipropionyl-, EtC(O)OOC(O)Et	Isooctane	353	—	8.10×10^{-6}	1
Dibenzoyl-, PhC(O)OOC(O)Ph	Isooctane	353	4.6	1.30×10^{-6}	18
Dibenzoyl-, PhC(O)OOC(O)Ph	Mineral oil	353	18	—	18
Acetyl 1,1-dimethylethyl-, MeC(O)OOCMe$_3$	Hexane	403	20	—	19
Acetyl 1,1-dimethylethyl-, MeC(O)OOCMe$_3$	Paraffin	403	40	—	19
Dicyclopropionyl-, 	Carbon tetrachloride	353	24	1.46×10^{-5}	1
Dicyclopropionyl-, 	Carbon tetrachloride	318	39	1.29×10^{-6}	1
Dicyclobutanoyl-, 	Carbon tetrachloride	353	3	3.26×10^{-5}	1
Dicyclobutanoyl-, 	Carbon tetrachloride	318	2.9	3.93×10^{-6}	1

(*continued overleaf*)

TABLE 2.1 (*continued*)

Peroxide	Solvent	T (K)	$f_r \times 100$	k_{sc} (s^{-1})	Reference
Dicyclopentanoyl-, 	Carbon tetrachloride	318	—	1.32×10^{-6}	1
Dicyclohexanoyl-, 	Carbon tetrachloride	318	—	2.00×10^{-6}	1
Dicaranoyl-, 	Carbon tetrachloride	353	14	1.48×10^{-5}	1
Diapocamphoryl-, 	Carbon tetrachloride	353	55	5.82×10^{-5}	1
Benzoylcyclopropyl-, 	Carbon tetrachloride	353	8.3	5.65×10^{-5}	1
Apocamphorylbenzoyl-, 	Carbon tetrachloride	343	7	7.00×10^{-5}	1

The existence of the cage effect was proved in experiments on the photolysis of optically active azo compounds. The photodecomposition of these compounds is accompanied by racemization.[1] For example, the partial (40%) photolysis of optically active 2-phenylazo-(2-phenyl)butane in the hexadecane solution provides racemization to 26%.[20] The fraction of geminate recombination was found to be

52% (hexadecane, room temperature):

$$\mathrm{PhMeEtC^{*}N{=}NPh} + h\nu \rightarrow [\mathrm{PhMeEtC^{\bullet}} + {}^{\bullet}\mathrm{NNPh}] \rightarrow \text{Products}$$

$$[\mathrm{PhMeEtC^{\bullet}} + {}^{\bullet}\mathrm{NNPh}] \rightarrow \mathrm{PhMeEtCN = NPh}$$

The (*E*)-isomer was found to be transformed into the (*Z*)-isomer due to geminate recombination:

$$(E)\text{-}\mathrm{PhMeEtCN{=}NPh} + h\nu \rightarrow [\mathrm{PhMeEtC^{\bullet}} + {}^{\bullet}\mathrm{NNPh}] \rightarrow \text{Products}$$

$$[\mathrm{PhMeEtC^{\bullet}} + {}^{\bullet}\mathrm{NNPh}] \rightarrow (Z)\text{-}\mathrm{PhMeEtCN{=}NPh}$$

The problem of retention of asymmetry of the formed free radical in the fast geminate recombination of radicals was studied by photolysis of the optically active azo compound $\mathrm{PhMeCHN{=}NCH_2Ph}$.[21,22] The radical pair of two alkyl radicals was initiated by the photolysis of the azo compound in benzene in the presence of 2-nitroso-2-methylpropane as a free radical acceptor. The yield of the radical pair combination product was found to be 28%. This product $\mathrm{PhMeHCCH_2Ph}$ was found to be composed of 31% (*S*,*S*)-(−)(double retention), 48% meso (one inversion), and 21% (*R*,*R*)(+) (double inversion). These results were interpreted in terms of the competition between recombination (k_c), diffusion (k_D), and rotation (k_{rot}) of one radical with respect to the other. The analysis of these data gave: $k_{rot}/k_c = 15$, $k_D/k_c = 2.5$.[22]

$$(-)(\mathrm{DD})\mathrm{R^1N{=}NR^2} \rightarrow (\mathrm{D})\mathrm{R^{1\bullet}} + \mathrm{D(R^{2\bullet})} + \mathrm{N_2} \rightarrow (-\mathrm{DD})\mathrm{R^1R^2} + \mathrm{N_2}$$

$$[(\mathrm{D})\mathrm{R^{1\bullet}} + (\mathrm{D})\mathrm{R^{2\bullet}}] \Leftrightarrow [(\mathrm{L})\mathrm{R^{1\bullet}} + (\mathrm{D})\mathrm{R^{2\bullet}}] \rightarrow (\mathrm{LD})\mathrm{R^1R^2}\ (\text{meso})$$

$$[(\mathrm{L})\mathrm{R^{1\bullet}} + (\mathrm{D})\mathrm{R^{2\bullet}}] \Leftrightarrow [(\mathrm{L})\mathrm{R^{1\bullet}} + (\mathrm{L})\mathrm{R^{2\bullet}}] \rightarrow (\mathrm{LL})\mathrm{R^1R^2}(+)$$

The study of the decomposition of the optically active peroxide of hydratropic acid proved that the product of the geminate radical pair recombination had some net retention.[23]

2.2.5 Influence of the Viscosity and Pressure on Decomposition of Initiators

When initiator splits into a pair of radicals, this pair can recombine with the formation of the parent molecule, for example,

$$\mathrm{RC(O)OOCMe_3} \Leftrightarrow [\mathrm{RCO_2^{\bullet}} + \mathrm{Me_3CO^{\bullet}}] \rightarrow \mathrm{R^{\bullet}} + \mathrm{CO_2} + \mathrm{Me_3CO^{\bullet}}$$

The higher the viscosity of the solvent, the higher proportion of the parent molecules that are formed due to the geminate recombination of radicals. The observed rate constant for decomposition of the initiator decreases with an increase in viscosity, which was observed at the decomposition of peresters and diacetyl peroxide in various solutions (see Tables 2.2 and 2.3). Subsequently, the fraction f_r of the radical pairs recombining to the parent molecule increases with an increase in the viscosity:

Diacetyl Peroxide, 353 K[a]			
Solvent	Isooctane	Dodecane	Octadecane
$f_r \times 100\%$	28	39	49
Acetyl 1,1-Dimethylethyl Peroxide, 403 K[b]			
Solvent	Hexane	Nonane	Paraffin
$f_r \times 100\%$	6	12	42

[a] See Ref. 17.
[b] See Ref. 19.

The introduction of a free radical acceptor (scavenger) helps to measure the probability (e) of radical pairs escaping from geminate combination and diffuse out of the cage (see Chapter 3). The value of e for the fixed initiator or photoinitiator depends on the viscosity η of solvent. The following empirical dependence for the photodecomposition of initiators was found:[25,26]

$$(1-e)^{-1} = 1.1 + 6.5 \times 10^{-6} T^{1/2} \eta^{-1} \qquad (CH_3N{=}NCH_3)$$

$$(1-e)^{-1} = 1.1 + 4.0 \times 10^{-5} T^{1/2} \eta^{-1} \qquad (CF_3N{=}NCF_3)$$

$$(1-e)^{-1} = 1.24 + 5.75 \times 10^{-5} T^{1/2} \eta^{-1} \qquad [PhMe_2CC(O)OOCMe_3]$$

There are initiators that split into only two radicals, for example,

$$Me_3COOCMe_3 \rightarrow Me_3CO^{\bullet} + Me_3CO^{\bullet}$$

TABLE 2.2 Rate Constants for the Decomposition of Peresters $RC(O)OOCMe_3$ in Solvents with Different Viscosities at $T = 403$ K

		$R = C_6H_5$[a]	$R = CH_3$[b]
Solvent	$\eta \times 10^3$ (Pa s)	$k_d \times 10^4$ (s^{-1})	$k_d \times 10^4$ (s^{-1})
Hexane	0.14	3.72	5.08
Isooctane	0.18	3.36	
Dodecane	0.39	3.08	
Hexane–Paraffin (40%)	0.38	3.39	4.43
Hexane–Paraffin (70%)	0.82	3.04	3.80
Paraffin	2.44	2.33	3.13

[a] See Ref. 27.
[b] See Ref 19.

TABLE 2.3 Rate Constants for the Diacetyl Peroxide Decomposition (k_d) in Various Solvents and Yield (y) of Products of Geminate Radical Pair Recombination

	353 K[a]	333 K[b]	C_2H_6[b]	MeC(O)OMe[b]
Solvent	$k_d \times 10^5$ (s^{-1})	$k_d \times 10^5$ (s^{-1})	$y \times 100$ (%)	$y \times 100$ (%)
Hexane		0.34	3.4	13
Heptane	7.72			
Octane	7.34	0.29	5.5	18
Decane	6.85			
Dodecane	6.15	0.23	7.1	21
Tetradecane	5.90	0.20	8.9	24
Hexadecane	5.39			
Octadecane		0.19	10	27

[a] See Ref. 17.
[b] See Ref. 24.

and initiators that dissociate with the formation of two radicals and one or two molecules, for example,

$$Me_2(CN)CN{=}NC(CN)Me_2 \rightarrow Me_2(CN)C^{\bullet} + N_2 + Me_2(CN)C^{\bullet}$$

$$Me_3COOC(O)C(O)OOCMe_3 \rightarrow Me_3CO^{\bullet} + CO_2 + CO_2 + Me_3CO^{\bullet}$$

The molecules formed simultaneously with radicals depend on the efficiency of initiation (see Table 2.4).

The pressure influence on the cage effect was studied by Neuman *et al.*[29–33] They measured such effects for the recombination–diffusion competition for the 1,1-dimethylethoxy radical pairs generated from bis(1,1-dimethylethyl)hyponitrite. The empirical activation volume difference ($\Delta V_d^{\#} - \Delta V_c^{\#}$) for the competition

TABLE 2.4 Ratio of Radical Pair Diffusion and Geminate Recombination for Various Radical Pairs (Influence of Inert Molecules)

Radical Pair	Solvent	T (K)	$e/(1-e)$
cyclo-$C_6H_{10}C{=}N^{\bullet}$, N_2, *cyclo*-$C_6H_{10}C{=}N^{\bullet}$	Chlorobenzene	353	1.51
cyclo-$C_6H_{10}C{=}N^{\bullet}$, *cyclo*-$C_6H_{10}C{=}N^{\bullet}$	Chlorobenzene	353	0.66
$Me_3CO^{\bullet}$, $Me_3CO^{\bullet}$	Isooctane	318	7.32
$Me_3CO^{\bullet}$, $Me_3CO^{\bullet}$	White oil	318	0.32
$Me_3CO^{\bullet}$, N_2, $Me_3CO^{\bullet}$	Isooctane	318	9.01
$Me_3CO^{\bullet}$, N_2, $Me_3CO^{\bullet}$	White oil	318	0.47
$Me_3CO^{\bullet}$, CO_2, CO_2, $Me_3CO^{\bullet}$	Isooctane	318	10.8
$Me_3CO^{\bullet}$, CO_2, CO_2, $Me_3CO^{\bullet}$	White oil	318	0.85

[a] See Refs. 22 and 28.

of initiator decomposition and radical pair recombination was found to depend on pressure (see Table 2.5). A fairly good correlation between the yield of the recombination product and the fluidity of the solvent (octane) at various pressures was obtained.

2.2.6 Spin Multiplicity Effects

Thermal and direct photolytic decomposition of initiator produces a radical pair in the singlet state when back geminate recombination occurs rapidly. The radical pair is formed in the triplet state when a triplet sensitizer is used. Before geminate recombination, this radical pair should evolve into the singlet state.[35,36] That is why the proportion of geminate recombination of the triplet pair is less than that of the singlet one. For example, direct photolysis of *N*-(1-cyanocyclohexyl)pentamethyleneketenimine gives 24% of succinonitryl in CCl_4, whereas triplet-sensitized photolysis gives only 8%.[1] The photolysis of phenyl benzoate in benzene gives 8% phenyl benzoate in geminate recombination, and in triplet sensitized photolysis gives only 3% of phenyl benzoate[1] Oxygen-18

TABLE 2.5 The Pressure Influence on the Cage Effect

Pressure (atm)	e	k_c/k_D	$\Delta V_D^{\#} - \Delta V_c^{\#}$
$Me_3CON = NOCMe_3$, *Solvent = Cumene*, $T = 352.6$ K[a]			
1	0.91	0.10	
1000	0.79	0.27	26
2000	0.68	0.46	15
3000	0.58	0.71	11
4000	0.53	0.88	8
$3-ClC_6H_4CH_2C(O)OOCMe_3$, *Solvent = Cumene*, $T = 352.6$ K[a]			
1	0.80	0.26	
1000	0.70	0.42	14
2000	0.64	0.57	8
3000	0.60	0.68	6
4000	0.55	0.82	5
$Me_2(CN)CN{=}NC(CN)Me_2$, *Solvent = Toluene*, $T = 335.3$ K[b]			
1	0.70	0.42	
1000	0.78	0.60	9.8
2000	0.57	0.74	5.7
3000	0.51	0.96	6.9
5000	0.46	1.20	6.3

[a] See Ref. 30.
[b] See Ref. 34.

randomization is also less important in the triplet-sensitized decomposition of diacyl peroxides.

Chemically induced dynamic nuclear polarization (DNP) opened the door to the study of the products formed from free radicals.[35] The ground for this study is the difference in nuclear magnetic resonance (NMR) spectra of normal molecules and those formed from free radicals and radical pairs. Molecules formed from radicals have an abnormal NMR spectrum with lines of emission and abnormal absorption.[35] The DNP spectra help to obtain the following mechanistic information:

1. The proof of radical ancestry for particular products.
2. The identity and characteristics of radical precursors.
3. The identity of pairs in which polarization occurs.
4. Some information on radical pair separation.
5. The direct observation of unstable diamagnetic reaction intermediates. For detailed information about DNP method, see Ref. 35.

2.3 MECHANISTIC SCHEMES OF CAGE EFFECT

The cage effect can be interpreted from a simple kinetic scheme.[3] For example, azo compounds decompose according to the following kinetic scheme:

$$\mathrm{RN{=}NR} \rightarrow [\mathrm{R}^\bullet + \mathrm{N_2} + \mathrm{R}^\bullet] \qquad (k_\mathrm{d})$$

$$[\mathrm{R}^\bullet + \mathrm{N_2} + \mathrm{R}^\bullet] \rightarrow \mathrm{RR} + \mathrm{N_2} \qquad (k_\mathrm{C})$$

$$[\mathrm{R}^\bullet + \mathrm{N_2} + \mathrm{R}^\bullet] \rightarrow \mathrm{R}^\bullet + \mathrm{N_2} + \mathrm{R}^\bullet \qquad (k_\mathrm{D})$$

The probability of the radical pair escaping from geminate recombination (e) depends on the rate constants according to Eq. (2.1):

$$e^{-1} = 1 + \frac{k_c}{k_D} = 1 + \frac{6\pi L r_R k_c \eta}{10^6 RT} = 1 + \text{const} \times \eta \qquad (2.1)$$

where r_R is the radius of the diffusing R$^\bullet$ radical.

The model of the cage effect at the photodissociation of the initiator was analyzed by Noyes.[37] Free radicals were assumed to be spherical particles, which move in a viscous continuum. The separation r_0 is the distance achieved during the initiating event. This separation is calculated by assuming that the initial kinetic energy has a magnitude greater than the average thermal energy. The second encounter of formed radicals is taken into account. The reciprocal of the total probability of geminate recombination has the following form:

$$\frac{1}{1-e} = \frac{r_0}{2r_R}\left\{1 + \frac{\alpha A_E + A_T}{\alpha\eta} + \frac{A_T A_E}{\alpha\eta^2}\right\} \qquad (2.2)$$

where $A_E = m_R^{1/2}(h\nu - E_I)^{1/2}/6\pi r_R^2$, $A_T = (1.5 m_R kT)^{1/2}/6\pi r_R^2$, α is the probability of the reaction between two R$^\bullet$ radicals per collision, m_R is the weight of radical R$^\bullet$, E_I is the dissociation energy of the initiator, and r_0 is the initial displacement of the formed radicals (which depends on the formation of the third particle due to initiator decomposition).

When free radicals formed from the initiator are unstable, they decompose in the cage, for example,

$$\mathrm{RC(O)OOCMe_3} \rightarrow [\mathrm{RCO_2}^\bullet + \mathrm{Me_3CO}^\bullet] \qquad (k_d)$$

$$[\mathrm{RCO_2}^\bullet + \mathrm{Me_3CO}^\bullet] \rightarrow [\mathrm{R}^\bullet + \mathrm{CO_2} + \mathrm{Me_3CO}^\bullet] \qquad (k_\beta)$$

$$[\mathrm{R}^\bullet + \mathrm{CO_2} + \mathrm{Me_3CO}^\bullet] \rightarrow \mathrm{ROCMe_3} + \mathrm{CO_2} \qquad (k_c)$$

$$[\mathrm{R}^\bullet + \mathrm{CO_2} + \mathrm{Me_3CO}^\bullet] \rightarrow \mathrm{R}^\bullet + \mathrm{CO_2} + \mathrm{Me_3CO}^\bullet \qquad (k_D)$$

The yield (y) for the product of geminate pair recombination (ROCMe$_3$) is a function of the subsequent rate constants:[38,39]

$$\frac{1}{y} - 1 = \frac{k_D}{k_c} + \frac{k_\beta}{k_c} \qquad (2.3)$$

If one takes into account the time dependence of k_D in the form ($r^2 = 2Dt$):

$$k_D = \frac{r}{r_R - r_0} \times \frac{1}{t} = \frac{\sqrt{2D}}{2r_R - r_0} \times \frac{1}{\sqrt{t}} \qquad (2.4)$$

where r_R is the radius of the formed radical R$^\bullet$, r_0 is the distance between two radicals at $t = 0$, D is the diffusion coefficient of the radical, and t is characteristic lifetime of existence of the radical pair in the cage. As well as $D \sim \eta^{-1}$, we obtain the equation

$$\frac{1}{y} - 1 = \frac{\text{const}}{\sqrt{\eta}} + \frac{k_\beta}{k_c} \qquad (2.5)$$

This equation helps us to make a choice between the concerted and nonconcerted decomposition of the initiator (for the concerted decomposition $k_\beta = 0$).

The cage effect was also analyzed for the model of diffusion of two particles (radical pair) in viscous continuum using the diffusion equation.[40] Due to initiator decomposition, two radicals R$^\bullet$ formed are separated by the distance r_0 at $t = 0$. The acceptor of free radicals Q is introduced into the solvent, it reacts with radicals with the rate constant k_a. Two radicals recombine with the rate constant k_c when they are brought together at the distance $2r_R$, where r_R is the radius of the radical R$^\bullet$. The solvent is treated as continuum with viscosity η. The distribution of radical pairs (n) as a function of the distance x between them obeys the equation of diffusion:

$$(D/x)d^2(nx)/dx^2 - 2\ k_a n[Q] = 0 \qquad (2.6)$$

The solution of Eq. (2.6) at $4k_{\mathrm{Q}}[\mathrm{Q}]r_{\mathrm{R}}/D \ll 1$ has the following simple form:

$$e = 1 - \frac{2r_R}{r_0}(1 + 8\pi r_R D/k_c)^{-1} \tag{2.7}$$

By substituting the diffusion coefficient D into its expression in the Stokes–Einstein equation, we have the equation

$$\frac{1}{1-e} = \frac{r_0}{2r_R}\left(1 + \frac{4 \times 10^6 RT}{3Lk_c\eta}\right) \tag{2.8}$$

2.4 CAGE EFFECT IN SOLID POLYMERS

Polyolefins are semicrystalline polymers, so that low molecular weight substances penetrate and diffuse only in the amorphous phase. Each particle or a pair of particles is surrounded by segments of the macromolecule. Since the segments in the amorphous phase are not packed as tightly as in the crystalline phase, there are holes moving through the polymer. Due to the high molecular weight of macromolecules, the holes "concentration" and the rate of their motion is lower in polymers than in liquids. This is the result of the diffusion rate of molecules in polymers being much lower than in liquids. Slow molecular diffusion in polymers leads to a high probability of free radical pair recombination in a polymer cage. In polymers, the probability of a free radical pair escaping recombination in the cage has a value of 0.1–0.01 and is lower in comparison with a value of 0.3–0.8 found in liquids. An attempt to estimate the cage effect in polymers was made in Ref. 41, which come from the cage effect in liquids and took into account slower diffusion in polymers. Indeed, according to the simple scheme (Scheme A)

$$\mathrm{AIBN} \rightarrow [\mathrm{R}^{\bullet} + \mathrm{R}^{\bullet}] + \mathrm{N_2}$$

$$[\mathrm{R}^{\bullet} + \mathrm{R}^{\bullet}] \rightarrow \mathrm{R}^{\bullet} + \mathrm{R}^{\bullet} \qquad (k_{\mathrm{D}})$$

$$[\mathrm{R}^{\bullet} + \mathrm{R}^{\bullet}] \rightarrow \mathrm{RR}$$

one obtains the following simple equation:

$$e_s = \frac{e_l k_{D_s}}{(1 - e_l)k_{D_l}} \tag{2.9}$$

at $e_{\mathrm{s}} \ll 1$, where indexes s and l denote the solid and liquid phases, respectively. The values of e_{s} calculated from this formula were found to be much lower than the experimental values.[41]

2.4.1 Schemes of the Cage Effect with Translational Motion of Particles

The cage effect in polymers was studied at the decomposition of AIBN in polypropylene.[42] The rate of free radicals formation, v_{i}, was measured by nitroxyl radical (2,2,6,6-tetramethyl-4-benzoyloxypiperidinoxyl-1) consumption using the technique of electron paramagnetic resonance (EPR). The kinetics of AIBN decomposition was studied manometrically by dinitrogen evolution (see Chapter 3). The value of e was estimated as the ratio $e = \nu_i k_d^{-1}[\mathrm{AIBN}]^{-1}$. It was proved that k_d is the same in the polymer and liquid (benzene) phases,[11] namely, $k_d(\mathrm{s}^{-1}) = 1.6 \times 10^{15} \exp(-129/RT)$. The molecular mobility in polymer samples was estimated as the frequency of nitroxyl radical rotation, ν_r, measured by its EPR spectrum.[43] To change the molecular mobility, chlorobenzene was introduced into the polymer samples as a plasticizer. Diffusion rate constant k_D of the nitroxyl radical was estimated on the frequency of their rotation ν_r by using the empirical equation: $\log k_D = 0.94 + 0.9 \log \nu_r$. The diffusion coefficient D is known to depend on the size (volume V) of a diffusing particle (1 and 2). This dependence is given by the equation: $\log(D_1/D_2) = 0.5 \log(V_2/V_1)$.[44] The ratio of the volumes of nitroxyl and cyanoisopropyl radicals is equal to 3.5. The values of e, ν_r, and k_{DR} are given in Table 2.6. According to the scheme of cage reactions A, $e = k_{DR}(k_{DR} + k_c)^{-1}$ or

$$e/k_{DR}(1 - e) = k_c. \tag{2.10}$$

However, the treatment of the experimental results obtained by this formula showed that the rate constant of radical pair recombination is a variable value (see Table 2.6). It implies that Scheme A is not valid for processes in the polymer cage.

Scheme A does not take into account the formation of two radicals and a nitrogen molecule between them at the decomposition of AIBN. The scheme with the formation of three particles at the AIBN decomposition was analyzed also (Scheme B):[42]

$$\mathrm{AIBN} \rightarrow [\mathrm{R}^\bullet + \mathrm{N}_2 + \mathrm{R}^\bullet] \qquad k_d$$

$$[\mathrm{R}^\bullet + \mathrm{N}_2 + \mathrm{R}^\bullet] \rightarrow \mathrm{R}^\bullet + \mathrm{R}^\bullet + \mathrm{N}_2 \qquad (k_{DR})$$

$$[\mathrm{R}^\bullet + \mathrm{N}_2 + \mathrm{R}^\bullet] \rightarrow [\mathrm{R}^\bullet + \mathrm{R}^\bullet] + \mathrm{N}_2 \qquad (k_{DN2})$$

$$[\mathrm{R}^\bullet + \mathrm{R}^\bullet] \rightarrow \mathrm{R}^\bullet + \mathrm{R}^\bullet \qquad (k_{DR})$$

$$[\mathrm{R}^\bullet + \mathrm{R}^\bullet] \rightarrow \mathrm{RR} \qquad (k_c)$$

The probability of radicals getting out of the cage in such a scheme depends not only on the values of k_{DR} and k_c, but also on the rate constant k_{DN2} or the ratio $\beta = k_{DN2}/k_{DR}$ in the following way:

$$\beta/[e(1 + \beta) - 1] = k_c/k_{DR} + 1 \tag{2.11}$$

The k_c values calculated from the experimental data in Eg. (2.10) are given in Table 2.6. It is seen that k_c is not constant, but increases with the growing molecular mobility. Hence, Scheme B does not give an adequate description of the experimental data on the cage effect at AIBN decomposition in the polymer. In a similar manner, the cage effects were investigated for lauroyl peroxide decomposition in polypropylene (353 K) using the nitroxyl radical as a free radical acceptor[45] and dodecane as a plasticizer. It was found that Schemes A and B do not describe the cage effect in this case.

2.4.2 Schemes of the Cage Effect with Translational and Rotational Motion of Particles

Free radicals in the cage execute translational and rotational motions. The latter can be important for free radicals to react, because such a reaction requires a pair of free radicals to be oriented in an appropriate manner for overlapping of odd electron orbitals and singlet spin orientation. One can expect that discrepancies between the above schemes and experimental data are the result of the important role of rotation in the cage effect. The following AIBN scheme of decomposition

TABLE 2.6 Cage Effect at AIBN Decomposition in Plasticized Polypropylene[a]

$\nu_r \times 10^{-7}$ (s^{-1})	$k_{DR} \times 10^{-8}$ (s^{-1})	$e \times 10^2$	$10^8 e/k_{DR}(1-e)$ (s^{-1}) (Scheme A)	$k_c \times 10^{-9}$ (s^{-1}) (Scheme B)
		$T = 333\ K$		
25	7.4	26.4	0.377	2.8
33	9.8	32.5	0.211	2.9
44	12.9	32.0	0.165	4.0
52	15.6	36.8	0.110	3.9
73	21.5	39.7	0.071	4.8
97	28.2	44.0	0.045	5.3
		$T = 343\ K$		
25.0	9.0	22.0	0.394	5.3
45.0	15.2	26.7	0.181	7.1
52.2	20.4	33.0	0.100	6.9
75.3	23.1	33.1	0.087	7.8
90.2	32.5	40.3	0.045	10.5
156	47.6	43.7	0.027	10.0
338	109	55.0	0.007	16.3
		$T = 353\ K$		
44.0	17.2	20.4	0.227	15.8
58.1	21.8	21.7	0.165	16.0
111.2	38.6	27.4	0.069	26.0
170.2	56.3	33.0	0.036	28.2
238	75.4	35.0	0.025	36.9

[a] See Ref. 42.

in a polymer was considered (Scheme C):[42]

$$\begin{array}{rcll}
\text{AIBN} & \rightarrow & [\text{R}^{\bullet} + \text{N}_2 + \text{R}^{\bullet}]^{*} & \alpha k_{\text{d}} \\
\text{AIBN} & \rightarrow & [\text{R}^{\bullet} + \text{N}_2 + \text{R}^{\bullet}] & (1-\alpha)k_{\text{d}} \\
[\text{R}^{\bullet} + \text{N}_2 + \text{R}^{\bullet}] & \rightarrow & \text{R}^{\bullet} + \text{R}^{\bullet} + \text{N}_2 & (k_{\text{DR}}) \\
[\text{R}^{\bullet} + \text{N}_2 + \text{R}^{\bullet}] & \rightarrow & [\text{R}^{\bullet} + \text{R}^{\bullet}] + \text{N}_2 & (k_{\text{DN2}}) \\
[\text{R}^{\bullet} + \text{R}^{\bullet}] & \rightarrow & \text{R}^{\bullet} + \text{R}^{\bullet} & (k_{\text{DR}}) \\
[\text{R}^{\bullet} + \text{R}^{\bullet}] & \rightarrow & [\text{R}^{\bullet} + \text{R}^{\bullet}]^{*} & \nu P \\
[\text{R}^{\bullet} + \text{R}^{\bullet}]^{*} & \rightarrow & [\text{R}^{\bullet} + \text{R}^{\bullet}] & \nu \\
[\text{R}^{\bullet} + \text{R}^{\bullet}]^{*} & \rightarrow & \text{RR} & (k_{\text{c}}{}^{*})
\end{array}$$

Four types of cages are suggested for reactions in the polymer matrix: primary cage $[\text{R}^{\bullet} + \text{N}_2 + \text{R}^{\bullet}]$, cage $[\text{R}^{\bullet} + \text{R}^{\bullet}]$ with random orientation of radicals, $[\text{R}^{\bullet} + \text{N}_2 + \text{R}^{\bullet}]^{*}$, and $[\text{R}^{\bullet} + \text{R}^{\bullet}]^{*}$ where free radicals are oriented conveniently for the reaction. Recombination of radicals occurs with the steric factor P. The cage $[\text{R}^{\bullet} + \text{R}^{\bullet}]^{*}$ transforms into $[\text{R}^{\bullet} + \text{R}^{\bullet}]$ with the frequency ν and back transformation occurs with the frequency νP. The probability of $[\text{R}^{\bullet} + \text{R}^{\bullet}]^{*}$ cage formation after AIBN decomposition is α and that of the $[\text{R}^{\bullet} + \text{R}^{\bullet}]$ cage formation is $(1 - \alpha)$. The rate constant of radicals recombination in the $[\text{R}^{\bullet} + \text{R}^{\bullet}]^{*}$ cage is equal to $k_C{}^{*}$. The ratio $k_{\text{DN2}}/k_{\text{DR}} = \beta$ and the ratio $\nu/k_{\text{DR}} = \gamma$. This scheme leads to the following dependence of e on the parameters of molecular mobility:

$$(\beta + 1)e - \frac{1}{(\beta + 1)(1 - e)} = \frac{\nu}{k_c{}^{*}(\gamma P + \alpha)} + \frac{1 - \alpha}{\gamma P + \alpha} \tag{2.12}$$

The experimental data on AIBN decomposition in polypropylene were found to agree with this scheme and Eq. (2.12). The following values were calculated for the parameters of this equation, and the $k_c{}^{*}$ values were calculated at $P = 0.1$:

T	333 K	343 K	353 K
$k_c^{*}(\gamma P + \alpha)(\text{s}^{-1})$	5.8×10^{10}	10.0×10^{10}	29×10^{10}
$(1 - \alpha)(\gamma P + \alpha)^{-1}$	0.165	0.125	0.065
$k_c^{*}(\text{s}^{-1})$	4.0×10^{10}	7.0×10^{10}	2.0×10^{11}

The data on dodecanoyl peroxide decomposition in polymers[45] were treated in the scope of the analogous scheme that takes into account the possibility of reverse recombination of radicals $\text{C}_{11}\text{H}_{23}\text{CO}_2{}^{\bullet}$, their decarboxylation with the rate constant k_{D}, and rotation of radicals in the cage. According to this scheme, the probability of free radical diffusion out of the cage was found to be

$$\nu(1 - e) = k_c^{*}(1 + 2.4P)e - k_c^{*}(1 - \alpha) \tag{2.13}$$

The experimental data on dodecanoyl peroxide decomposition is in agreement with the dependence of e on the molecular mobility ν (polypropylene, 353 K).[14] Assuming $P = 0.1$, we find $k_c^* = 2.7 \times 10^{10}$ s^{-1}, $\alpha = 0.96$. Thus, the experimental data on the cage effect at the decomposition of AIBN and dodecanoyl peroxide in comparison with the molecular mobility in the polymer matrix proves that the fate of a radical pair in a polymer cage depends on the rate constant of radical recombination (disproportionation) and their translational and rotational diffusion. The lower the rate of rotation, the more important the influence of rotation of particles on the cage effect. So, the important role of rotational diffusion in the cage effect (which is not important in liquids) is specific for a polymer matrix.

2.4.3 Role of the Cage Shape in the Polymer Matrix at Initiator Decomposition

Unlike liquids, polymer samples can have one or another shape, for example, the polymer films can be stretched. In this case, the polymer acquires a microfibrillic structure where each microfibrille is oriented along the direction of the drawing and consists of a sequence of crystalline and amorphous parcels.[46] Macromolecules stretch in the amorphous phase and the "hole" may be expected to acquire a cylindric shape as well. The question about the way it influences the cage effect was studied.[47] The cage effects were studied at AIBN decomposition in oriented polypropylene with the degree of stretching $\lambda = 1$ (powder), 4 and 8 (oriented films) in the temperature range of 330–360 K. It was found that the rate constant of initiation k_i in oriented samples is higher than that in the nonoriented polymer.

The kinetics of nitrogen evolution showed that the rate constant of AIBN decomposition is independent of the polymer samples orientation. So, an increase in k_i in oriented polymers implies the growing of e ($k_i = 2ek_d$). The more mobile the polymer segments, the higher the probability of radicals getting out of the cage. However, in oriented polymer samples the molecular mobility is lower, as was shown by the EPR spectrum of the nitroxyl radical measured in these samples. The increase in e at polymer orientation can be due to the shape of the cage. The following scheme can qualitatively explain these data. At the decomposition of AIBN in nonoriented polymer, the cage is close to a sphere form and nitrogen diffuses rapidly from the cage. [$R^\bullet$, N_2, $R^\bullet$], after the free radicals, recombine with a high probability. The cage in the oriented polymer has a presumably cylindric shape. When an AIBN molecule decomposes in such a cage, nitrogen diffuses slowly because two free radicals at the ends of the cylindric hole interfere with its motion out of the cage. On the other side, a molecule of nitrogen placed between two radicals does not permit them to recombine. It leads to an increase in the probability of a radical pair getting out of the cage. The thermal motion of segments makes the walls of the cage more permeable for diffusion of nitrogen. That is why, the higher the temperature, the lower the difference of e values in oriented and isotropic polymers (see below), which is the reason for e having a negative temperature coefficient in oriented polymers.[47]

γ	A_i (s^{-1})	E/(kJ mol^{-1})	e ($T = 323$ K)
1	3.7×10^{15}	141	0.024
4	1.6×10^{10}	104	0.093
8	1.3×10^{9}	96	0.17

2.4.4 Concept of a Hard Cage of Polymer Matrix

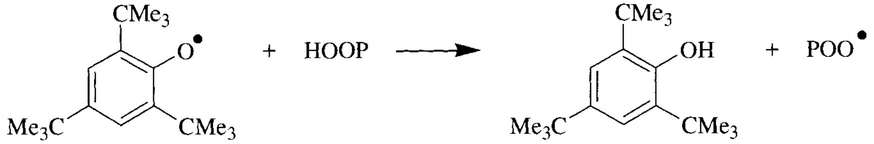
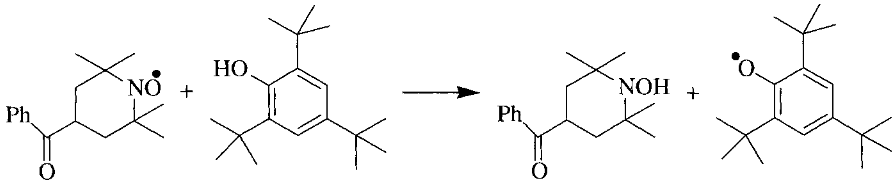
Another phenomenon specific to polymers is the cage effect in slow bimolecular reactions. It is well known that the viscosity of liquids does not influence the rate of slow bimolecular reaction, which occurs with an activation energy and is not controlled by the rate of diffusion of reagents. However, slow reactions in the polymer matrix occur more slowly than in the liquid under the same conditions, which was proved by comparison of the experimental rate constants of the reactions as shown in Table 2.7 (POOH is the hydroperoxide group of polymer).[48-54]

Rate constants for these reactions were found to correlate with the molecular mobility that was calculated from the EPR spectra of the nitroxyl radical. The higher the molecular mobility, the higher the rate constant of the reaction.

These experimental data encouraged us to put forward the model of the hard cage of a polymer matrix.[55-60] The medium of the polymer matrix affects the bimolecular reaction differently than in the liquid phase. The interaction of two reagents in the liquid phase occurs in the cage formed by labile molecules. All geometric shapes of such a cage are energetically equivalent due to the high flexibility of molecules surrounding the pair of reacting particles, and this cage may be regarded as "soft". The formation of a transition state in the soft cage of the nonpolar liquid does not need an additional energy for the reorganization of the molecules surrounding the pair of reactants.

In the polymer matrix, each particle or a pair of particles is surrounded by segments of the macromolecule. This segment is connected by C—C bonds to form a rigid cage. In such a rigid cage, there are geometrically and energetically unequal orientations of particles. This is why a pair of reactants reacting in the polymer matrix needs an additional energy to assume the necessary orientation to react in a rigid cage. Therefore, the rate constant of a bimolecular reaction in the polymer matrix includes an additional coefficient F_S, which describes the influence of the cage walls on the mutual orientation of reactants: $k_S = A \times F_S \exp(-E/RT)$. This coefficient must depend on the temperature because it includes the Boltzmann factor, which is equal to $\exp(-U_{or}/RT)$,

TABLE 2.7 The Dependence of Rate Constants for Bimolecular Reactions on the Molecular Mobility (ν) of Polymer Matrix (POOH is the Hydroperoxide Group of Polymer)[a]

Media	$\nu \times 10^{-7}$ (s^{-1})	k(295 K) ($L\,mol^{-1}\,s^{-1}$)	E ($kJ\,mol^{-1}$)	$\log A$, A ($L\,mol^{-1}\,s^{-1}$)
				
PP	6.7	3.5×10^{-3}	67	9.4
PP + 8% PhCl	240	0.38	52	7.8
PE	44	0.014	69	10.4
C_6H_6	850	0.115	45	7.1
				
PE	42	1.0×10^{-4}		
PE + 36% PhCl	350	7.0×10^{-4}		
PP	23	1.0×10^{-4}	75	8.7
PP + 2% PhCl	60	3.1×10^{-4}		
C_6H_6	5400	1.4×10^{-3}	42	4.1

[a] See Refs. 48–54.

where U_{or} is the difference between the energy of the energetically most convenient orientation of particles and that necessary for the reaction to occur. A particle in the polymer cage is regarded as being in the field of forces of intermolecular interaction, which is approximated by a cosine function (the reaction is regarded in one plane):

$$U(\theta) = 0.5U_0(1 - \cos n_\theta \theta) \tag{2.14}$$

where U_0 is the energy barrier dividing two energetically convenient positions of the particle in the cage, and $2n_\theta$ is the number of such positions. For the reaction to occur, particle A must be oriented in the cage under an angle of $\theta_A \pm \Delta\theta_A$.

The preexponential factor of the bimolecular reaction in the polymer in the scope of such a model is the following:

$$A_S = \frac{A\exp(-U_{or}/RT)}{4\pi^2 I_0(U_0/2RT)\exp(-U_0/2RT)} \quad (2.15)$$

where $I_0(x)$ is the modified Bessel function with respect to an imaginary argument. In liquids, all orientations of reactants are energetically equivalent. Therefore, the ratio of rate constants in the polymer and liquid is

$$\frac{k_s}{k_l} = \frac{\exp(-U_{or}/RT)}{\exp(-U_0/2RT)I_0(U_0/2RT)} \quad (2.16)$$

This cage model gives a simple equation for the frequency of rotation of the particle in the polymer ν_S and liquid ν_l:

$$\nu_s = \nu_l \exp(-U_0/RT) \quad (2.17)$$

Such a model explains the above mentioned peculiarities of free radical reactions in polymers. First, the reaction occurs more slowly in a polymer than in a liquid on account of the reorganization of the surrounding polymer segments to achieve the transition state (potential U_{or}). Second, the correlation between k_S and molecular mobility ν_S finds a natural explanation because k_S and ν_S depend on the same potential U_0:

$$\ln\frac{k_l}{k_s(\nu_s/\nu_l)^{1/2}I_0[0.5\ln(\nu_l/\nu_s)]} = m\ln\frac{\nu_l}{\nu_s} \quad (2.18)$$

where $m = U_{or}/U_0$). Experimental data are in good agreement with this formula (see Table 2.8).

As seen from Table 2.8, the parameter m is constant in all experiments and lies in the limits of 0.5–0.75. The energetic barrier for orientation varies from 7 to 12 kJ mol^{-1}. This model also explains the compensating effect, that is, the increasing of the preexponential factor with growing activation energy.[20] An empirical linear correlation between the rate constant of the bimolecular reaction in a polymer matrix and the transition state volume was found.[53,54]

$$RT\ln(k_l/k_s)(\text{kJ mol}^{-1}) = a(V^{\#} - b) \quad (2.19)$$

T(K)	303	333	363
$a \times 10^2$ kJ cm^{-3}	2.50	2.23	1.98
$b(\text{cm}^3\ \text{mol}^{-1})$	127	110	117

TABLE 2.8 Comparison of Rate Constants and Molecular Mobility in the Polymer Matrix and Liquids, Values of U_0 and U_{0r}[a]

Polymer	ν_s/ν_l	k_s/k_l	U_0 (kJ mol^{-1})	m	U_{or} (kJ mol^{-1})
Reaction of 2,4,6(1,1-Dimethylethyl)phenoxyl with Hydroperoxide Groups					
$T = 295$ K					
PE	5.62×10^{-3}	8.40×10^{-2}	12.7	0.74	9.3
PP	1.22×10^{-3}	3.12×10^{-3}	36.8	0.74	12.2
PP + 2% PhCl	1.43×10^{-2}	0.125	10.4	0.78	8.1
PP + 8% PhCl	5.00×10^{-2}	0.332	7.3	0.72	5.2
Reaction of 4-Benzoyloxy-2,2,6,6-tetramethylpiperidine-N-oxyl with 2,6-bis(1,1-Dimethylethyl)phenol					
$T = 313$ K					
PE	8.93×10^{-3}	7.25×10^{-2}	13.1	0.81	10.7
PE + 5.5% PhCl	1.07×10^{-2}	0.123	11.7	0.74	8.6
PE + 36% PhCl	6.67×10^{-2}	0.502	10.7	0.69	7.4
PP	4.25×10^{-3}	7.25×10^{-2}	14.1	0.73	10.3
PP 2% PhCl	1.11×10^{-3}	7.22×10^{-2}	11.7	0.61	7.1
$T = 323$ K					
PE	8.93×10^{-3}	0.267	12.6	0.55	6.9
PE 4% PhCl	1.56×10^{-2}	0.370	11.1	0.52	5.8
PP	4.31×10^{-3}	0.125	14.6	0.63	9.2
PP 1% PhCl	6.45×10^{-3}	0.208	13.5	0.57	7.6
$T = 333$ K					
PE	1.11×10^{-2}	0.345	12.4	0.51	6.5
PP	6.67×10^{-3}	0.251	13.8	0.53	7.4
PP + 1% PhCl	9.61×10^{-3}	0.345	13.0	0.51	6.6
PP + 2% PhCl	1.39×10^{-2}	0.417	11.8	0.49	5.7
PS + 9% PhCl	2.08×10^{-3}	0.133	17.0	0.56	9.5
PS + 38% PhCl	4.17×10^{-3}	0.526	8.8	0.52	4.6
Reaction of 4-Benzoyloxy-2,2,6,6-tetramethylpiperidine-N-oxyl with 1-Naphthol					
$T = 333$ K					
PE + 6% PhCl	1.39×10^{-3}	7.04×10^{-2}	18.1	0.63	11.4
PS + 18% PhCl	4.59×10^{-3}	0.252	14.9	0.52	7.9
PS + 50% PhCl	6.67×10^{-2}	0.588	7.4	0.55	4.1

[a] See Refs. 49–52.

The following peculiarities of the cage effect in the solid polymer and liquid can be formulated:[55–57]

Liquid	**Polymer**
Molecules that are moving intensively form the cage. The diffusion of molecules is relatively fast $D \approx 10^{-5}$–10^{-6} cm^2 s^{-1}.	The cage is formed by segments of a macromolecule. Molecules diffuse in the amorphous phase of a polymer relatively slowly with $D \approx 10^{-7}$–10^{-10} cm^2 s^{-1}.
The time of the radical pair stay in the cage depends on the processes of recombination and translational motion. Schemes of the cage taking into account the translational diffusion of radicals describe the empirical dependence of the cage effect on viscosity.	The evolution of a radical pair in the cage depends on recombination, translational, and rotational diffusions. Agreement with the experiment gives such schemes, which take into account not only translational, but also rotational diffusion of radicals.
The molecules of a liquid move rapidly, so the cage changes its shape very promptly.	The cage in oriented polymers has a preferentially stretched shape with two radicals separated by a molecule, which influences the cage effect.
The cage does not influence the bimolecular elementary act, if $k \ll k_D$ and $E \gg E_D$.	Slow bimolecular reactions occur in the polymer at a lower rate than in the liquid, which is the result of a “rigid” cage formed by polymer segments.

REFERENCES

1. T. Koenig and H. Fischer, in *Free Radicals*, J. K. Kochi (Eds.), John Wiley & Sons, Inc., New York, 1973, Vol. 1, p. 157.
2. A. M. North, *The Collision Theory of Chemical Reactions in Liquids*, Methuen, London, 1964.
3. E. T. Denisov, in *Itogi Nauki I Tekhniki, Ser. Kinetika Kataliz* (Russian), VINITI, Moscow, 1981, Vol. 9.
4. E. T. Denisov, O. M. Sarkisov, and G. I. Likhtenshtein, *Chemical Kinetics* (Russian), Khimiya, Moscow, 2000.
5. J. Frank and E. Rabinowitch, *Trans. Faraday Soc.* **30**, 120 (1934).
6. R. M. Noyes, *Z. Electrochem.* **69**, 153 (1960).
7. R. L. Strong, *J. Am. Chem. Soc.* **87**, 3563 (1965).
8. J. P. Fisher, G. Mucke, and G. V. Schulz, *Ber. Bunsenges. Phys. Chem.* **73**, 154 (1969).

9. L. Herk, M. Feld, and M. Szwarc, *J. Am. Chem. Soc.* **83**, 2998 (1961).
10. P. D. Bartlett, G. N. Fickes, F. C. Haupt, and R. Hegelson, *Acc. Chem. Res.* **3**, 177 (1970).
11. J. C. Bevington, *Trans. Faraday Soc.* **51**, 1392 (1955).
12. R. K. Lyon and D. H. Levy, *J. Am. Chem. Soc.* **83**, 4290 (1961).
13. R. E. Rebert and P. Ausloos, *J. Phys. Chem.* **66**, 2253 (1962).
14. J. C. Martin and J. W. Taylor, *J. Am. Chem. Soc.* **89**, 6904 (1969).
15. T. Koenig and R. Cruthoff, *J. Am. Chem. Soc.* **91**, 2562 (1969).
16. J. C. Martin and S. A. Dombchik, *Adv. Chem. Ser.* **75** (1), 269 (1968).
17. W. Pryor and K. Smith, *J. Am. Chem. Soc.* **92**, 5403 (1970).
18. D. Booth and R. M. Noyes, *J. Am. Chem. Soc.* **82**, 1872 (1960).
19. T. Koenig, J. Huntington, and R. Cruthoff, *J. Am. Chem. Soc.* **92**, 5413 (1970).
20. D. Gegion, K. Muszkat, and E. Fischer, *J. Am. Chem. Soc.* **90**, 12 (1968).
21. K. R. Kopecky and T. Gillan, *Can. J. Chem.* **47**, 2371 (1969).
22. F. D. Greene, M. A. Berwick, and T. C. Stowell, *J. Am. Chem. Soc.* **92**, 867 (1970).
23. F. D. Greene, *J. Am. Chem. Soc.* **77**, 4689 (1955).
24. W. Braun, L. Rajbenback, and E. R. Eirich, *J. Phys. Chem.* **66**, 1591 (1962).
25. O. Dobis, I. Nemes, and M. Szwarc, *Lecture on International Conference on Mechanism of Reactions in Solution*, Kent, England, 1970.
26. F. E. Herkes, J. Friedman, and P. D. Barlett, *Int. J. Chem. Kinet.* **1**, 193 (1969).
27. T. Koenig, M. Deinzer, and J. A. Hoobler, *J. Am. Chem. Soc.* **93**, 938 (1971).
28. C. S. Wu, G. S. Hammound, and J. M. Wright, *J. Am. Chem. Soc.* **82**, 5386 (1960).
29. R. C. Neuman and J. V. Behar, *J. Am. Chem. Soc.* **91**, 6024 (1969).
30. R. C. Neuman and E. S. Alhadeff, *J. Org. Chem.* **35**, 3401 (1970).
31. R. C. Neuman and R. G. Bussey, *J. Am. Chem. Soc.* **92**, 2440 (1970).
32. R. C. Neuman and R. C. Pankratz, *J. Am. Chem. Soc.*, **95**, 8372 (1973).
33. R. C. Neuman and J. V. Behar, *J. Org. Chem.* **36**, 657 (1971).
34. M. Ya. Botnikov, V. M. Zhulin, L. G. Bubnova, and G. A. Stashina, *Izv. AN SSSR, Ser. Khim.* 229 (1977).
35. H. R. Ward, in *Free Radicals*, J. K. Kochi (Eds.), John Wiley & Sons, Inc., New York, 1973, Vol. 1, p. 239.
36. A. L. Buchachenko, *Chemical Polarisation of Electrons and Nucleus* (Russian), Nauka, Moscow, 1974.
37. R. M. Noyes, *Prog. React. Kinet.* **1**, 129 (1961).
38. T. Koenig and M. Deinzer, *J. Am. Chem. Soc.* **90**, 7014 (1968).
39. T. Koenig, *J. Am. Chem. Soc.* **91**, 2558 (1969).
40. Kh. S. Bagdasaryan, *Zh. Fiz. Khim.* **41**, 1697 (1967).
41. B. R. Smirnov and V. D. Sukhov, *Vysokomolek. Soed.* **19A**, 236 (1977).
42. A. P. Griva, L. N. Denisova, and E. T. Denisov, *Vysokomolek. Soed.* **19A**, 219 (1977).
43. A. L. Buchachenko and A. M. Vasserman, *Stabilnye Radikaly* (Russian), Khimiya, Moscow, 1973.
44. I. I. Barashkova, A. M. Vasserman, and A. L. Kovarskii, *Vysokomolek. Soed.* **23B**, 434 (1981).

45. A. P. Griva, L. N. Denisova, and E. T. Denisov, *Zh. Fiz. Khim.* **58**, 577 (1984).
46. *Structure and Properties of Oriented Polymers*, J. M. Ward, John Wiley & Sons, Inc., New York, 1975.
47. B. E. Krisyuk, E. N. Ushakov, A. P. Griva, and E. T. Denisov, *Dokl. AN SSSR* **277**, 630 (1984).
48. N. V. Zolotova and E. T. Denisov, *Zh. Fiz. Khim.* **46**, 2008 (1972).
49. A. P. Griva and E. T. Denisov, *J. Polym. Sci., Polym. Chem. Ed.* **14**, 1051 (1976).
50. A. P. Griva and E. T. Denisov, *Dokl. AN SSSR* **232**, 1343 (1977).
51. A. P. Griva, L. N. Denisova, and E. T. Denisov, *Kinet Katal.* **19**, 309 (1978).
52. A. P. Griva, L. N. Denisova, and E. T. Denisov, *Zh. Fiz. Khim.* **63**, 2601 (1989).
53. S. D. Grinkina, E. T. Denisov, and A. P. Griva, *Kinet Katal.* **35**, 523 (1994).
54. S. D. Grinkina, A. P. Griva, E. T. Denisov, V. D. Sen', and I. K. Yakuschenko, *Kinet Katal.* **34**, 245 (1993).
55. E. T. Denisov, in *General Aspects of the Chemistry of Radicals*, Z. B. Alfassy, John Wiley & Sons, Chichester, U.K., 1999.
56. E. T. Denisov, *Zh. Fiz. Khim.* **49**, 2475 (1975).
57. E. T. Denisov, *Izv. AN SSSR, Ser. Khim.* 51 (1976).
58. A. P. Griva and E. T. Denisov, *Dokl. AN SSSR* **219**, 640 (1974).
59. E. T. Denisov and A. P. Griva, *Zh. Fiz. Khim.* **53**, 2417 (1979).
60. E. T. Denisov, *Macromol. Chem., Suppl.* **8**, 63 (1984).

Handbook of Free Radical Initiators. E.T. Denisov, T.G. Denisova, T.S. Pokidova
Copyright © 2003 John Wiley & Sons, Inc.
ISBN: 0-471-20753-5

3

METHODS OF STUDY OF INITIATOR DECOMPOSITION AND FREE RADICAL GENERATION

3.1 KINETIC DECAY OF INITIATOR (KDI)

A simple and widely used method for measuring rate constants is the monitoring of the kinetic curve of decomposition of the starting initiator I.[1,2] Unimolecular decomposition of initiator obeys the exponential law:

$$[\mathrm{I}] = [\mathrm{I}]_0 \exp(-k_\mathrm{d}t) \tag{3.1}$$

$$\ln([\mathrm{I}]_0/[\mathrm{I}]) = k_\mathrm{d}t \tag{3.2}$$

The rate constant is calculated as the slope of the straight line plotted in the coordinates $\ln([\mathrm{I}]_0/[\mathrm{I}])$ versus time t. It is evident that k_d should not depend on the initial concentration of the initiator. Nevertheless, in some cases along with unimolecular decomposition, an induced chain decomposition of the initiator occurs (see Section 1.6). For example, benzoyl peroxide decomposes monomolecularly ($v = k_\mathrm{d}[\mathrm{I}]$) and in some solvents it is attacked by free radicals with the additional rate $v_\mathrm{ind} = k_\mathrm{ind}[\mathrm{I}]^{3/2}$. The rate constant k_expl calculated from Eq. (3.2) was found to be $k_\mathrm{expl} = k_\mathrm{d} + k_\mathrm{ind}[\mathrm{I}]_0^{1/2}$. In this case, the rate constant of unimolecular decomposition k_d is found by the extrapolation

$$k_\mathrm{d} = \lim k_\mathrm{expl} \quad \text{at} \quad [\mathrm{I}]_0^{1/2} \to 0 \tag{3.3}$$

The following methods are used for monitoring the concentration of the decomposing initiator:

1. Chemical analysis of the initiator, for example, the iodometric method for peroxides.

2. Gas–liquid and liquid chromatography (GLC).
3. Visual, ultraviolet (UV), and infrared (IR) spectroscopy.
4. NMR spectroscopy.
5. Electrochemical methods (e.g., polarography).

3.2 KINETIC PRODUCT FORMATION (KPF)

If the stable product (P) is formed as a result of initiator decomposition, the rate and kinetics of P formation is used for the estimation of k_d.[1,2] The rate of end-product accumulation is the following:

$$\frac{d[\mathrm{P}]}{dt} = f_p k_d[\mathrm{I}] = f_p k_d([\mathrm{P}]_\infty - [\mathrm{P}]) \tag{3.4}$$

where f_p is the stoichiometric coefficient of P formation and $[\mathrm{P}]_\infty = [\mathrm{P}]$ at $t \rightarrow \infty$, $f_p = [\mathrm{P}]_\infty/[\mathrm{I}]_0$. The kinetics of end-product accumulation is described by Eq. (3.5).

$$\ln \frac{[\mathrm{P}]_\infty}{[\mathrm{P}]_\infty - [\mathrm{P}]} = f_p k_d t \tag{3.5}$$

The production $f_p k_d$ is found from the slope of the straight line in the coordinates $\ln\{[\mathrm{P}]_\infty/([\mathrm{P}]_\infty - [\mathrm{P}])\}$ versus time and the value of f_p is found from the proportion $[\mathrm{P}]_\infty/[\mathrm{I}]_0$. This method was used particularly in studying the decomposition of azo compounds that decompose with dinitrogen evolution:

$$\mathrm{RN=NR} \rightarrow \mathrm{R}^\bullet + \mathrm{N_2} + \mathrm{R}^\bullet$$

The reaction kinetics is monitored by measuring the volume V of the evolved gas. The rate constant of $\mathrm{RN_2R}$ decomposition is found from Eq. (3.6).

$$\ln \frac{V_\infty}{V_\infty - V} = k_d t \tag{3.6}$$

The stoichiometric coefficient $f_p = 1$ for this initiator.

3.3 ACCEPTORS OF FREE RADICALS (AFR)

Since free radicals are formed as the result of initiator decomposition, the rate of their formation can be measured using free radical acceptors.[1–4] Acceptors are molecules or stable radicals that react very rapidly with free radicals. The most popular radical acceptors (scavengers) are listed in Table 3.1. Stable radicals react with radicals with the stoichiometric coefficient (f) equal to unity, for example,

TABLE 3.1 Stoichiometric Coefficients and Rate Constants k_a of Radical Acceptors Reactions with Free Radicals

Acceptor	Radical	Solvent	T (K)	f	k_a (L mol^{-1} s^{-1})	Ref.
Diphenylpicrylhydrazyl	$\sim CH_2C^{\bullet}MeCO_2Me$	Methyl methacrylate	317	1.0	9.4×10^5	5
Phenoxyl, 2,6-bis(1,1-dimethylethyl)-4-benzoyl-	$Me_2(CN)CO_2^{\bullet}$	Benzene	333	1.0	1.9×10^8	6
Phenoxyl, 2,6-bis(1,1-dimethylethyl)-4-chloro-	$Me_2(CN)CO_2^{\bullet}$	Benzene	333	1.0	1.7×10^8	6
Phenoxyl, 2,6-bis(1,1-dimethylethyl)-4-cyano-	$Me_2(CN)CO_2^{\bullet}$	Benzene	333	1.0	2.7×10^8	6
Phenoxyl, 2,6-bis(1,1-dimethylethyl)-4-dimethylethoxy-	$Me_2(CN)CO_2^{\bullet}$	Benzene	333	1.0	4.1×10^8	6
Phenoxyl, 2,6-bis(1,1-dimethylethyl)-4-methoxy-	$Me_2(CN)CO_2^{\bullet}$	Benzene	333	1.0	7.2×10^8	6
Phenoxyl, 2,6-bis(1,1-dimethylethyl)-4-methyl-	$\sim CH_2C^{\bullet}HCO_2Me$	Methyl acrylate	333	1.0	1.2×10^8	7
Phenoxyl, 2,6-bis(1,1-dimethylethyl)-4-phenyl-	$Me_2(CN)CO_2^{\bullet}$	Benzene	333	1.0	6.0×10^8	6
Phenoxyl, 2,4,6-tris(1,1-dimethylethyl)-	$PhMe_2CO_2^{\bullet}$	Cumene	303	1.0	2.0×10^8	8
Phenoxyl, 2,4,6-tris(1,1-dimethylethyl)-	$\sim CH_2C^{\bullet}HCO_2Me$	Methyl acrylate	333	1.0	7.0×10^7	7
Phenoxyl, 2,4,6-tris(1,1-dimethylethyl)-	$Me_2(CN)CO_2^{\bullet}$	Benzene	333	1.0	3.2×10^8	6
Phenoxyl, 2,4,6-tris(1,1-dimethylethyl)-	$\sim CH_2C^{\bullet}HCO_2Me$	Methyl acrylate	333	1.0	7.0×10^7	7

(continued overleaf)

TABLE 3.1 (*continued*)

Acceptor	Radical	Solvent	T (K)	f	k_a (L mol^{-1} s^{-1})	Ref.
Piperidine, 2,2,6,6-tetramethyl-*N*-oxyl-	$Me_3(CH_2)_7C^{\bullet}H_2$	Water	270–317	1.0	$2.5 \times 10^{10}\exp(-7.5/RT)$	9
Piperidine, 2,2,6,6-tetramethyl-*N*-oxyl-	$Me_3CC^{\bullet}H_2$	Isooctane	293	1.0	9.6×10^8	10
Piperidine, 2,2,6,6-tetramethyl-*N*-oxyl-	$PhC^{\bullet}H_2$	Isooctane	293	1.0	4.9×10^8	10
Piperidine, 2,2,6,6-tetramethyl-*N*-oxyl-	$PhC^{\bullet}HMe$	Isooctane	293	1.0	1.6×10^8	10
Piperidine, 2,2,6,6-tetramethyl-*N*-oxyl-	$PhMe_2C^{\bullet}$	Isooctane	293	1.0	1.2×10^9	10
Piperidine, 2,2,6,6-tetramethyl-*N*-oxyl-	$\sim CH_2C^{\bullet}HPh$	Styrene	323	1.0	2.1×10^4	11
Piperidine, 4-benzoyloxy-2,2,6,6-tetramethyl-*N*-oxyl-	$\sim CH_2C^{\bullet}HPh$	Benzene	333	1.0	3.0×10^5	11
Piperidine, 4-benzoyloxy-2,2,6,6-tetramethyl-*N*-oxyl-	$\sim CH_2C^{\bullet}MeCO_2Me$	Methyl methacrylate	333	1.0	6.0×10^5	11
Piperidine, 4-(2′-hydroxybenzoyloxy)-2,2,6,6-tetramethyl-*N*-oxyl-	$\sim CH_2C^{\bullet}HPh$	Styrene	333	1.0	7.0×10^5	11
Piperidine, 4-(2′-hydroxybenzoyloxy)-2,2,6,6-tetramethyl-*N*-oxyl-	$\sim CH_2C^{\bullet}MeCO_2Me$	Methyl methacrylate	333	1.0	6.8×10^5	11

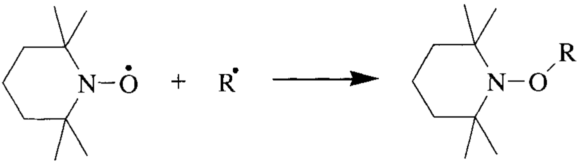
3,4-Benzopyrrolidine, 2,2,5,5-tetramethyl-*N*-oxyl-	$Me_3C^\bullet$	Isooctane	293	1.0	8.8×10^8	10
3,4-Benzopyrrolidine, 2,2,5,5-tetramethyl-*N*-oxyl-	$C^\bullet H_3$	Cyclohexane	333–398	1.0	$2.5 \times 10^7 \exp(-4.6/RT)$	12
3,4-Benzopyrrolidine, 2,2,5,5-tetramethyl-*N*-oxyl-	$CH_2{=}CH(CH_2)_3C^\bullet H_2$	Cyclohexane	333–398	1.0	$5.0 \times 10^9 \exp(-3.8/RT)$	12
3,4-Benzopyrrolidine, 2,2,5,5-tetramethyl-*N*-oxyl-	$PhC^\bullet H_2$	Isooctane	293	1.0	$5.5 \times 10^8 \exp(-3.8/RT)$	10
Pyrrolidine, 3-acetamido-2,2,5,5-tetramethyl-*N*-oxyl-	$C^\bullet H_3$	Water	298	1.0	5.1×10^7	9
Pyrrolidine, 3-acetamido-2,2,5,5-tetramethyl-*N*-oxyl-	*cyclo*-$[C^\bullet H(CH_2)_4]$	Water	298	1.0	3.5×10^8	9
Pyrrolidine, 3-acetamido-2,2,5,5-tetramethyl-*N*-oxyl-	$HOC^\bullet H_2$	Water	298	1.0	4.6×10^8	9
Pyrrolidine, 3-acetamido-2,2,5,5-tetramethyl-*N*-oxyl-	$CH_3C^\bullet HOH$	Water	298	1.0	4.3×10^8	9
Pyrrolidine, 3-acetamido-2,2,5,5-tetramethyl-*N*-oxyl-	$Me_2C^\bullet HOH$	Water	298	1.0	3.3×10^8	9
Diphenylnitrone	$Me(CH_2)_{11}C^\bullet HMe$	Tetradecane	323–343	2.0	$6.0 \times 10^{10} \exp(-35.1/RT)$	13
Diphenylnitrone	$Me(CH_2)_{11}CO_2{}^\bullet HMe$	Tetradecane	323–353	0.9	$5.75 \times 10^8 \exp(-31.2/RT)$	13

(continued overleaf)

TABLE 3.1 (*continued*)

Acceptor	Radical	Solvent	T (K)	f	k_a (L mol^{-1} s^{-1})	Ref.
Diphenylcarbamoylnitrone	$Me(CH_2)_{11}C^•HMe$	Tetradecane	323–353	2.1	$3.7 \times 10^{11} exp(-41.8/RT)$	13
Diphenylcarbamoylnitrone	$Me(CH_2)_{11}CO_2{}^•HMe$	Tetradecane	323–353	1.0	$1.7 \times 10^{9} exp(-37.2/RT)$	13
p-Benzoquinone	$C^•H_3$	Toluene	338	2.0	1.03×10^8	14
p-Benzoquinone	$\sim CH_2C^•HPh$	Styrene	323	2.0	1.01×10^5	15
p-Benzoquinone	$\sim CH_2C^•HCO_2Me$	Methyl acrylate	317	2.0	1.20×10^3	16
p-Benzoquinone	$\sim CH_2C^•MeCO_2Me$	Methyl methacrylate	317	2.0	2.58×10^3	17
p-Benzoquinone, 2,6-dichloro-	$C^•H_3$	Toluene	338	2.0	2.62×10^8	14
p-Benzoquinone, 2,6-dichloro-	$\sim CH_2C^•MeCO_2Me$	Methyl methacrylate	317	2.0	1.65×10^4	16
p-Benzoquinone, 2,6-dichloro-	$\sim CH_2C^•HCO_2Me$	Methyl acrylate	317	2.0	1.67×10^4	16
Diiodine	$C^•H_3$	Water	295	2.0	6.0×10^9	18
1,4-Naphthoquinone	$C^•H_3$	Toluene	338	2.0	3.30×10^7	14
1,4-Benzenediol	$PhMe_2CO_2{}^•$	Cumene	338	1.8	$6.4 \times 10^7 exp(-19.7/RT)$	19
1,4-Benzenediol	$Me_3CO^•$	Benzene	295	2.0	3.2×10^9	20
1-Naphthol	$PhMe_2CO_2{}^•$	Cumene	338	2.0	$3.2 \times 10^7 exp(-15.7/RT)$	19
1-Naphthol	$Me_3CO^•$	Benzene	295	2.0	2.0×10^9	20
2-Naphthol	$PhMe_2CO_2{}^•$	Cumene	338	1.8	$3.2 \times 10^7 exp(-20.6/RT)$	19
2-Naphthol	$Me_3CO^•$	Benzene	295	2.0	1.0×10^9	20

Phenol	$PhMe_2CO_2^\bullet$	Cumene	338	2.0	$3.2 \times 10^7 \exp(-29.4/RT)$	19
Phenol	$Me_3CO^\bullet$	Benzene	295	2.0	3.3×10^8	20
Phenol, 2,6-bis(1,1-dimethylethyl)-4-methyl-	$PhMe_2CO_2^\bullet$	Cumene	338	2.0	$3.2 \times 10^7 \exp(-21.3/RT)$	19
Phenol, 2,6-bis(1,1-dimethylethyl)-4-methyl-	$Me_3CO^\bullet$	Benzene	295	2.0	1.2×10^8	20
Phenol, 4-methyl-	$PhMe_2CO_2^\bullet$	Cumene	338	2.2	$3.2 \times 10^7 \exp(-24.3/RT)$	19
Phenol, 4-methyl-	$Me_3CO^\bullet$	Chlorobenzene	395	2.0	1.65×10^9	21
Phenol, 4-methyl-	$Me_3CO^\bullet$	Benzene	295	2.0	5.5×10^8	20
Phenol, 2,4,6-tris(1,1-dimethylethyl)-	$PhMe_2CO_2^\bullet$	Cumene	333	2.1	$3.2 \times 10^7 \exp(-17.9/RT)$	19
Phenol, 2,4,6-tris(1,1-dimethylethyl)-	*cyclo*-$C_6H_{11}O^\bullet$	Benzene	323	2.0	1.1×10^8	22
1.4-Benzenediamine, *N*,*N*′-bis-2′-naphthalenyl-	$(PhCH_2)_2NCHPhO_2^\bullet$	Tribenzylamine	333	2.0	$2.0 \times 10^8 \exp(-11.4/RT)$	23
1.4-Benzenediamine, *N*,*N*′-diphenyl	$PhMe_2CO_2^\bullet$	Cumene	338	2.2	$2.0 \times 10^8 \exp(-15.5/RT)$	23
1-Naphthalenamine	*cyclo*-$C_6H_{11}O_2^\bullet$	Cyclohexane	323	2.0	$2.0 \times 10^8 \exp(-24.5/RT)$	23
1-Naphthalenamine	$Me_3CO^\bullet$	Benzene	293	2.0	1.9×10^8	24
2-Naphthalenamine	$Me(CH_2)_4CHMeO_2^\bullet$	Heptane	347	2.0	$2.0 \times 10^8 \exp(-27.0/RT)$	23
2-Naphthalenamine	$Me_3CO^\bullet$	Benzene	293	2.0	6.0×10^8	24



Generally, the molecular acceptor reacts with free radicals with $f = 2$, for example,

$$R^{\bullet} + Q \rightarrow RQ^{\bullet}$$

$$R^{\bullet} + RQ^{\bullet} \rightarrow RQR$$

To measure the rate of free radical generation, the acceptor is introduced into the solvent together with the initiator. Free radicals generated by the initiator partially recombine in the cage (see Chapter 2) and partially go into the bulk. The acceptor reacts only with those radicals that have escaped into the bulk volume. Due to a cage effect, the rate constant of initiation k_i can be measured by the disappearance of the acceptor. This rate constant $k_i = 2ek_d$, where e is the probability of the formed radical pair to escape the cage recombination. If the initial rate of initiation is measured, the rate constant is calculated from the kinetic curve of acceptor (Q) decay:

$$-\frac{d[Q]}{f\,dt} = k_i[I]_0 \quad \text{and} \quad [Q] = [Q]_0 - f^{-1}k_i[I]_0 t \qquad (3.7)$$

In the general case, one should take into account the reactions of free radicals with the acceptor (k_a) and reactions of free radical recombination with the rate equal to $2k_t[R^{\bullet}]^2$. The rates of free radical generation and disappearance are the following under the steady-state conditions:

$$k_i[I]_0 = f^{-1}k_a[Q][R^{\bullet}] + 2k_t[R^{\bullet}]^2 \qquad (3.8)$$

To measure the initiation rate of the acceptor disappearance, one should take an acceptor in a high enough concentration so that the acceptor will scavenge virtually all of the free radicals formed.

$$f^{-1}k_a[Q] \gg 2k_t[R^{\bullet}] \quad \text{and} \quad k_a[Q] \gg \sqrt{2k_t k_i[I]_0} \qquad (3.9)$$

For example, when $2k_t = 10^9\ \mathrm{L\,mol^{-1}\,s^{-1}}$ (recombination of radicals is diffusionally controlled) and $k_i[I]_0 = 10^{-7}\ \mathrm{mol\,L^{-1}\,s^{-1}}$, the scavenger concentration [Q] should be $> 10 f k_a^{-1}$, and at $k_a = 10^5\ \mathrm{L\,mol^{-1}\,s^{-1}}$ and $f = 2$ we should introduce Q in the concentration: $[Q]_0 \gg 2 \times 10^{-4}\ \mathrm{mol\,L^{-1}}$, for example, $5 \times 10^{-3}\ \mathrm{mol\,L^{-1}}$. On the other side, the initial concentration of the scavenger should not be very high because its decay should be measured during time t of the experiment. Suppose that at the end of the experiment (time t) the concentration of the acceptor should be 90% lower than $[Q]_0$. This implies that $0.1[Q]_0 < k_i[I]_0t$. So, the concentration of the chosen acceptor should obey the following conditions:

$$10f^{-1}k_i[I]_0t \gg [Q]_0 \gg fk_a^{-1}\sqrt{2k_tk_i[I]_0} \tag{3.10}$$

When the initiator decomposes with only the formation of free radicals, its rate constant of initiation is $k_i = 2ek_d$ and $e = k_i/2k_d$. Combination with Eq. (2.1) leads to Eq. (3.11).

$$\frac{k_d}{k_i} = \frac{1}{2} + \text{const } \times \eta \tag{3.11}$$

The estimation of k_i and k_d in solvents with different viscosities opens the way for us to check on whether the initiator decomposes homolytically or not. If the initiator decomposes to free radicals with the rate constant k_d and to molecules with k_m, we should observe the following dependence:

$$\frac{k_{\text{expl}}}{k_i} = \frac{k_m + k_d}{k_i} = \frac{1}{2} + \frac{k_m}{k_i} + \text{const } \times \eta \tag{3.12}$$

The extrapolation of the ratio k_{expl}/k_i as a function of η to $\eta \to 0$ gives a value that helps us to differentiate both cases: $\lim(k_{\text{expl}}/k_i)_{\eta\to0} = \frac{1}{2}$ when $k_{\text{expl}} = k_d$ and const $> \frac{1}{2}$, when $k_{\text{expl}} = k_d + k_m$.

When the initial rate of acceptor consumption is measured, only k_i can be determined. If the experiment is conducted in such a manner that all the initiator has decomposed during this time, then the kinetic curve for the consumption of the acceptor can be used to determine both k_d and e.[2] Here the acceptor is added in excess, so that all the radicals formed from the initiator react with the acceptor. The rate of acceptor consumption is

$$-\frac{d[Q]}{dt} = 2ek_df^{-1}[I]_0e^{-k_dt} \tag{3.13}$$

and the kinetics of acceptor consumption is described by Eq. (3.14):

$$[Q] = [Q]_0 - 2ef^{-1}[I]_0[1 - \exp(-k_dt)] \tag{3.14}$$

or

$$\ln\frac{[Q]_0 - [Q]_\infty}{[Q] - [Q]_\infty} = k_dt \tag{3.15}$$

The rate constant k_d is found from the straight-line slope in the coordinates: $\ln([Q]_0 - [Q]_\infty)/([Q] - [Q]_\infty)$ versus t. The value of e is calculated from Eq. (3.16).

$$e = f[([Q]_0 - [Q]_\infty)/[I]_0] \tag{3.16}$$

3.4 KINETIC CHAIN INITIATED REACTION (KIR)

Initiators are widely used for the initiation of chain reactions in solution, for example, radical polymerization[5,11] and oxidation of hydrocarbons by dioxygen.[3] The chain mechanism of the last reaction includes the following elementary steps:[3,23]

$$\mathrm{I} \rightarrow \mathrm{r}^{\bullet} + \mathrm{r}^{\bullet} \qquad (2ek_d)$$

$$\mathrm{r}^{\bullet} + \mathrm{RH} \rightarrow \mathrm{rH} + \mathrm{R}^{\bullet} \qquad \text{(fast)}$$

$$\mathrm{R}^{\bullet} + \mathrm{O_2} \rightarrow \mathrm{RO_2}^{\bullet} \qquad \text{(fast)}$$

$$\mathrm{RO_2}^{\bullet} + \mathrm{RH} \rightarrow \mathrm{ROOH} + \mathrm{R}^{\bullet} \qquad (k_p)$$

$$\mathrm{RO_2}^{\bullet} + \mathrm{RO_2}^{\bullet} \rightarrow \mathrm{ROOR} + \mathrm{O_2} \qquad (2k_t)$$

The reaction of an alkyl radical with dioxygen occurs with a diffusionally controlled rate constant and at $[\mathrm{O_2}] \geq 10^{-4}$ mol L^{-1} it does not limit chain propagation. The limiting stage of chain propagation is the reaction of $\mathrm{RO_2}^{\bullet}$ with RH (rate constant k_p). Chains are terminated by the reaction of two peroxyl radicals with the rate equal to $2k_t[\mathrm{RO_2}^{\bullet}]$. When the initiator I is the single source of free radicals and the length ν of the chain is great ($\nu > 10$), the initial rate of chain oxidation $V_{\mathrm{O_2}}$ obeys Eq. (3.17) (under steady-state conditions)

$$V_{\mathrm{O_2}} = \frac{d\Delta[\mathrm{O_2}]}{dt} = k_p\left[[\mathrm{RH}]\sqrt{\frac{2k_d e[\mathrm{I}]_0}{2k_t}}\right] \qquad (3.17)$$

where $\Delta[\mathrm{O_2}]$ is the amount of consumed dioxygen, and

$$\Delta[\mathrm{O_2}] = (k_p\sqrt{2k_t})[\mathrm{RH}]\sqrt{2k_d e[\mathrm{I}]_0} \times t \qquad (3.18)$$

In the absence of initiators, free radicals are generated in the reaction of a hydrocarbon with dioxygen (see Chapter 11) with the rate v_{i0}. So, in the general case, the rate of initiated oxidation is expressed by Eq. (3.19):

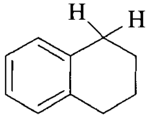
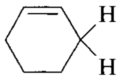
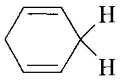
$$V_{\mathrm{O_2}} = (k_p\sqrt{2k_t})[\mathrm{RH}]\sqrt{2k_d e[\mathrm{I}] + v_{i0}} \qquad (3.19)$$

and at $v_{i0} \ll 2k_d e[\mathrm{I}]_0$ this equation transforms into Eq. (3.18). From experiments on RH oxidation with different concentrations of the initiator, we find the value of $k_i = 2ek_d$ from the slope and v_{i0} from the interception on coordinates $V_{\mathrm{O_2}}^2 - [\mathrm{I}]_0$ according to Eq. (3.20).

$$V_{\mathrm{O_2}}^2 = (k_p^2/2k_t)[\mathrm{RH}]^2(2ek_d[\mathrm{I}]_0 + v_{i0}) \qquad (3.20)$$

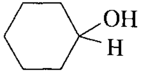
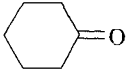
The values of $k_p/\sqrt{2k_t}$ for the oxidation of hydrocarbons and radical polymerization of monomers are listed in Tables 3.2 and 3.3.

TABLE 3.2 Ratio Values $k_p/\sqrt{2k_t}$ for Initiated Oxidation of Organic Compounds

Oxidizing Compound	Solvent	T (K)	$k_p/\sqrt{2k_t}$ (L/mol s)$^{1/2}$	Reference
Pentane $Me(CH_2)_3Me$	Pentane	253–303	$1.34 \times 10^5 \exp(-59.0/RT)$	25
Decane $Me(CH_2)_8Me$	Decane	283–355	$2.97 \times 10^5 \exp(-58.3/RT)$	26
2-Methylbutane $(Me)_2CHCH_2Me$	2-Methylbutane	387–423	$5.9 \times 10^3 \exp(-50.6/RT)$	27
Pentane, 2,4-dimethyl- $(Me)_2CHCH_2CH(Me)_2$	2,4-Dimethylpentane	323–398	$1.0 \times 10^4 \exp(-44.8/RT)$	28
Cyclohexane *cyclo*-C_6H_{12}	Cyclohexane	403–433	$1.9 \times 10^4 \exp(-54.0/RT)$	29
Ethylbenzene $PhCH_2Me$	Ethylbenzene/chlorobenzene	338–358	$4.0 \times 10^3 \exp(-44/RT)$	30
Propane, 2-phenyl-$PhCH(Me)_2$	Cumene	308–338	$1.7 \times 10^2 \exp(-29.9/RT)$	31
1,1-Diphenylethane Ph_2CHMe	1,1-Diphenylethane	313–353	$1.07 \times 10^3 \exp(-36.0/RT)$	32
Tetralin	Tetralin	286–323	$4.4 \times 10^1 \exp(-25.1/RT)$	33
				
1-Butene $CH_2{=}CHCH_2Me$	1-Butene	333	$1.68 \times 10^4 \exp(-45.8/RT)$	34
2-Butene, 2,3-dimethyl- $(Me)_2C{=}C(Me)_2$	2,3-Dimethyl butene-2	333	$2.73 \times 10^5 \exp(-47.4/RT)$	34
Cyclohexene	Cyclohexene	323	$1.0 \times 10^2 \exp(-26.5/RT)$	35
				
1,4-Cyclohexadiene	Decane	303	$3.61 \times 10^4 \exp(-38.3/RT)$	36
				

(*continued overleaf*)

TABLE 3.2 (*continued*)

Oxidizing Compound	Solvent	T (K)	$k_p/\sqrt{2k_t}$ (L/mol s)$^{1/2}$	Reference
Styrene $CH_2{=}CHPh$	Styrene/chlorobenzene	308–343	88.2 exp($-23.7/RT$)	37
Propene, 2-phenyl-$CH_2{=}CMePh$	α-Methylstyrene	286–323	3.5×10^2exp($-25.8/RT$)	38
Methyl acrylate $CH_2{=}CHCO_2Me$	Methyl acrylate	303–323	2.73×10^3exp($-42.1/RT$)	39
Methyl methacrylate $CH_2{=}CMeCO_2Me$	Methyl methacrylate	293–323	8.37×10^5exp($-48.5/RT$)	39
Butyl methacrylate $CH_2{=}CMeCO_2Bu$	Butyl methacrylate	293–323	6.31×10^4exp($-45.6/RT$)	39
Ethanol, 1-methyl-$(Me)_2CHOH$	Ethanol, 1-methyl-	363–400	3.0×10^4exp($-50.2/RT$)	40
Propanol, 1-methyl- $MeCH(OH)CH_2Me$	Propanol, 1-methyl-	338–348	1.0×10^5exp($-54.4/RT$)	41
Cyclohexanol 	Cyclohexanol	333–348	5.0×10^3exp($-45.2/RT$)	42
Benzyl alcohol $PhCH_2OH$	Benzyl alcohol	303–358	1.3×10^5exp($-50.0/RT$)	43
1-Phenylethanol $PhCH(OH)Me$	1-Phenyl	338–368	1.1×10^4exp($-43.9/RT$)	41
2-Butanone $MeC(O)CH_2Me$	2-Butanone	308–348	2.8×10^1exp($-31.77/RT$)	42
Benzyl phenyl ketone $PhC(O)CH_2C_6H_5$	Deoxybenzoin/ *o*-dichlorobenzene	333–363	2.5×10^1exp($-26.0/RT$)	43
Cyclohexanone 	Cyclohexanone	328–353	4.6×10^3exp($-46.9/RT$)	44

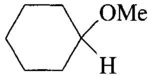
2-Propanone, 1,3-diphenyl- $(PhCH_2)_2CO$	Dibenzyl ketone/ *o*-dichlorobenzene	333–363	$2.0 \times 10^3 \exp(-37.3/RT)$	44
Decanal $Me(CH_2)_8CHO$	Decane	275–318	$3.44 \times 10^2 \exp(-17.6/RT)$	45
Benzaldehyde PhCHO	Benzaldehyde	278–293	$3.46 \times 10^5 \exp(-7.5/RT)$	46
Dibutyl ether $[Me(CH_2)_3]_2O$	Butyl ether	348	$6.3 \times 10^2 \exp(-37.2/RT)$	47
Diethoxymethane $CH_2(OCH_2Me)_2$	Diethoxymethane	303–343	$8.9 \times 10^3 \exp(-45.6/RT)$	48
Methoxycyclohexane 	Methoxycyclohexane	323–353	$1.6 \times 10^3 \exp(-41.0/RT)$	49
Dibenzyl ether $(PhCH_2)_2O$	Dibenzyl ether	348	$7.9 \times 10^3 \exp(-37.2/RT)$	47
Propanoic acid, 2-methyl-, methyl ester $(Me)_2CHC(O)OMe$	Methyl isobutyrate	338–353	$2.3 \times 10^7 \exp(-69.0/RT)$	50
Linoleic acid, methyl ester $Me(CH_2)_4CH{=}CHCH_2CH{=}CH$ $(CH_2)_7C(O)OMe$	Chlorobenzene	303–333	$5.9 \times 10^1 \exp(-20.8/RT)$	51
Oleic acid, methyl ester $Me(CH_2)_7CH{=}CH(CH_2)_7$ $C(O)OMe$	Chlorobenzene	303–333	$8.9 \times 10^2 \exp(-34.1/RT)$	51

TABLE 3.3 Kinetic Parameter Values of $a = vv_i^{-1/2} = k_p[PH](2k_t)^{-1/2}$ for Oxidation of Solid Polymers

Polymer[a]	Crystallinity (%)	Initiator	T (K)	a, (kg$^{-1/2}$ mol$^{1/2}$ s$^{-1/2}$)	References
PE	65	DCP	389–402	$1.0 \times 10^{10}\exp(-88/RT)$	52
PE	75	^{60}Co	318	8.1×10^{-4}	53
PE	75	^{60}Co	295	8.5×10^{-4}	54
PE	40	DBP	365	5.4×10^{-3}	52
PP	0	DBP	358–378	$8.5 \times 10^{8}\exp(-71/RT)$	55
PP	65	DBP, DCP	349–401	$3.0 \times 10^{6}\exp(-57/RT)$	52,56
PP	60	AIBN	317–365	$4.3 \times 10^{2}\exp(-27/RT)$	57,58
PP	0	DBP	344–378	$1.1 \times 10^{2}\exp(-26/RT)$	59
PP	70	^{60}Co	295	9.0×10^{-3}	60
PP	70	^{60}Co	353	1.9×10^{-2}	61
PP	70	^{60}Co	343	1.4×10^{-2}	61
PP	49	DCP	383	6.3×10^{-2}	62
PP	49	DCP	388	8.0×10^{-2}	62
PP	50	POOH	383–413	$1.2 \times 10^{4}\exp(-38/RT)$	63
PP	0	DBP	387	0.21	52
PP	0	DBPO	295–318	$2.2 \times 10^{5}\exp(-44/RT)$	64

[a] PE = Polyethylene. PP = Polypropylene.

If the initiator is the sole source of radical formation in the studied system and the ratio $k_p/\sqrt{2k_t}$ does not change during the time of experiment, the chain reaction kinetics can be used to determine k_d and e for the studied initiator, carrying out the experiment up to full consumption of the initiator.[1–3,5] The rate of chain reaction measured as the rate of consumption of dioxygen in oxidation is the following:

$$\frac{d\Delta[O_2]}{dt} = (k_p\sqrt{2k_t})[RH]\sqrt{2k_d e[I]_0}\,e^{-(1/2)k_d t} \tag{3.21}$$

The consumption of dioxygen (in oxidation of RH) obeys the kinetic law

$$\Delta[O_2] = \Delta[O_2]_{max}(1 - e^{-0.5k_d t}) \tag{3.22}$$

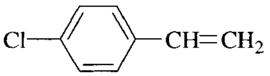
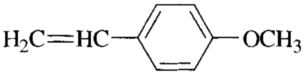
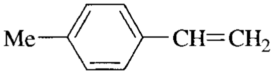
where

$$\Delta[O_2]_{max} = \frac{2k_p[RH]}{\sqrt{k_t k_d}}\sqrt{e[I]_0}$$

From the slope in the coordinates

$$\ln\frac{\Delta[O_2]_{max}}{\Delta[O_2]_{max} - \Delta[O_2]} \text{ versus } t \tag{3.23}$$

TABLE 3.4 Ratio values $k_p/\sqrt{2k_t}$ for Homopolymerization of Monomers in Bulk

Compound	T (K)	$k_p/\sqrt{2k_t}$ ((L/mol s)$^{1/2}$)	References
Acrylamide $CH_2{=}CHC(O)NH_2$	298	4.73	65
Acrylic acid $CH_2{=}CHCOOH$	296	0.45	66
Acrylonitrile $CH_2{=}CHC{\equiv}N$	298–333	$1.2 \times 10^{-2} \exp(-26.8/RT)$	67
Methacrylonitrile $CH_2{=}CMeC{\equiv}N$	298	$3.32 \times 10^{2} \exp(-27.2/RT)$	68
Methyl acrylate $CH_2{=}CHC(O)OMe$	303–333	$0.53 \exp(-32.0/RT)$	69,70
Methyl methacrylate $CH_2{=}C(CH_3)C(O)OMe$	323–363	$93.2 \exp(-22.6/RT)$	71
Styrene, $PhCH{=}CH_2$	253–303	$46.2 \times \exp(-22.5/RT)$	72
Styrene, 4-chloro-	303	1.71×10^{-2}	73
			
Styrene, 4-methoxy-	303	1.24×10^{-2}	74
			
Styrene, 4-methyl-	303	1.03×10^{-2}	74
			
Vinyl acetate $CH_2{=}CHOC(O)Me$		$3.81 \times 10^{2} \exp(-19.6/RT)$	71
Vinyl chloride $CH_2{=}CHCl$	298–323	$72.2 \exp(-15.5/RT)$	75

one calculates the value of k_d and from the value of $\Delta[O_2]_{max}$ one finds the value of e:

$$e = \frac{\Delta[O_2]^2_{max} k_t k_d}{4k_p^2[RH]^2[I]_0} \tag{3.24}$$

Another method to determine k_d from the kinetics of the initiated chain reaction is to measure the rate of chain reaction as it changes during the experiment due to initiator consumption:[1,2]

$$v = (k_p/\sqrt{2k_t})[RH](2k_d e[I]_0)^{1/2}\exp(-0.5k_d t) \tag{3.25}$$

hence

$$\ln(v_0/v) = \tfrac{1}{2}k_d t \tag{3.26}$$

From the slope in the coordinates $\ln(v_0/v)$ versus t, one calculates the rate constant k_d.

The initiation rate can be measured in experiments with a chain reaction (polymerization or oxidation) initiated by the initiator and simultaneously retarded by the radical acceptor that inhibits this reaction. Acceptors of alkyl radicals are used as inhibitors of polymerization and acceptors of peroxyl radicals are used as inhibitors of oxidation. The induction period τ of the chain reaction is measured in these experiments.[2,3] Induction period

$$\tau = f[\mathrm{InH}]_0/v_\mathrm{i} \tag{3.27}$$

if the initiation rate $v_\mathrm{i} = \mathrm{const}$ during the induction period and the free radical acceptor is very active in reactions with free radicals that propagate the chains. If the initiator is the lone generator of free radical, the rate $v_\mathrm{i} = 2ek_\mathrm{d}[\mathrm{I}]_0$, and we calculate $k_\mathrm{i} = 2ek_\mathrm{d}$ according to Eq. (3.28).

$$2ek_\mathrm{d} = \tau[\mathrm{I}]_0/f[\mathrm{InH}]_0 \tag{3.28}$$

The linear dependence of the product $\tau[\mathrm{I}]_0$ on $[\mathrm{InH}]_0$ shows that the initiator is the main generator of free radicals and InH consumes all formed free radicals. If an additional generation of free radicals $v_{\mathrm{i}0}$ exists, the dependence of the induction period τ on $[\mathrm{I}]_0$ and $[\mathrm{InH}]_0$ has the following form:

$$\frac{f[\mathrm{InH}]_0}{\tau} = (k_\mathrm{i}[\mathrm{I}]_0 + v_{\mathrm{i}0}) \tag{3.29}$$

and one finds the value of $k_\mathrm{i} = 2ek_\mathrm{d}$ from the slope in the coordinates, $f[\mathrm{InH}]_0$ versus $[\mathrm{I}]_0$. This equation is correct when the amount of the initiator decomposed during the induction period is negligible (<3%). If the induction period is long enough, one should take into account the decay of the initiator. In this case,

$$-\frac{d[\mathrm{InH}]}{dt} = f^{-1}k_\mathrm{i}[\mathrm{I}]_0 e^{-k_\mathrm{d}t} \tag{3.30}$$

and

$$\frac{f[\mathrm{InH}]_0}{\tau[\mathrm{I}]_0} = 2k_\mathrm{d}e - k_\mathrm{d}^2 e\tau \tag{3.31}$$

at $\tau < k_\mathrm{d}^{-1}$. One finds k_d and e from the slope and interception ratio $f[\mathrm{InH}]_0\tau[\mathrm{I}]_0$ as function of τ.

3.5 CHEMILUMINESCENCE (CL) METHOD

The oxidation of hydrocarbons with oxidized $>\mathrm{CH_2}$ or $-\mathrm{CH_3}$ groups is accompanied by a weak chemiluminescence.[3,76,77] This luminescence is generated by triplet ketone or aldehyde production in the reaction of two peroxyl radical recombinations:

$$2\mathrm{R^1R^2CHO_2^\bullet} \rightarrow \mathrm{R^1R^2C(O)^*} + \mathrm{R^1R^2CHOH} + \mathrm{O_2}$$

$$\mathrm{R^1R^2C(O)^*} \rightarrow \mathrm{R^1R^2C(O)} + h\nu$$

The intensity of chemiluminescence $I_{\mathrm{chl}} = 2k_t\eta[\mathrm{RO_2}^\bullet]^2$, where η is the quantum yield in this reaction. The yield of chemiluminescence η can be increased by the addition of photosensitizer, for example, 9,10-dibromoanthracene. If an initiator is added to the oxidized hydrocarbon and radicals are generated only from this initiator during the entire experiment, then by measuring the chemiluminescence intensity I_{chl}, one can measure the rate constant of initiation by this initiator

$$I_{\mathrm{chl}} = \eta 2k_t[\mathrm{RO_2}^\bullet]^2 = \eta 2ek_d[\mathrm{I}]_0e^{-k_dt} \tag{3.32}$$

and

$$\ln(I_{\mathrm{chl,0}}/I_{\mathrm{chl,t}}) = k_dt \tag{3.33}$$

The light intensity is recorded in this experiment. From the plot of ln I_{chl} versus t, one finds the rate constant of initiator decomposition k_d. This method can be used to determine k_d in substances that are subject to oxidation accompanied by chemiluminescence. The conditions are selected in such a way that the oxidation products (peroxides) give practically no radical generation in comparison with that of the added initiator. The chemiluminescence can be used for monitoring the peroxyl radicals concentration in an oxidized substance in the presence of initiator I and inhibitor InH. Induction period τ is measured and can be used for the calculation of the rate constant of initiation [see Eqs. (3.27–3.30)].

REFERENCES

1. E. T. Denisov, *Liquid-Phase Reaction Rate Constant*, IFI/Plenum, New York, 1974.
2. E. T. Denisov, in *Itogi Nauki i Tekhniki, Kinetika i Kataliz* (Russian), VINITI, Moscow, 1983, Vol. 9, p. 1.
3. N. M. Emanuel, E. T. Denisov, and Z. K. Maizus, *Liquid-Phase Oxidation of Hydrocarbons*, Plenum Press, New York, 1967.
4. T. Koenig and H. Fischer, in *Free Radicals*, J. K. Kochi (Ed.), John Wiley & Sons, Inc., New York, 1973, Vol. 1, p. 157.
5. G. Odian, *Principles of Polymerization*, Mc Graw-Hill Book Co., New York, 1970.
6. V. I. Rubtsov, V. A. Roginskii, V. Z. Dubinskii, and V. B. Miller, *Kinet. Katal.* **19**, 1140 (1978).
7. R. D. Parnell and K. E. Russell, *J. Polym. Sci., Polym. Chem. Ed.* **12**, 347 (1974).
8. A. P. Griva and E. T. Denisov, *Int. J. Chem. Kinet.* **5**, 869 (1973).
9. S. Nigam, K.-D. Asmus, and R. L. Willson, *J. Chem. Soc., Faraday Trans. I*, 2314 (1976).
10. J. Chateauneuf, J. Lusztyk, and K. U. Ingold, *J. Org. Chem.* **53**, 1629 (1988).
11. E. T. Denisov and V. V. Azatyan, *Inhibition of Chain Reactions*, Gordon and Breach, London, 2000.
12. A. L. J. Beckwith and V. W. Bowry, *J. Org. Chem.* **53**, 1632 (1988).
13. A. Ya. Gerchikov, I. Sh. Nasyrov, N. A. Akmanova, V. S. Martemiyanov, and E. T. Denisov, *React. Kinet. Catal. Lett.* **33**, 317 (1987).

14. A. Remboum and M. Szwarc, *J. Am. Chem. Soc.* **77**, 4468 (1955).
15. F. Tudos and L. Shimandi, *Vysokomol. Soedin.* **4**, 1271 (1962).
16. J. L. Kice, *J. Polym. Sci.* **19**, 123 (1956).
17. J. L. Kice, *J. Am. Chem. Soc.* **76**, 6274 (1954).
18. J. K. Thomas, *J. Phys. Chem.* **71**, 1919 (1967).
19. E. T. Denisov and T. I. Drozdova, *Kinet. Catal.* **35**, 155 (1994).
20. P. K. Das, M. V. Encinas, S. Steeken, and J. C. Scaiano, *J. Am. Chem. Soc.* **103**, 4162 (1981).
21. K. U. Ingold, *Can. J. Chem.* **41**, 2816 (1963).
22. V. A. Roginskii and V. A. Belyakov, *Izv. AN SSSR, Ser. Khim.* 1980 (1982).
23. E. T. Denisov and T. G. Denisova, *Handbook of Antioxidants*, CRC Press, Boca Raton, FL, 2000.
24. E. Leyva, M. S. Platz, B. Niu, and J. Wirz, *J. Phys. Chem.* **91**, 1919 (1967).
25. S. L. Khursan, R. L. Safiullin, and S. Yu. Serenko, *Khim. Fiz.* **9**, 375 (1990).
26. S. I. Maslennikov, A. I. Nikolaev, and V. D. Komissarov, *Kinet. Katal.* **20**, 326 (1979).
27. T. G. Degtyareva, *Mechanism of oxidation of 2-methylbutane*, Ph.D. Thesis (Russian), Institute of Chemistry and Physics, Chernogolovka, USSR, 1972.
28. T. Mill and G. Montorsi, *Int. J. Chem. Kinet.* **5**, 119 (1973).
29. A. E. Semenchenko, V. M. Solyanikov, and E. T. Denisov, *Neftekhimiya* **11**, 555 (1971).
30. I. A. Opeida, A. G. Matvienko, I. V. Yefimova, and I. O. Kachurin, *Zh. Org. Khim.* **24**, 572 (1988).
31. D. G. Hendry, *J. Am. Chem. Soc.* **89**, 5433 (1967).
32. A. F. Guk, V. F. Tsepalov, V. F. Shuvalov, and V. Ya. Shlyapintokh, *Izv. AN SSSR, Ser. Khim.* 2250 (1968).
33. J. A. Howard and K. U. Ingold, *Can. J. Chem.* **44**, 1119 (1966).
34. L. Sajus, *Adv. Chem. Ser.* **75**, 59 (1968).
35. A. V. Nikitin, L. I. Murza, I. F. Rusina, and V. L. Rubailo, *Neftekhimiya* **30**, 639 (1990).
36. J. A. Howard and K. U. Ingold, *Can. J. Chem.* **45**, 785 (1967).
37. N. N. Pozdeeva, I. K. Yakuschenko, A. L. Aleksandrov, V. B. Luzhkov, and E. T. Denisov, *Kinet. Katal.* **30**, 31 (1989).
38. J. A. Howard and K. U. Ingold, *Can. J. Chem.* **44**, 1113 (1966).
39. M. M. Mogilevich and E. M. Pliss, *Oxidation and oxidative polymerization of non-saturated compounds* (Russian) Khimiya, Moscow, 1990.
40. E. T. Denisov and V. M. Solyanikov, *Neftekhimiya* **3**, 360 (1963).
41. C. Parlant, *Rev. Inst. Fr. Petrole Ann. Combust. Liquides* **19**, 1 (1964).
42. G. E. Zaikov, A. A. Vichutinskii, and Z. K. Maizus, *Kinet. Katal.* **8**, 675 (1967).
43. A. A. Fokin, *Oxidation of aromatic ketones in liquid phase by dioxygen*, Ph.D. Thesis (Russian), Kemerovo State University, Kemerovo, USSR, 1985.
44. A. L. Aleksandrov and E. T. Denisov, *Kinet. Katal.* **10**, 904 (1969).
45. H. R. Cooper and H. W. Melville, *J. Chem. Soc.* 1994 (1951).

46. T. A. Ingles and H. W. Melville, *Proc. R. Soc. London, Ser. A.*, **218**, 163 (1953).
47. V. I. Timokhin, *Reactivity and selectivity of free radicals and molecules of hydrocarbons in reaction of hydrogen atom abstraction*, Doctor Diss. Thesis (Russian), L'vov Polytech. Institute, L'vov, USSR, 1991.
48. D. L. Rakhmankulov, R. A. Karakhanov, S. S. Zlotskii, U. B. Imashev, E. A. Kantor, and A. M. Syrkin, in *Itogi Nauki i Techniki, Technology of organic compounds* (Russian), VINITI, Moscow, 1983, Vol. 7, p. 94.
49. G. A. Kovtun and A. L. Aleksandrov, *Izv. AN SSSR, Ser. Khim.* 1946 (1973).
50. B. I. Chernyak, I. M. Krip, and G. I. Donets, *Ukrain. Khim. Zh.* **47**, 1103 (1981).
51. V. A. Roginskii, *Kinet. Katal.* **31**, 546 (1990).
52. Yu. B. Shilov and E. T. Denisov, *Vysokomol. Soedin. A*, **11**, 1812 (1969).
53. C. Dekker, F. Mayo, and H. Richardson, *J. Polym. Sci.* **11**, 2875 (1973).
54. N. Ya. Rapoport, A. S. Goniashvily, and M. S. Akutin, *Vysokomol. Soedin. A*, **23**, 393 (1981).
55. A. V. Tobolsky, P. M. Norling, N. H. Frick, and M. Yu, *J. Am. Chem. Soc.* **86**, 3925 (1964).
56. Yu. B. Shilov and E. T. Denisov, *Vysokomol. Soedin. A*, **14**, 2385 (1972).
57. V. A. Roginskii, *Oxidation of polyolefins inhibited by sterically hindered phenols*, Doctor Diss. Thesis (Russian), Institute of Chemistry and Physics, Chernogolovka, USSR, 1983.
58. E. L. Shanina, V. A. Roginskii, and V. B. Miller, *Vysokomol. Soedin. A*, **18**, 1160 (1976).
59. J. C. W. Chien and D. S. F. Wang, *Macromolecules* **8**, 920 (1975).
60. B. Loy, *J. Phys. Chem.* **65**, 58 (1961).
61. N. Ya. Rapoport, A. Sh. Goniashvili, M. S. Akutin, and V. B. Miller, *Vysokomol. Soedin. A*, **20**, 1432 (1978).
62. A. V. Kirgin, Yu. B. Shilov, E. T. Denisov, and A. A. Efimov, *Vysokmol. Soedin. A*, **28**, 2236 (1986).
63. J. C. W. Chien and R. Boss, *J. Polym. Sci. A-1* N **12**, 3091 (1967).
64. E. Niki, C. Decker, and F. Mayo, *J. Polym. Sci. Polymer Chem. Ed.* **11**, 2813 (1973).
65. F. S. Dainton and M. Tordoff, *Trans. Faraday Soc.* **53**, 499 (1957).
66. V. A. Kabanov, D. A. Topchiev, and T. M. Karaputadze, *J. Polym. Sci., Part C*, **42**, 173 (1973).
67. A. F. Revzin and K. S. Bagdasaryan, *Zh. Fiz. Khim.* **38**, 1020 (1964).
68. N. Grassie and E. Vance, *Trans. Faraday Soc.* **52**, 727 (1956).
69. M. S. Matheson, E. E. Auer, E. B. Bevilacqua, and E. J. Hart, *J. Chem. Soc.* **73**, 5395 (1951).
70. Z. A. Sinitsyna and K. S. Bagdasaryan, *Zh. Fiz. Khim.* **32**, 1319 (1958).
71. S. E. Bresler, E. N. Kazbekov, and V. N. Shadrin, *Macromol. Chem.* **175**, 2875 (1974).
72. M. S. Matheson, E. E. Auer, E. B. Bevilacqua, and E. J. Hart, *J. Chem. Soc.* **73**, 1700 (1951).
73. M. Kinoshita, *Kobunshi Kagaku* **20**, 237 (1963).
74. M. Kinoshita, *Kobunshi Kagaku* **20**, 231 (1963).

75. G. M. Burnett and W. W. Wright, *Proc. R. Soc. London, Ser. A*, **211**, 41 (1954).
76. R. F. Vasiliev, *Prog. Reaction Kinet.* **4**, 305 (1967).
77. V. Ya. Shlyapintokh, O. N. Karpukhin, L. M. Postnikov, V. F. Tsepalov, A. A. Vichutinskii, and I. V. Zakharov, *Chemiluminescence Techniques in Chemical Reactions*, Consultants Bureau, New York, 1968.

Handbook of Free Radical Initiators. E.T. Denisov, T.G. Denisova, T.S. Pokidova
Copyright © 2003 John Wiley & Sons, Inc.
ISBN: 0-471-20753-5

4

DIALKYL PEROXIDES AND HYDROPEROXIDES

Peroxides are formed as active intermediate products in oxidation processes of organic compounds.[1-8] The chemistry of peroxides was intensely studied during the entire twentieth century.[1,2,9-15] Peroxides are widely used in chemical technology, first, as initiators of free radical polymerization, for the modification of polymers and second as network creation in elastomers and natural resins.[16-21] Inorganic peroxides are used for bleaching textiles and other products. Peroxides are used as reactants for olefin epoxidation and the production of phenol.[22] Peroxides are used as initiators of various liquid-phase chain reactions. They are produced as intermediates of oxidation processes in living organisms and participate in the creation of pathological processes. They are also formed in the atmosphere as products of the photochemical oxidation of volatile organic molecules.

4.1 DIALKYL PEROXIDES

Dialkyl peroxides are formed as products of autoxidation of hydrocarbons with tertiary C—H bonds as the result of the following peroxyl radical reactions:[3-8]

$$RO^{\bullet} + RH \rightarrow ROH + R^{\bullet}$$

$$R^{\bullet} + O_2 \rightarrow RO_2^{\bullet}$$

$$RO_2^{\bullet} + RO_2^{\bullet} \rightarrow ROOOOR$$

$$ROOOOR \rightarrow [RO^{\bullet} + RO^{\bullet}] + O_2$$

$$[RO^{\bullet} + RO^{\bullet}] \rightarrow ROOR$$

$$[RO^{\bullet} + RO^{\bullet}] \rightarrow RO^{\bullet} + RO^{\bullet}$$

They are also formed by the decomposition of tertiary hydroperoxides:[6]

$$ROOH \rightarrow RO^{\bullet} + HO^{\bullet}$$

$$RO^{\bullet} + HOOR \rightarrow ROH + RO_2^{\bullet}$$

$$RO_2^{\bullet} + RO_2^{\bullet} \rightarrow ROOR + O_2$$

4.1.1 Synthesis and Analysis

A number of methods for dialkyl peroxide synthesis was developed (see Table 4.1).

Physical properties of selected dialkyl peroxides are given in Table 4.2 and trade names are given in Table 4.3.

Different analytical techniques are known for the evaluation of dialkyl peroxides. The iodometric technique has been used for a long time.[23] According to this method, peroxide is reduced by hydrogen iodine with formation of diiodine in stoichiometric quantity. The amount of produced diiodine is measured by its reduction with thiosulfate using any titrometric technique or photometrically.

$$ROOR + 2HI \rightarrow 2ROH + I_2$$

$$2Na_2S_2O_3 + I_2 \rightarrow 2NaI + Na_2S_4O_6$$

Dialkyl peroxides possess low reactivity toward HI. The following procedure was proposed for analytical estimation of ROOR.[24] Reduction of peroxide by NaI occurs in a solution of acetic acid saturated with CO_2 in the presence of HCl at 320 K for 1 h. The evolved I_2 is estimated titrometrically. Its relative standard deviation is equal to 1%.

TABLE 4.1 Synthetic Methods of Production of Dialkyl Peroxides[a]

Reaction	Reactants	Catalyst
$RX + R^1OOK \rightarrow R^1OOR + KX$	RX, R^1OOH, H_2O_2	KOH
$Me_3COOH + Me_2C{=}CHMe \rightarrow Me_3COOCMe_2CH_2Me$	Me_3COOH, olefin	H_2SO_4, $HClO_4$
$ROOH + R^1OSO_3H \rightarrow ROOR^1 + H_2SO_4$	ROOH, R^1OSO_3H	
$ROOH + R^1COH \rightarrow ROOR^1 + H_2O$	ROOH, R^1COH	H_2SO_4, $HClO_4$
ROOH + *cyclo*-$[R^1CHCMe_2O] \rightarrow ROOCMe_2CHR^1OH$	ROOH, epoxide	
$ROOH + MeC(OR^1)_2 \rightarrow ROOC(OR^1)Me + R^1OH$	ROOH, $MeC(OR^1)_2$	

[a] See Refs. 11–15.

TABLE 4.2 Physical Properties of Some Dialkyl Peroxides[a]

Peroxide	CAS Registry Number	Belstein Registry Number	MW	bp (K)	mp (K)	ρ (kg m^{-3})	n_D^{293}
Dimethyl-, MeOOMe	690-02-8	1730817	62.07	287	173	867.7	1.3503
Diethyl-, EtOOEt	628-37-5	1731371	90.12	338	203	824.0	1.3715
Bis(1,1-dimethylethyl)-, $Me_3COOCMe_3$	110-05-4	1735581	146.23	384	233	704.2	1.3890
Bis(2-methylpropyl)-, $[Me_2CHCH_2O]_2$	32752-09-3	1735586	146.23	308			1.3996
Bis(1,1-dimethylpropyl)-, $[EtMe_2CO]_2$	10508-09-5	1738675	174.28	331	218	808.2	1.4095
Bis(1-methyl-1-phenylethyl)-, $[PhMe_2CO]_2$	80-43-3	2056090	270.37	373	312	1084.1	

[a] See Ref. 14.

TABLE 4.3 Trade Names of Dialkyl Peroxides and Hydroperoxides

Compound	Trade Name	Company
Peroxide		
Bis(1,1-dimethylethyl)-, $Me_3COOCMe_3$	Luperox DI	Elf atochem
	Peroximon DI	Elf atochem
	Perbutyl D	Nippon Oil & Fats Co
	Trigonox B	Akzo
	Interox DTB	Interox
Bis(1,1-dimethylpropyl)-, $EtMe_2COOCMe_2Et$	Luperox DTA	Elf atochem
Bis(1-methyl-1-phenylethyl)-, $PhMe_2COOCMe_2Ph$	Luperox DC	Elf atochem
	Peroximon DCSC	Elf atochem
	Percumyl D	Nippon Oil & Fats Co
	Perkadox SB	Akzo
	Interox DCUP	Interox
1,1-Dimethylethyl 1-methyl-1-phenylethyl-, $PhMe_2COOCMe_3$	Luperox 801	Elf atochem
	Perbutyl C	Nippon Oil & Fats Co
	Trigonox T	Akzo
	Interox BCUP	Interox
2,5-Dimethyl-2,5-bis(1,1-dimethylethylperoxy)hexane-, $Me_3COOCMe_2CH_2CH_2$-CMe_2OOCMe_3	Luperox 101	Elf atochem
	Perhexa 25B	Nippon Oil & Fats Co
	Interox DHBP	Interox
2,5-Dimethyl-2,5-bis(1,1-dimethylethylperoxy)hexyne-3, $Me_2(Me_3COO)CC\equiv CC(OOCMe_3)Me_2$	Luperox 130	Elf atochem
	Perhexyne 25B	Nippon Oil & Fat Co

(continued overleaf)

TABLE 4.3 (*continued*)

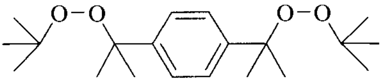
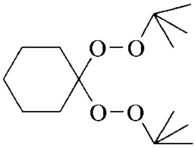
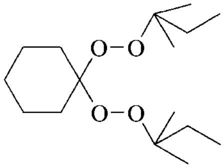
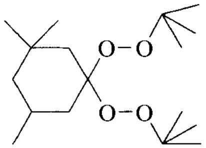
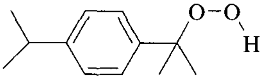
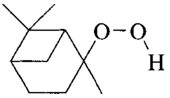
Compound	Trade Name	Company
1,4-Bis(1-methyl-1-(1,1-dimethylethyldioxy)ethylbenzene)-, 	Luperox F Perbutyl P Perkadox 14	Elf atochem Nippon Oil & Fats Co Akzo
Perketales		
1,1-Bis(1,1-dimethylethylperoxy)-cyclohexane 	Luperox 331 Peroximon 331 Perhexa C Trigonox 22 Interox CH	Elf atochem Elf atochem Nippon Oil & Fats Co Akzo Interox
1,1-Bis(1,1-dimethylpropylperoxy)-cyclohexane 	Luperox 531	Elf atochem
2,2-Bis(1,1-dimethylethylperoxy)butane, $Me_3COOCMeEtOOCMe_3$	Luperox 220 Peroxymon 220 Perhexa 22 Interox BU	Elf atochem Elf atochem Nippon Oil & Fats Co Interox
1,1-Bis(1,1-dimethylethylperoxy)-3,3,5-trimethylcyclohexane, 	Luperox 231 Peroximon 231 Perhexa 3M Trigonox 29	Elf atochem Elf atochem Nippon Oil & Fats Co Akzo
2,2-Bis(1,1-dimethylethylperoxy)octane, $(Me_3COO)_2MeC(CH_2)_5Me$	Perhexa O	Nippon Oil & Fats Co
Butyl-4,4-bis(1,1-dimethylethylperoxy)valerate, $(Me_3COO)_2MeC(CH_2)_2C(O)OBu$	Luperox 230 Perhexa V	Elf atochem Nippon Oil & Fats Co
Butyl-3,3-bis(1,1-dimethylethylperoxy)butyrate, $(Me_3COO)_2MeCCH_2C(O)OBu$	Luperox 233	Elf atochem

TABLE 4.3 (*continued*)

Compound	Trade Name	Company
Hydroperoxide		
1,1-Dimethylethyl-,	Luperox TBH 70X	Elf atochem
Me_3COOH	Peroximon TBH 70X	Elf atochem
	Perbutyl H	Nippon Oil & Fats Co
	Trigonox A-W-70	Akzo
	Interox TBHP	Interox
1,1-Dimethylpropyl-, $EtMe_2COOH$	Luperox TAH 85	Elf atochem
Cumyl-, $Me_2PhCOOH$	Luperox CU 80	Elf atochem
	Percumyl H	Nippon Oil & Fats Co
	Trigonox K	Akzo
	Interox CUHP	Interox
2-(4-Methylethylphenyl)-2-propyl-,	Percumyl P	Nippon Oil & Fats Co
	Trigonox M	Akzo
2,5-Dimethylhexane-2,5- dimethylhexane-2,5-di-, $HOOCMe_2CH_2CH_2CMe_2OOH$	Perhexa 25H	Nippon oil & Fats Co
1,1,3,3-Tetramethylbutyl-, $Me_3CCH_2CMe_2OOH$	Perocta H	Nippon Oil & Fats Co
Pinyl-, 	Interox PIHP	Interox

Polarography is used for measuring diacyl peroxides.[23] The reduction of peroxide performs according to the following electrochemical equation:

$$ROOR + 2e^- \rightarrow 2RO^-$$

The individual polarographic characteristic of analyzed compounds is the potential $E_{1/2}$ at which the current strength equals 50% of its maximum. The binary solvent benzene/methanol or benzene/ethanol is used. The amount of peroxide is proportional to the maximum strength of the electric current at peroxide concentration in solution <0.01 mol L^{-1}. The values of $E_{1/2}$ for dialkyl peroxides (ROOR) in benzene/ethanol solution (1/1) at [LiCl] $= 0.3$ mol L^{-1} are the following:[25]

R	Me_3C	$Me_3CCH_2Me_2C$	*p*-Menthyl-	Pinyl-	$PhMe_2C$
$E_{1/2}$ (V)	−2.10	−1.93	−1.75	−1.88	−1.60

Liquid and paper chromatography as well as MS are used for identification and analysis of dialkyl peroxides.[23] NMR spectroscopy is used for identification of dialkyl peroxides.

4.1.2 Structure of Dialkyl Peroxides

The structure of dialkyl peroxides was studied by experimental [rentgen structural analysis (RSA) and electronography (EG)] and theoretical [quantum chemical calculation (QCH)] methods. The results of experimental measurements and theoretical calculations are collected in Table 4.4.

Dialkyl peroxides possess weak UV absorption at $\lambda \approx 300$ nm.[23] Peroxides with chromophorous groups have an intense UV and visual absorption at λ that is characteristic of this group (C=O, NO_2, etc.). Quinolide peroxide has an intense absorption band at $\lambda = 239$ nm, which is due to the quinone system.[23] Analysis of the IR spectrum of dialkyl peroxides (ROOR) gives the O—O valence vibration a frequency that varies from 820 to 890 cm^{-1} and decreases with increasing the weight of peroxide.[23]

R	Et	Bu	EtMeCH	Me_3C	MePrCH	Me_2PhC
ν(O—O) (cm^{-1})	882	846	854	878	854	855

For the values of dipole moments and polarization of dialkyl peroxides, see Table 4.5.

4.1.3 Thermochemistry of Dialkyl Peroxides

The values for enthalpies of dialkyl peroxide formation in the gas and liquid phases are presented in Table 4.6. The value for the increment of formation enthalpy (gas phase) of ROOR $\Delta H[(O){-}O{-}(C)] = -19.2\ kJ\,mol^{-1}$, in the liquid phase $\Delta H[(O){-}O{-}(C)] = -28.14\ kJ\,mol^{-1}$, and additional increments for the di-*tert*-alkyl structure $\Delta H[(C)_3C{-}OO{-}C(C)_3] = -5.72\ kJ\,mol^{-1}$.[34]

The O—O bond dissociation energies of ROOR D(O—O) ($kJ\,mol^{-1}$) are equal.[35,36]

R	Et	n-C_3H_7	Me_2CH	Me_3C	Me_2PhC	CF_3
D(O—O)	161.5	161.5	163.6	162.7	158.8	195.8

4.1.4 Decomposition of Dialkyl Peroxides

Dialkyl peroxides decompose with splitting of the weakest O—O bond. The pair of forming alkoxyl radicals recombine or disproportionate in the cage or leave the cage (see Chapter 2).

$$ROOR \rightarrow [RO^{\bullet} + RO^{\bullet}]$$

$$[RO^{\bullet} + RO^{\bullet}] \rightarrow ROOR$$

TABLE 4.4 Bond Lengths and Bond Angles in Dialkyl Peroxides

	Bond Length (10^{-10} m)		Bond Angles (°)				
Peroxide	O–O	O–C	O–O–C	O–C–C	C–OO–C	Method	Reference
Bis(1,1-dimethylethyl)-, $Me_3COOCMe_3$	1.478	1.439	100.7	110.8	164.0	RSA	26
Bis(1,1-dimethylethyl)-, $Me_3COOCMe_3$			104.0	106.5		QCH	26
Bis(1,1-dimethylethyl)-, $Me_3COOCMe_3$	1.480	1.460		108.1	165.8	ED	27
Bis(1-methyl-1-phenylethyl)-, $PhMe_2COOCMe_2Ph$	1.486	1.442	102.0	110.1	180.0	RSA	28
Bis(triphenylmethyl)-, $Ph_3COOCPh_3$	1.479	1.459	100.0	109.9	180.0	RSA	29
Bis(triphenylmethyl)-, $Ph_3COOCPh_3$	1.480	1.461		107.5	180	RSA	15
Dimethyl-, MeOOMe	1.462	1.448	105.8	110.7	122.0	QCH	30
Bis(trifluoromethyl)-, CF_3OOCF_3	1.408	1.368	105.2	111.5	122.4	QCH	30
Bis(trifluoromethyl)-, CF_3OOCF_3	1.419	1.399	107.2		123.3	EG	15

(*continued overleaf*)

TABLE 4.4 (*continued*)

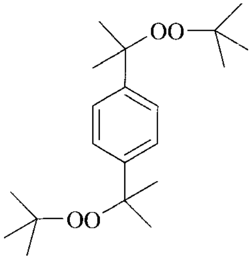
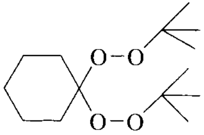
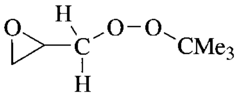
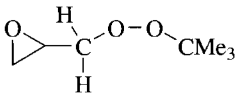
Peroxide	Bond Length $(10^{-10}$ m)		Bond Angles (°)			Method	Reference
	O–O	O–C	O–O–C	O–C–C	C–OO–C		
Diperoxide, bis(1,1-dimethylethyl) 1,4-(2-propylidene)benzene, 	1.480	1.443	101.4	110.8	152.6	RSA	31
Diperoxide, bis(1,1-dimethylethyl) 1,1-cyclohexylidene, 	1.482	1.449	101.3		153.6	RSA	31

TABLE 4.5 Dipole Moments (μ) and Polarization (P) of Dialkyl Peroxides in Benzene[a]

Peroxide	T (K)	μ (D)	P ($cm^3\ mol^{-1}$)
Butyl 1,1-dimethylethyl-, $BuOOCMe_3$	303	1.19	70.95
Bis(1,1-dimethylethyl)-, $Me_3COOCMe_3$	298	0.92	60.78
Bis(1,1-dimethylethyl)-, $Me_3COOCMe_3$	303	0.94	60.86
Bis(1,1-dimethylethyl)-, $Me_3COOCMe_3$	323	0.95	60.05
1,1-Dimethylethyl dimethylaminomethyl-, $Me_3COOCH_2NMe_2$	298	0.95	
1,1-Dimethylethyl *N*,*N*-bis(1-methylethyl)aminomethyl-, $Me_3COOCH_2N(CHMe_2)_2$	298	1.28	

[a] See Refs. 32 and 33.

TABLE 4.6 Enthalpies ΔH_f^0 and Entropies S^0 of Dialkyl Peroxide Formation in the Gas and Condensed Phases

Peroxide	Phase	$-\Delta H_f^0$ ($kJ\,mol^{-1}$)	S^0 ($J\,mol^{-1}\,K$)	References
Dimethyl-, MeOOMe	Gas	125.9	312.1	37
Diethyl-, EtOOEt	Gas	192.8	390.8	38
Diethyl-, EtOOEt	Liquid	223.4		37
Bis(1,1-dimethylethyl)-, $Me_3COOCMe_3$	Gas	349.1	469	39
Bis(1,1-dimethylethyl)-, $Me_3COOCMe_3$	Gas	340.7		15
Bis(1,1-dimethylethyl)-, $Me_3COOCMe_3$	Liquid	381.2		37
1,1-Dimethylethyl oxyranylmethyl-, 	Gas	267.4		40,41
1,1-Dimethylethyl oxyranylmethyl-, 	Liquid	321.3		40
1,1-Dimethylethyl hydroxymethyl-, Me_3COOCH_2OH	Gas	397.3		41,42
1,1-Dimethylethyl hydroxymethyl-, Me_3COOCH_2OH	Liquid	460.6		42
1,1-Dimethylethyl 2-hydroxyethyl-, $Me_3COOCH_2CH_2OH$	Gas	445.4		41,42
1,1-Dimethylethyl 2-hydroxyethyl-, $Me_3COOCH_2CH_2OH$	Liquid	511.7		43

(*continued overleaf*)

TABLE 4.6 (*continued*)

Peroxide	Phase	$-\Delta H_f^0$ (kJ mol^{-1})	S^0 (J mol^{-1} K)	References
1,1-Dimethylpropyl 2-hydroxyethyl-, $\mathrm{EtMe_2COOCH_2CH_2OH}$	Gas	463.8		41,42
1,1-Dimethylpropyl 2-hydroxyethyl-, $\mathrm{EtMe_2COOCH_2CH_2OH}$	Liquid	534.2		42
1,1-Dimethylethyl 2,3-dihydroxypropyl-, $\mathrm{Me_3COOCH_2CH(OH)CH_2OH}$	Gas	631.7		41,42
1,1-Dimethylethyl 2,3-dihydroxypropyl-, $\mathrm{Me_3COOCH_2CH(OH)CH_2OH}$	Liquid	719.2		42
1,1-Dimethylethyl 4-hydroxy-1,1,4-trimethyl-pentyl,- $\mathrm{Me_3COOCMe_2CH_2CH_2Me_2COH}$	Gas	622.7		41,43
1,1-Dimethylethyl 4-hydroxy-1,1,4-trimethyl-pentyl,- $\mathrm{Me_3COOCMe_2CH_2CH_2Me_2COH}$	Liquid	696.9		43
Diperoxide, bis(1,1-dimethylethyl) 1,1,4,4-tetramethyltetramethylene-, $\mathrm{Me_3COOCMe_2CH_2CH_2Me_2COOCMe_3}$	Gas	656.3		41,43
Diperoxide, bis(1,1-dimethylethyl) 1,1,4,4-tetramethyltetramethylene-, $\mathrm{Me_3COOCMe_2CH_2CH_2Me_2COOCMe_3}$	Liquid	725.2		43
Diperoxide, bis(1,1-dimethylethyl) 1,1,4,4,7,7,10,10-octamethyl-5,6-dioxa-1,10-decalidene- $\mathrm{Me_3COO[CMe_2CH_2CH_2Me_2COO]_2CMe_3}$	Gas	990.2		41,44
Diperoxide, bis(1,1-dimethylethyl) 1,1,4,4,7,7,10,10-octamethyl-5,6-dioxa-1,10-decalidene- $\mathrm{Me_3COO[CMe_2CH_2CH_2Me_2COO]_2CMe_3}$	Liquid	1059.1		44
1,1-Dimethylethyl 1,1-dimethylpent-2-yn-4-enyl-, $\mathrm{Me_3COOCMe_2C{\equiv}CCH{=}CH_2}$	Gas	−26.0		41,45
1,1-Dimethylethyl 1,1-dimethylpent-2-yn-4-enyl-, $\mathrm{Me_3COOCMe_2C{\equiv}CCH{=}CH_2}$	Liquid	28.8		45
1,1-Dimethylethyl 1-methyl-1-phenylethyl-, $\mathrm{PhMe_2COOCMe_3}$	Gas	200.4		41,46
1,1-Dimethylethyl 1-methyl-1-phenylethyl-, $\mathrm{PhMe_2COOCMe_3}$	Liquid	263.0		46
Bis(1-methyl-1-phenylethyl)-, $\mathrm{[PhMe_2CO]_2}$	Gas	58.0		47
Bis(1-methyl-1-phenylethyl)-, $\mathrm{[PhMe_2CO]_2}$	Solid	166.0		47

$$[\mathrm{RO}^{\bullet} + \mathrm{RO}^{\bullet}] \rightarrow \mathrm{ROH} + \text{carbonyl compound}$$

$$[\mathrm{RO}^{\bullet} + \mathrm{RO}^{\bullet}] \rightarrow \mathrm{RO}^{\bullet} + \mathrm{RO}^{\bullet}$$

The rate constants of dialkyl peroxides decomposition are presented in Tables 4.7–4.11. The value of the probability of formed radical pairs to leave a cage ($e = k_i/2k_d$) are given in Table 4.12.

TABLE 4.7 Rate Constants for the Thermal Decay of Bis(1,1-dimethylethyl) Peroxide in the Gas Phase and Various Solvents

Phase, Solvent	T (K)	E (kJ mol^{-1})	log A, A (s^{-1})	k_d, k_i (400 K) (s^{-1})	Reference
		k_d			
Gas phase	374–418	161.9	16.40	1.81×10^{-5}	48
Gas phase	433–551	160.2	16.08	1.45×10^{-5}	49
Gas phase	403–433	156.5	15.60	1.46×10^{-5}	50
Gas phase	418–453	159.4	16.13	2.06×10^{-5}	51
Gas phase	363–403	158.2	15.80	1.39×10^{-5}	52
Gas phase	363–623	158.6	15.81	1.26×10^{-5}	52
Gas phase	413–433	163.6	16.50	1.37×10^{-5}	53
Gas phase	528–677	152.3	15.50	4.09×10^{-5}	54
Gas phase	500–600	156.5	15.60	1.46×10^{-5}	55
Acetic acid	388–403	137.1	13.54	4.33×10^{-5}	56
Acetonitrile	388–403	133.0	13.00	4.29×10^{-5}	56
Aniline, *N*,*N*-dimethyl-	393–408	160.1	16.27	2.31×10^{-5}	56
Benzene	393–408	151.0	15.10	2.41×10^{-5}	56
Benzene	393			1.39×10^{-5}	57
Benzoic acid, ethyl ester	393–408	151.7	15.19	2.40×10^{-5}	56
Carbon tetrachloride	393			9.0×10^{-6}	58
Cyclohexane	393–408	174.1	17.98	1.76×10^{-5}	56
Cyclohexene	393			8.30×10^{-6}	58
Cyclohexene	393–408	159.7	16.11	1.80×10^{-5}	56
Decane	383			2.63×10^{-6}	59
Ethanol, 1,1-dimethyl-	393–408	146.3	14.60	3.13×10^{-5}	56
Neopentyl butanoate	408–438	122.0	11.65	5.23×10^{-5}	60
Neopentyl 2,2-dimethylpropanoate	408–438	144.8	14.32	2.58×10^{-5}	60
Neopentyl 3,3-dimethylbutanoate	408–438	141.5	14.05	3.73×10^{-5}	60
Neopentyl 2,2-dimethylbutanoate	408–438	148.2	14.74	2.44×10^{-5}	60

(*continued overleaf*)

TABLE 4.7 ***(continued)***

Phase, Solvent	T (K)	E (kJ mol^{-1})	log A, A (s^{-1})	k_d, k_i (400 K) (s^{-1})	Reference
Neopentyl 2-methylbutanoate	408–438	115.2	10.73	4.86×10^{-5}	60
Neopentyl 2-methylpropanoate	408–438	135.7	13.18	2.88×10^{-5}	60
Nitrobenzene	393–408	152.3	15.41	3.33×10^{-5}	56
Nitroethane	393–408	151.9	15.31	2.98×10^{-5}	56
Propanol, 1,1-dimethyl-	393–408	159.7	16.11	1.80×10^{-5}	56
Tetrahydrofuran	393–408	158.6	16.13	2.63×10^{-5}	56
Toluene	393			1.34×10^{-5}	57
Triethylamine	393–408	172.6	17.87	2.14×10^{-5}	56
		$k_i = 2ek_d$			
Benzene	373–398	150.6	15.10	2.72×10^{-5}	61
Ethanol, 1-methyl-	359–411	146.4	14.64	3.33×10^{-5}	62
Styrene	313–371	146.4	14.45	2.15×10^{-5}	63
Styrene	353–373	161.5	16.21	1.32×10^{-5}	64
Styrene	363–373	157.3	15.86	2.08×10^{-5}	65
Benzene/Styrene (1:1 V/V)	333–353	146.4	14.12	1.01×10^{-5}	66

TABLE 4.8 Rate Constants for the Thermal Decay of Bis(1-methyl-1-phenylethyl) Peroxide in Various Solvents

Solvent	T (K)	E (kJ mol^{-1})	log A, A (s^{-1})	k_d, k_i(400 K) (s^{-1})	Reference
		k_d			
Benzene	398			1.38×10^{-5}	57
Carbon tetrachloride	398			8.91×10^{-6}	57
Cumene	383–423	144.3	14.63	6.12×10^{-5}	67
Cyclohexane	398			8.32×10^{-6}	57
Decane	373–413	143.5	14.57	6.78×10^{-5}	56
Dodecane	401–431	140.2	14.17	7.28×10^{-5}	68
Styrene	368–378	166.9	17.76	9.24×10^{-5}	67
Toluene	398			1.35×10^{-6}	57
		$k_i = 2ek_d$			
Benzene	373–398	146.0	14.70	4.31×10^{-5}	61
Chlorobenzene	368–398	133.8	13.18	5.10×10^{-5}	69

TABLE 4.8 (*continued*)

Solvent	T (K)	E (kJ mol^{-1})	log A, A (s^{-1})	k_d, k_i(400 K) (s^{-1})	Reference
Paraffin oil	393–423	135.6	13.51	6.35×10^{-5}	70
Octadiene-1,7 2,6-dimethyl-	393–423	133.9	13.26	5.95×10^{-5}	71
(Z)-1,4-Polyisoprene	393–423	135.9	13.15	2.53×10^{-5}	72
Mineral oil	393–423	141.8	14.43	8.19×10^{-5}	73
PE	384–402	156.0	15.94	3.71×10^{-5}	74
PE	378–403	143.0	14.15	3.00×10^{-5}	75
PE	388			8.1×10^{-6}	76

4.2 HYDROPEROXIDES AND PERACIDS

Hydroperoxides are formed primarily as stable products of the chain oxidation of hydrocarbon RH and other organic compounds by dioxygen. The chain mechanism of hydrocarbon oxidation with hydroperoxide formation is the following:[4–8]

$$R^{\bullet} + O_2 \rightarrow RO_2^{\bullet}$$

$$RO_2^{\bullet} + RH \rightarrow ROOH + R^{\bullet}$$

Peracids RC(O)OOH are produced primarily as molecular products of aldehyde oxidation by dioxygen[5,6]

$$RC^{\bullet}(O) + O_2 \rightarrow RC(O)OO^{\bullet}$$

$$RC(O)OO^{\bullet} + RCHO \rightarrow RC(O)OOH + RC^{\bullet}(O)$$

Hydroperoxides decomposing to free radicals result in the acceleration of autooxidation of hydrocarbons.

4.2.1 Synthesis and Analysis of Hydroperoxides

Two synthetic methods of hydroperoxides are widely used: autoxidation of hydrocarbons and different reactions of the alkylation of hydrogen peroxide (see Table 4.13). Physical properties of some hydroperoxides are collected in Table 4.14 and trade names are given in Table 4.3.

Many different analytical techniques are known for the estimation of hydroperoxides and peracids. Among them, the iodometric technique has been used for a long time.[23] According to this method, peroxide is reduced by HI and I_2 is formed in stoichiometric quantity. The amount of formed I_2 is measured by reduction with thiosulfate by using any titrometric technique or photometrically.

$$ROOH + 2HI \rightarrow ROH + H_2O + I_2$$

$$2Na_2S_2O_3 + I_2 \rightarrow 2NaI + Na_2S_4O_6$$

TABLE 4.9 Rate Constants for the Thermal Decay of Dialkyl Peroxides in the Gas Phase and Various Solvents

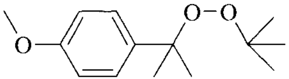
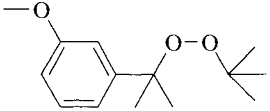
Peroxide	Solvent	T (K)	E (kJ mol^{-1})	log A, A (s^{-1})	k_d, k_i (400 K) (s^{-1})	Reference
			k_d			
Dimethyl-, MeOOMe	Gas phase	428–453	154.4	15.61	2.80×10^{-5}	77
Dimethyl-, MeOOMe	Gas phase	393–435	147.7	15.20	8.18×10^{-5}	78
Dimethyl-, MeOOMe	Gas phase	403–460	155.2	15.70	2.71×10^{-5}	79
Dimethyl-, MeOOMe	Gas phase	430–510	159.2	16.10	2.05×10^{-5}	80
Dimethyl-, MeOOMe	Gas phase		154.4	15.60	2.74×10^{-5}	81
Dimethyl-, MeOOMe	Gas phase		147.7	15.20	8.18×10^{-5}	82
Dimethyl-, MeOOMe	Gas phase		155.2	15.70	2.71×10^{-5}	83
Dimethyl-, MeOOMe	Gas phase		159.0	16.10	2.17×10^{-5}	84
Diethyl-, EtOOEt	Gas phase	433–513	125.1	12.04	5.06×10^{-5}	85
Diethyl-, EtOOEt	Gas phase	473–518	132.6	13.30	9.65×10^{-5}	86
Diethyl-, EtOOEt	Gas phase	403–443	127.2	12.68	1.17×10^{-4}	87
Diethyl-, EtOOEt	Gas phase	407–441	156.0	16.10	5.36×10^{-5}	88
Dipropyl-, PrOOPr	Gas phase	373–423	146.4	14.96	6.96×10^{-5}	89
Bis(1-methylethyl)-, $Me_2CHOOCHMe_2$	Gas phase	421–458	155.2	15.40	1.36×10^{-5}	88
Bis(1-methylethyl)-, $Me_2CHOOCHMe_2$	Gas phase	378–422	154.0	15.15	1.10×10^{-5}	90
Dibutyl-, BuOOBu	Gas phase	423–473	160.2	16.20	1.91×10^{-5}	91
Bis(1-methylpropyl)-, EtMeCHOOCHEtMe	Gas phase	373–413	150.6	15.25	3.84×10^{-5}	92
Bis(1,1-dimethylpropyl)-, $EtMe_2COOCEtMe_2$	Gas phase	523–633	152.3	15.80	8.17×10^{-5}	55

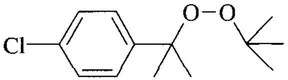
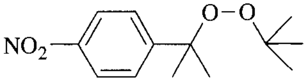
Dinonyl-, $[Me(CH_2)_7CH_2O]_2$	Gas phase	423–473	152.6	15.60	4.71×10^{-5}	91
Bis(1,1,2,2-tetramethylpropyl)-, $Me_3CMe_2COOCMe_2CMe_3$	Cumene	398			4.84×10^{-4}	93
Bis(trifluoromethyl)-, CF_3OOCF_3	Gas phase		193.3	15.20	9.08×10^{-11}	94
Bis(trifluoromethyl)-, CF_3OOCF_3	Gas phase		193.7	16.10	6.39×10^{-10}	95
Bis(trifluoromethyl)-, CF_3OOCF_3	Gas phase		193.3	15.90	4.55×10^{-10}	96
		$k_i = 2ek_d$				
Diethyl-, EtOOEt	Benzene/styrene[a]	333–353	142.7	14.16	3.35×10^{-5}	97
Dipropyl-, PrOOPr	Styrene	333			2.70×10^{-9}	98
Bis(1-methylethyl)-, $Me_2CHOOCHMe_2$	Benzene/styrene[a]	333–353	156.0	15.27	7.92×10^{-6}	97
Dibutyl-, BuOOBu	Benzene/styrene[a]	333–353	143.5	13.98	1.74×10^{-5}	99
Bis(1-methylpropyl)-, EtMeCHOOCHEtMe	Benzene/styrene[a]	333–353	142.3	13.56	9.50×10^{-6}	97
Bis(1,1-dimethylpropyl)-, $EtMe_2COOCMe_2Et$	Styrene	353–373	145.6	15.48	2.93×10^{-4}	64
Bis(1,1-dimethylpropyl)-, $EtMe_2COOCEtMe_2$	Styrene	353–383	157.8	16.19	3.83×10^{-5}	65
Bis(1-methyl-1-ethylpropyl)-, $Et_2MeCOOCEt_2Me$	Styrene	353–383	159.0	16.55	6.12×10^{-5}	65

---

[a] Benzene/styrene (1:1 *V*/*V*).

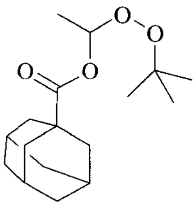
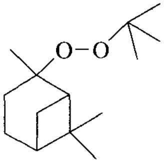
TABLE 4.10 Rate Constants for the Thermal Decay of Me_3COOR Peroxides in Various Solvents

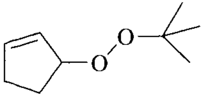
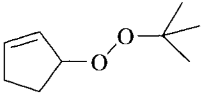
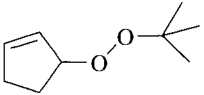
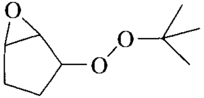
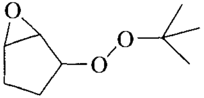
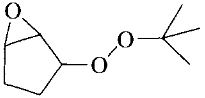
Peroxide, 1,1-Dimethylethyl-[a]	Solvent	T (K)	E (kJ mol^{-1})	log A, A (s^{-1})	k_d, k_i (400 K) (s^{-1})	Reference
		k_d				
1,1-Dimethylpropyl-, $Me_3COOCEtMe_2$	Decane	383–403	126.8	12.26	5.03×10^{-5}	59
1,1-Dimethylpropyl-, $Me_3COOCEtMe_2$	Cumene	383–413	163.2	16.83	3.30×10^{-5}	100
1,1-Dimethylbutyl-, $Me_3COOCMe_2Pr$	Cumene	383–413	159.9	15.91	1.07×10^{-5}	100
1,1,2,2-Tetramethylpropyl-, $Me_3COOCMe_2CMe_3$	Cumene	393–413	150.8	15.61	8.28×10^{-5}	100
1,1,2-Trimethylpropyl-, $Me_3COOC(Me)_2CHMe_2$	Cumene	383–413	152.9	15.70	5.42×10^{-5}	100
2-Chloro-1,1-dimethylethyl-, $Me_3COOCMe_2CH_2Cl$	Cumene	393–423	159.5	16.4	3.73×10^{-5}	100
1,1-Dimethyl-2-phenylethyl-, $Me_3COOCMe_2CH_2Ph$	Cumene	383–413	153.9	15.64	3.49×10^{-5}	100
1-Methyl-1-phenylethyl-, $Me_3COOCMe_2Ph$	Decane	383–403	151.8	15.40	3.78×10^{-5}	59
1-Methyl-1-phenylethyl-, $Me_3COOCMe_2Ph$	Cumene	398			3.04×10^{-5}	93
1-Methyl-1-(4′-methoxyphenyl)ethyl-, 	Cumene	398			3.72×10^{-5}	93
1-Methyl-1-(3′-methoxyphenyl)ethyl-, 	Cumene	398			3.22×10^{-5}	100

1-Methyl-1-(4′-chlorophenyl)ethyl-, 	Cumene	398			3.42×10^{-5}	100
1-Methyl-(4′-nitrophenyl)ethyl-, 	Cumene	398			2.20×10^{-5}	100
Methoxyphenylmethyl-, $Me_3COOCH(OMe)Ph$	Tetradecane	383–423	165.3	17.53	8.80×10^{-5}	101
Methoxyphenylmethyl-, $Me_3COOCH(OMe)Ph$	Chlorobenzene	373–433	166.9	17.55	5.69×10^{-5}	101
Methoxyphenylmethyl-, $Me_3COOCH(OMe)Ph$	Dimethyl phthalate	373–433	164.4	17.34	7.45×10^{-5}	101
1-Methoxyheptyl-, $Me_3COOCH(OMe)(CH_2)_5Me$	Tetradecane	383–423	174.1	18.84	1.27×10^{-4}	101
1-Methoxyheptyl-, $Me_3COOCH(OMe)(CH_2)_5Me$	Chlorobenzene	373–433	174.9	18.91	1.22×10^{-4}	101
1-Methoxyheptyl-, $Me_3COOCH(OMe)(CH_2)_5Me$	Dimethyl phthalate	373–433	175.7	19.03	1.15×10^{-4}	101
Hydroxymethyl-, Me_3COOCH_2OH	Cumene	383–423	126.6	12.92	2.44×10^{-4}	102
1-Acetoxyethyl-, $Me_3COOCHMe(OAc)$	Chlorobenzene	383–413	89.5	8.20	3.26×10^{-4}	103
1-Propanoyloxyethyl-, $Me_3COOCHMe(OC(O)Et)$	Chlorobenzene	383–413	96.9	9.00	2.22×10^{-4}	103

(*continued overleaf*)

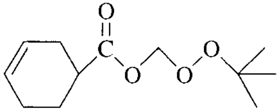
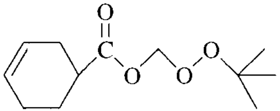
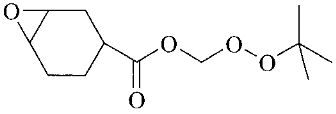
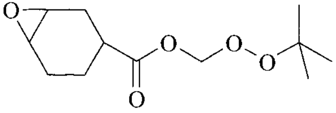
TABLE 4.10 (*continued*)

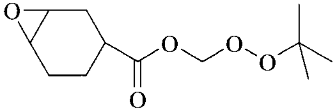
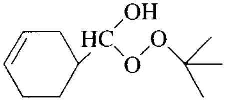
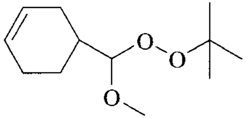
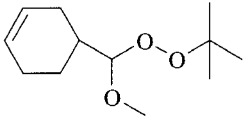
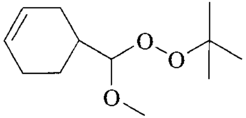
Peroxide, 1,1-Dimethylethyl-[a]	Solvent	T (K)	E (kJ mol^{-1})	log A, A (s^{-1})	k_d, k_i (400 K) (s^{-1})	Reference
1-Pentanoyloxyethyl-, $Me_3COOCHMeOC(O)Bu$	Chlorobenzene	383–413	85.7	7.60	2.56×10^{-4}	103
1-Nonanoyloxyethyl-, $Me_3COOCHMeOC(O)(CH_2)_7Me$	Chlorobenzene	383–413	122.5	12.80	6.36×10^{-4}	103
1-(1′,1′-Dimethylpropanoyloxy)ethyl-, $Me_3COOCHMeOC(O)CMe_3$	Chlorobenzene	383–413	116.1	11.70	3.46×10^{-4}	103
1-Adamantyl-1-carboxyethyl-, 	Chlorobenzene	383–413	124.2	12.40	1.52×10^{-4}	103
1-Benzoyloxyethyl-, $Me_3COOCHMeOC(O)Ph$	Chlorobenzene	383–413	134.8	14.10	3.14×10^{-4}	103
1-Pinyl-, 	Decane	383–400	121.3	11.48	4.37×10^{-5}	59

3-Cyclopentenyl-, 	Butanol	383–408	143.1	14.37	4.82×10^{-5}	104
3-Cyclopentenyl-, 	Chlorobenzene	393–413	152.3	15.64	5.65×10^{-5}	104
3-Cyclopentenyl-, 	*N*,*N*-Dimethylformamide	393–413	151.9	15.43	3.93×10^{-5}	104
2,3-Epoxycyclopentyl-, 	Butanol	383–408	139.7	14.26	1.04×10^{-4}	104
2,3-Epoxycyclopentyl-, 	Chlorobenzene	393–413	153.1	15.73	5.46×10^{-5}	104
2,3-Epoxycyclopentyl-, 	*N*,*N*-Dimethylformamide	393–413	155.6	15.43	1.29×10^{-5}	104

(*continued overleaf*)

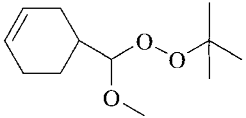
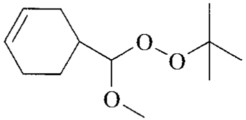
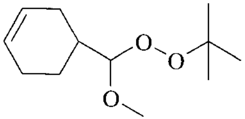
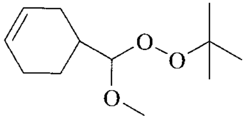
TABLE 4.10 (*continued*)

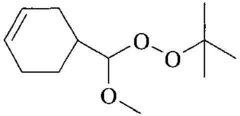
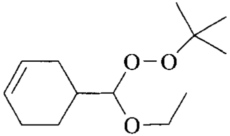
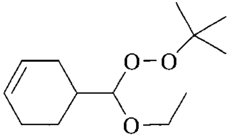
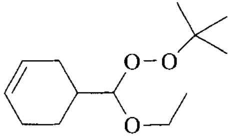
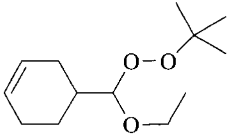
Peroxide, 1,1-Dimethylethyl-[a]	Solvent	T (K)	E (kJ mol^{-1})	log A, A (s^{-1})	k_d, k_i (400 K) (s^{-1})	Reference
3-Cyclohexenylcarboxymethyl-, 	Nitrobenzene	388–398	123.0	12.52	2.87×10^{-4}	104
3-Cyclohexenylcarboxymethyl-, 	*N*,*N*-Dimethylformamide	378–398	117.2	11.30	9.90×10^{-5}	104
3,4-Epoxycyclohexylcarboxymethyl-, 	Chlorobenzene	388–403	132.2	12.69	2.67×10^{-5}	104
3,4-Epoxycyclohexylcarboxymethyl-, 	Nitrobenzene	388–398	131.4	13.63	2.96×10^{-4}	104

3,4-Epoxycyclohexylcarboxymethyl, 	*N*,*N*-Dimethylformamide	378–398	128.9	13.75	8.27×10^{-4}	104
3-Cyclohexenylhydroxymethyl-, 	Dimethyl phthalate	398–408	135.1	12.84	1.50×10^{-5}	101
3-Cyclohexenylmethoxymethyl-, (eq) 	Tetradecane	398–423	160.2	17.52	3.98×10^{-4}	101
3-Cyclohexenylmethoxymethyl-, (eq) 	Chlorobenzene	373–398	150.6	16.23	3.66×10^{-4}	101
3-Cyclohexenylmethoxymethyl-, (eq) 	Dimethyl phthalate	373–408	156.9	17.20	5.14×10^{-4}	101

(continued overleaf)

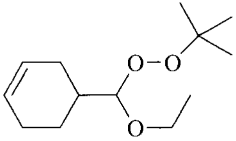
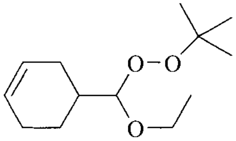
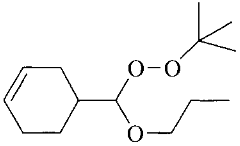
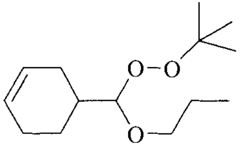
TABLE 4.10 (*continued*)

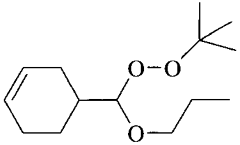
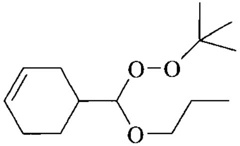
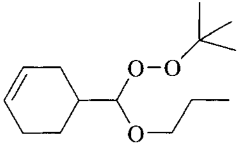
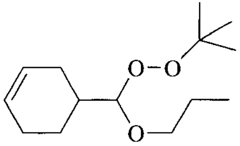
Peroxide, 1,1-Dimethylethyl-[a]	Solvent	T (K)	E (kJ mol^{-1})	log A, A (s^{-1})	k_d, k_i (400 K) (s^{-1})	Reference
3-Cyclohexenylmethoxymethyl-, (eq) 	1-Nonanol	373–398	156.1	17.01	4.22×10^{-4}	101
3-Cyclohexenylmethoxymethyl-, (ax) 	Tetradecane	398–423	170.3	18.55	2.05×10^{-4}	101
3-Cyclohexenylmethoxymethyl-, (ax) 	Chlorobenzene	388–408	160.2	17.27	2.24×10^{-4}	101
3-Cyclohexenylmethoxymethyl-, (ax) 	Dimethyl phthalate	418–433	164.0	17.99	3.75×10^{-4}	101

3-Cyclohexenylmethoxymethyl-, (ax) 	1-Nonanol	408–423	167.8	18.39	3.01×10^{-4}	101
3-Cyclohexenylethoxymethyl-, (eq) 	Tetradecane	383–388	154.8	16.54	2.12×10^{-4}	101
3-Cyclohexenylethoxymethyl-, (eq) 	Chlorobenzene	373–398	146.9	16.02	6.87×10^{-4}	101
3-Cyclohexenylethoxymethyl-, (eq) 	Dimethyl phthalate	373–408	149.8	16.08	3.30×10^{-4}	101
3-Cyclohexenylethoxymethyl-, (eq) 	Tetradecane	398–423	164.0	17.66	1.75×10^{-4}	101

(continued overleaf)

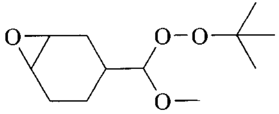
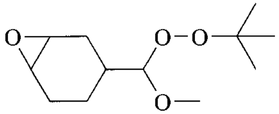
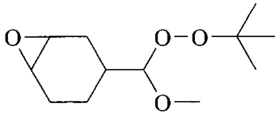
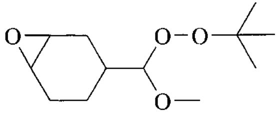
TABLE 4.10 (*continued*)

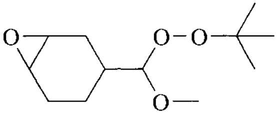
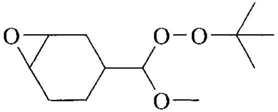
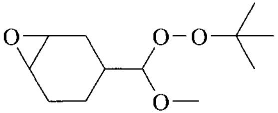
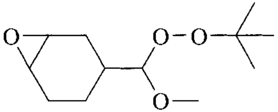
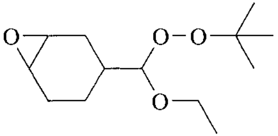
Peroxide, 1,1-Dimethylethyl-[a]	Solvent	T (K)	E (kJ mol^{-1})	log A, A (s^{-1})	k_d, k_i (400 K) (s^{-1})	Reference
3-Cyclohexenylethoxymethyl-, (eq) 	Chlorobenzene	373–398	154.4	16.77	4.05×10^{-4}	101
3-Cyclohexenylethoxymethyl-, (eq) 	Dimethyl phthalate	418–433	157.3	16.86	2.15×10^{-4}	101
3-Cyclohexenylpropoxymethyl-, (eq) 	Tetradecane	383–388	151.0	16.11	2.46×10^{-4}	101
3-Cyclohexenylpropoxymethyl-, (eq) 	Chlorobenzene	373–393	145.6	15.68	4.64×10^{-4}	101

3-Cyclohexenylpropoxymethyl-, (eq) 	Dimethyl phthalate	373–408	144.3	15.43	3.86×10^{-4}	101
3-Cyclohexenylpropoxymethyl-, (ax) 	Tetradecane	398–423	158.2	17.03	2.35×10^{-4}	101
3-Cyclohexenylpropoxymethyl-, (ax) 	Chlorobenzene	408–433	151.5	16.40	4.14×10^{-4}	101
3-Cyclohexenylpropoxymethyl-, (ax) 	Dimethyl phthalate	418–433	153.3	16.59	3.73×10^{-4}	101

(continued overleaf)

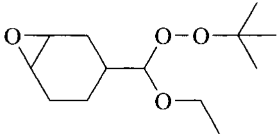
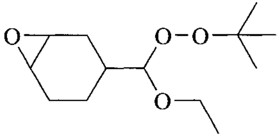
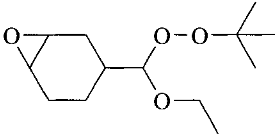
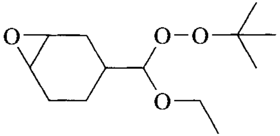
TABLE 4.10 (*continued*)

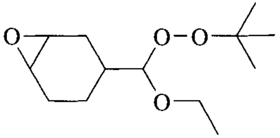
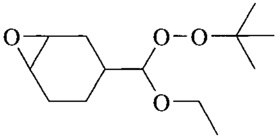
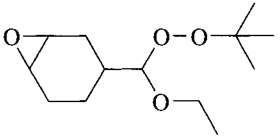
Peroxide, 1,1-Dimethylethyl-[a]	Solvent	T (K)	E (kJ mol^{-1})	log A, A (s^{-1})	k_d, k_i (400 K) (s^{-1})	Reference
3,4-Epoxycyclohexylmethoxymethyl-, (eq) 	Tetradecane	383–388	163.2	17.75	2.75×10^{-4}	101
3,4-Epoxycyclohexylmethoxymethyl-, (eq) 	Chlorobenzene	373–398	151.9	16.29	2.85×10^{-4}	101
3,4-Epoxycyclohexylmethoxymethyl-, (eq) 	Dimethyl phthalate	373–408	156.9	17.04	3.56×10^{-4}	101
3,4-Epoxycyclohexylmethoxymethyl-, (eq) 	1-Nonanol	373–398	159.4	17.45	4.31×10^{-4}	101

3,4-Epoxycyclohexylmethoxymethyl-, (ax) 	Tetradecane	393–423	172.0	18.89	2.69×10^{-4}	101
3,4-Epoxycyclohexylmethoxymethyl-, (ax) 	Chlorobenzene	408–433	162.3	17.57	2.38×10^{-4}	101
3,4-Epoxycyclohexylmethoxymethyl-, (ax) 	Dimethyl phthalate	418–433	164.4	17.96	3.10×10^{-4}	101
3,4-Epoxycyclohexylmethoxymethyl-, (ax) 	1-Nonanol	408–423	169.9	18.34	1.42×10^{-4}	101
3,4-Epoxycyclohexylethoxymethyl-, (eq) 	Tetradecane	383–388	161.5	17.44	2.24×10^{-4}	101

(*continued overleaf*)

TABLE 4.10 (*continued*)

Peroxide, 1,1-Dimethylethyl-[a]	Solvent	T (K)	E (kJ mol^{-1})	log A, A (s^{-1})	k_d, k_i (400 K) (s^{-1})	Reference
3,4-Epoxycyclohexylethoxymethyl-, (eq) 	Chlorobenzene	373–398	150.2	16.19	3.77×10^{-4}	101
3,4-Epoxycyclohexylethoxymethyl-, (eq) 	Dimethyl phthalate	373–408	154.0	16.39	1.91×10^{-4}	101
3,4-Epoxycyclohexylethoxymethyl-(eq) 	1-Nonanol	373–398	159.0	17.35	3.86×10^{-4}	101
3,4-Epoxycyclohexylethoxymethyl-, (ax) 	Tetradecane	398–423	169.5	18.34	1.61×10^{-4}	101

3,4-Epoxycyclohexylethoxymethyl-, (ax) 	Chlorobenzene	408–433	158.6	17.18	2.95×10^{-4}	101
3,4-Epoxycyclohexylethoxymethyl-, (ax) 	Dimethyl phthalate	418–433	160.7	17.14	1.43×10^{-4}	101
3,4-Epoxycyclohexylethoxymethyl-, (ax) 	1-Nonanol	408–423	169.0	18.35	1.91×10^{-4}	101
2-Trimethylsilyloxyethyl-, $Me_3SiOCH_2CH_2OOCMe_3$	Benzene	403–423	123.9	11.97	6.17×10^{-5}	102
2-Trimethylsilyloxypropyl-, $Me_3SiOCHMeCH_2COOCMe_3$	Benzene	403–423	122.6	11.92	8.13×10^{-5}	102
Trimethylsilyloxyethyl-, $Me_3SiOCH_2OOCMe_3$	Cumene	383–413	122.6	12.44	2.69×10^{-4}	102

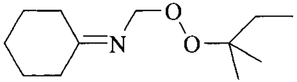
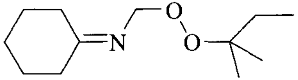
(*continued overleaf*)

TABLE 4.10 (*continued*)

Peroxide, 1,1-Dimethylethyl-[a]	Solvent	T (K)	E (kJ mol^{-1})	log A, A (s^{-1})	k_d, k_i (400 K) (s^{-1})	Reference
2-Triphenylsilyloxyethyl-, $Ph_3SiOCH_2CH_2OOCMe_3$	Benzene	403–423	130.2	12.83	6.73×10^{-5}	102
		$k_i = 2ek_d$				
2,4-Dioxapentyl-, $Me_3COOCH_2OCH_2OMe$	Styrene	353–373	130.1	12.79	6.32×10^{-5}	65
2,4-Dioxahexyl-, $Me_3COOCH_2OCH_2OEt$	Styrene	353–373	133.1	13.19	6.44×10^{-5}	65
2,4-Dioxaheptyl-, $Me_3COOCH_2OCH_2OPr$	Styrene	353–373	136.8	13.67	6.40×10^{-5}	65
5-Methyl-2,4-dioxahexyl-, $Me_3COOCH_2OCH_2OCHMe_2$	Styrene	353–373	139.7	14.18	8.65×10^{-5}	65
2,4-Dioxaoctyl-, $Me_3COOCH_2OCH_2OBu$	Styrene	353–373	133.5	13.25	6.56×10^{-5}	65
Hydroxymethyl-, Me_3COOCH_2OH	Tetradecane	388–403	136.8	11.09	1.68×10^{-7}	105
Hydroxymethyl-, Me_3COOCH_2OH	Nitrobenzene	363–383	104.6	7.66	1.00×10^{-6}	105

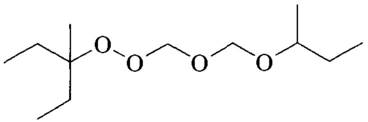
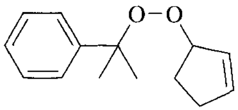
[a] ax = axial, eq = equatorial.

TABLE 4.11 Rate Constants of Thermal Decay of R^1OOR^2 Peroxides in Various Solvents

Peroxide	Solvent	T (K)	E (kJ mol^{-1})	log A, A (s^{-1})	k_d, k_i (400 K) (s^{-1})	Reference
		k_d				
1,1-Dimethylbutyl *N*,*N*-dimethylaminomethyl-, $PrCMe_2OOCH_2NMe_2$	Nitrobenzene	373			5.5×10^{-8}	105
1,1-Dimethylbutyl *N*,*N*-dimethylaminomethyl-, $PrCMe_2OOCH_2NMe_2$	Tetradecane	383			7.1×10^{-8}	105
1,1-Dimethylpropyl *N*-cyclohexyliminomethyl-, 	Nitrobenzene	368–382	83.3	4.36	3.04×10^{-7}	105
1,1-Dimethylpropyl *N*-cyclohexyliminomethyl-, 	Tetradecane	373–383	101.7	7.1	6.60×10^{-7}	105
1,1-Dimethylbutyl dibutylphosphinatomethyl-, $PrCMe_2OOCH_2OP(O)Bu_2$	Nitrobenzene	363–362	60.7	1.43	3.19×10^{-7}	105
1,1-Diphenylethyl 1-methyl-1-phenylethyl-, $PhMe_2COOCPh_2Me$	Decane	383–403	123.0	13.09	1.07×10^{-3}	59

(*continued overleaf*)

TABLE 4.11 (*continued*)

Peroxide	Solvent	T (K)	E (kJ mol^{-1})	log A, A (s^{-1})	k_d, k_i (400 K) (s^{-1})	Reference
		$k_i = 2ek_d$				
1,1-Dimethylpropyl 2-oxa-3-oxononyl-, $EtCMe_2OOCH_2OC(O)(CH_2)_5Me$	Nitrobenzene	363–373	73.2	3.42	7.26×10^{-7}	105
1,1-Dimethylpropyl 2-oxa-3-oxononyl-, $EtCMe_2OOCH_2OC(O)(CH_2)_5Me$	Tetradecane	383–402	97.9	5.96	1.50×10^{-7}	105
1,1-Dimethylpropyl 2-oxahexyl-, $EtC(Me)_2OOCH_2OBu$	Nitrobenzene	383–402	105.9	7.08	1.78×10^{-7}	105
1,1-Dimethylpropyl 2-oxahexyl-, $EtCMe_2OOCH_2OBu$	Tetradecane	358–373	134.7	12.35	5.76×10^{-6}	105
1,1-Dimethylpropyl 2,4-dioxanonyl-, $EtCMe_2OOCH_2OCH_2OBu$	Styrene	353–373	141.8	14.57	1.13×10^{-4}	65
1-Ethyl-1-methylpropyl 5-methyl-2,4-dioxaheptyl-  	Styrene	353–373	141.0	14.52	1.28×10^{-4}	65
2-Cyclopentenyl 1-methyl-1-phenylethyl-,  	Ethylbenzene	383–403	141.4	14.80	2.16×10^{-4}	106

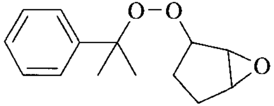
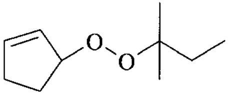
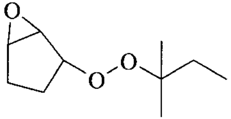
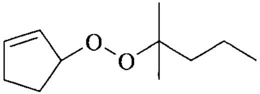
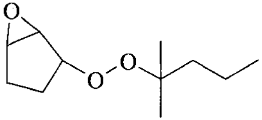
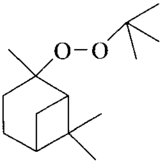
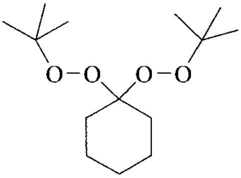
2,3-Epoxycyclopentyl 1-methyl-1-phenylethyl-, 	Ethylbenzene	383–403	142.3	14.80	1.65×10^{-4}	106
1,1-Dimethylpropyl 2-cyclopentenyl-, 	Ethylbenzene	383–403	151.5	15.90	1.31×10^{-4}	106
1,1-Dimethylpropyl 2,3-epoxycyclopentyl-, 	Ethylbenzene	383–403	146.4	16.50	2.41×10^{-3}	106
2-Cyclopentenyl 1,1-dimethylbutyl-, 	Ethylbenzene	383–403	153.1	16.70	5.10×10^{-4}	106
1,1-Dimethylbutyl 2,3-epoxycyclopentyl-, 	Ethylbenzene	383–403	148.1	16.30	9.13×10^{-4}	106

TABLE 4.12 The Probability of the Radical Pair Escaping the Cage *e* in the Thermal Decay of Peroxides

Peroxide	Solvent	*T* (K)	*e*	Reference
Bis(1,1-dimethylethyl)-, $Me_3COOCMe_3$	Decane	383	0.47	59
Bis(1-methyl-1-phenylethyl)-, $PhCMe_2OOCMe_2Ph$	Decane	383	0.51	59
1,1-Dimethylethyl-1-methyl-1-phenylethyl-, $Me_3COOCMe_2Ph$	Decane	383	0.63	59
1,1-Dimethylethyl 1,1-dimethylpropyl-, $Me_3COOCMe_2Et$	Decane	383	0.53	59
1,1-Diphenyl 1-methyl-1-phenylethyl-, $PhCMe_2OOCPh_2Me$	Decane	383	0.72	59
1,1-Dimethylethyl pinyl-, 	Decane	383	0.92	59
Diperoxide, bis(1,1-dimethylethyl)-cyclohexylidene- 	Decane	383	0.79	59

The following analytical procedures for an accurate estimation of hydroperoxides and peracids were proposed.[24] Reduction of peroxide occurs in the solution of isopropanol saturated with NaI in the presence of acetic acid and a CO_2 atmosphere at 373 K (in a water bath). The reaction is finished in 15 min and the relative standard deviation equals 0.2%.

The fast reduction of hydroperoxide by Sn(II) is used in a stannometric technique of ROOH estimation.

$$\mathrm{ROOH} + \mathrm{SnCl_2} + 2\mathrm{HCl} \rightarrow \mathrm{ROH} + \mathrm{H_2O} + \mathrm{SnCl_4}$$

The following is the analytical procedure.[107] Acetic acid is added to the sample of hydroperoxide, then dissolved air is removed by vacuum, the vessel is filled with dinitrogen, and an aqueous solution of $SnCl_2$ is added. Reaction occurs for 1 h at room temperature. Next, one introduces an excess of solution of $NH_4Fe(SO_4)_2$

TABLE 4.13 Synthesis of Hydroperoxides[a]

Reaction	Reactants	Catalyst
$RH + O_2 \rightarrow ROOH$ (chain reaction)	RH, O_2	I, $h\nu$
$Me_2CH(CH_2)_nCHMe_2 + O_2 \rightarrow Me_2C(OOH)(CH_2)_nC(OOH)Me_2$ $n = 1,2,3$ (chain reaction)	RH, O_2	I, $h\nu$
$ROH + H_2O_2 \rightarrow ROOH + H_2O$	ROH, H_2O_2	Acid
$R^1_2C{=}CHR^2 + H_2O_2 \rightarrow R^1_2C(OOH)CH_2R^2$	R^1_2 $C{=}CHR^2, H_2O_2$	Acid
$(RO)_2SO_2 + H_2O_2 \rightarrow ROOH + ROSO_2H$	$(RO)_2SO_2, H_2O_2$	KOH
$RCl + H_2O_2 \rightarrow ROOH + HCl$	RCl, H_2O_2	KOH
$RMgCl + O_2 \rightarrow ROOMgCl$	$RMgCl, O_2$	
$ROOMgCl + H_2O \rightarrow ROOH + HOMgCl$		
$RCHO + O_2 \rightarrow RC(O)OOH$ (chain reaction)	$RCHO, O_2$	I, $h\nu$
$RC(O)OH + H_2O_2 \rightarrow RC(O)OOH + H_2O$	$RC(O)OH, H_2O_2$	Acid
$RC(O)Cl + H_2O_2 \rightarrow RC(O)OOH + HCl$	$RC(O)Cl, H_2O_2$	KOH
$RC(O)OOC(O)R + NaOR^1 \rightarrow RC(O)OONa + RC(O)OR^1$	$RC(O)OOC(O)R$,	
$RC(O)OONa + H_2O \rightarrow RC(O)OOH + NaOH$	R^1ONa	
$[MeC(O)O]_2BOB[OC(O)Me]_2 + 4H_2O_2 \rightarrow 2MeC(O)OOH + 2H_3BO_3$	$[MeC(O)]_2O, H_2O_2$	

[a] See Refs. 11–15.

and in 30 min estimates the amount of formed Fe(II) by titration with potassium dichromate.

A spectrophotometric technique of hydroperoxide estimation was developed with triphenyl phosphite.[108]

$$ROOH + Ph_3P \rightarrow ROH + Ph_3PO$$

Triphenyl phosphite is added in excess and the rest is estimated colorimetrically after introduction of formaldehyde and HCl. Hydrogen chloride forms colored triphenyl phosphonyl chloride, $[Ph_3PCH_2OH]^+$ Cl^-.

Polarography is successfully used for the estimation of hydroperoxides and peracids.[23] The reduction of hydroperoxide performs according to the electrochemical equation:

$$ROOH + 2e^- \rightarrow RO^- + HO^-$$

The $E_{1/2}$ potential is the individual polarographic characteristic of an analyzed compound, where the current strength equals 50% of its maximum value. The binary solvent benzene/methanol or benzene/ethanol is used. The amount of peroxide is proportional to the maximum strength of the electric current at peroxide concentration in solution <0.01 mol L^{-1}. The values of $E_{1/2}$ for several hydroperoxides (ROOH) in benzene/ethanol solution (1:1 V/V) at $[LiCl] = 0.3$ mol L^{-1} are the following:[23]

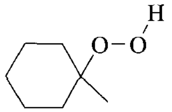
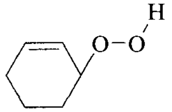
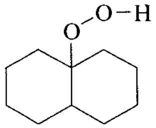
R−	Me_3C−	$EtMe_2C$−	Pinyl−	Me_2PhC−	Ph_2CH−	Tetralyl−
$E_{1/2}$ (V)	−1.22	−1.19	−1.03	−0.97	−0.82	−0.88

Liquid and paper chromatography as well as MS are used for the identification and analysis of hydroperoxides.[23] NMR spectroscopy is used for the identification of diacyl peroxides.

4.2.2 Structure of Hydroperoxides

The structure of hydroperoxides was studied by the RSA method. The results of experimental measurements are collected in Table 4.15.

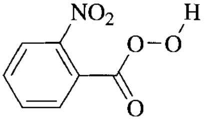
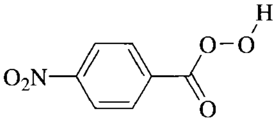
TABLE 4.14 Physical Properties of Some Hydroperoxides[a]

Hydroperoxide	MW	BP [p (Torr)] (K)	ρ [T(K)] ($kg\,m^{-3}$)	n_D^{293}
Methyl-, MeOOH	48.04	311 (60)	996.7 (288 K)	1.3638
Methylethyl-, Me_2CHOOH	76.10	381 (760)	892.9 (294 K)	1.4361
1,1-Dimethylethyl-, Me_3COOH	90.12	308 (17)	896.0 (293 K)	1.4014
1,1-Dimethylpropyl-, $EtMe_2COOH$	104.15	299 (3.5)	903.0 (293 K)	1.4161
1,1-Diethylpropyl-, Et_3COOH	132.21	301 (2.0)	914.0 (293 K)	1.4379
1-Methylcyclohexyl-, 	130.19	326 (0.1)	996.1 (293 K)	1.4692
2-Cyclohexenyl-, 	114.15	303 (1.0)	1063.8 (293 K)	1.4900
1,1-Dimethyl-2-propynyl-, $HC{\equiv}CC(OOH)Me_2$	100.12	315 (17)	954 (298 K)	1.4295 (298)
1-Phenylethyl-, PhMeCHOOH	138.17	339 (0.5)		1.5250
1-Methyl-1-phenylethyl-, $PhMe_2COOH$	152.2	317 (0.05)	1054.5 (293 K)	
(E)-9-Decalyl-, 	162.19	376 (1.2)	1150 (293 K)	1.550

---

[a] See Refs. 2 and 14.

TABLE 4.15 Bond Lengths and Angles of Hydroperoxides (Method RSA)[a]

Compound	Length (10^{-10} m)		Angle (°)		
	O–O	O–C	O–O–H	O–O–C	C–OO–H
Hydrogen peroxide, H_2O_2	1.453	0.97(O–H)	94.8		90.2
Hydrogen peroxide, H_2O_2	1.464	0.965(O–H)	99.4		
Hydroperoxide					
Methyl-, MeOOH	1.443	1.437	99.6	105.7	114
Trifluoromethyl-, CF_3OOH	1.447	1.376	100.0	107.6	95
1,1-Dimethylethyl-, Me_3COOH	1.472	1.463	100	109.6	100
1-Methyl-1-phenylethyl-, $PhMe_2COOH$	1.477	1.461	100.9	108.7(Me), 109.7(Ph)	109
Triphenylmethyl-, Ph_3COOH	1.455	1.454	102.9	109.7(Ph)	101
Peracid					
Nonanoic-, $Me(CH_2)_7C(O)OOH$	1.44	1.35		112	133.7
2-Nitrobenzoic-, 	1.478	1.337		108.9	146
4-Nitrobenzoic-, 	1.48	1.37		107	170

[a] See Refs. 15 and 30.

Analysis of the IR spectrum of hydrogen peroxide and cumyl hydroperoxide gave the following values for frequencies (cm^{-1}) of valence and bond angles vibration.[23]

Bond, Angle	O–O	O–H	C–O	θ(C–O–O)	θ(O–O–H)
H_2O_2	880	3598 (symm) 3610 (nonsym)			1390 (symm) 1266 (nonsym)
$Me_2PhCOOH$	880	3350	1270	585	

The hydrogen bond decreases the frequency of the O–H bond valence vibration (see Section 4.2.3). Two (*E*)- and one (*Z*)- configuration of a tertiary hydroperoxide are known.[30] The activation barrier for transition from (*Z*)- to (*E*)- configuration is found to be equal to 195 kJ mol^{-1} (quantum chemical calculation).[30]

Peracids form intramolecular hydrogen bonds and have lower frequencies of OH bond vibration. The carbonyl group vibration is very intensive. The following table lists the data on the valence vibration frequencies (cm^{-1}) in peracids (RC(O)OOH):[23]

R	Phase	ν(O−O) (cm^{-1})	ν(C=O) (cm^{-1})	ν(O−H) (cm^{-1})
H	Liquid	855	1739	3378
CH_3	Liquid	858	1750	3310
CH_3CH_2	Gas	875	1760	3280
$CH_3CH_2CH_2$	Gas	862	1760	3280
C_nH_{2n+1}, $n = 7–15$	CCl_4	865	1747	3280
C_6H_5	CCl_4		1732	3250

The dipole moment of hydrogen peroxide $\mu = 1.573$ D.[30] The values of dipole moments and the polarization of hydroperoxides and peracids are given in Table 4.16.

4.2.3 Thermochemistry of Hydroperoxides and Peracids

The values for enthalpies of hydroperoxide formation are in Table 4.17.

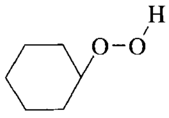
The increments of groups in the additive scheme of enthalpy ΔH_f calculation for hydroperoxides have the following values:[47] $\Delta H[O-(C)(O)] = -19.2 \pm 0.81$ kJ mol^{-1}, $\Delta H[(O)-OH] = -54.7$ kJ mol^{-1}, and additional increments of the tertiary atom C $\Delta H[(C)_3C-OO-C(C)_3] = -5.72$. The increments of

TABLE 4.16 Dipole Moments and Polarization of Hydroperoxides and Peracids in Benzene[a]

Peroxides	T (K)	μ (D)	P (cm^3 mol^{-1})
Hydroperoxide			
1,1-Dimethylethyl-, Me_3COOH	303	1.82	91.1
1,1-Dimethylethyl-, Me_3COOH	323	1.81	86.5
1-Methyl-1-phenylethyl-, $Me_2PhCOOH$	303	1.76	106.1
Peracid			
Nonanoic-, $Me(CH_2)_7C(O)OOH$	303	2.38	160.9
Decanoic-, $Me(CH_2)_8C(O)OOH$	303	2.27	155.6
Dodecanoic-, $Me(CH_2)_{10}C(O)OOH$	303	2.28	165.0
Tetradecanoic-, $Me(CH_2)_{12}C(O)OOH$	303	2.27	172.8
Hexadecanoic-, $Me(CH_2)_{14}C(O)OOH$	303	2.30	184.9

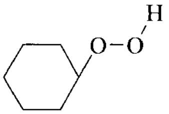
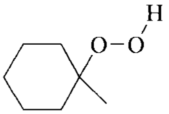
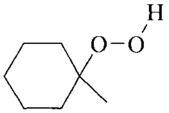
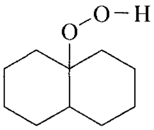
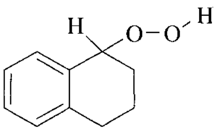
[a] See Refs. 33 and 109.

TABLE 4.17 Enthalpies of Formation ΔH_f^0 (Gas, 298 K) and Evaporation ΔH_v of Hydroperoxides

Hydroperoxide	$-\Delta H_f^0$ (kJ mol^{-1})	$-\Delta H_v$ (kJ mol^{-1})	ΔS^0 (J mol^{-1} K^{-1})	References
Hydrogen peroxide, H_2O_2	136.4	51.0	232.8	110
Methyl-, MeOOH	130.5		282.4	110
Methyl-, MeOOH	133.9			111
Ethyl-, EtOOH	169.4	43.7	321.8	111
1-Methylethyl-, Me_2CHOOH	198.3		358.7	111
Butyl-, BuOOH	205.0		393.8	110
1,1-Dimethylethyl-, Me_3COOH	242.7		360.6	110
1,1-Dimethylethyl-, Me_3COOH	236.4	48.7		111
1,1-Dimethylethyl-, Me_3COOH	243.3			112
1,1-Dimethylethyl-, Me_3COOH	245.8			15
1,1-Dimethylethyl-, Me_3COOH	218.3			113
1,1-Dimethylethyl-, Me_3COOH	225.7			47
Pentyl-, $Me(CH_2)_3CH_2OOH$	217.6		433.2	110
1-Methylbutyl-, MePrCHOOH	234.3		430.7	110
1-Hexyl-, $Me(CH_2)_4CH_2OOH$	238.5		472.6	110
1-Hexyl-, $Me(CH_2)_4CH_2OOH$	237.1	62.7		114
1-Hexyl-, $Me(CH_2)_4CH_2OOH$	259.2			15
1-Methylpentyl-, $Me(CH_2)_3CH(OOH)Me$	255.2		470.1	110
1-Methylpentyl-, $Me(CH_2)_3CH(OOH)Me$	250.1	60.1		114
1-Methylpentyl-, $Me(CH_2)_3CH(OOH)Me$	267.5			15
1-Ethylbutyl-, $Me(CH_2)_2CH(OOH)Et$	245.1	60.1		114
1-Ethylbutyl-, $Me(CH_2)_2CH(OOH)Et$	263.3			15
1-Heptyl-, $Me(CH_2)_5CH_2OOH$	288.7		512.0	110
1-Heptyl-, $Me(CH_2)_5CH_2OOH$	275.7	67.5		114
1-Methylhexyl-, $Me(CH_2)_4CH(OOH)Me$	276.1		509.5	110
1-Methylhexyl-, $Me(CH_2)_4CH(OOH)Me$	281.6	64.9		114
1-Ethylpentyl-, $Me(CH_2)_3CH(OOH)Et$	282.1	64.9		114
1-Propylbutyl-, $Me(CH_2)_2CH(OOH)Pr$	269.1	64.9		114
1,1-Dimethyl-2-pentyn-4-enyl-, $CH_2{=}CHC{\equiv}CCMe_2OOH$	−127.1	63.5		46
Cyclohexyl-, 	214.9	58.5		114

(*continued overleaf*)

TABLE 4.17 (*continued*)

Hydroperoxide	$-\Delta H_f^0$ (kJ mol^{-1})	$-\Delta H_v$ (kJ mol^{-1})	ΔS^0 (J mol^{-1} K^{-1})	References
Cyclohexyl-, 	229.9			15
1-Methylcyclohexyl-, 	270.3	60.2		114
1-Methylcyclohexyl-, 	263.3			110
(*E*)-9-Decalyl-, 	277.8	67.2		115
1-Methyl-1-phenylethyl-, PhMe$_2$COOH	82.5	66.0		112
1-Methyl-1-phenylethyl-, PhMe$_2$COOH	87.9	66.0		116
1-Methyl-1-phenylethyl-, PhMe$_2$COOH	85.4	66.0		117
1-Tetralyl-, 	104.5	77.2		114
1,1,4,4-Tetramethyl-1,4-dihydroperoxybutane, HOOCMe$_2$(CH$_2$)$_2$CMe$_2$OOH	428.6	138.6		47
1,1,4,4-Tetramethyl-1,4-dihydroperoxybutyne-2 HOOCMe$_2$C≡CCMe$_2$OOH	130.2	127.4		47
Peracid				
1-Decanoic-, Me(CH$_2$)$_8$C(O)OOH	509.3	117.2		44,118
1-Undecanoic-, Me(CH$_2$)$_9$C(O)OOH	548.9	131.4		44,118
1-Tridecanoic-, Me(CH$_2$)$_{11}$C(O)OOH	599.7	150.1		44,118

groups for the calculation of enthalpy ΔH_υ of peroxides evaporation are ΔH[(O)–O–(C)] = 6.26 kJ mol^{-1}, ΔH_υ[(O)–OC(O)–(C_B)] = 25.4 kJ mol^{-1}, ΔH_υ[(O)–OH] = 27.4 kJ mol^{-1}, and ΔH_υ[(O)–OC(O)–(C)] = 18.3 kJ mol^{-1}.[119] The linear correlation between ΔH_f(ROOH) and ΔH_f(ROH) was found to be[120]

$$\Delta H_f^0(\text{ROOH}) = \Delta H_f^0(\text{ROH}) - 80.3\ \text{kJ mol}^{-1}$$

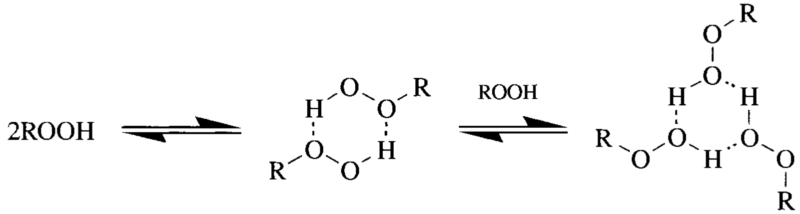
Dissociation energies for the O–O bond in hydroperoxides ROOH are the following:

R	Me	Et	Me_3C	Me_2PhC
D (kJ mol^{-1})	191.0	193.0	182.5	175.0

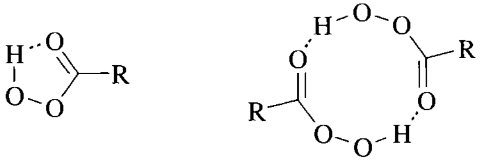
Dissociation energy for the O–H bond depends on the structure of R and equals: 365.5 kJ mol^{-1}(R = *sec*-R), 358.6 kJ mol^{-1} (R = *tert*-R), 406.1 kJ mol^{-1} [R = PhC(O)], 418.0 kJ mol^{-1} (R = CF_3), 407.2 kJ mol^{-1} (CCl_3), 407.2 kJ mol^{-1} (R = CCl_3CCl_2).[121,122]

4.2.4 Hydrogen Bonding and Acidity of Hydroperoxides and Peracids

Hydroperoxides form dimers and trimers connected by hydrogen bonds. The following scheme of self-association was proposed:[15]



In nonpolar solution, peracids exist in monomeric form with intramolecular hydrogen bonds between the hydroxyl group and the carbonyl oxygen. In the crystalline state, they form dimers with two hydrogen bonds:



The equilibrium constants K_H and the thermodynamic parameters for self-association of several hydroperoxides and peracids are given in Table 4.18.

Polar molecules and molecules with π bonds form with hydroperoxides and peracids complexes via hydrogen bond, for example,

$$R^1OOH + NR_3 \Leftrightarrow R^1OOH \cdots NR_3$$

Equilibrium constant values for K_H are listed in Table 4.18.

Peracids and hydroperoxides have an OOH group and possess acidic properties. The pK_a values fall into a rather narrow range of 11.5–13.2 for hydroperoxides and 7.2–8.2 for peracids in water. The pK_a values for hydroperoxides ROOH in water at 298 K are presented below.[15]

R	Me	Et	Me_3C	$PhCMe_2$	$PhCH_2CMe_2$	Ph_2CMe	Ph_2CEt	Ph_3C
pK_a	11.50	11.80	13.27	13.08	13.25	12.94	13.02	13.07

The pK_a values for some peracids RC(O)OOH in H_2O at 298 K have the following values:[15]

R	Me	Et	Me_3C	Ph	p-$MeOC_6H_4$	p-MeC_6H_4	p-FC_6H_4	p-ClC_6H_4
pK_a	8.2	8.1	8.23	7.78	8.07	7.95	7.76	7.67

4.2.5 Unimolecular Decomposition of Hydroperoxides

Hydroperoxides react with many organic substances with free radicals generation (see Chapter 11). In addition, they react with free radicals and can be decomposed in chain reactions (see Section 4.2.4). That is why the kinetics of thermal decomposition of hydroperoxides is difficult to interpret in most cases. Decay of hydroperoxides in the gas phase can be accelerated by catalytic decomposition on the wall of the reactor. The rate constants of the unimolecular decomposition of some hydroperoxides in the gas phase and solution are presented in Table 4.19. The acceleration of 1,1-dimethylethyl hydroperoxide decay in solution, probably demonstrates the interaction of ROOH with the solvent. Data on the decomposition of hydroperoxide groups in polymers are collected in Tables 4.20 and 4.21.

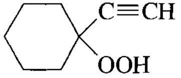
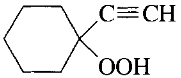
4.2.6 Chain Decomposition of Hydroperoxides

Different chain mechanisms of hydroperoxide decomposition are known. Tertiary hydroperoxides are decomposed under the action of intermediate alkoxyl radicals.[6]

$$Me_3COOH \rightarrow Me_3CO^{\bullet} + HO^{\bullet}$$

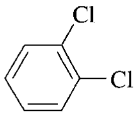
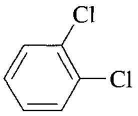
$$2Me_3COOH \rightarrow Me_3CO_2^{\bullet} + H_2O + Me_3CO^{\bullet}$$

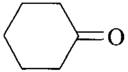
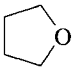
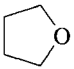
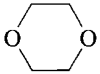
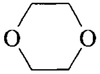
TABLE 4.18 Equilibrium Constants (K_H), Enthalpies (ΔH), and Entropies (ΔS) of Hydrogen Bonding ROOH + Y ⇔ ROOH···Y

Hydroperoxide	Y	Solvent	T (K)	$-\Delta H$ (kJ mol^{-1})	$-\Delta S$ (J mol^{-1} K^{-1})	K_H (298 K) (L mol^{-1})	Reference
1-Acetylethyl-, MeC(O)CH(OOH)Me	Me_3COH	MeC(O)Et	343			0.65	123
1-Acetylethyl-, MeC(O)CH(OOH)Me	MeC(O)OH	MeC(O)Et	343			3.11	123
1-Etynylcyclohexyl-, 		CCl_4	258–312	17.6	48.9	0.29	23
1,1-Dimethylethyl-, Me_3COOH	Me_3COOH	n-C_7H_{16}	363			1.90	124
1,1-Dimethylethyl-, Me_3COOH	Me_3COOH	CCl_4	258–313	23.8	82.0	0.77	125
1,1-Dimethylethyl-, Me_3COOH	Me_3COOH	CCl_4	303	24.9	77.0	2.20	126
1,1-Dimethylethyl-, Me_3COOH	Me_3COOH	C_6H_6	343	6.6	37.7	0.15	126
1,1-Dimethylethyl-, Me_3COOD	Me_3COOD	CCl_4	303	20.5	62.8	2.06	15
1,1-Dimethylethyl-, Me_3COOD	Me_3COOD	C_6H_6	343			0.64	127
1,1-Dimethylethyl-, Me_3COOH	Me_3COOH	CCl_4	313	26.4	90.4	0.80	15
1,1-Dimethylethyl-, Me_3COOH	$2Me_3COOH$	CCl_4	313	11.7	28.9	3.48	15

(continued overleaf)

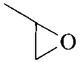
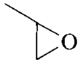
TABLE 4.18 (*continued*)

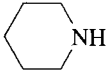
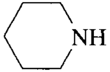
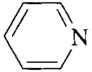
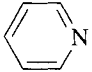
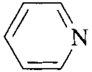
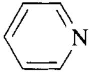
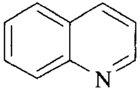
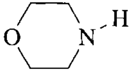
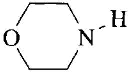
Hydroperoxide	Y	Solvent	T (K)	$-\Delta H$ (kJ mol^{-1})	$-\Delta S$ (J mol^{-1} K^{-1})	K_H (298 K) (L mol^{-1})	Reference
1,1-Dimethylethyl-, Me_3COOH	$2Me_3COOH$	*cyclo*-C_6H_{12}	288–343	50.2	108.7	1.32×10^3	128
1,1-Dimethylethyl-, Me_3COOH	$2Me_3COOH$	C_7H_{14}	258–343	50.2	111.3	9.67×10^2	128
1,1-Dimethylethyl-, Me_3COOH	$2Me_3COOH$	*cyclo*-$C_6H_{11}CH_3$	288–343	50.2	112.1	8.78×10^2	128
1,1-Dimethylethyl-, Me_3COOH	$2Me_3COOH$	CCl_4	258–343	46.9	106.3	4.66×10^2	128
1,1-Dimethylethyl-, Me_3COOH	C_6H_6	C_6H_6	303–343	6.6	37.7	0.15	126
1,1-Dimethylethyl-, Me_3COOH	C_6H_6	C_6H_6	288–343	8.2	42.3	0.17	128
1,1-Dimethylethyl-, Me_3COOH	$PhCH_3$	$PhCH_3$	288–343	5.7	29.9	0.27	128
1,1-Dimethylethyl-, Me_3COOH	$PhCHMe_2$	$PhCHMe_2$	288–343	11.7	52.1	0.21	128
1,1-Dimethylethyl-, Me_3COOH	C_6H_5Cl	C_6H_5Cl	288–343	7.6	42.5	0.13	128
1,1-Dimethylethyl-, Me_3COOH	C_6H_5Cl	C_6H_5Cl	343			0.10	127
1,1-Dimethylethyl-, Me_3COOH			343			0.13	127
1,1-Dimethylethyl-, Me_3COOH	$PhCH{=}CH_2$	$PhCH{=}CH_2$	303–343	10.0	43.9	0.29	126

1,1-Dimethylethyl-, Me_3COOH	$PhCH{=}CH_2$	$PhCH{=}CH_2$	288–343	7.5	35.4	0.29	128
1,1-Dimethylethyl-, Me_3COOD	$PhCH{=}CH_2$	$PhCH{=}CH_2$	343			0.50	127
1,1-Dimethylethyl-, Me_3COOH	MeCOMe	CCl_4	249–293	12.5	31.0	3.73	129
1,1-Dimethylethyl-, Me_3COOH	MeCOEt	MeCOEt	288–343	15.0	57.9	0.40	128
1,1-Dimethylethyl-, Me_3COOH	MeOH	CCl_4	249–293	12.5	31.4	3.55	129
1,1-Dimethylethyl-, Me_3COOH		CCl_4	249–293	9.2	18.8	4.27	129
1,1-Dimethylethyl-, Me_3COOH	EtOEt	EtOEt	233–289	13.0	25.5	8.84	130
1,1-Dimethylethyl-, Me_3COOH	EtOEt	EtOEt	288–343	19.7	68.9	0.71	128
1,1-Dimethylethyl-, Me_3COOH	$Me_2CHOCHMe_2$	Me_2COCMe_2	288–343	20.5	67.9	1.11	128
1,1-Dimethylethyl-, Me_3COOH	BuOBu	BuOBu	288–343	19.5	68.2	0.72	128
1,1-Dimethylethyl-, Me_3COOH	$Me_2EtCHOCHMe_2Et$	$Me_2EtCHOCHMe_2Et$	288–343	19.7	66.1	1.00	128
1,1-Dimethylethyl-, Me_3COOH			288–343	21.8	81.5	0.37	128
1,1-Dimethylethyl-, Me_3COOH			288–343	17.8	66.9	0.42	128

(continued overleaf)

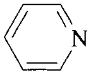
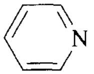
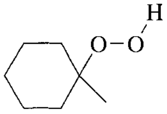
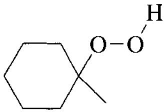
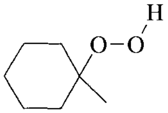
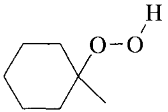
TABLE 4.18 (*continued*)

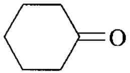
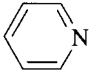
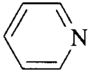
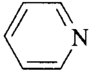
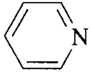
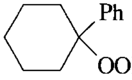
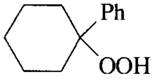
Hydroperoxide	Y	Solvent	T (K)	$-\Delta H$ (kJ mol^{-1})	$-\Delta S$ (J mol^{-1} K^{-1})	K_H (298 K) (L mol^{-1})	Reference
1,1-Dimethylethyl-, Me_3COOH	$MeOCH_2CH_2OMe$	$MeOCH_2CH_2OMe$	288–343	18.0	70.4	0.30	128
1,1-Dimethylethyl-, Me_3COOH	PhOMe	PhOMe	288–343	10.6	30.0	1.95	128
1,1-Dimethylethyl-, Me_3COOH	PhOEt	PhOEt	288–343	10.5	29.6	1.97	128
1,1-Dimethylethyl-, Me_3COOH	$PhCH_2OMe$	$PhCH_2OMe$	288–343	20.1	67.7	0.97	128
1,1-Dimethylethyl-, Me_3COOH	$Me_3COOCMe_3$	$Me_3COOCMe_3$	288–343	13.5	43.7	1.21	128
1,1-Dimethylethyl-, Me_3COOH			288–343	17.3	61.6	0.65	128
1,1-Dimethylethyl-, Me_3COOH	$PhNH_2$	$PhNH_2$	298	3.3	−7.28	9.09	131
1,1-Dimethylethyl-, Me_3COOH	PhNHEt	PhNHEt	298	4.8	−0.83	7.67	131
1,1-Dimethylethyl-, Me_3COOH	$AcNMe_2$	CCl_4	294–341	22.6	51.1	19.6	132
1,1-Dimethylethyl-, Me_3COOH	AcNHBu	CCl_4	292–341	23.9	55.7	19.0	132
1,1-Dimethylethyl-, Me_3COOH	$AcNHCHMe_2$	CCl_4	294–332	14.7	43.5	2.02	132
1,1-Dimethylethyl-, Me_3COOH	$Me_2NC(O)H$	$Me_2NC(O)H$	288–343	22.0	93.1	9.84×10^{-2}	128
1,1-Dimethylethyl-, Me_3COOH	$CH_2{=}CHCOOMe$	$CH_2{=}CHCOOMe$	293–343	13.8	35.6	3.62	133

1,1-Dimethylethyl-, Me$_3$COOH	CH$_2$=CMeCOOMe	CH$_2$=CMeCOOMe	293–343	18.8	52.3	3.66	133
1,1-Dimethylethyl-, Me$_3$COOH	MeCN	MeCN	288–343	12.0	44.3	0.62	128
1,1-Dimethylethyl-, Me$_3$COOH	CH$_2$=CHCN	CH$_2$=CHN	293–343	12.5	33.5	2.76	133
1,1-Dimethylethyl-, Me$_3$COOH			298	28.8	85.8	3.68	131
1,1-Dimethylethyl-, Me$_3$COOH			248–289	28.0	72.0	14.03	130
1,1-Dimethylethyl-, Me$_3$COOH			298	11.0	9.7	26.39	131
1,1-Dimethylethyl-, Me$_3$COOH		Me$_3$COOH	298	10.7	12.0	17.73	131
1,1-Dimethylethyl-, Me$_3$COOH			298	21.4	52.5	10.20	131
1,1-Dimethylethyl-, Me$_3$COOH	Me$_2$SO	Me$_2$SO	288–343	23.7	107.6	3.42×10^{-2}	128
1,1-Dimethylpropyl-, EtMe$_2$COOH	EtMe$_2$COOH	CCl$_4$	258–313	22.6	75.3	1.07	125
1,1-Dimethylpropyl, EtMe$_2$COOH	MeCOMe	MeCOMe	270–313	15.9	37.2	6.98	130
1,1-Dimethylpropyl-, EtMe$_2$COOH	EtOEt	EtOEt	248–288	10.5	10.9	18.66	130

(*continued overleaf*)

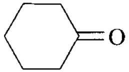
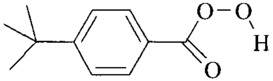
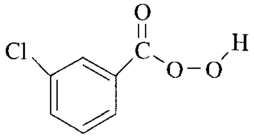
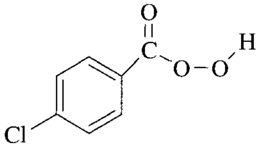
TABLE 4.18 (*continued*)

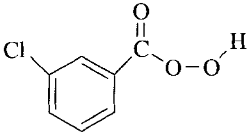
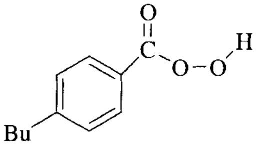
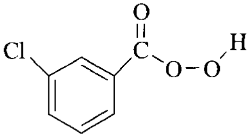
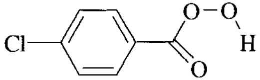
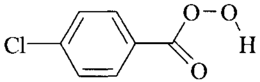
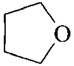
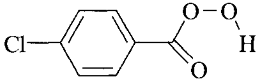
Hydroperoxide	Y	Solvent	T (K)	$-\Delta H$ (kJ mol^{-1})	$-\Delta S$ (J mol^{-1} K^{-1})	K_H (298 K) (L mol^{-1})	Reference
1,1-Dimethylpropyl-, $EtMe_2COOH$			253–288	28.0	74.0	11.03	130
1-Methylcyclohexyl- 		n-$C_{10}H_{14}$	293	23.4	79.5	0.89	15
1-Methylcyclohexyl- 		n-$C_{10}H_{14}$	293	11.7	26.8	4.48	15
1-Methyl-1-phenylethyl-, $Me_2PhCOOH$	$Me_2PhCOOH$	Me_2PhCH	273–313	25.1	66.6	8.33	132
1-Methyl-1-phenylethyl-, $Me_2PhCOOH$	$Me_2PhCOOH$	CCl_4	265–323	28.5	96.2	0.93	125
1-Methyl-1-phenylethyl-, $Me_2PhCOOH$	$PhOCH_3$	CCl_4	293			0.46	15
1-Methyl-1-phenylethyl-, $Me_2PhCOOH$	MeCOMe	CCl_4	249–293	15.1	53.5	0.43	129
1-Methyl-1-phenylethyl-, $Me_2PhCOOH$	MeCOMe	MeCOMe	270–313	15.9	35.1	9.00	130
1-Methyl-1-phenylethyl-, $Me_2PhCOOH$	MeOH	CCl_4	249–293	15.9	50.2	1.46	129

1-Methyl-1-phenylethyl-, $Me_2PhCOOH$		CCl_4	249–293	10.9	30.1	0.46	129
1-Methyl-1-phenylethyl-, $Me_2PhCOOH$	EtOEt	EtOEt	248–288	13.8	25.5	12.2	130
1-Methyl-1-phenylethyl-, $Me_2PhCOOH$	$PhNH_2$	$PhNH_2$	298	8.0	13.7	4.86	131
1-Methyl-1-phenylethyl-, $Me_2PhCOOH$	$AcNMe_2$	CCl_4	294–350	20.9	49.8	11.54	132
1-Methyl-1-phenylethyl-, $Me_2PhCOOH$	AcNHBu	CCl_4	294–337	20.5	49.0	10.81	132
1-Methyl-1-phenylethyl-, $Me_2PhCOOH$	$AcNHCHMe_2$	CCl_4	294–332	21.3	55.6	6.75	132
1-Methyl-1-phenylethyl-, $Me_2PhCOOH$			298	17.7	49.4	3.33	131
1-Methyl-1-phenylethyl-, $Me_2PhCOOH$	$CH_2{=}CHCOOMe$	$CH_2{=}CHCOOMe$	293–343	14.6	37.2	4.13	133
1-Methyl-1-phenylethyl-, $Me_2PhCOOH$	$CH_2{=}CMeCOOMe$	$CH_2{=}CMeCOOMe$	293–343	13.8	42.7	1.54	133
1-Methyl-1-phenylethyl-, $Me_2PhCOOH$	$CH_2{=}CHCN$	$CH_2{=}CHCN$	293–343	12.5	33.5	2.76	133
1-Methyl-1-phenylethyl-, $Me_2PhCOOH$			253–289	29.3	75.3	15.9	130
1-Phenylcyclohexyl-, 		CCl_4	269–312	21.8	83.6	0.28	125

(continued overleaf)

TABLE 4.18 (*continued*)

Hydroperoxide	Y	Solvent	T (K)	$-\Delta H$ (kJ mol^{-1})	$-\Delta S$ (J mol^{-1} K^{-1})	K_H (298 K) (L mol^{-1})	Reference
1,1-Dimethyl-2-butenyl-, $Me_2C(OOH)CH{=}CHMe$	$Me_2C(OOH)\ CH{=}CHMe$	CCl_4	269–304	18.8	73.7	0.28	134
Triphenylmethyl-, Ph_3COOH	Ph_3COOH	CCl_4	269–313	23.8	82.0	0.77	135
Triphenylmethyl-, Ph_3COOH	MeCOMe	CCl_4	269–313	14.6	50.2	0.86	129
Triphenylmethyl-, Ph_3COOH	MeOH	CCl_4	269–313	16.3	54.4	1.04	129
Triphenylmethyl-, Ph_3COOH		CCl_4	269–313	10.9	31.4	1.86	129
Peracid,							
4-(1,1-dimethylethyl) benzoic-, 	$AcNMe_2$	CCl_4	298	26.4	77.1	3.98	15
3-Chlorobenzoic-, 		CCl_4	298	29.7	80.6	9.90	136

3-Chlorobenzoic-, 		CCl_4	298	26.3	76.7	4.01	136
3-Chlorobenzoic-, 	$AcNMe_2$	CCl_4	298	29.7	80.6	9.90	15
4-Chlorobenzoic-, 	$AcNMe_2$	CCl_4	298	27.6	74.8	8.52	15
4-Chlorobenzoic-, 		CCl_4	298	24.3	74.6	2.30	15
4-Chlorobenzoic-, 	$HC(O)NMe_2$	CCl_4	298	25.1	69.3	6.02	15

$$HO^{\bullet} + HOOCMe_3 \rightarrow H_2O + Me_3CO_2^{\bullet}$$

$$Me_3CO^{\bullet} + HOOCMe_3 \rightarrow Me_3COH + Me_3CO_2^{\bullet}$$

$$Me_3CO_2^{\bullet} + Me_3CO_2^{\bullet} \rightarrow 2Me_3CO^{\bullet} + O_2$$

$$Me_3CO_2^{\bullet} + Me_3CO_2^{\bullet} \rightarrow Me_3COOCMe_3 + O_2$$

The rate of tertiary hydroperoxide decomposition is equal to

$$v = k_1[ROOH] + 2k_2[ROOH]^2(1 + k_3/k_4) \qquad (4.1)$$

The ratio $k_3/k_4 > 1$, for example, $k_3/k_4 = 7.2 \pm 1.1$ for the decay of 1,1-dimethylethyl hydroperoxide in benzene at 318 K,[163] $k_3/k_4 = 10$ for MeEtCHOOH in chlorobenzene (318 K).[164] Secondary hydroperoxides are decomposed in oxidizing hydrocarbons in a chain reaction with peroxyl radicals.[165]

$$R^1R^2CHOOH + RO_2^{\bullet} \rightarrow ROOH + R^1R^2C{=}O + HO^{\bullet}$$

$$HO^{\bullet} + RH \rightarrow H_2O + R^{\bullet}$$

$$R^{\bullet} + O_2 \rightarrow RO_2^{\bullet}$$

TABLE 4.19 Rate Constants for the Unimolecular Decomposition of Hydroperoxides and Peracids

Peroxide	Solvent	T (K)	E (kJ mol^{-1})	log A, A (s^{-1})	k (400 K) (s^{-1})	Reference
Hydroperoxide						
Methyl-, MeOOH	Gas	565–651	180.0	14.91	2.54×10^{-9}	111
Ethyl-, EtOOH	Gas	553–653	180.0	15.35	6.99×10^{-9}	111
1-Methylethyl-, Me_2CHOOH	Gas	553–653	180.0	15.50	9.88×10^{-9}	111
1,1-Dimethylethyl-, Me_3COOH	Gas	553–653	180.0	15.60	1.24×10^{-8}	111
1,1-Dimethylethyl-, Me_3COOH	Toluene	423	180.0	16.10	3.94×10^{-8}	110
Peracid						
Acetic-, MeC(O)OOH	Gas	403–553	136.0	13.1	2.19×10^{-5}	111
Propionic-, EtC(O)OOH	Gas	443–503	139.0	13.1	8.88×10^{-6}	111
Butyric-, PrC(O)OOH	Gas	443–503	137.0	13.0	1.29×10^{-5}	111
Methylpropionic-, $Me_2CHC(O)OOH$	Gas	443–503	137.0	13.2	2.04×10^{-5}	111

TABLE 4.20 Rate Constants for Hydroperoxide Group Decomposition to Free Radicals Measured by the Kinetics of Polymer Autooxidation and Free Radical Acceptor Method

Polymer	Conditions of Oxidation	T (K)	E (kJ mol^{-1})	log A, A (s^{-1})	k (400 K) (s^{-1})	References
PE	Chlorobenzene (383 K)	351–403	146.0	14.20	1.36×10^{-5}	137
PE	Solid phase (363 K)	365			5.0×10^{-6}	138
PE	Melt	430			1.0×10^{-4}	139
PP	Cumene (single OOH)	383–403	133.9	12.40	8.22×10^{-6}	137
PP	Solid phase (single OOH)	383–413	120.0	10.71	1.10×10^{-5}	137
PP	Chlorobenzene (associated OOH)	388			3.5×10^{-5}	137
PP	Solid phase (associated OOH)	383–403	102.2	6.18	6.82×10^{-8}	137
PP	Solid phase	365–387	92.0	7.84	6.70×10^{-5}	138
PP	Solid phase	393–413	75.1	5.64	6.81×10^{-5}	140
PP	Solid phase	383–413	91.9	8.61	4.06×10^{-4}	141
PP	Solid phase	365			1.4×10^{-5}	142
PP	Solid phase	348–387	88.1	7.34	6.85×10^{-5}	138
PP	Solid phase	403			6.0×10^{-5}	143
PP	Solid phase	339–362	128.5	10.93	1.41×10^{-6}	144
		Oligomeric peroxides: $RCH_2CH_2O(OCHRCH_2O)_n$				
$PhCH{=}CH_2$	Benzene	353	110.0	9.16	6.25×10^{-6}	145,146
$CH_2{=}CMeCOOMe$	Benzene	353	119.2	10.41	6.99×10^{-6}	132
$CH_2{=}CClCH = CH_2$	Benzene	353	76.7	7.36	2.21×10^{-3}	147

TABLE 4.21 Rate Constants of Polymer Hydroperoxide Group Decay

Polymer	Medium	T (K)	E (kJ mol^{-1})	log A, A (s^{-1})	k (400 K) (s^{-1})	$k_i/2k_d$	Reference
PE	Chlorobenzene	373–408	104.0	8.04	2.88×10^{-6}	0.10	148
PE	Chlorobenzene	393–408	113.0	8.08	2.11×10^{-7}		148
PE	Chlorobenzene	383–403	146.0	15.93	7.32×10^{-4}	0.01	137
PE	Chlorobenzene	373–393	84.0	8.28	2.05×10^{-3}	0.07	137
PE	Solid phase	333–373	92.0	8.34	2.12×10^{-4}		149
PE	Solid phase	373–393	162.5	17.79	3.72×10^{-4}		150
PE	Solid phase	413–443	146.0	14.40	2.16×10^{-5}		151
PE	Solid phase, O_2	430			2.6×10^{-3}		139
PE	Solid phase	403			4.7×10^{-4}		152
PE	Solid phase, O_2	403			5.3×10^{-3}		152
PP	Solid phase	363–393	113.0	11.98	1.67×10^{-5}		153
PP	Solid phase	363–393	115.0	12.36	2.20×10^{-3}		154
PP	Chlorobenzene	398			6.0×10^{-4}	0.035	137
PP	Benzene	392–407	109.0	10.58	2.22×10^{-4}	0.015	137
PP	Solid phase	393–413	109.0	10.87	4.39×10^{-4}		155
PP	Solid phase	393			2.85×10^{-4}		156
PP	Solid phase	403			7.7×10^{-4}		157
PP	Solid phase	403			11.5×10^{-4}		158
PP	Solid phase		100.0	10.11	1.13×10^{-3}		159
PP	Solid phase		129.0	12.23	2.42×10^{-5}		159
PP	Solid phase		104.0	10.34	5.74×10^{-4}	0.14	160
PP	Solid phase	365–387	114.0	11.50	4.11×10^{-4}		144
PP	Solid phase, O_2	403			8.7×10^{-4}		140
PP	Solid phase	398			1.8×10^{-4}	0.03	137
PS	Solid phase	453–473	150.7	13.91	1.70×10^{-6}		161
SR	Solid phase	353–403	77.0	7.34	1.93×10^{-3}		162

In the absence of dioxygen, when hydroperoxide initiates the formation of alkyl radicals, the following chain reaction of ROOH decomposition occurs:[166]

$$\mathrm{ROOH} \rightarrow \mathrm{RO}^{\bullet} + \mathrm{HO}^{\bullet}$$

$$\mathrm{RO}^{\bullet} + \mathrm{R}^1\mathrm{H} \rightarrow \mathrm{ROH} + \mathrm{R}^{1\bullet}$$

$$\mathrm{R}^{1\bullet} + \mathrm{ROOH} \rightarrow \mathrm{R}^1\mathrm{OH} + \mathrm{RO}^{\bullet}$$

$$\mathrm{R}^{1\bullet} + \mathrm{R}^{1\bullet} \rightarrow \mathrm{R}^1\mathrm{R}^1$$

Chain length $\nu = 3.6$ (n-decane, 393 K, $[\mathrm{ROOH}]_0 = 0.6$ mol L^{-1}).[149] Chain decomposition of hydroperoxide was proved for the hydroperoxide of dimethylacetamide. The rate of chain decay $v_\nu = k_{\mathrm{ind}}[\mathrm{ROOH}]_0^{3/2}$.[167] The values of the effective rate constant k_{ind} in dimethylacetamide were found to be the following:[167,168]

ROOH	Me_3COOH	$Me_2PhCOOH$	$AcN(Me)CH_2OOH$
T (K)	405	405	300–405
k_{ind} ($L^{-1/2}$ $mol^{-1/2}$ s^{-1})	2.0×10^{-4}	9.0×10^{-4}	8.5×10^{-7} $\exp(-87.0/RT)$

The induced decomposition of hydroperoxide groups was observed in polymers in the absence and presence of dioxygen. The values of k_{ind}, k_d, and k_i are presented in Table 4.22.

Primary and secondary alcohols induce the chain decomposition of hydroperoxides with participation of ketyl radicals that are very active as reducing intermediates.[169,170]

$$ROOH \rightarrow RO^{\bullet} + HO^{\bullet}$$

$$RO^{\bullet} + R^1CH(OH)R^2 \rightarrow ROH + R^1C^{\bullet}(OH)R^2$$

$$R^1C^{\bullet}(OH)R^2 + ROOH \rightarrow R^1R^2C(O) + H_2O + RO^{\bullet} \qquad (k_p)$$

$$2R^1C^{\bullet}(OH)R^2 \rightarrow R^1C(O)R^2 + R^1CH(OH)R^2 \qquad (k_t)$$

The rate of chain decomposition of hydroperoxide is $v = (k_p(2k_t)^{-1/2})[ROOH]\, v_i^{1/2}$. Dioxygen reacts with ketyl radicals with the formation of hydroxyperoxyl radicals. The latter is decomposed to ketone and $HO_2^{\bullet}$.

Hydroperoxyl and hydroxyalkylperoxyl radicals also possess the reducing activity and induce chain decomposition of hydroperoxide.[169]

TABLE 4.22 Kinetic Parameters of Hydroperoxide Group Induced Decomposition in the Solid Phase[a]

Atmosphere	Polymer	T (K)	$k_d \times 10^4$ (s^{-1})	$k_i \times 10^5$ (s^{-1})	e	$k_{ind} \times 10^2$ ($kg^{1/2}$ $mol^{-1/2}$ $s^{-1/2}$)
N_2	PP, OOH group (associated)	387	1.4	2.8	0.10	13.0
N_2	PP, OOH group (associated)	365	0.21	0.5	0.12	4.5
O_2, 10^5 Pa	PP, OOH group (associated)	387	1.4	2.8	0.10	13.6
O_2, 2.6×10^4 Pa	PP, OOH group (associated)	365	0.19	0.5	0.13	12.0
O_2, 10^5 Pa	PP, OOH group (associated)	365	0.21	0.5	0.12	2.9
N_2	IPP, OOH group (single)	387	0.10	0.21	0.11	9.6
N_2	IPP, OOH group (single)	365	0.039	0.017	0.02	3.0
N_2	PE	365	0.05	0.5	0.5	0.36
O_2, 10^5 Pa	PE	365	0.05	0.5	0.5	0.81
N_2	PE	393	4.6	33	0.37	11.0

[a] See Ref. 138.

$$RO_2^{\bullet} + R^1CH(OH)R^2 \rightarrow ROOH + R^1C^{\bullet}(OH)R^2$$

$$R^1C^{\bullet}(OH)R^2 + O_2 \rightarrow R^1C(OH)(OO^{\bullet})R^2$$

$$R^1C(OH)(OO^{\bullet})R^2 \rightarrow R^1C(O)R^2 + HO_2^{\bullet}$$

$$R^1C(OH)(OO^{\bullet})R^2 + ROOH \rightarrow R^1C(O)R^2 + H_2O + RO^{\bullet} + O_2$$

$$HO_2^{\bullet} + ROOH \rightarrow H_2O + RO^{\bullet} + O_2 \qquad (k_p)$$

$$2R^1C(OH)(OO^{\bullet})R^2 \rightarrow R^1C(O)R^2 + O_2 + R^1C(OH)(OOH)R^2 \qquad (k_t)$$

The rate of chain decomposition of hydroperoxide in the presence of alcohol and dioxygen is $\nu = [k_p(2k_t]^{-1/2})[ROOH]v_i^{1/2}$. The value of rate constants for chain propagation in chain reactions of ROOH decomposition are collected in Table 4.23.

TABLE 4.23 Rate Constants of Free Radical Reactions with Hydroperoxides in Hydrocarbon Solution Calculated by the IPM Method[a]

Radical	Hydroperoxide	E (kJ mol^{-1})	log A, A (L mol^{-1} s^{-1})	k (400 K) (L mol^{-1} s^{-1})
		$R^{\bullet} + R_1OOH \rightarrow ROH + R_1O^{\bullet}$[b]		
$C^{\bullet}H_3$	H_2O_2	36.7	9.30	3.22×10^4
$MeC^{\bullet}H_2$	H_2O_2	35.4	9.30	4.77×10^4
$Me_2C^{\bullet}H$	H_2O_2	32.8	9.30	1.04×10^5
$Me_3C^{\bullet}$	H_2O_2	33.6	9.30	8.19×10^4
$PhC^{\bullet}H_2$	H_2O_2	48.6	9.30	9.01×10^2
$C^{\bullet}H_3$	Me_3COOH	27.5	9.00	2.56×10^5
$CH_3C^{\bullet}H_2$	Me_3COOH	26.4	9.00	3.57×10^5
$Me_2C^{\bullet}H$	Me_3COOH	24.1	9.00	7.13×10^5
$Me_3C^{\bullet}$	Me_3COOH	24.8	9.00	5.77×10^5
$PhC^{\bullet}H_2$	Me_3COOH	37.9	9.00	1.12×10^4
		$RCH_2C^{\bullet}H_2 + ROOH \rightarrow RCH{=}CH_2 + H_2O + RO^{\bullet}$[c]		
$CH_3C^{\bullet}H_2$	Me_3COOH	47.0	8.54	2.55×10^2
$Me_2C^{\bullet}H$	Me_3COOH	46.2	8.85	6.58×10^2
$EtMeC^{\bullet}H$	Me_3COOH	43.4	8.40	5.38×10^2
$Me_3C^{\bullet}$	Me_3COOH	47.4	9.00	6.46×10^2
$MePhC^{\bullet}H$	Me_3COOH	64.7	8.48	1.06
$EtPhC^{\bullet}H$	Me_3COOH	62.0	8.30	1.60
		$RC^{\bullet}HOH + ROOH \rightarrow RCHO + H_2O + RO^{\bullet}$[d]		
$MeC^{\bullet}HOH$	H_2O_2	12.8	8.88	1.62×10^7
$Me_2C^{\bullet}OH$	H_2O_2	11.8	8.90	2.30×10^7
$PhC^{\bullet}HOH$	H_2O_2	20.5	8.78	1.26×10^6
$MePhC^{\bullet}OH$	H_2O_2	19.4	8.79	1.82×10^6
$MeC^{\bullet}HOH$	Me_3COOH	3.3	8.89	2.89×10^8

TABLE 4.23 (*continued*)

Radical	Hydroperoxide	E (kJ mol^{-1})	log A, A (L mol^{-1} s^{-1})	k (400 K) (L mol^{-1} s^{-1})
$Me_2C^{\bullet}OH$	Me_3COOH	2.4	8.95	4.37×10^8
$PhC^{\bullet}HOH$	Me_3COOH	9.8	8.65	2.36×10^7
$MePhC^{\bullet}OH$	Me_3COOH	8.8	8.67	3.33×10^7
	$HO_2^{\bullet} + ROOH \rightarrow RO^{\bullet} + H_2O + O_2$[e]			
$HO_2^{\bullet}$	H_2O_2	47.1	8.60	2.83×10^2
$HO_2^{\bullet}$	ROOH	33.2	8.30	9.24×10^3
	$RO_2^{\bullet} + R^1CH(OOH)R^2 \rightarrow ROOH + HO^{\bullet} + R^1C(O)R^2$[f]			
cyclo-$C_6H_{11}O_2^{\bullet}$	*cyclo*-$C_6H_{11}OOH$	38.0	6.97	1.01×10^2
cyclo-$C_6H_9O_2^{\bullet}$	$PhCH(OOH)CH_3$	55.0	9.01	67.7

[a] See Chapter 9.
[b] See Ref. 172.
[c] See Ref. 169.
[d] See Refs. 170 and 173.
[e] See Refs. 170 and 174.
[f] See Refs. 165 and 171.

4.2.7 Interaction of Hydroperoxides with Ketones

Hydroperoxides undergo reversible addition across the carbonyl group of a ketone with the formation of a new peroxide:

$$ROOH + R^1C(O)R^2 \Leftrightarrow R^1C(OH)(OOR)R^2$$

The formed hydroxyperoxide decomposes to free radicals much more rapidly than alkyl hydroperoxide.[175] So, the equilibrium addition of the hydroperoxide to the ketone changes the rate of formation of radicals. This effect was first observed for cyclohexanone and 1,1-dimethylethyl hydroperoxide.[175] In this system, the rate radical formation increases with an increase in the ketone concentration. The mechanism of radical formation is described by the following scheme:

$$ROOH \rightarrow RO^{\bullet} + HO^{\bullet} \qquad (k_{i1})$$

$$ROOH + R^1C(O)R^2 \Leftrightarrow R^1C(OH)(OOR)R^2 \qquad (K)$$

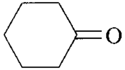
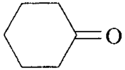
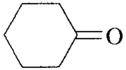
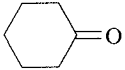
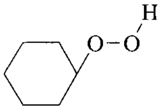
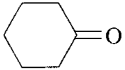
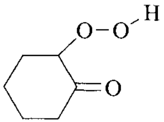
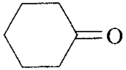
$$R^1C(OH)(OOR)R^2 \rightarrow R^1C(OH)(O^{\bullet})R^2 + RO^{\bullet} \qquad (k_{i2})$$

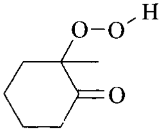
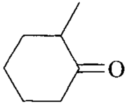
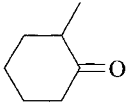
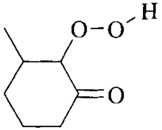
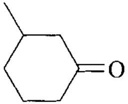
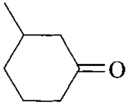
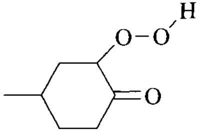
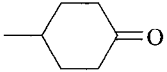
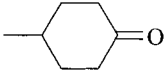
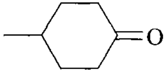
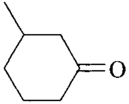
and the rate of radical generation is given by Eq (4.2)

$$\begin{aligned} v_i &= 2ek_1[ROOH] + 2ek_2[R^1C(OH)(OOR)R^2] \\ &= (2ek_1 + 2ek_2K[R^1C(O)R^2])[ROOH](1 + K[R^1COR^2])^{-1} \end{aligned} \qquad (4.2)$$

The values of k_1, k_2, and K are collected in Table 4.24.

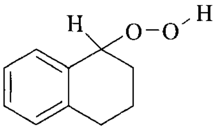
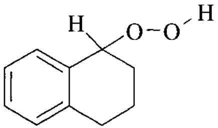
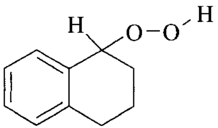
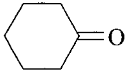
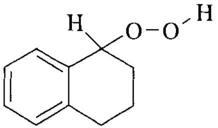
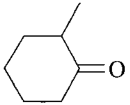
TABLE 4.24 Rate Constants for the Decomposition of ROOH (k_1) and $R^1C(OH)(OOR)R^2$ (k_2) and the Equilibrium Constant K of the Hydroxyalkyl Peroxide Formation from ROOH and Ketone

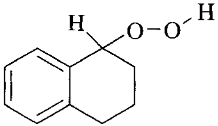
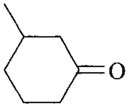
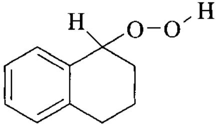
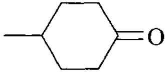
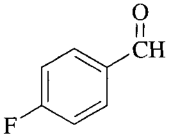
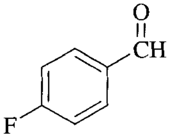
Hydroperoxide	Ketone	Solvent	T (K)	k_1 (s^{-1})	k_2 (s^{-1})	K (L mol^{-1})	Reference
1,1-Dimethylethyl-, Me_3COOH		Chlorobenzene	383–400	$k_1 = 3.6 \times 10^{12} \exp(-138.1/RT)$ $k_2 = 3.6 \times 10^{9} \exp(-108.8/RT)$ $K = 6.9 \times 10^{-7} \exp(46.0/RT)$			175
1,1-Dimethylethyl-, Me_3COOH		Carbon tetrachloride	295–313	$K = 7.61 \times 10^{-3} \exp(10.5/RT)$			176
1-Methyl-1-phenyl ethyl-, $Me_2PhCOOH$		Chlorobenzene	393	$k_1 = 2.1 \times 10^{-6}$ $k_2 = 5.7 \times 10^{-6}$, $K = 1.0$			177
1-Methyl-1-phenyl ethyl-, $Me_2PhCOOH$		Carbon tetrachloride	295–313	$K = 1.56 \times 10^{-3} \exp(12.5/RT)$			176
Cyclohexyl-, 		Chlorobenzene	353–383	$k_1 = 6.3 \times 10^{11} \exp(-133.9/RT)$ $k_2 = 4.0 \times 10^{4} \exp(-63.6/RT)$ $K = 1.4 \times 10^{-5} \exp(33.0/RT)$			178
2-Oxocyclohexyl-, 		Chlorobenzene	393	$k_1 = 1.2 \times 10^{-5}$ $k_2 = 3.0 \times 10^{7} \exp(-85.3/RT)$			178
1-Acetylethyl-, MeC(O)CH(OOH)Me	MeC(O)Et	Benzene	293–343	$k_1 = 3.4 \times 10^{12} \exp(-114.6/RT)$ $k_2 = 1.15 \times 10^{10} \exp(96.2/RT)$ $K = 0.8$ (293 K)			179

1-Methyl-2-oxocyclohexyl-, 			373–403	$k_2 = 1.9 \times 10^6 \exp(-76.1/RT)$	5
2-Methyl-5-oxocyclohexyl-, 			373–403	$k_2 = 6.9 \times 10^6 \exp(-79.5/RT)$	5
3-Methyl-5-oxocyclohexyl-, 			373–403	$k_2 = 8.9 \times 10^5 \exp(-72.4/RT)$	5
1,1-Dimethylethyl-, Me_3COOH		Carbon tetrachloride	295–313	$K = 7.60 \times 10^{-3} \exp(10.5/RT)$	176
1,1-Dimethylethyl-, Me_3COOH		Carbon tetrachloride	295–313	$K = 1.17 \times 10^{-2} \exp(8.4/RT)$	176

(continued overleaf)

TABLE 4.24 (*continued*)

Hydroperoxide	Ketone	Solvent	T (K)	k_1 (s^{-1})	k_2 (s^{-1})	K ($L\,mol^{-1}$)	Reference
1-Tetralyl-, 	MeC(O)Me	Carbon tetrachloride/Tetralin (1:1)	293	$K = 0.53$			176
1-Tetralyl-, 	Me(CO)Et	Carbon tetrachloride/Tetralin (1:1)	293	$K = 0.38$			176
1-Tetralyl-, 		Carbon tetrachloride/Tetralin (1:1)	293–313	$K = 4.07 \times 10^{-2} \exp(10.5/RT)$			176
1-Tetralyl-, 		Carbon tetrachloride/Tetralin (1:1)	293	$K = 0.29$			176

1-Tetralyl-, 		Carbon tetrachloride/Tetralin (1:1)	293–313	$K = 0.23 \exp(8.4/RT)$	176
1-Tetralyl-, 		Carbon tetrachloride/Tetralin (1:1)	293–313	$K = 4.74 \times 10^{-2} \exp(9.6/RT)$	176
Hydrogen peroxide H_2O_2	PhCH(O)	PhCH(O)	333–348	$k_2 = 1.15 \times 10^{14} \exp(-122.5/RT)$	180
Hydrogen peroxide H_2O_2			323–343	$k_2 = 2.69 \times 10^{15} \exp(-129.2/RT)$	180
Hydrogen peroxide H_2O_2	$F_5C_6CH(O)$	$F_5C_6CH(O)$	353–373	$k_2 = 1.93 \times 10^{18} \exp(-160.0/RT)$	180

REFERENCES

1. A. Rieche, *Die Bedeutung der Organischen Peroxyde fur die Chemische Wissenschaft und Technik*, Enke, Stuttgart, Germany, 1936.
2. K. I. Ivanov, *Intermediate Products and Reactions of Hydrocarbon Autoxidation* (Russian) Gostopthekhizdat, Moscow, 1949.
3. G. Scott, *Atmospheric Oxidation and Antioxidants*, Elsevier, Amsterdam, The Netherlands, 1965.
4. N. M. Emanuel, E. T. Denisov, and Z. K. Maizus, *Liquid-Phase Oxidation of Hydrocarbons*, Plenum Press, New York, 1967.
5. E. T. Denisov, N. I. Mitskevich, and V. E. Agabekov, *Liquid-Phase Oxidation of Oxygen-Containing Compounds*, Consultants Bureau, New York, 1977.
6. *Liquid-Phase Oxidation in Comprehensive Chemical Kinetics*, C. H. Bamford and C. F. H. Tipper (Eds.), Elsevier, Amsterdam, The Netherlands, 1980, Vol. 16.
7. E. T. Denisov and T. G. Denisova, *Handbook of Antioxidants*, CRC Press, Boca Raton, FL, 2000.
8. E. T. Denisov and V. V. Azatyan, *Inhibition of Chain Reactions*, Gordon and Breach, London, 2000.
9. A. Rieche, *Alkylperoxide und Ozonide*, Steinkopff, Dresden, Germany, 1931.
10. A. V. Tobolsky and R. B. Mesrobian, *Organic Peroxides: their Chemistry, Decomposition and Role in Polymerisation*, Wiley-Interscience, New York, 1954.
11. E. G. E. Hawkins, *Organic Peroxides*, Spon LTD, London, 1961.
12. A. G. Davies, *Organic Peroxides*, Butterwork, London, 1961.
13. *Organic Peroxides*, D. Swern (Ed.), Wiley-Interscience, New York, 1970.
14. V. L. Antonovskii, *Organic Peroxides as Initiators* (Russian), Khimiya, Moscow, 1972.
15. S. Patai, *The Chemistry Peroxides*, John Wiley & Sons, Inc., New York, 1983.
16. C. Walling, *Free Radicals in Solution*, John Wiley & Sons, Inc., New York, 1962.
17. G. Odian, *Principles of Polymerisation*, Mc Graw-Hill Book Co., New York, 1970.
18. Kh. S. Bagdasaryan, *Theory of Radical Polymerisation* (Russian), Izd-vo Akad. Nauk SSSR, Moscow, 1966.
19. R. Houwink and A. J. Staverman, *Chemie und Technologie der Kunstoffe*, Akademische Verlagsgesellschaft, Leipzig, Germany, 1962.
20. *Free-Radical Polymerisation, in Comprehensive Chemical Kinetics*, C. H. Bamford and C. F. H. Tipper (Eds.), Elsevier, Amsterdam, The Netherlands, 1976, Vol. 14 A.
21. F. Moad and D. H. Solomon, *The Chemistry of Free Radical Polymerisation*, Pergamon, New York, 1995.
22. J. M. Tedder, A. Nechvatal, and A. H. Jubb, *Basic Organic Chemistry, Part 5: Industrial Products*, John Wiley & Sons, Inc., London, 1975.
23. V. L. Antonovskii and M. M. Buzlanova, *Analytical Chemistry of Organic Peroxides* (Russian), Khimiya, Moscow, 1978.
24. C. Wagner, R. Smith, and D. Peters, *Analyt. Chem.* **19**, 976 (1947).
25. R. D. Mair and R. T. Hall, *Treatise on Analytical Chemistry*, John Wiley & Sons, Inc., New York, 1971, Vol. 14, Part 11, p. 444.

26. Yu. L. Slovokhotov, T. V. Timofeeva, and M. Yu. Antipin, *Mol. Structure* **112**, 127 (1984).
27. D. Kass, H. Oberhammer, and D. Brandes, *Mol. Structure* **40**, 65 (1977).
28. A. Yu. Kosnikov, V. L. Antonovskii, and N. A. Turovskii, *Izv. AN SSSR, Ser. Khim.* 791 (1988).
29. A. I. Yanovskii, T. V. Timofeeva, and N. G. Furmanova, *Kristallografiya* **26**, 203 (1981).
30. W. Gase and I. Boggs, *J. Mol. Structure* **116**, 207 (1984).
31. V. L. Antonovskii, *Vestnik Nizhegorodskogo Gosudarstvennogo Universiteta, Organic and Elementoorganic Peroxides* (Russian), Izdatelstvo Nizhegorodskogo Universiteta, Nizhnii Novgorod, Russia, 1996, p. 3.
32. M. F. Rogers and T. W. Campbell, *J. Am. Chem. Soc.* **74**, 4742 (1952).
33. W. Lobuncze and J. R. Rittenhouse, *J. Am. Chem. Soc.* **80**, 3505 (1958).
34. E. S. Dombrovsky and E. D. Hearing, *J. Phys. Chem. Ref. Data* **22**, 805 (1993).
35. E. T. Denisov and T. G. Denisova, *Zh. Fiz. Khim.* **62**, 304 (1988).
36. V. L. Antonovskii, *Progress in Chemistry of Organic Peroxides* (Russian), TSNII Eneftekhim, Moscow, 1992.
37. G. Baker, J. H. Littlefair, R. Show, and J. C. J. Thynne, *J. Chem. Soc.* 6970 (1965).
38. E. I. Blat, M. I. Gerber, and M. B. Neuman, *Acta Physicochim. URSS* **10**, 273 (1939).
39. A. C. Egerton, W. Emte, and G. J. Minkoff, *Discuss. Faraday Soc.* **10**, 278 (1951).
40. Yu. Ya. Van-Chin-Syan and N. S. Kachurina, *Zh. Fiz. Khim.* **61**, 1196 (1987).
41. Yu. Ya. Van-Chin-Syan, Yu. P. Pavlovskii, and N. S. Kachurina, *Zh. Fiz. Khim.* **64**, 553 (1990).
42. Yu. Ya. Van-Chin-Syan, N. S. Kachurina, and G. A. Petrovskaya, *Zh. Fiz. Khim.* **57**, 2888 (1983).
43. Yu. Ya. Van-Chin-Syan, V. F. Korotyuk, and Yu. V. Panchenko, *Zh. Fiz. Khim.* **57**, 2856 (1983).
44. H. A. Swain, Kwan Chi-Yin, and Sung Ho-Nan, *J. Chem. Phys.* **84**, 1347 (1980).
45. Yu. Ya. Van-Chin-Syan, T. N. Dolbneva, and V. P. Vasiliev, *Zh. Fiz. Khim.* **56**, 2833 (1982).
46. Yu. Ya. Van-Chin-Syan, T. N. Dolbneva, and M. A. Dikii, *Zh. Fiz. Khim.* **58**, 2937 (1984).
47. Yu. Ya. Van-Chin-Syan and N. S. Kachurina, *Vestnik Nizhegorodskogo Gosudarstvennogo Universiteta, Organic and Elementoorganic Peroxides* (Russian), Izd-vo Nizhegorodskogo Universiteta, Nizhnii Novgorod, Russia, 1996, p. 29.
48. A. R. Blake and K. O. Kutschke, *Can. J. Chem.* **37**, 1462 (1959).
49. M. F. R. Mulcahy and D. J. Williams, *Austr. J. Chem.* **14**, 534 (1961).
50. L. Batt and S. W. Benson, *J. Chem. Phys.* **36**, 895 (1962).
51. J. Long and G. Skirrow, *Trans. Faraday Soc.* **58**, 1403 (1962).
52. D. H. Shaw and H. O. Pritchard, *Can. J. Chem.* **46**, 2721 (1968).
53. J. H. Ralley, F. F. Rust, and W. E. Vaughan, *J. Am. Chem. Soc.* **40**, 88 (1948).
54. D. K. Lewis, *Can. J. Chem.* **54**, 581 (1976).
55. M. J. Perona and D. M. Golden, *Int. J. Chem. Kinet.* **5**, 55 (1973).
56. E. S. Huyser and R. M. Van Scoy, *J. Org. Chem.* **33**, 3524 (1968).

57. C. Walling and H. P. Wait, *J. Phys. Chem.* **71**, 2361 (1967).
58. C. Walling and G. Metzger, *J. Am. Chem. Soc.* **81**, 5365 (1959).
59. V. L. Antonovskii and L. D. Bezborodova, *Zh. Fiz. Khim.* **44**, 1224 (1970).
60. J. R. L. Smith, E. Nagatomi, A. Stead, D. J. Waddington, and S. D. Beviere, *J. Chem. Soc., Perkin Trans. 2*, 1193 (2000).
61. S. M. Kavun and A. L. Buchachenko, *Izv. AN SSSR, Ser. Khim.* 1483 (1966).
62. E. T. Denisov and V. M. Solyanikov, *Neftekhimiya* **3**, 360 (1963).
63. J. A. Offenbach and A. V. Tobolsky, *J. Am. Chem. Soc.* **79**, 278 (1957).
64. V. V. Zaitseva, A. J. Yurzhenko, and V. D. Enaliev, *Zh. Org. Khim.* **4**, 1402 (1968).
65. O. M. Mashnenko, A. E. Batog, N. J. Mironenko, and M. K. Romantsevich, *Vysokomol. Soed. B*, **10**, 444 (1968).
66. W. A. Pryor, A. Lee, and C. E. Witt, *J. Am. Chem. Soc.* **86**, 4229 (1964).
67. H. C. Bailey and G. W. Godin, *Trans. Faraday Soc.* **52**, 68 (1956).
68. M. S. Kharasch, A. Fono and W. Nudenberg., *J. Org. Chem.* **16**, 105 (1951).`
69. P. A. Ivanchenko, V. V. Kharitonov, and E. T. Denisov, *Vysokomol. Soedin. A*, **11**, 1622 (1969).
70. E. M. Dannenberg, M. E. Jordan, and H. M. Cole, *J. Pol. Sci.* **31**, 127 (1958).
71. C. R. Parks and O. Lorenz, *J. Pol. Sci.* **50**, 287 (1961).
72. D. K. Thomas, *J. Appl. Pol. Sci.* **6**, 613 (1963).
73. B. M. E. Van der Hoff, *Ind. Eng. Chem. Prod. Res. Develop.* **2**, 273 (1963).
74. Yu. B. Shilov, *Kinetics and Mechanism of Initiated Oxidation of PP and PE in Solid Phase,* Ph.D. Thesis (Russian), Institute of Chemical Physics, Chernogolovka, USSR, 1979.
75. Yu. B. Shilov and E. T. Denisov, *Vysokomol. Soedin. A*, **20**, 1849 (1978).
76. A. P. Griva and E. T. Denisov, *Kinet. Katal.* **17**, 1465 (1976).
77. Y. Takezaki and C. Takenchi, *J. Chem. Phys.* **22**, 1527 (1954).
78. P. L. Hanst and J. G. Calvert, *J. Phys. Chem.* **63**, 104 (1959).
79. J. H. Barker, S. W. Benson, and D. M. Golden, *Int. J. Chem. Kinet.* **9**, 31 (1977).
80. L. Batt and G. N. Rattray, *Int. J. Chem. Kinet.* **11**, 1183 (1979).
81. Y. Ogata, K. Tomizawa, K. Furuta, and H. Kato, *J. Chem. Soc., Perkin Trans. 2*, 110 (1981).
82. Y. Ogata and K. Tomizawa, *J. Org. Chem.* **43**, 261 (1978).
83. Y. Ogata and E. Hayashi, *Bull. Chem. Soc. Jpn.* **50**, 323 (1974).
84. Y. Ogata, K. Tokagi, and E. Hayashi, *J. Org. Chem.* **44**, 856 (1979).
85. K. Moriya, *Rep. Phys. Chem. Jpn.* 143 (1946).
86. R. E. Rebbert and K. J. Laidler, *J. Chem. Phys.* **20**, 574 (1952).
87. J. R. Harrison, Ph. D. Thesis, University of London, London, 1952.
88. C. Legget and J. C. J. Thynne, *Trans. Faraday Soc.* **63**, 2504 (1967).
89. R. L. East and L. Phillips, *J. Chem. Soc. A* 331 (1970).
90. G. A. Hughes and L. Phillips., *J. Chem. Soc. A* 894 (1967).
91. K. A. Sahetchian and R. Rigny, *J. Chem. Soc., Faraday Trans. 2*, **83**, 2035 (1987).
92. R. F. Walker and L. Phillips, *J. Chem. Soc. A*, **9**, 2103 (1968).

93. W. H. Hendrickson, Ch. C. Nguyen, J. T. Nguyen, and K. T. Simons, *Tetrahedron Lett.* **36**, 7217 (1995).
94. C. Buxton and W. K. Wilmarth, *J. Phys Chem.* **67**, 2835 (1963).
95. R. Livingston and H. Zeldes, *J. Chem. Phys.* **44**, 1245 (1966).
96. R. Livingston, J. K. Dohrmann, and H. Zeldes, *J. Chem. Phys.* **53**, 2448 (1970).
97. W. A. Pryor, D. M. Huston, T. R. Fiske, T. L. Rickering, and E. Ciuffarin, *J. Am. Chem. Soc.* **86**, 4237 (1964).
98. W. A. Pryor and E. P. Pultinas, *J. Am. Chem. Soc.* **85**, 133 (1963).
99. W. A. Pryor and G. L. Kaplan, *J. Am. Chem. Soc.* **86**, 4234 (1964).
100. K. Matsuyama and Y. Higuchi, *Bull. Chem. Soc. Jpn.* **64**, 259 (1991).
101. A. I. Serdyuk, *Study of Thermal Decomposition of Semi-tert-butyl Peroxyacetates*, Ph.D. Thesis (Russian), Donetsk, USSR, 1975.
102. V. A. Fomin, V. S. Etlis, and I. V. Pettrukhin, *Zh. Obshch. Khim.* **53**, 812 (1983).
103. A. V. Navrotskii, *Oxyperoxides and its Esters. Synthesis and reactions*, Doctor Diss. Thesis (Russian), VGTU, Volgograd, 1999.
104. A. M. Ustinova, *The Synthesis and Study of Some Cycloolefins and their Epoxy Compounds*, Ph.D. Thesis (Russian), DGU, Donetsk, USSR, 1974.
105. A. A. Turovskii, *The Study of Dependence between Thermodynamic Characteristics of Reactants and Transition State of Free Radical Reactions*, Ph.D. Thesis (Russian) L'vov State University, L'vov, USSR, 1968.
106. N. A. Turovskii, *The Study of Structure and Reactivity Peresters and Some Dialkylperoxides in the Thermal Decomposition*, Ph.D. Thesis (Russian), Institute of Physical-Organic Chemistry, Donezk, USSR, 1978.
107. D. Barnard and N. Hargrave, *Anal. Chim. Acta* **10**, 476 (1951).
108. L. Dulog and K.-H. Burg, *Z. Anal. Chem.* **203**, 184 (1964).
109. J. R. Rittenhouse, *J. Am. Chem. Soc.* **80**, 4850 (1958).
110. S. G. Lias, J. F. Liebman, R. D. Levin, and S. A. Kafafi, *NIST Standard Reference Database*, 19A, NIST Positive Ion Energetics, Version 2.0, NIST, Gaithersburg, MD, 1993.
111. S. W. Benson and H. E. O'Neal, *Kinetic Data on Gas Phase Unimolecular Reactions*, NSRDS, Washington, D.C., 1970.
112. N. A. Kozlov and I. B. Rabinovich, in *Trudy po Khimii i Khimicheskoy Tekhnologii* (Russian), Gorkiy State University, Gorkiy, 1964, Vol. 2 (10), p. 189.
113. E. R. Bell, F. H. Dickey, and J. H. Raley, *Ind. Eng. Chem.* **41**, 2597 (1949).
114. W. Pritzkow and K. A. Muller, *Chem. Ber.* **89**, 2318 (1956).
115. J. W. Breitenbach and J. Derkosch, *Monatsh. Chem.* **81**, 689 (1950).
116. J. P. Fortuin and H. I. Waterman, *Chem. Eng. Sci.* **2**, 182 (1953).
117. W. Pritzkow and R. Hoffman, *J. Prakt. Chem.* N **14**, 13 (1961).
118. H. A. Swain, L. S. Silbert, and J. C. Miller, *J. Am. Chem. Soc.* **86**, 2562 (1984).
119. Yu. A. Lebedev and E. A. Miroshnichenko, *Thermochemistry of Evaporation of Organic Compounds* (Russian), Nauka, Moscow, 1981.
120. E. T. Denisov and T. G. Denisova, *Zh. Fiz. Khim,* **57**, 304 (1988).
121. J. L. Holmes, F. P. Lossing, and P. M. Mayer, *J. Am. Chem. Soc.* **113**, 9723 (1991).
122. E. T. Denisov and T. G. Denisova, *Kinet. Catal.* **34**, 173 (1993).

123. G. E. Zaikov, Z. K. Maizus, and N. M. Emanuel, *Izv. AN SSSR, Ser. Khim.* 256 (1968).

124. E. T. Denisov, *Zh. Fiz. Khim.* **38**, 2085 (1964).

125. O. P. Yablonskii, N. S. Lastochkina, and V. A. Belyaeva, *Neftekhimiya* **13**, 851 (1973).

126. C. Walling and L. Heaton, *J. Am. Chem. Soc.* **87**, 48 (1965).

127. C. Walling and L. Heaton, *J. Am. Chem. Soc.* **87**, 38 (1965).

128. G. L. Bitman, *Intermolecular Association of tert.-Butyl Hydroperoxide*, Ph.D. Thesis (Russian), Institute of Fine Chemical Technology, Moscow, 1973.

129. I. F. Franchuk and L. I. Kalinina, *Teor. Experim. Khimiya* **8**, 553 (1972).

130. O. P. Yablonskii, A. K. Kobyakov, and V. A. Belyaeva, *Neftekhimiya* **14**, 446 (1974).

131. E. I. Solov'eva, *Physico-Chemical Study of Associative Interaction of Organic Peroxides with Bases*, Ph.D. Thesis (Russian), Gor'kiy State University, Gor'kiy, USSR, 1979.

132. T. I. Drozdova, V. T. Varlamov, V. P. Lodygina, and A. L. Aleksandrov, *Zh. Fiz. Khim.* **52**, 735 (1978).

133. M. M. Mogilevich and E. M. Pliss, *Oxidation and Oxidizing Polymerization of Nonsaturated Compounds* (Russian), Khimiya, Moscow, 1990.

134. O. P. Yablonskii, L. F. Lapuka, N. M. Rodionova, Z. A. Pokrovskaya, and V. A. Belyaeva, *Neftekhimiya* **14**, 101 (1974).

135. I. F. Franchuk and L. I. Kalinina, *Zh. Prikl. Spektroskopii* **15**, 896 (1971).

136. B. Plesnicar, V. Menart, and M. Hodoscek, *J. Chem. Soc., Perkin Trans. 2*, **9**, 1397 (1986).

137. N. V. Zolotova and E. T. Denisov, *J. Polym. Sci.* **9**, 3311 (1971).

138. Yu. B. Shilov and E. T. Denisov, *Vysokomol. Soedin. A*, **19**, 1244 (1977).

139. M. Iring, T. Kelen, and F. Tudos. *Makromol Chem.* **175**, 467 (1974).

140. V. S. Pudov, B. A. Gromov, E. T. Sklyarova, and M. B. Neiman, *Neftekhimiya* **3**, 743 (1963).

141. J. C. W. Chien and C. R., Boss, *J. Polym. Sci. A 1*, **12**, 3091 (1967).

142. E. L. Shanina and V. A. Roginskii, *Vysokomol. Soedin. B*, **20**, 145 (1978).

143. N. Y. Rapoport and V. B. Miller, *Vysokomol. Soedin. A*, **18**, 2343 (1976).

144. A. P. Griva, L. N. Denisova, Yu. B. Shilov, and E. T. Denisov, *Vysokmol. Soedin. B*, **28**, 658 (1986).

145. F. R. Mayo and A. A. Miller, *J. Am. Chem. Soc.* **78**, 1023 (1956).

146. F. R. Mayo, *J. Am. Chem. Soc.* **80**, 2465 (1958).

147. D. G. Hendry, F. R. Mayo, and D. A. Gones, *Ind. Eng. Chem. Prod. Res. Develop.* **7**, 145 (1968).

148. J. C. W. Chien, *J. Polym. Sci. Part 1*, **6**, 375 (1968).

149. N. M. Emanuel, S. G. Kiryushkin, and A. P. Mar'in, *Dokl. Akad. Nauk SSSR* **275**, 408 (1984).

150. A. M. Tolks, *Kinetics and Mechanism of Hydroperoxide Groups in Polymers*, Ph.D. Thesis (Russian) Polytechnical Institute, Riga, USSR, 1973.

151. V. M. Goldberg, V. I. Esenin, and I. A. Krasochkina, *Vysokomol. Soedin. A*, **19**, 1729 (1977).
152. I. G. Latyshkaeva, G. N. Belov, T. A. Bogaevskaya, and Y. A. Shlyapnikov, *Vysokmol. Soedin. B*, **24**, 70 (1982).
153. Z. Manyasek, D. Beren, and M. Michko, *Vysokomol. Soed.* **3**, 1104 (1961).
154. V. V. Dudorov, A. L. Samvelyan, and A. F. Lukovnikov., *Izv. AN Arm. SSR, Ser. Khim.* **15**, 1104 (1962).
155. *Ageing and Stabilization of Polymers* (Russian), A. S. Kuzminskii, Khimiya (Ed.), Moscow, 1966.
156. T. V. Monakhova, T. A. Bogaevskaya, B. A. Gromov, and Y. A. Shlyapnikov, *Vysokomol. Soedin. B*, **16**, 91 (1974).
157. S. G. Kiryushkin and Y. A. Shlyapnikov, *Dokl. AN SSSR* **220**, 1364 (1975).
158. S. G. Kiryushkin and Y. A. Shlyapnikov, *Vysokomol. Soedin. B*, **16**, 702 (1974).
159. J. C. W. Chien and H. Jabloner, *J. Polym. Sci. Part. A-1*, **6**, 393 (1968).
160. V. S. Pudov and M. B. Neiman, *Neftekhimiya* **2**, 918 (1962).
161. V. M. Goldberg, V. N. Esenin, and I. A. Krasochkina, *Vysokomol. Soedin. A*, **19**, 1720 (1977).
162. E. A. Il'ina, S. M. Kavun, and Z. I. Tarasova, *Vysokomol. Soedin. B*, **17**, 388 (1975).
163. R. Hiatt, J. Clipsham, and T. Visser, *Can. J. Chem.* **42**, 2754 (1964).
164. T. G. Degtyareva, V. M. Solyanikov, E. T. Denisov, and V. V. Komkin, *Neftekhimiya* **13**, 229 (1973).
165. A. E. Semenchenko, V. M. Solyanikov, and E. T. Denisov, *Neftekhimiya* **11**, 555 (1971).
166. M. L. Poutsma, in *Free Radicals*, J. K. Kochi (Ed.), John Wiley & Sons, Inc., New York, 1973, Vol. 2, p. 113.
167. T. I. Drozdova, A. L. Aleksandrov, and E. T. Denisov, *Izv. AN SSSR, Ser. Khim.* 967 (1978).
168. T. I. Drozdova, A. L. Aleksandrov, and E. T. Denisov, *Izv. AN SSSR, Ser. Khim.* 1213 (1978).
169. E. T. Denisov, *Neftekhimiya* **39**, 434 (1999).
170. E. T. Denisov, *Kinet. Catal.* **40**, 217 (1999).
171. I. P. Hajdu, I. Nemes, D. Gal, V. L. Rubailo, and N. M. Emanuel, *Can. J. Chem.* **55**, 2677 (1977).
172. T. S. Pokidova and E. T. Denisov, *Neftekhimia* **38**, 269 (1998).
173. J. S. B. Park, P. M. Wood, B. C. Gilbert, and A. C. Whitwood, *J. Chem. Soc., Perkin Trans. 2*, 923 (1999).
174. P. Ulanski and C. von Sonntag, *J. Chem. Soc., Perkin Trans. 2*, 165 (1999).
175. E. T. Denisov, *Dokl. AN SSSR* **146**, 394 (1962).
176. V. L. Antonovskii and V. A. Terentiev, *Zh. Fiz. Khim.* **43**, 2727 (1969).
177. E. T. Denisov, *Zh. Fiz. Khim.* **37**, 1896 (1963).
178. E. T. Denisov and L. N. Denisova, *Izv. AN SSSR, Ser. Khim.* 1731 (1963).
179. G. E. Zaikov, Z. K. Maizus, and N. M. Emanuel, *Izv. AN SSSR, Ser. Khim.* 53 (1968).
180. A. I. Rakhimov, *Vestnik Nizhegorodskogo Gosudarstvennogo Universiteta* (Russian), Izd-vo Nizhegorodskogo Universiteta, Nizhnii Novgorod, Russia, 1996, p. 115.

Handbook of Free Radical Initiators. E.T. Denisov, T.G. Denisova, T.S. Pokidova
Copyright © 2003 John Wiley & Sons, Inc.
ISBN: 0-471-20753-5

5

DIACYL PEROXIDES, PEROXY ESTERS, POLYATOMIC, AND ORGANOMETALLIC PEROXIDES

5.1 DIACYL PEROXIDES

5.1.1 Synthesis and Analysis

Diacyl peroxides are widely used as radical initiators in synthesis, kinetic experiments, and chemical engineering at moderate temperatures (350–400 K). They are formed as products of aldehyde oxidation by dioxygen. Several methods of their synthesis from hydrogen peroxide and peroxy acids were developed (see Table 5.1).[1–5] The physical properties of selected diacyl peroxides are listed in Table 5.2 and their trade names are in Table 5.3.

A great variety of different analytical techniques for the estimation of diacyl peroxides are known. Among them, the iodometric technique has been used for a long time.[7] According to this method, peroxide is reduced by HI and iodine is formed in stoichiometric amounts. The amount of formed I_2 is measured by reduction with thiosulfate using any titrometric technique or photometrically.

$$\mathrm{RC(O)OOC(O)R + 2HI \rightarrow 2RC(O)OH + I_2}$$

$$\mathrm{2Na_2S_2O_3 + I_2 \rightarrow 2NaI + Na_2S_4O_6}$$

A few analytic procedures for accurate estimation of diacyl peroxides were proposed:

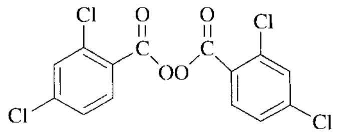
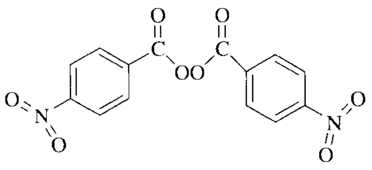
1. Reduction of peroxide occurs in a solution of isopropyl alcohol saturated with NaI in the presence of acetic acid and a CO_2 atmosphere at 373 K (in water bath).[8] The reaction is finished in 15 min. Relative standard deviation equals 0.2%.

TABLE 5.1 Synthetic Methods of Production of Diacyl Peroxides[a]

Reaction	Reactants	Catalyst
$2RC(O)Cl + M_2O_2 \rightarrow RC(O)OOC(O)R + 2MCl$	$RC(O)Cl$, $H_2O_2(Na_2O_2, BaO_2)$	$(Na_2CO_3$, pyridine, alkalis)
$(RCO)_2O + M_2O_2 \rightarrow RC(O)OOC(O)R + M_2O$	$(RCO)_2O$, $H_2O_2(Na_2O_2, BaO_2)$	$(Na_2CO_3$, pyridine, alkalis)
$2RCOOH + H_2O_2 + 2C_6H_{11}N{=}C{=}NC_6H_{11} \rightarrow RC(O)OOC(O)R + 2C_6H_{11}NHC(O)NHC_6H_{11}$	$RCOOH$, H_2O_2, $C_6H_{11}N{=}C{=}NC_6H_{11}$	
$R^1C(O)OOH + RC(O)Cl \rightarrow R^1C(O)OOC(O)R + HCl$	$RC(O)OOH$, $RC(O)Cl$	(NaOH, pyridine)
$R^1C(O)OOH + (RCO)_2O \rightarrow R^1C(O)OOC(O)R + RC(O)OH$	$R^1C(O)OOH$, $(RCO)_2O$	H_2SO_4
$R^1CHO + O_2 + (RCO)_2O \rightarrow R^1C(O)OOC(O)R + RC(O)OH$	R^1CHO, $(RCO)_2O$, O_2	Peroxide, *hν*, O_3, MeCOONa

[a] See Refs. 1–5.

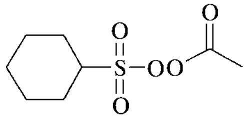
TABLE 5.2 Physical Properties of Selected Diacyl Peroxides[a]

Peroxide	CAS Registry Number	Belstein Registry Number	MW	bP (K)	mp (K)
Diacetyl-, MeC(O)OOC(O)Me	[110-22-5]	1753975	116.01	336	303
Dibenzoyl-, PhC(O)OOC(O)Ph	[94-36-0]	984320	242.06		378
Bis(2,4-dichlorobenzoyl)-, 	[133-4-2]	2008711	377.90		379
Bis(4-nitrobenzoyl)-, 	[1712-84-1]	1916959	332.03		429
Didodecanoyl-, $Me(CH_2)_{10}C(O)OOC(O)(CH_2)_{10}Me$	[105-74-8]	1804936	398.34		322
Acetyl benzoyl-, PhC(O)OOC(O)Me	[644-31-5]	1911081	180.04	403	310

[a] See Ref. 6.

2. A sample with peroxide is inserted into the vessel containing acetic anhydride (10 mL) and 1 g of KI. In 20 min, 50 mL of water is added and a titrometric estimation of the formed diiodine using starch as an indicator is performed.[9]
3. A sample of peroxide is introduced into the vessel with 20 mL of acetone. Solid dry CO_2 is added and solution is heated to room temperature. Then 1 mL of saturated solution of NaI in acetone is added, and a reaction occurs in seconds. The formed diiodine is estimated titrometrically. The relative standard deviation is equal to 0.5%.[10]

TABLE 5.3 Trade Names of Diacyl Peroxides and Peroxydicarbonates

Peroxide	Trade name	Company
Acetyl cyclohexylsulfonyl	Luperox 228	Elf atochem
	Perhexa ACS	Nippon Oil & Fats Co
	Interox ACSP	Interox
Bis(2-methylpropanoyl)-, $Me_2CHC(O)OOC(O)CHMe_2$	Peroyl IB	Nippon Oil & Fats Co
Bis(succinic acid)-, $HOC(O)CH_2CH_2C(O)OOC(O)CH_2CH_2C(O)OH$	Peroyl SA	Nippon Oil & Fats Co
Bis(3,5,5-trimethylhexanoyl)-, $Me_3CCH_2CH(Me)CH_2C(O)OOC(O)CH_2CH(Me)CH_2CMe_3$	Luperox 219	Elf atochem
	Trigonox 36	Akzo
	Peroyl D	Nippon Oil & Fats Co
	Interox INP	Interox
Diacetyl-, $MeC(O)OOC(O)Me$	Peroyl A	Nippon Oil & Fats Co
	Interox AP	Interox
Dibenzoyl-, $PhC(O)OOC(O)Ph$	Luperox A75	Elf atochem
	Lucidol	Akzo
	Nyper	Nippon Oil & Fats Co
	Interox BP	Interox
Didecanoyl-, $Me(CH_2)_8C(O)OOC(O)(CH_2)_8Me$	Luperox DEC	Elf atochem
	Perkadox SE 10	Akzo
	Peroyl D	Nippon Oil & Fats Co

(continued overleaf)

TABLE 5.3 (*continued*)

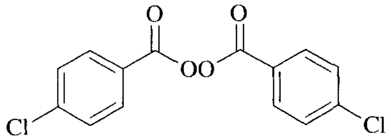
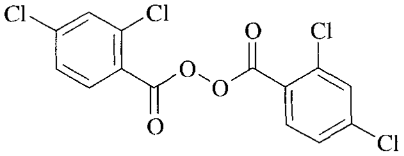
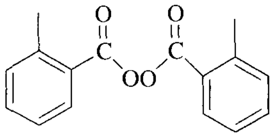
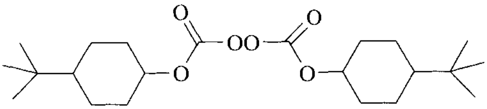
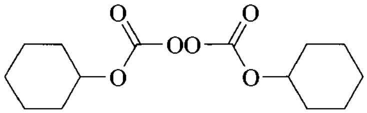
Peroxide	Trade name	Company
Didodecanoyl-, $Me(CH_2)_{10}C(O)OOC(O)(CH_2)_{10}Me$	Interox DP Luperox LP Laurox Peroyl L	Interox Elf atochem Akzo Nippon Oil & Fats Co
Dioctanoyl-, $Me(CH_2)_6C(O)OOC(O)(CH_2)_6Me$	Interox LP Perkadox SE Peroyl O	Interox Akzo Nippon Oil & Fats Co
Dipropanoyl-, $EtC(O)OOC(O)Et$	Interox OP Trigonox 19 Peroyl A	Interox Akzo Nippon Oil & Fats Co
Bis(4-chlorobenzoyl)-, 	Interox CLBP	Interox
Bis(2,4-dichlorobenzoyl)-, 	Perkadox SD Nyper CS Interox DCLBP	Akzo Nippon Oil & Fats Co Interox
Bis(2-methylbenzoyl)-, 	Nuper MT-80 Interox MBP	Nippon Oil & Fats Co Interox
Peroxydicarbonate, Bis[4-(1′,1′-dimethylethyl)-cyclohexyl]-, 	Perkadox 16 Interox BCHPC	Akzo Interox
Bis(2-ethoxyethyl)-, $EtO(CH_2)_2OC(O)OOC(O)O(CH_2)_2OEt$	Peroyl EPP	Nippon Oil & Fats Co
Bis(2-ethylhexyl)-, $[Me(CH_2)_3CH(Et)CH_2OC(O)O]_2$		

TABLE 5.3 (*continued*)

Peroxide	Trade name	Company
	Luperox 223	Elf atochem
	Peroyl OPP	Nippon Oil & Fats Co
	Trigolox EHP	Akzo
	Intepox EHPC	Interox
Bis(3-methoxy-3-methylbutyl)-, $Me_2(MeO)CCH_2CH_2OC(O)O\text{-}OC(O)OCH_2CH_2CMe_2(OMe)$	Peroyl SOP	Nippon Oil & Fats Co
Bis(1-methyl-2-methoxyethyl)-, $[MeOCH_2CHMeOC(O)O]_2$	Peroyl MIP	Nippon Oil & Fats Co
Bis(1-methylethyl)-, $Me_2CHOC(O)OOC(O)OCHMe_2$	Peroyl IPP	Nippon Oil & Fats Co
	Perkadox IPP	Akzo
	Intepox IPPC	Interox
Bis(1-methylpropyl)-, $EtCH(Me)OC(O)OOC(O)OCH(Me)Et$	Trigonox SBP	Akzo
	Interox SBPC	Interox
Dibutyl-, $BuOC(O)OOC(O)OBu$	Trigonox NBP	Akzo
	Interox NBPC	Interox
Dicyclohexyl-, 	Perkadox 18	Akzo
	Interox CHPC	Interox
Dihexadecyl-, $Me(CH_2)_{15}OC(O)OOC(O)O(CH_2)_{15}Me$	Interox CEPC	Interox
Dipropyl-, $PrOC(O)OOC(O)OPr$	Peroyl NPP	Nippon Oil & Fats Co
Ditetradecyl-, $Me(CH_2)_{13}OC(O)OOC(O)O(CH_2)_{13}Me$	Interox MYPC	Interox

Diacyl peroxides react rapidly with hydroxylamine with formation of hydroxamic acid. The latter forms the complex with Fe(III) intensively colored.

$$RC(O)OOC(O)R + 2NH_2OH \rightarrow 2RC(O)NHOH + 2H_2O$$

$$3RC(O)NHOH + Fe^{3+} \rightarrow [RC(O)NHO]_3Fe + 3H^+$$

The analytic procedure is the following.[7] One adds 3 mL of hydroxylamine alcohol solution to the sample containing diacyl peroxide. Reaction occurs in 30 min at room temperature. Then a solution of $Fe(ClO_4)_3$ in isopropylalcohol/water is added and the amount of formed complex is estimated spectrophotometrically.

The amount of estimated diacyl peroxide lies in 2 $\times 10^{-5}$–5 $\times$ 10^{-4} mol. The relative standard deviation is equal to 2%.

A volumetric technique of diacyl peroxide estimation was developed using $LiAlH_4$.[7]

$$2RC(O)OOC(O)R + 3LiAlH_4 \rightarrow LiAl(OCH_2R)_4 + 2H_2 + 2LiAlO_2$$

$LiAlH_4$ is added to the sample in the form of a 0.15 *M* solution in diethyl ether. Evolved hydrogen is measured volumetrically. The amount of estimated diacyl peroxide lies in 1.5 $\times 10^{-5}$ $\div$ 1.5 $\times$ 10^{-4} mol. The relative standard deviation is equal to 3%.

Polarography is used for estimation of diacyl peroxides.[7] The reduction of peroxide performs according to the electrochemical equation:

$$RC(O)OOC(O)R + 2e^- \rightarrow 2RC(O)O^-$$

The individual polarographic characteristic of the analyzed compound is the potential $E_{1/2}$ at which the current strength is equal to 50% of its maximum. The mixed-solvent benzene/methanol or benzene/ethanol is used. The amount of peroxide is proportional to the maximum strength of the electric current at peroxide concentration in solution <0.01 mol L^{-1}. The values of $E_{1/2}$ for several diacyl peroxides [RC(O)OOC(O)R] in a benzene/ethanol solution (1 : 1) at [LiCl] = 0.3 mol L^{-1} are the following:[7]

R	n-C_6H_{13}	n-$C_{11}H_{23}$	n-$C_{17}H_{35}$	Ph	o-ClC_6H_4	p-ClC_6H_4
$E_{1/2}$ (V)	−0.20	−0.22	−0.22	−0.16	−0.124	−0.134

Liquid and paper chromatography as well as MS are used for identification and analysis of diacyl peroxides.[7] NMR spectroscopy is used for identification of diacyl peroxides.

5.1.2 Structure of Diacyl Peroxides

The structure of diacyl peroxides was studied experimentally.[11–17] The values of bond lengths and bond angles in diacyl peroxides are collected in Table 5.4. The length of the O—O bond is practically the same as in dialkyl peroxides (see Table 4.4) and the C—O bond is a little shorter (1.39 10^{-10} m vs 1.45 10^{-10} m in diacyl peroxides). The length of the O—O bond in peroxy dicarbonates is 0.03 10^{-10} m shorter than in diacyl peroxides.

The characteristic frequencies of bonds vibration in diacyl peroxides are given in Table 5.5. Since diacyl peroxide has two adjacent carbonyl groups that interact, the double line of the carbonyl group is observed.

TABLE 5.4 Bond Lengths and Bond Angles in Diacyl Peroxides $R^1C_{(1)}(O)OOC_{(2)}(O)R^2$

		Bond Length (10^{-10} m)			Bond Angles (°)		
R^1	R^2	O–O	$C_{(1)}$–O	$C_{(2)}$–O	C–O–O	C–O–O–C	Reference
Me	Me	1.455	1.388	1.388	110.8	84.9	11
Me	Ph	1.455	1.371	1.382	(1) 111.2 (2) 122.7	86.6	12
Me	Ph	1.445	1.382		110.9	86.6	5
Ph	Ph	1.46	1.38	1.38	110	91	13
Ph	Ph	1.435				91.3	5
2-BrC_6H_4	2-BrC_6H_4	1.45	1.35	1.35	111	112	5
2-ClC_6H_4	2-ClC_6H_4	1.45	1.41	1.41	107	106	5
4-ClC_6H_4	4-ClC_6H_4	1.48	1.32	1.32		81	5
4-$MeOC_6H_4$	4-$MeOC_6H_4$	1.462	1.40	1.40	108.9	86.7	14
2-IC_6H_4	2-IC_6H_4	1.52	1.33	1.33	106	110	5
2-IC_6H_4	3-BrC_6H_4	1.47	1.41		111	86	15
2-IC_6H_4	3-ClC_6H_4	1.46	1.32	1.32	111	117	5
$(Ph)_3CCH_2$	$(Ph)_3CCH_2$	1.476	1.276	1.276	110	180	16
cyclo-$C_6H_{11}O$	*cyclo*-$C_6H_{11}O$	1.433	1.379	1.386	90	86.1	17

TABLE 5.5 Frequencies of Valence Vibration of Peroxide Groups in Diacyl Peroxides[a]

	ν (cm^{-1})	
Bond	$[Me(CH_2)_nC(O)O]_2, n = 2–16, CCl_4$	$PhC(O)OOC(O)Ph, CCl_4$
O–O	887÷906	
C(O)–OO–C(O)	1062	997
C=O	1817	1792
C=O	1788	1768
C–O	1127	1224

[a] See Ref. 7.

Due to polar character of the peroxide groups, diacyl peroxides have dipole moments.[7]

5.1.3 Thermochemistry of Diacyl Peroxides

The enthalpies of formation (ΔH_f°) of diacyl peroxides are collected in Table 5.7. The value of the increment formation enthalpy of the acyl peroxide group $\Delta H[(O){-}O{-}C(O)] = -90.6$ kJ mol^{-1} (gas phase), $\Delta H[(O){-}O{-}C(O)] = -206.1$ kJ mol^{-1} (liquid phase), and $\Delta H[(O){-}O{-}C(O)] = -237.6$ kJ mol^{-1} (solid phase).[20] The O–O bond dissociation energies in diacyl peroxides

RC(O)OOC(O)R are the following:

R	Me	Et	Bu	*cyclo*-$C_6H_{11}O$	Ph
D(O−O) (kJ mol^{-1})	131.6	131.2	129.8	123.5	124.4

TABLE 5.6 Dipole Moments and Polarization of Some Diacyl Peroxides[a]

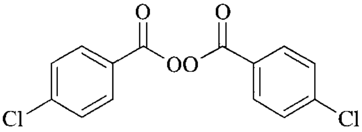
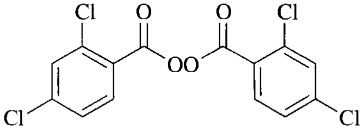
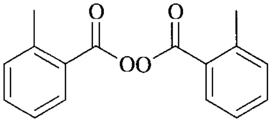
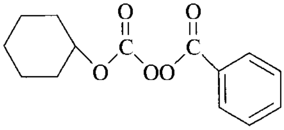
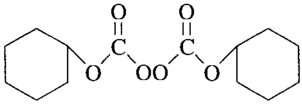
Peroxide	$[Me(CH_2)_{10}C(O)O]_2$	$[PhC(O)O]_2$	$[4\text{-}ClC_6H_4C(O)O]_2$
T (K)	293	303	293
Dipole moment (D)	1.32	1.60	1.36
Polarization (cm^3/mol)	152.3	115.4	114.4

[a] See Ref. 7.

TABLE 5.7 The Formation Enthalpies (ΔH_f°) of Diacyl Peroxides and Peroxydicarbonates in Gas and Condensed Phases

Peroxide	Phase	$-\Delta H_f^\circ$ (kJ mol^{-1})	Reference
Diacetyl-,	Gas	503.3	18
Me(O)OOC(O)Me	Liquid	550.3	
Diacetyl-,	Gas	497.4	5
Me(O)OOC(O)Me			
Dipropanoyl-,	Gas	578.7	19
EtC(O)OOC(O)Et	Liquid	620.1	
Dipropanoyl-,	Gas	580.6	5
EtC(O)OOC(O)Et			
Dibutanoyl-,	Gas	627.0	5
PrC(O)OOC(O)Pr			
Bis(2-methylpropanoyl)-,	Gas	640.1	18
$Me_2CHC(O)OOC(O)CHMe_2$	Liquid	701.8	
Dioctanoyl-,	Gas	829.0	18
$Me(CH_2)_6C(O)OOC(O)(CH_2)_6Me$	Liquid	929.0	
Didecanoyl-,	Gas	871.0	18
$Me(CH_2)_8C(O)OOC(O)(CH_2)_6Me$	Liquid	986.0	
Didodecanoyl-,	Gas	912.6	18
$Me(CH_2)_{10}C(O)OOC(O)(CH_2)_{10}Me$	Liquid	1044.5	
Dibenzoyl-,	Gas	271.7	19
PhC(O)OOC(O)Ph	Liquid	357.4	

TABLE 5.7 (*continued*)

Peroxide	Phase	$-\Delta H_f^\circ$ (kJ mol^{-1})	Reference
Bis(4-chlorobenzoyl)-, 	Gas Liquid	329.7 449.3	18
Bis(2,4-dichlorobenzoyl)-, 	Gas Liquid	384.4 502.4	18
Bis(2-methylbenzoyl)-, 	Gas Liquid	293.4 396.5	18
Benzoyl cyclohexyloxycarbonyl-, 	Gas Liquid	644.4 740.6	20
Benzoyl phenyloxycarbonyl-, PhOC(O)OOC(O)Ph	Gas Liquid	438.9 526.8	18
Dicyclohexylperoxydicarbonate, 	Gas Liquid	1002.6 1103.0	20

5.1.4 Decomposition of Diacyl Peroxides

The homolytic decomposition of diacyl peroxides proceeds via splitting of the weakest O—O bond. The forming acyloxy radicals are very unstable and a cascade of cage reactions (see Chapter 2) succeeds this decomposition.[1-5]

$$\mathrm{MeC(O)OOC(O)Me} \rightarrow [\mathrm{MeCO_2}^\bullet + \mathrm{MeCO_2}^\bullet]$$

$$[\mathrm{MeCO_2^{\bullet}} + \mathrm{MeCO_2^{\bullet}}] \rightarrow \mathrm{MeC(O)OOC(O)Me}$$

$$[\mathrm{MeCO_2^{\bullet}} + \mathrm{MeCO_2^{\bullet}}] \rightarrow \mathrm{MeCO_2^{\bullet}} + \mathrm{MeCO_2^{\bullet}}$$

$$[\mathrm{MeCO_2^{\bullet}} + \mathrm{MeCO_2^{\bullet}}] \rightarrow [\mathrm{Me^{\bullet}} + \mathrm{MeCO_2^{\bullet}}] + \mathrm{CO_2}$$

$$[\mathrm{C^{\bullet}H_3} + \mathrm{CH_3CO_2^{\bullet}}] \rightarrow \mathrm{C^{\bullet}H_3} + \mathrm{CH_3CO_2^{\bullet}}$$

$$[\mathrm{C^{\bullet}H_3} + \mathrm{CH_3CO_2^{\bullet}}] \rightarrow \mathrm{CH_3C(O)OCH_3}$$

$$[\mathrm{C^{\bullet}H_3} + \mathrm{CH_3CO_2^{\bullet}}] \rightarrow [\mathrm{C^{\bullet}H_3} + \mathrm{C^{\bullet}H_3}] + \mathrm{CO_2}$$

$$[\mathrm{C^{\bullet}H_3} + \mathrm{C^{\bullet}H_3}] \rightarrow \mathrm{C^{\bullet}H_3} + \mathrm{C^{\bullet}H_3}$$

$$[\mathrm{C^{\bullet}H_3} + \mathrm{C^{\bullet}H_3}] \rightarrow \mathrm{C_2H_6}$$

For data on the cage effect in diacyl peroxides decomposition see Chapter 2. The yield of cage reaction products increases with increasing viscosity of solvent. The decomposition of diacyl peroxides was the object of intensive study. The values of rate constants of peroxide decomposition (k_d) and initiation ($k_i = 2ek_d$) are collected in Tables 5.8–5.15.

TABLE 5.8 The Rate Constants for the Decomposition of Diacetyl Peroxide in Different Solvents

Solvent	T (K)	E (kJ mol^{-1})	log A, A (s^{-1})	k (353 K) (s^{-1})	Reference
		k_d			
Gas phase	363–463	123.4	14.25	9.78×10^{-5}	21
Acetic acid	328–358	126.4	14.51	6.40×10^{-5}	22
Benzene	328–358	135.1	15.93	8.69×10^{-5}	22
Benzene	353			8.71×10^{-5}	23
Carbon tetrachloride	353			5.66×10^{-5}	23
Carbon tetrachloride	333–373	139.7	16.43	5.73×10^{-5}	24
Carbon tetrachloride/water (3:1 V/V)	353			9.29×10^{-5}	23
Cyclohexane	328–358	131.4	15.27	6.71×10^{-5}	22
Cyclohexene	333–373	133.5	15.59	6.85×10^{-5}	23
1-Hexene	343–373	132.6	15.56	8.69×10^{-5}	23
Isooctane	328–358	134.7	15.82	7.73×10^{-5}	22
2-Methyl-1-pentene	343–373	126.8	14.75	9.71×10^{-5}	23
1-Pentene	343–363	133.9	15.71	7.88×10^{-5}	23
Propionic acid	337.9–358.2	122.6	14.1	9.09×10^{-5}	22
Toluene	323–353	138.1	16.31	7.50×10^{-5}	25
Toluene	323–353	129.7	15.05	7.21×10^{-5}	26
		$k_i = 2ek_d$			
Styrene	343			2.02×10^{-5}	27

TABLE 5.9 The Rate Constants of the Decomposition of Dibenzoyl Peroxide in Different Solvents and Polymers

Medium	T (K)	E (kJ mol^{-1})	log A, A (s^{-1})	k_d, k_i (353 K) (s^{-1})	Reference
k_d					
Acetic acid	353			8.13×10^{-5}	28
Acetic anhydride	333–353	128.5	14.90	7.69×10^{-5}	28
Anisole	353			3.59×10^{-5}	28
Benzene	353–363	128.5	14.04	1.06×10^{-5}	29
Benzene	333–353	123.8	13.64	2.10×10^{-5}	30
Benzene	353			4.04×10^{-5}	23
tert-Butylbenzene	353–363	127.2	14.48	4.55×10^{-5}	29
tert-Butylbenzene	353			3.28×10^{-5}	28
Cumene	318–353	120.5	13.08	1.78×10^{-5}	31
Cumene	353			4.22×10^{-5}	23
Cumene	353			1.95×10^{-5}	32
Cyclohexane	353			1.93×10^{-5}	28
Cyclohexane	353–363	118.0	13.48	1.05×10^{-4}	29
Dioxane	333–353	125.5	14.18	4.07×10^{-5}	33
Ethylbenzene	346.5–358	130.3	14.90	4.16×10^{-5}	34
Ethylbenzene	353			1.85×10^{-5}	32
Ethyl acetate	353			8.97×10^{-5}	28
Iodoethane	353			4.03×10^{-5}	28
Methylcyclohexane	353–363	128.5	14.79	5.97×10^{-5}	29
Nitrobenzene	353			3.28×10^{-5}	28
Phenyl acetate	343–367.5	126.4	14.33	4.23×10^{-5}	35
Styrene	343–363	137.0	15.99	5.22×10^{-5}	36
Styrene	346–358	129.7	14.76	3.70×10^{-5}	34
Toluene	353			3.28×10^{-5}	28
Vinyl acetate	318–353	118.4	13.42	7.94×10^{-5}	37
p-Xylene	353			1.75×10^{-5}	32
Poly(vinyl chloride) + O_2	338–350	171	20.23	8.45×10^{-6}	38
Polyethylene + O_2	353–367	173	20.50	7.96×10^{-6}	39
Polyethylene + N_2	333–363	211	26.42	1.58×10^{-5}	40
Polystyrene + O_2	343–353	149	17.09	1.10×10^{-5}	38
Polystyrene + O_2	353–363	124			38
Polystyrene + O_2	329–356	151	17.46	1.31×10^{-5}	41
Polystyrene + O_2	356–364	126			41
Polystyrene + O_2	353	150	17.20	1.01×10^{-5}	42
Polystyrene + N_2	353	150	17.72	3.34×10^{-5}	42
Triacetyl cellulose + O_2	365–388	117	12.19	7.54×10^{-6}	43
Triacetyl cellulose + vacuum	353–371	117	12.35	1.09×10^{-5}	44
Polyisobutylene + N_2	338–368	148	17.00	1.26×10^{-5}	45
Polycarbonate + CO_2	359–373	125	13.66	1.46×10^{-5}	46
Polypropylene (isotactic) + vacuum	353	125	13.73	1.71×10^{-5}	47
Polypropylene (atactic) + O_2	344–365	124	13.87	3.32×10^{-5}	48
Polypropylene (atactic) + N_2	338–360	125	13.94	2.78×10^{-5}	49
Polypropylene (atactic) + vacuum	353	125	14.33	6.82×10^{-5}	47
Poly(1-butene) + O_2	344–365	124	13.89	3.48×10^{-5}	48

(*continued overleaf*)

TABLE 5.9 ***(continued)***

Medium	T (K)	E (kJ mol^{-1})	log A, A (s^{-1})	k_d, k_i (353 K) (s^{-1})	Reference
Poly(4-methyl-1-pentene) + O_2	344–365	123	13.86	4.57×10^{-5}	48
Polyamide + He	348–371	138	16.08	4.57×10^{-5}	50
Polyamide + O_2	353–371	125	13.76	1.84×10^{-5}	51
Poly(ethyl acrylate) + O_2	358–383	124	13.86	3.25×10^{-5}	52
Poly(methyl methacrylate) + O_2	373	125	13.54	1.01×10^{-5}	53
Poly(methyl methacrylate) + N_2	353	125	13.62	1.33×10^{-5}	54
Poly(methyl methacrylate) + N_2	345–378	169	15.51	5.66×10^{-5}	55
Poly(methyl methacrylate) + N_2	345–398	134			55
Polyformaldehyde + O_2	353–373	124	13.69	2.20×10^{-5}	56
Polyformaldehyde + vacuum	353–373	124	14.33	9.58×10^{-5}	56
	$k_i = 2ek_d$				
Acetone	373–393	130.1	15.31	1.15×10^{-4}	57
Benzene	324–349	123.8	13.48	1.45×10^{-5}	58
Carbon tetrachloride	332–350	136.8	15.68	2.74×10^{-5}	59
Chlorobenzene	378–388	110.2	12.12	6.51×10^{-5}	60
Methyl acetate	322–327	123.8	13.82	3.17×10^{-5}	58
Nitrobenzene	322–343	123.8	13.66	2.19×10^{-5}	58
Styrene	333–353	128.0	14.26	2.09×10^{-5}	61
Styrene	313–343	140.6	16.30	3.13×10^{-5}	27
Toluene	322–343	123.8	13.86	3.48×10^{-5}	58
Toluene	333			9.22×10^{-6}	62
Polyethylene (solid)	365			4.50×10^{-5}	63
Polypropylene (solid)	360			5.90×10^{-5}	64

TABLE 5.10 The Rate Constants for the Decomposition of Symmetrically Substituted Dibenzoyl Peroxides $RC_6H_4C(O)OOC(O)C_6H_4R$ in Different Solvents

Substituent (R)	Solvent	T (K)	E (kJ mol^{-1})	log A, A (s^{-1})	k_d, k_i (353) (s^{-1})	Reference
		k_d *(T = 353 K)*				
3-Br–	Dioxane	353			2.57×10^{-5}	33
4-Br–	Dioxane	353			3.23×10^{-5}	33
2-Me–	Phenyl acetate	335–353	126.4	15.20	3.14×10^{-4}	35
3-Me–	Dioxane	353			4.86×10^{-5}	33
3-Me–	Phenyl acetate	353–368	126.4	14.39	4.62×10^{-5}	35
4-Me–	Dioxane	353			6.13×10^{-5}	33
4-Me–	Phenyl acetate	346.4–368	125.1	14.3	6.15×10^{-5}	35
2-MeO–	Phenyl acetate	323–353	113.8	14.18	2.66×10^{-3}	35
3-MeO–	Phenyl acetate	346.0–363	125.1	14.3	6.16×10^{-5}	35

TABLE 5.10 (*continued*)

Substituent (R)	Solvent	T (K)	E (kJ mol^{-1})	log A, A (s^{-1})	k_d, k_i (353) (s^{-1})	Reference
3-MeO–	Dioxane	353			5.75×10^{-5}	33
4-MeO–	Dioxane	353			1.17×10^{-4}	33
4-MeO–	Phenyl acetate	345.4–360	120.1	13.98	1.62×10^{-4}	35
2-Cl–	Phenyl acetate	333.4–360	123.0	14.79	3.89×10^{-4}	35
3-Cl–	Dioxane	353			2.63×10^{-5}	33
3-Cl–	Phenyl acetate	353–371	128.5	14.67	4.53×10^{-5}	35
4-Cl–	Dioxane	353			3.62×10^{-5}	33
4-Cl–	Phenyl acetate	353–376	127.2	14.43	4.06×10^{-5}	35
3-CN–	Dioxane	353			1.70×10^{-5}	33
4-CN–	Dioxane	353			2.03×10^{-5}	33
4-CN–	Phenyl acetate	353–371	130.5	14.99	4.78×10^{-5}	35
4-Me_3C–	Dioxane	353			5.01×10^{-5}	33
2-NO_2–	Phenyl acetate	339–353	119.7	14.70	9.72×10^{-4}	35
3-NO_2–	Phenyl acetate	353–379	126.4	14.27	3.69×10^{-5}	35
4-NO_2–	Phenyl acetate	353–370	126.8	14.40	4.34×10^{-5}	35
3,5-$(NO_2)_2$–	Phenyl acetate	353–368	130.5	14.71	2.51×10^{-5}	35
2-PhO–	Phenyl acetate	330.5–353	121.3	14.66	5.14×10^{-4}	35
2-CF_3–	Chlorobenzene	373–393	116.5	12.40	1.45×10^{-5}	65
3-CF_3–	Chlorobenzene	410			2.30×10^{-4}	65
4-CF_3–	Chlorobenzene	373–393	145.4	16.02	3.20×10^{-6}	65
2-CF_2HO–	Chlorobenzene	373–393	141.2	15.73	6.86×10^{-6}	65
4-CF_2HO–	Chlorobenzene	373–393	129.5	14.21	1.12×10^{-5}	65
4-CF_3O–	Chlorobenzene	383			2.79×10^{-4}	65
4-C_2F_5O–	Chlorobenzene	373–393	128.6	14.0	9.35×10^{-6}	65
2-C_3F_7–	Chlorobenzene	373–393	135.5	14.9	7.08×10^{-6}	65
		$k_i = 2ek_d$				
2-Br–	Styrene	343			8.51×10^{-5}	27
3-Br–	Styrene	343			3.80×10^{-6}	27
4-Br–	Styrene	343			5.24×10^{-6}	27
2-CH_3–	Styrene	343			2.78×10^{-4}	27
3-CH_3–	Styrene	343			6.00×10^{-6}	27
4-CH_3–	Styrene	343			1.09×10^{-5}	27
3,5-Me_2–	Styrene	343			7.76×10^{-6}	27
2-MeO–	Styrene	343			1.38×10^{-4}	27
3-MeO–	Styrene	343			9.00×10^{-6}	27
4-MeO–	Styrene	343			1.85×10^{-5}	27
2-Cl–	Styrene	343			2.82×10^{-5}	27
3-Cl–	Styrene	343			3.60×10^{-6}	27
4-Cl–	Styrene	343			5.40×10^{-6}	27
4-Et–	Styrene	343			9.90×10^{-6}	27
2-EtO–	Styrene	343			1.19×10^{-4}	27

(*continued overleaf*)

TABLE 5.10 (*continued*)

Substituent (R)	Solvent	T (K)	E (kJ mol^{-1})	log A, A (s^{-1})	k_d, k_i (353) (s^{-1})	Reference
4-EtO–	Styrene	343			1.86×10^{-5}	27
2-F–	Styrene	343			1.01×10^{-5}	27
3-F–	Styrene	343			3.60×10^{-6}	27
4-F–	Styrene	343			5.30×10^{-6}	27
2-I–	Styrene	343			1.10×10^{-7}	27
3-I–	Styrene	343			3.63×10^{-6}	27
4-I–	Styrene	343			5.37×10^{-6}	27
4-Me_2CH–	Styrene	343			1.07×10^{-5}	27
4-Me_3C–	Styrene	343			1.26×10^{-5}	27
4-$Me(CH_2)_7O$–	Styrene	343			1.82×10^{-5}	27
4-MeC(O)O–	Styrene	343			6.06×10^{-6}	27
2-MeC(O)O–	Styrene	343			1.00×10^{-5}	27
2-NO_2–	Styrene	343			8.01×10^{-7}	27
3-NO_2–	Styrene	343			7.08×10^{-7}	27
4-NO_2–	Styrene	343			2.07×10^{-7}	27
4-Ph–	Styrene	343			8.51×10^{-6}	27
2-$PhCH_2O$–	Styrene	343			1.86×10^{-5}	27
4-CN–	Styrene	343			3.63×10^{-7}	27
4-CH_2=CH–	Styrene	343			6.46×10^{-6}	27
3,4-$(MeO)_2$–	Styrene	343			8.91×10^{-6}	27
2,3-$(MeO)_2$–	Styrene	343			4.79×10^{-6}	27
2,3,4,5-$(Cl)_4$–	Styrene	343			8.51×10^{-6}	27

TABLE 5.11 The Rate Constants for the Decomposition of Unsymmetrically Substituted Dibenzoyl Peroxides $R^1C_6H_4C(O)OOC(O)C_6H_4R^2$ in Different Solvents

Substituents		Solvent	T (K)	E (kJ mol^{-1})	log A, A (s^{-1})	k_i, k_d (353 K) (s^{-1})	Reference
R^1	R^2			k_d			
2-Me–	H–	Carbon tetrachloride	353			1.10×10^{-4}	66
4-MeO–	H–	Dioxane	353			7.59×10^{-5}	33
3-MeO–	H–	Dioxane	353			4.78×10^{-5}	33
4-CN–	H–	Dioxane	353			2.69×10^{-5}	33
2-Ph–	H–	Carbon tetrachloride	353			2.19×10^{-4}	66
2-$PhCH_2$–	H–	Carbon tetrachloride	353			1.32×10^{-4}	66
2-$PhCH_2$–	H–	Carbon tetrachloride	353			2.57×10^{-4}	66
2-I–	H–	Iodomethane	298–318	83.7	9.25	7.32×10^{-4}	67

TABLE 5.11 (*continued*)

Substituents		Solvent	T (K)	E (kJ mol^{-1})	log A, A (s^{-1})	k_i, k_d (353 K) (s^{-1})	Reference
4-NO_2–	2-I–	Acetone	298			3.02×10^{-4}	68
4-NO_2–	2-I–	Acetonitrile	298			2.08×10^{-4}	68
4-NO_2–	2-I–	Benzene	298			5.69×10^{-5}	68
4-NO_2–	2-I–	Carbon tetrachloride	298			3.39×10^{-5}	68
4-NO_2–	2-I–	Chloroform/ ethanol	298			2.82×10^{-4}	68
4-NO_2–	2-I–	Nitrobenzene	298			6.17×10^{-4}	68
				$k_i = 2ek_d$			
3-NO_2–	H–	Styrene	343			1.20×10^{-6}	28
4-NO_2–	H–	Styrene	343			2.29×10^{-6}	28
4-Cl–	H–	Styrene	308–373	118.4	13.24	5.25×10^{-5}	69
2,4-Cl_2–	H–	Styrene	308–373	117.6	13.92	3.30×10^{-4}	69

5.2 PEROXY ESTERS

5.2.1 Synthesis and Analysis

Peroxy esters as diacyl peroxides are widely used as radical initiators in synthesis, kinetic experiments, and chemical engineering at moderate temperatures (360–420 K). The synthetic methods are similar to those for esters with substitution of alcohol by hydroperoxide (see Table 5.16).[1–5] For the physical properties of selected peroxy esters, see Table 5.17 and their trade names, Table 5.18.

Several different analytical methods of perester estimation are known. The most popular is the iodometric technique.[7] According to this method, peroxide is reduced by HI and I_2 is formed in stoichiometric quantity according to the reactions

$$RC(O)OOR^1 + 2HI \rightarrow RC(O)OH + R^1OH + I_2$$

$$2Na_2S_2O_3 + I_2 \rightarrow 2NaI + Na_2S_4O_6$$

The amount of I_2 formed is measured by its reduction with thiosulfate using any titrometric or photometric technique. The following procedure was proposed for *tert*-butyl perester estimation.[112] A sample of perester is dissolved in chloroform free dioxygen. A portion of acetic acid solution containing $FeCl_3$ is added to this solution. Then the reaction occurs in 10 min in the dark. After that, one adds water and perform a titrometric estimation of evolved diiodine.

Polarography is also used for the estimation of peresters.[7] The reduction of peroxide occurs according to the electrochemical equation:

$$RC(O)OOR^1 + 2e^- \rightarrow RC(O)O^- + R^1O^-$$

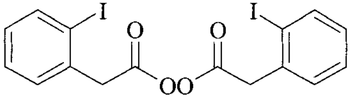
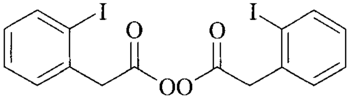
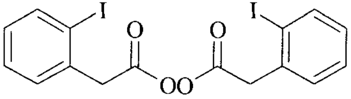
TABLE 5.12 The Rate Constants of the Decomposition of Diacyl Peroxides Rc(O)OOC(O)R in the Gas, Liquid, and Solid Phases

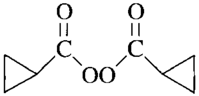
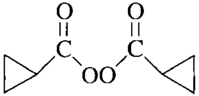
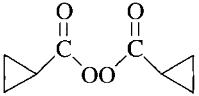
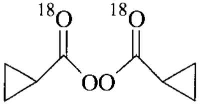
Peroxide	Solvent	T (K)	E (kJ mol^{-1})	log$A$, A (s^{-1})	k_d, k_i (353 K) (s^{-1})	Reference
	k_d					
Dipropanoyl-, EtC(O)OOC(O)Et	Gas phase	373–464	125.5	14.4	6.76 × 10^{-5}	70
Dipropanoyl-, EtC(O)OOC(O)Et	Ethylbenzene	346–363	126.4	14.80	1.24 × 10^{-4}	71
Dibutanoyl-, PrC(O)OOC(O)Pr	Gas phase	370–452	123.8	14.28	9.15 × 10^{-5}	70
Dibutanoyl-, PrC(O)OOC(O)Pr	Ethylbenzene	346–328	124.7	14.68	1.69 × 10^{-4}	71
Dibutanoyl-, PrC(O)OOC(O)Pr	Ethylbenzene	346–363	126.4	14.78	1.19 × 10^{-4}	72
Bis(2-methylpropanoyl)-, $Me_2CHC(O)OOC(O)CHMe_2$	Benzene	313			2.4 × 10^{-4}	73
Bis(2-methylpropanoyl)-, $Me_2CHC(O)OOC(O)CHMe_2$	Carbon tetrachloride	313–343	109.5	14.18	9.48 × 10^{-3}	73
Bis(2-methylpropanoyl)-, $Me_2CHC(O)OOC(O)CHMe_2$	Chlorobenzene	313			1.73 × 10^{-4}	73
Bis(2-methylpropanoyl)-, $Me_2CHC(O)OOC(O)CHMe_2$	Cyanobenzene	313			4.2 × 10^{-4}	73
Bis(2-methylpropanoyl)-, $Me_2CHC(O)OOC(O)CHMe_2$	*p*-Xylene	313			1.40 × 10^{-4}	73
Bis(2-methylpropanoyl)-, $Me_2CHC(O)OOC(O)CHMe_2$	*tert*-Butanol	313			2.51 × 10^{-4}	73
Bis(2-methylpropanoyl)-, $Me_2CHC(O)OOC(O)CHMe_2$	Ethylbenzene	313–328	103.8	11.84	3.02 × 10^{-4}	71
Bis(2-methylpropanoyl)-, $Me_2CHC(O)OOC(O)CHMe_2$	Ethylbenzene	313–328	103.8	11.78	2.65 × 10^{-4}	72
Bis(2-methylpropanoyl)-, $Me_2CHC(O)OOC(O)CHMe_2$	Isooctane	313			3.2 × 10^{-5}	73
Bis(2-methylpropanoyl)-, $Me_2CHC(O)OOC(O)CHMe_2$	Cyclohexane	313			4.5 × 10^{-5}	73
Bis(2-methylpropanoyl)-, $Me_2CHC(O)OOC(O)CHMe_2$	Isopropylalcohol	313			3.0 × 10^{-4}	73
Bis(2-methylpropanoyl)-, $Me_2CHC(O)OOC(O)CHMe_2$	Nitrobenzene	313			5.8 × 10^{-4}	73
Bis(2-methylpropanoyl)-, $Me_2CHC(O)OOC(O)CHMe_2$	Tetralin	313			1.75 × 10^{-4}	73
Bis(2-methylpropanoyl)-, $Me_2CHC(O)OOC(O)CHMe_2$	Toluene	313			1.43 × 10^{-4}	73

Bis(2-methylpropanoyl)-, $Me_2CHC(O)OOC(O)CHMe_2$	Chloroform	313			7.50×10^{-5}	73
Dipentanoyl-, $[Me(CH_2)_3C(O)O]_2$	Ethylbenzene	346–358	123.8	14.55	1.70×10^{-4}	71
Dihexanoyl-, $[Me(CH_2)_4C(O)O]_2$	Ethylbenzene	346–358	128.9	15.34	1.84×10^{-4}	71
Dihexanoyl-, $[Me(CH_2)_4C(O)O]_2$	Ethylbenzene	348–368	128.4	15.00	1.00×10^{-5}	71
Diheptanoyl-, $[Me(CH_2)_5C(O)O]_2$	Ethylbenzene	346–358	125.9	14.89	1.82×10^{-4}	71
Diheptanoyl-, $[Me(CH_2)_5C(O)O]_2$	Styrene	348–368	128.4	15.06	1.15×10^{-4}	71
Dioctanoyl-, $[Me(CH_2)_6C(O)O]_2$	Ethylbenzene	346–358	125.1	14.78	1.86×10^{-4}	71
Dioctanoyl-, $[Me(CH_2)_6C(O)O]_2$	Styrene	348–368	125.1	14.55	1.09×10^{-4}	71
Dinonanoyl-, $[Me(CH_2)_7C(O)O]_2$	Styrene	348–368	124.3	14.46	1.17×10^{-4}	71
Dinonanoyl-, $[Me(CH_2)_7C(O)O]_2$	Ethylbenzene	346–358	125.5	14.87	1.99×10^{-4}	71
Didecanoyl-, $[Me(CH_2)_8C(O)O]_2$	Ethylbenzene	346–358	126.4	14.98	1.89×10^{-4}	71
Didecanoyl-, $[Me(CH_2)_8C(O)O]_2$	Styrene	348–368	125.9	14.68	1.12×10^{-4}	71
Didodecanoyl-, $[Me(CH_2)_{10}C(O)O]_2$	Styrene	348–368	125.9	14.68	1.12×10^{-4}	71
Didodecanoyl-, $[Me(CH_2)_{10}C(O)O]_2$	Ethylbenzene	346–358	126.4	14.99	1.93×10^{-4}	71
Didodecanoyl-, $[Me(CH_2)_{10}C(O)O]_2$	Benzene	333–348	134.0	15.91	1.21×10^{-4}	74
Didodecanoyl-, $[Me(CH_2)_{10}C(O)O]_2$	Benzene/butanol (5 vol %)	348			1.84×10^{-4}	74
Didodecanoyl-, $[Me(CH_2)_{10}C(O)O]_2$	Benzene/butanol (10 vol %)	348			2.80×10^{-4}	74
Didodecanoyl-, $[Me(CH_2)_{10}C(O)O]_2$	Benzene/butanol (15 vol %)	348			6.27×10^{-4}	74
Didodecanoyl-, $[Me(CH_2)_{10}C(O)O]_2$	Cyclohexane	333–348	125.0	14.38	7.65×10^{-5}	74
Didodecanoyl-, $[Me(CH_2)_{10}C(O)O]_2$	Chlorobenzene	333–348	129.0	15.66	3.73×10^{-4}	74
Didodecanoyl-, $[Me(CH_2)_{10}C(O)O]_2$	Butanol	348			1.93×10^{-3}	74
Didodecanoyl-, $[Me(CH_2)_{10}C(O)O]_2$	Nitrobenzene	348			1.34×10^{-3}	74
Dihexadecanoyl-, $[Me(CH_2)_{14}C(O)O]_2$	Ethylbenzene	346–358	126.4	15.20	3.14×10^{-4}	71
Dihexadecanoyl-, $[Me(CH_2)_{14}C(O)O]_2$	Styrene	348–368	125.5	14.63	1.15×10^{-4}	71

(continued overleaf)

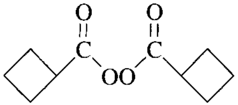
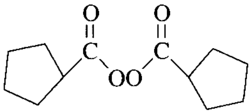
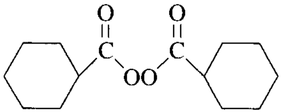
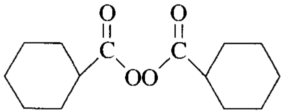
TABLE 5.12 (*continued*)

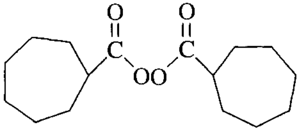
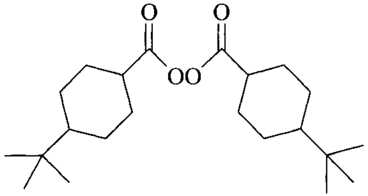
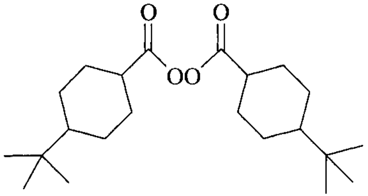
Peroxide	Solvent	T (K)	E (kJ mol^{-1})	log$A$, A (s^{-1})	k_d, k_i (353 K) (s^{-1})	Reference
Dioctadecanoyl-, $[Me(CH_2)_{16}C(O)O]_2$	Ethylbenzene	346–358	125.5	14.86	1.95×10^{-4}	71
Dioctadecanoyl-, $[Me(CH_2)_{16}C(O)O]_2$	Styrene	348–368	125.1	14.61	1.26×10^{-4}	71
Diphenylacetyl-, $PhCH_2C(O)OOC(O)CH_2Ph$	Ethylbenzene	346–358	92.0	9.33	5.21×10^{-5}	71
Diphenylacetyl-, $PhCH_2C(O)OOC(O)CH_2Ph$	Benzene	318–333	133.1	17.09	2.48×10^{-3}	75
Diphenylacetyl-, $PhCH_2C(O)OOC(O)CH_2Ph$	Dibutyl phthalate	318–333	134.3	17.25	2.39×10^{-3}	75
Bis(2′-iodophenyl)acetyl-,	Chloroform	273			3.98×10^{-5}	76
						
Bis(2′-iodophenyl)acetyl-,	Toluene	273			1.30×10^{-5}	76
						
Bis(2′-iodophenyl)acetyl-,	Methyl acetate	273			2.60×10^{-3}	76
						
Bis(3-phenylpropanoyl)-, $[Ph(CH_2)_2C(O)O]_2$	Ethylbenzene	346–358	124.7	14.76	2.03×10^{-4}	71
Bis(4-phenylbutanoyl)-, $[Ph(CH_2)_3C(O)O]_2$	Ethylbenzene	346–358	126.4	14.18	3.00×10^{-5}	71

Bis(5-phenylpentanoyl)-, $[Ph(CH_2)_4C(O)O]_2$	Carbon tetrachloride	343–358	130.1	15.25	9.98×10^{-5}	77
Bis(3-phenylpropynoyl)-, $PhC{\equiv}CC(O)OOC(O)C{\equiv}CPh$	Toluene	343			5.89×10^{-5}	78
Dicyclopropylcarbonyl-, 	4-Methyl cymene	343–386	124.7	14.04	3.87×10^{-5}	79
Dicyclopropylcarbonyl-, 	Ethylbenzoate	343			7.94×10^{-6}	80
Dicyclopropylcarbonyl-, 	Carbon tetrachloride	336–349	118.8	12.74	1.45×10^{-5}	81
Dicyclopropylcarbonyl (O^{18}-labeled)-, 	Carbon tetrachloride	338–348	137.5	16.03	4.83×10^{-5}	82

(continued overleaf)

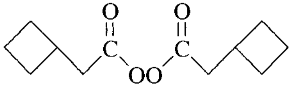
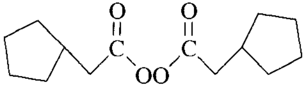
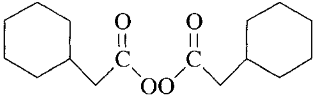
TABLE 5.12 (*continued*)

Peroxide	Solvent	T (K)	E (kJ mol^{-1})	log$A$, A (s^{-1})	k_d, k_i (353 K) (s^{-1})	Reference
Dicyclobutylcarbonyl-, 	Carbon tetrachloride	338–348	79.8	8.09	1.91×10^{-4}	81
Dicyclopentylcarbonyl-, 	Carbon tetrachloride	313–328	97.2	11.39	1.02×10^{-3}	81
Dicyclohexylcarbonyl-, 	Carbon tetrachloride	308–318	98.9	12.23	3.94×10^{-3}	80
Dicyclohexylcarbonyl-, 	Benzene	323	77.9	9.48	8.96×10^{-3}	73

Dicycloheptylcarbonyl-, 	Benzene	313–323	76.3	8.86	3.71×10^{-3}	79
Bis[4-(1′,1′-dimethylethyl)cyclohexylcarbonyl] (*Z*)-, 	Carbon tetrachloride	313–324	78.5	9.01	2.48×10^{-3}	81
Bis[4-(1′,1′-dimethylethyl)cyclohexylcarbonyl] (*E*)-, 	Carbon tetrachloride	313–323	84.5	9.74	1.72×10^{-3}	81

(continued overleaf)

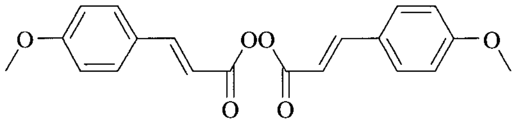
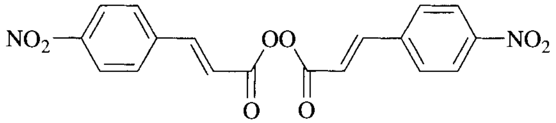
TABLE 5.12 (*continued*)

Peroxide	Solvent	T (K)	E (kJ mol^{-1})	log$A$, A (s^{-1})	k_d, k_i (353 K) (s^{-1})	Reference
Dicyclobutylacetyl-, 	Carbon tetrachloride	338–348	100.7	10.71	6.45×10^{-5}	80
Dicyclopentylacetyl-, 	Carbon tetrachloride	338–348	118.6	13.52	9.35×10^{-5}	80
Dicyclohexylacetyl-, 	Carbon tetrachloride	338–348	102.4	10.96	6.42×10^{-5}	80

	$k_i = 2ek_d$					
Dipropanoyl-, $EtC(O)OOC(O)Et$	Ethylbenzene	346–358	126.4	14.75	1.11×10^{-4}	83
Dipropanoyl-, $EtC(O)OOC(O)Et$	Styrene	436–358	128.5	14.81	6.25×10^{-5}	34
Dibutanoyl-, $PrC(O)OOC(O)Pr$	Ethylbenzene	346–358	124.7	14.64	1.54×10^{-4}	83
Dibutanoyl-, $PrC(O)OOC(O)Pr$	Styrene	436–358	117.9	13.36	8.21×10^{-5}	34
Dibutanoyl-, $PrC(O)OOC(O)Pr$	Styrene	343			1.91×10^{-5}	27
Dipentanoyl-, $[Me(CH_2)_3C(O)O]_2$	Styrene	346–558	119.2	13.56	8.35×10^{-5}	34
Dihexanoyl-, $[Me(CH_2)_4C(O)O]_2$	Styrene	346–358	124.3	14.40	1.07×10^{-4}	34
Dihexanoyl-, $[Me(CH_2)_4C(O)O]_2$	Styrene	343			1.86×10^{-5}	27
Diheptanoyl-, $[Me(CH_2)_5C(O)O]_2$	Styrene	346–358	117.2	13.36	1.04×10^{-4}	34
Diheptanoyl-, $[Me(CH_2)_5C(O)O]_2$	Cumene	323–353	143.8	17.41	1.35×10^{-4}	84
Dioctanoyl-, $[Me(CH_2)_6C(O)O]_2$	Styrene	346–358	119.7	13.68	9.29×10^{-5}	34
Dioctanoyl-, $[Me(CH_2)_6C(O)O]_2$	Styrene	343			2.10×10^{-5}	27
Dinonanoyl-, $[Me(CH_2)_7C(O)O]_2$	Cumene	323–353	143.0	17.42	1.82×10^{-4}	84
Didecanoyl-, $[Me(CH_2)_8C(O)O]_2$	Styrene	346–358	122.2	14.02	8.67×10^{-5}	34
Didecanoyl-, $[Me(CH_2)_8C(O)O]_2$	Styrene	343			1.86×10^{-5}	27
Didodecanoyl-, $[Me(CH_2)_{10}C(O)O]_2$	Styrene	308–348	120.9	14.16	1.86×10^{-5}	85

(*continued overleaf*)

TABLE 5.12 (*continued*)

Peroxide	Solvent	T (K)	E (kJ mol^{-1})	log$A$, A (s^{-1})	k_d, k_i (353 K) (s^{-1})	Reference
Didodecanoyl-, $[Me(CH_2)_{10}C(O)O]_2$	Styrene	346–358	118.0	13.40	8.70×10^{-5}	34
Didodecanoyl-, $[Me(CH_2)_{10}C(O)O]_2$	Cumene	323–353	120.5	13.96	1.26×10^{-4}	84
Didodecanoyl-, $[Me(CH_2)_{10}C(O)O]_2$	Polyethylene	353			4.4×10^{-4}	86
Didodecanoyl-, $[Me(CH_2)_{10}C(O)O]_2$	Polystyrene	353			3.5×10^{-4}	86
Ditetradecanoyl-, $[Me(CH_2)_{12}C(O)O]_2$	Styrene	343			1.54×10^{-5}	34
Diphenylacetyl-, $PhCH_2C(O)OOC(O)CH_2Ph$	Styrene	343			9.5×10^{-5}	27
Bis(3-phenylpropanoyl)-, $[Ph(CH_2)_2C(O)O]_2$	Styrene	346–358	105.0	11.50	8.18×10^{-5}	34
Bis(4-phenylbutanoyl)-, $[Ph(CH_2)_3C(O)O]_2$	Styrene	346–358	118.4	13.16	4.37×10^{-5}	34
Bis(4-phenylbutanoyl)-, $[Ph(CH_2)_3C(O)O]_2$	Styrene	343			2.01×10^{-5}	73
Bis(3-phenylpropenoyl)-, $[PhCH{=}CHC(O)O]_2$	Styrene	346–358	116.3	13.19	9.57×10^{-5}	34
Bis(3-phenylpropenoyl)-, $[PhCH{=}CHC(O)O]_2$	Styrene	343			1.60×10^{-5}	27
Bis[3-(4′-methoxyphenyl)propenoyl]-, 	Styrene	343			1.9×10^{-5}	27
Bis[3-(4′-nitrophenyl)propenoyl]-, 	Styrene	343			6.92×10^{-5}	27

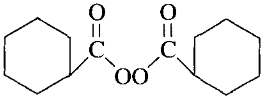
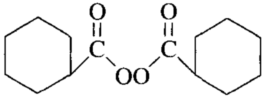
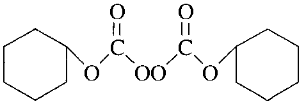
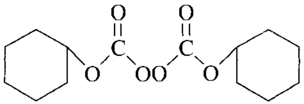
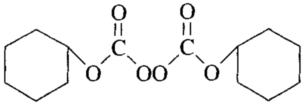
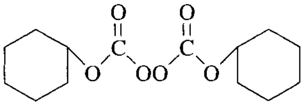
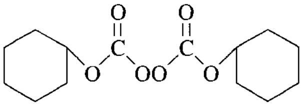
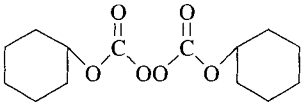
Bis(3-phenylpropynoyl)-, $[PhC{\equiv}CC(O)O]_2$	Styrene	343			1.8×10^{-5}	27
Bis(9,10-dibromoundecanoyl)- $[Me(CHBr)_2(CH_2)_7C(O)O]_2$	Styrene	343			1.7×10^{-5}	27
Bis(9,10-dibromoctadecanoyl)- $[Me(CH_2)_7(CHBr)_2(CH_2)_7C(O)O]_2$	Styrene	343			1.5×10^{-5}	27
Dicyclohexylcarbonyl-, 	Benzene	303–333	87.0	11.03	1.43×10^{-2}	87
Dicyclohexylcarbonyl-, 	Styrene	313–343	131.8	16.9	2.50×10^{-3}	69

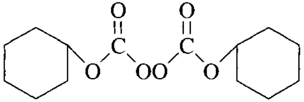
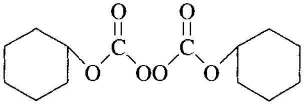
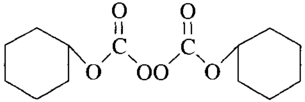
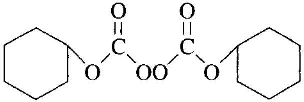
TABLE 5.13 The Rate Constants for the Decomposition of Peroxydicarbonates ROC(O)OOC(O)OR in Different Solvents

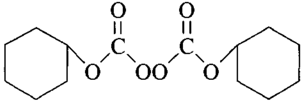
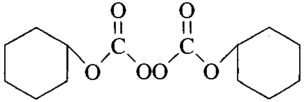
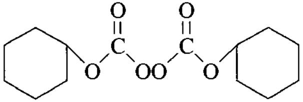
Peroxydicarbonate	Solvent	T (K)	E (kJ mol^{-1})	log A, A (s^{-1})	k_d, k_i(323 K) (s^{-1})	Reference
	k_d					
Diethyl-, EtOC(O)OOC(O)OEt	2,2′-Oxyethylenebis allylcarbonate	313–333	126.2	15.89	3.03×10^{-5}	88
Diethyl-EtOC(O)OOC(O)OEt	Carbon dioxide (supercritical)	338–358	132.0	16.80	2.84×10^{-5}	89
Bis(1-methylethyl)-, $[Me_2CHOC(O)O]_2$	Toluene	313–333	116.6	14.25	2.35×10^{-5}	88
Bis(1-methylethyl)-, $[Me_2CHOC(O)O]_2$	Toluene	323			2.92×10^{-5}	88
Bis(2-methyl-2-nitrobutyl)-, $[EtC(NO_2)(Me)CH_2O\text{-}C(O)O]_2$	Toluene	323			2.24×10^{-5}	88
Dicyclohexyl-, 	Acetonitrile	323			2.8×10^{-5}	90
Dicyclohexyl-, 	Benzene	318–333	124.3	16.01	8.11×10^{-5}	75

Dicyclohexyl-, 	Benzene	323–338	126.5	16.35	7.82×10^{-5}	91
Dicyclohexyl-, 	Benzene	318–348	120.1	14.9	3.01×10^{-5}	92
Dicyclohexyl-, 	Benzene	323			2.20×10^{-5}	90
Dicyclohexyl-, 	Chlorobenzene	318–348	135.6	17.4	2.96×10^{-5}	92

(*continued overleaf*)

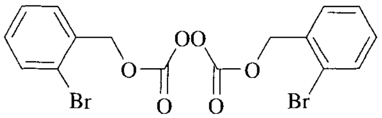
TABLE 5.13 (*continued*)

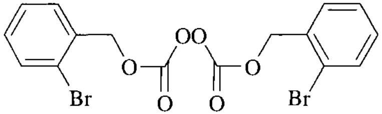
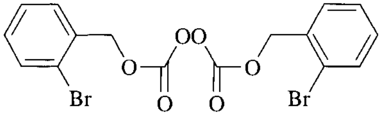
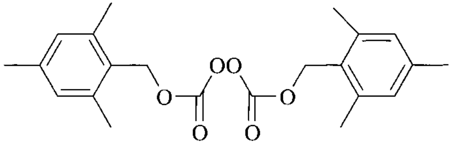
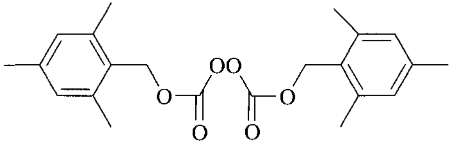
Peroxydicarbonate	Solvent	T (K)	E (kJ mol^{-1})	log A, A (s^{-1})	k_d, k_i(323 K) (s^{-1})	Reference
Dicyclohexyl-, 	Decane	318–348	124.3	15.4	1.99×10^{-5}	92
Dicyclohexyl-, 	Dibutyl phthalate	343–363	111.3	13.87	7.43×10^{-5}	93
Dicyclohexyl-, 	Toluene	323			1.2×10^{-5}	90
Dicyclohexyl-, 	Freon-113	313–333	133.9	17.05	2.49×10^{-5}	94

Dicyclohexyl-, 	Methyl 3′-methylbutanoate	343–363	96.3	11.8	1.69×10^{-4}	93
Dicyclohexyl-, 	Isopropyl alcohol	303–313	77.4	9.73	1.63×10^{-3}	95
Dicyclohexyl-, 	Polyformaldehyde	323–343	133.9	17.24	3.86×10^{-5}	96
Diphenyl-, PhOC(O)OOC(O)OPh	Acetonitrile	333			1.50×10^{-4}	92
Diphenyl-, PhOC(O)OOC(O)OPh	Benzene	318–348	120.1	14.9	3.00×10^{-5}	92
Diphenyl-, PhOC(O)OOC(O)OPh	Benzene	333–353	103.8	12.58	6.22×10^{-3}	97
Diphenyl-, PhOC(O)OOC(O)OPh	Carbon tetrochloride	308–323	119.2	15.45	1.49×10^{-4}	95

(continued overleaf)

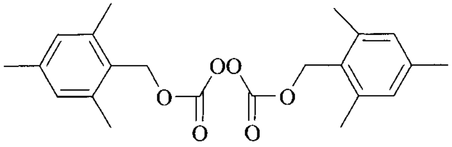
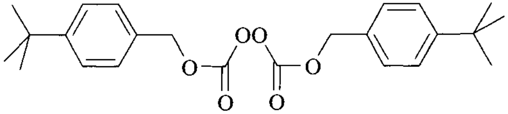
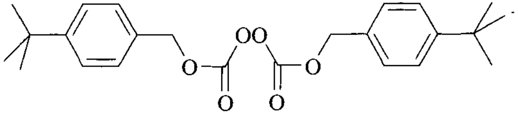
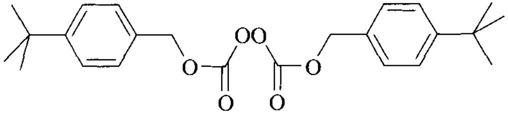
TABLE 5.13 (*continued*)

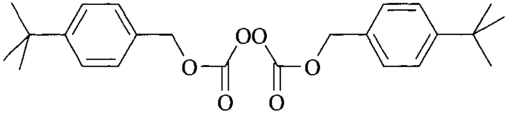
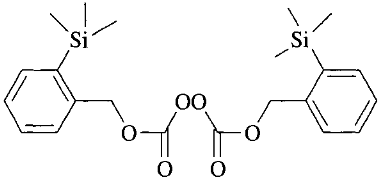
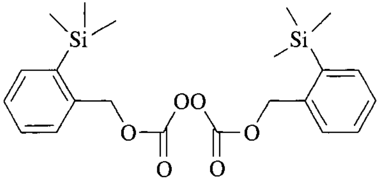
Peroxydicarbonate	Solvent	T (K)	E (kJ mol^{-1})	log A, A (s^{-1})	k_d, k_i(323 K) (s^{-1})	Reference
Diphenyl-, PhOC(O)OOC(O)OPh	Chlorobenzene	318–348	136.5	17.4	1.99×10^{-5}	92
Diphenyl-, PhOC(O)OOC(O)OPh	Cumene	338			1.90×10^{-4}	97
Diphenyl-, PhOC(O)OOC(O)OPh	Cyclohexane	338			3.20×10^{-4}	92
Diphenyl-, PhOC(O)OOC(O)OPh	Cyclohexane	333			7.00×10^{-5}	92
Diphenyl-, PhOC(O)OOC(O)OPh	Decane	318–348	124.3	15.4	1.99×10^{-5}	92
Diphenyl-, PhOC(O)OOC(O)OPh	Dioxane	338			1.92×10^{-3}	97
Diphenyl-, PhOC(O)OOC(O)OPh	Ethyl acetate	328–343	159.3	21.2	2.75×10^{-5}	97
Diphenyl-, PhOC(O)OOC(O)OPh	2-Butanol	303–318	121.3	16.14	3.34×10^{-4}	95
Diphenyl-, PhOC(O)OOC(O)OPh	Tetrahydrofuran	323			1.44×10^{-3}	97
Dibenzyl-, $[PhCH_2OC(O)O]_2$	Benzene	308–323	103.3	13.12	2.60×10^{-4}	97
Dibenzyl-, $[PhCH_2OC(O)O]_2$	Benzene	318–333	133.1	17.09	3.68×10^{-5}	75
Dibenzyl-, $[PhCH_2OC(O)O]_2$	Benzene	333–353	103.8	12.58	6.22×10^{-5}	97
Dibenzyl-, $[PhCH_2OC(O)O]_2$	Benzyl alcohol	308–333	112.1	14.51	2.41×10^{-4}	75
Dibenzyl-, $[PhCH_2OC(O)O]_2$	Dibutyl phthalate	318–333	134.3	17.25	3.40×10^{-5}	75
Dibenzyl-, $[PhCH_2OC(O)O]_2$	Dioxane	338			1.92×10^{-3}	97
Dibenzyl-, $[PhCH_2OC(O)O]_2$	Ethyl acetate	328–343	159.3	21.2	2.75×10^{-5}	97
Dibenzyl-, $[PhCH_2OC(O)O]_2$	Heptane	308–323	104.6	13.01	1.24×10^{-4}	98
Dibenzyl-, $[PhCH_2OC(O)O]_2$	Tetrahydrofuran	323			1.44×10^{-3}	97
Dibenzyl-, $[PhCH_2OC(O)O]_2$	Toluene	323			2.92×10^{-5}	88
Bis(2-bromobenzyl)-,  	Benzene	338			2.3×10^{-4}	97

Bis(2-bromobenzyl)-, 	Cyclohexane	338	3.1×10^{-4}	97
Bis(2-bromobenzyl)-, 	Ethyl acetate	338	2.1×10^{-4}	97
Bis(2,4,6-trimethylbenzyl)- 	Benzene	338	1.1×10^{-4}	99
Bis(2,4,6-trimethylbenzyl)- 	Cumene	338	1.1×10^{-4}	99

(*continued overleaf*)

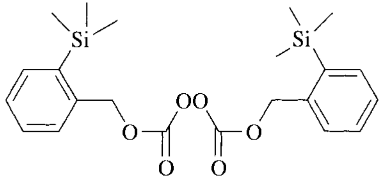
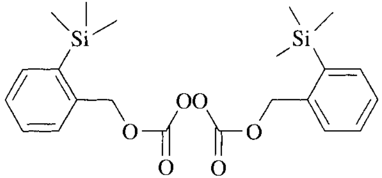
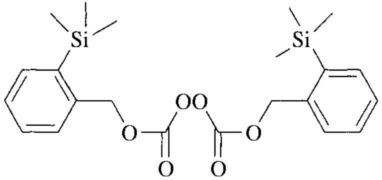
TABLE 5.13 (*continued*)

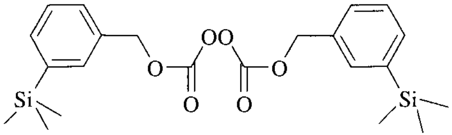
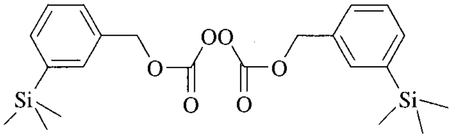
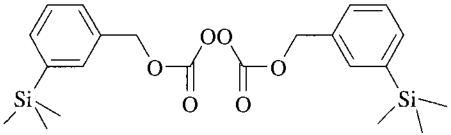
Peroxydicarbonate	Solvent	T (K)	E (kJ mol^{-1})	log A, A (s^{-1})	k_d, k_i(323 K) (s^{-1})	Reference
Bis(2,4,6-trimethylbenzyl)- 	Tetrahydrofuran	338			1.5×10^{-4}	99
Bis[4-(1′,1′-dimethylethyl)benzyl]-, 	Cumene	338			2.2×10^{-4}	99
Bis[4-(1′,1′-dimethylethyl)benzyl]-, 	Dioxane	338			2.3×10^{-4}	99
Bis[4-(1′,1′-dimethylethyl)benzyl]-, 	Benzene	333–358	85.7	9.75	7.78×10^{-5}	97

Bis[4-(1′,1′-dimethylethyl)benzyl-, 	Ethyl acetate	328–348	139.1	18.10	4.03×10^{-5}	97
Bis[2-(trimethylsilyl)benzyl]-, 	Benzene	338			1.90×10^{-4}	99
Bis[2-(trimethylsilyl)benzyl]-, 	Benzene	318–353	106.7	12.77	3.27×10^{-5}	97

(*continued overleaf*)

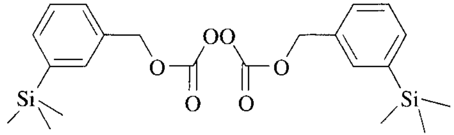
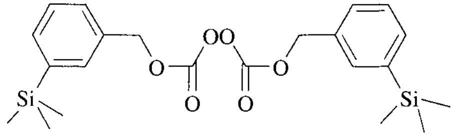
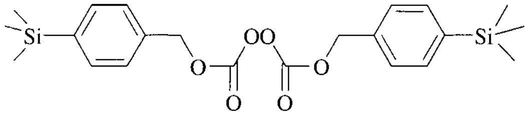
TABLE 5.13 (*continued*)

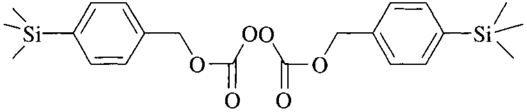
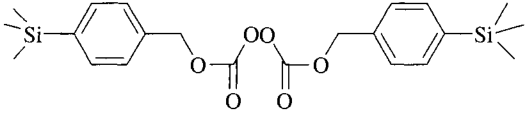
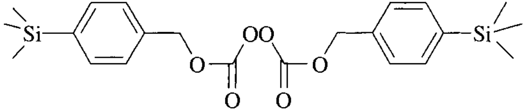
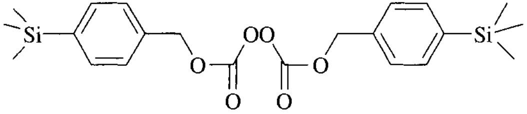
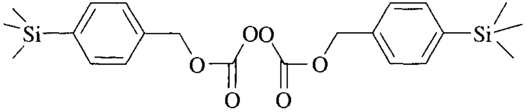
Peroxydicarbonate	Solvent	T (K)	E (kJ mol^{-1})	log A, A (s^{-1})	k_d, k_i(323 K) (s^{-1})	Reference
Bis[2-(trimethylsilyl)benzyl]-, 	Cumene	338			1.90×10^{-4}	97
Bis[2-(trimethylsilyl)benzyl]-, 	Cyclohexane	328–338	92.3	10.63	5.06×10^{-5}	97
Bis[2-(trimethylsilyl)benzyl]-, 	Dioxane	338			1.70×10^{-4}	99

Bis[3-(trimethylsilyl)benzyl]-,	Benzene	338			2.40×10^{-4}	99
					
Bis[3-(trimethylsilyl)benzyl]-,	Benzene	318–353	62.5	6.35	1.75×10^{-4}	97
Bis[3-(trimethylsilyl)benzyl]-,	Cumene	338			1.90×10^{-4}	99
					
Bis[3-(trimethylsilyl)benzyl]-,	Cyclohexane	323–338	95.3	11.2	6.15×10^{-4}	97
					

(*continued overleaf*)

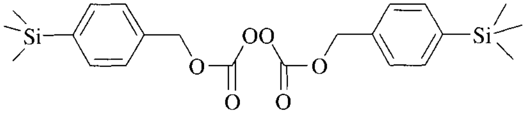
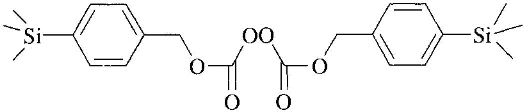
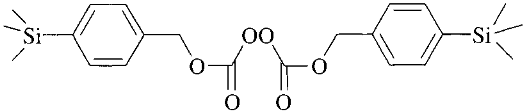
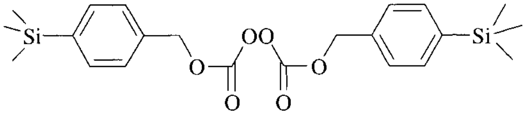
TABLE 5.13 (*continued*)

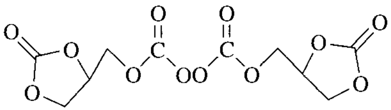
Peroxydicarbonate	Solvent	T (K)	E (kJ mol^{-1})	log A, A (s^{-1})	k_d, k_i(323 K) (s^{-1})	Reference
Bis[3-(trimethylsilyl)benzyl]-, 	Dioxane	338			1.90×10^{-4}	99
Bis[3-(trimethylsilyl)benzyl]-, 	Ethyl acetate	328–348	128.6	16.14	2.21×10^{-5}	97
Bis[4-trimethylsilyl)benzyl]-, 	Benzene	338			2.40×10^{-4}	99

Bis[4-(trimethylsilyl)benzyl]-, 	Benzene	318–353	71.2	7.89	2.38×10^{-4}	97
Bis[4-(trimethylsilyl)benzyl]-, 	Cumene	338			1.70×10^{-4}	97
Bis[4-(trimethylsilyl)benzyl]-, 	Cumene	328–358	90.1	10.23	4.57×10^{-5}	97
Bis[4-(trimethylsilyl)benzyl]-, 	Cyclohexane	328–358	81.9	9.20	9.03×10^{-5}	97
Bis[4-(trimethylsilyl)benzyl]-, 	Dioxane	303–343	53.2	5.52	8.26×10^{-4}	97

(*continued overleaf*)

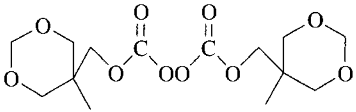
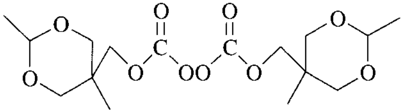
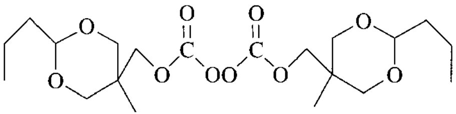
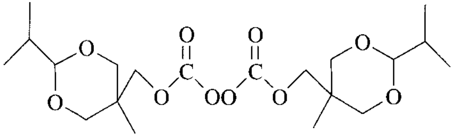
TABLE 5.13 (*continued*)

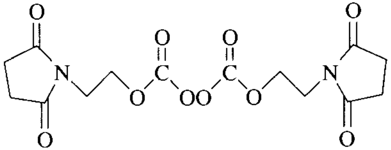
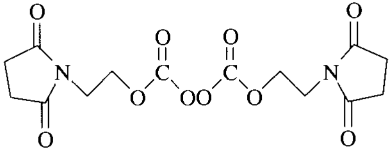
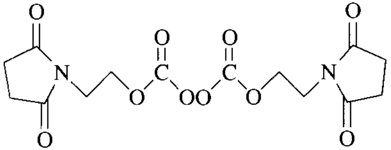
Peroxydicarbonate	Solvent	T (K)	E (kJ mol^{-1})	log A, A (s^{-1})	k_d, k_i(323 K) (s^{-1})	Reference
Bis[4-(trimethylsilyl)benzyl]-, 	Dioxane	338			2.10 × 10^{-4}	99
Bis[4-(trimethylsilyl)benzyl]-, 	Ethyl acetate	328–333	121.3	15.47	7.15 × 10^{-5}	97
Bis[4-(trimethylsilyl)benzyl]-, 	Tetrahydrofuran	338			2.10 × 10^{-4}	99
Bis[4-(trimethylsilyl)benzyl]-, 	Tetrahydrofuran	328–338	109	14.56	8.57 × 10^{-4}	97
Bis(3,6-dioxaheptyl)-, $[Me(OCH_2CH_2)_2OC(O)O]_2$	Benzene	313–328	105.0	13.67	4.90 × 10^{-4}	100
Bis(3,6-dioxaheptyl)-, $[Me(OCH_2CH_2)_2OC(O)O]_2$	Benzene	333			1.20 × 10^{-4}	99

Bis(6-phenyl-3,6-dioxahexyl)-, $[Ph(OCH_2CH_2)_2OC(O)O]_2$	Benzene	323–338	121.0	15.61	1.10×10^{-4}	100
Bis(6-phenyl-3,6-dioxahexyl)-, $[Ph(OCH_2CH_2)_2OC(O)O]_2$	Benzene	333			1.10×10^{-4}	99
Bis(7-phenyl-3,6-dioxaheptyl)-, $[PhCH_2(OCH_2CH_2)_2OC(O)O]_2$	Benzene	313–328	111.0	14.78	6.76×10^{-4}	100
Bis(1,4-dimethyl-7-phenyl-3,6-dioxaheptyl)-, $[PhCH_2(OCH_2CHMe)_2OC(O)O]_2$	Benzene	333–348	110.0	13.56	5.91×10^{-5}	100
Bis(dimethylmethoxycarbonylmethyl)-, $[MeOC(O)CMe_2OC(O)O]_2$	Benzene	333–348	120.5	14.39	8.01×10^{-6}	101
Bis(dimethylmethoxycarbonylmethyl)-, $[MeOC(O)CMe_2OC(O)O]_2$	Isopropanol	303–318	76.6	8.91	3.33×10^{-4}	101
Bis(dimethylethoxycarbonylmethyl)-, $[EtOC(O)CMe_2OC(O)O]_2$	Benzene	333–348	109.2	12.82	1.45×10^{-4}	101
Bis(dimethylethoxycarbonylmethyl)-, $[EtOC(O)CMe_2OC(O)O]_2$	Isopropyl alcohol	298–313	72.8	8.68	8.08×10^{-4}	101
Bis[(1,3-dioxolan-2-on-4-yl)methyl]-, 	Dimethylformamide	308–323	99.6	12.77	4.61×10^{-4}	102

(*continued overleaf*)

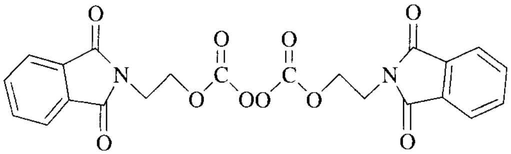
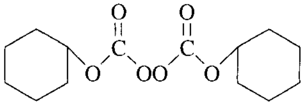
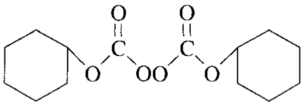
TABLE 5.13 (*continued*)

Peroxydicarbonate	Solvent	T (K)	E (kJ mol^{-1})	log A, A (s^{-1})	k_d, k_i(323 K) (s^{-1})	Reference
Bis[(5-methyl-1,3-dioxane-5-yl)methyl]-, 	Benzene	303–328	97.1	12.21	3.21×10^{-4}	103
Bis[(2,5-dimethyl-1,3-dioxane-5-yl)methyl]-, 	Benzene	308–328	79.5	9.39	3.42×10^{-4}	103
Bis[(2-propyl-5-methyl-1,3-dioxane-5-yl)methyl]-, 	Benzene	308–328	125.9	16.87	3.24×10^{-4}	103
Bis{[2-(1-methylethyl)-5-methyl-1,3-dioxane-5-yl]methyl}-, 	Benzene	308–328	79.5	9.35	3.12×10^{-4}	103

Bis[2-(*N*-succinimidyl)ethyl]-, 	Benzene	323–338	121.2	15.23	4.27×10^{-5}	104
Bis[2-(*N*-succinimidyl)ethyl]-, 	Benzene	333			0.90×10^{-4}	99
Bis[2-(*N*-succinimidyl)ethyl]-, 	Dimethylformamide	303–318	91.6	12.11	1.98×10^{-3}	104

(*continued overleaf*)

TABLE 5.13 (*continued*)

Peroxydicarbonate	Solvent	T (K)	E (kJ mol^{-1})	log A, A (s^{-1})	k_d, k_i(323 K) (s^{-1})	Reference
Bis[2-(*N*-phthalimidyl)ethyl]-	Dimethylformamide	303–318	99.5	13.43	2.18×10^{-3}	105
						
	$k_i = 2ek_d$					
Bis(2-ethylhexyl)-, $[Me(CH_2)_3CHEtCH_2O\ C(O)O]_2$	Cumene	323–373	110.8	13.68	5.78×10^{-5}	105
Dihexadecyl-, $[Me(CH_2)_{15}OC(O)O]_2$	Cumene	323–373	120.1	14.98	3.62×10^{-5}	84
Dicyclohexyl-,	Benzene	328–348	117.2	14.78	6.72×10^{-5}	105
						
Dicyclohexyl-,	2-Butanone	328–348	87.9	10.39	1.50×10^{-4}	105
						

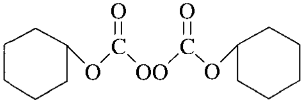
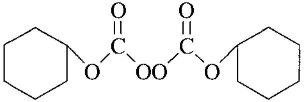
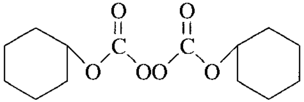
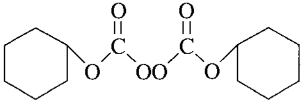
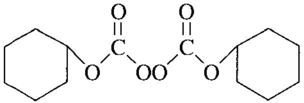
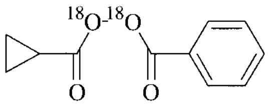
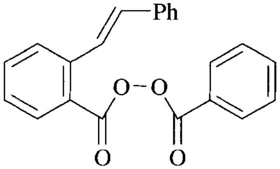
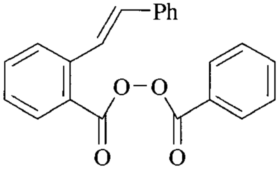
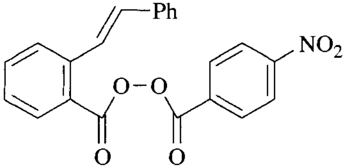
Dicyclohexyl-, 	Chlorobenzene	348			1.82×10^{-3}	105
Dicyclohexyl-, 	Cumene	323–353	135.8	17.57	4.07×10^{-5}	84
Dicyclohexyl-, 	Cyclohexanone	348			1.41×10^{-3}	105
Dicyclohexyl-, 	Ethylbenzene	333–353	123.8	15.43	2.56×10^{-5}	106
Dicyclohexyl-, 	Heptane	328–348	100.4	12.04	6.37×10^{-5}	105

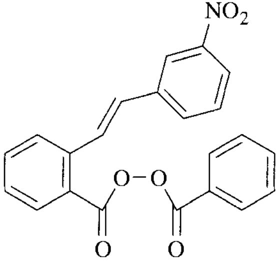
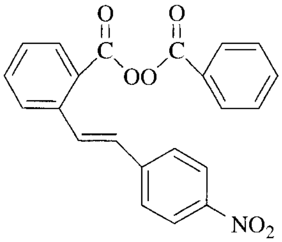
TABLE 5.14 The Rate Constants for the Decomposition of Unsymmetrical Diacylic Peroxides $R^1C(O)OOC(O)R^2$ in Different Solvents

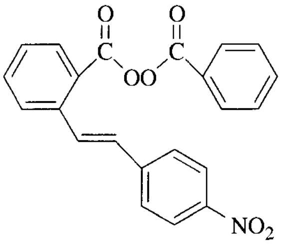
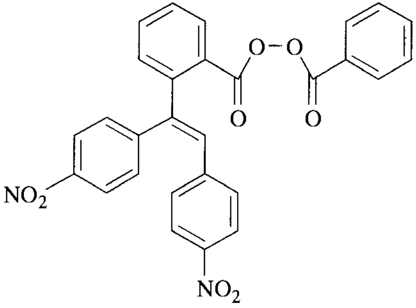
Peroxide	Solvent	T (K)	E (kJ mol^{-1})	log A, A (s^{-1})	k_d, k_i (353K) (s^{-1})	Reference
		k_d				
Acetyl benzoyl-, $MeC(O)OOC(O)Ph$	Chlorobenzene	343			2.00×10^{-5}	72
Benzoyl cyclopropylcarbonyl (^{18}O-labeled)-	Carbon tetrochloride	353			5.65×10^{-5}	82
						
Butanoyl 5-phenyl-4-pentenoyl, $PrC(O)OOC(O)(CH_2)_2CH{=}CHPh$	Carbon tetrochloride	333–343	112.5	13.15	3.19×10^{-4}	73
Butanoyl 5-phenyl-4-pentenoyl-, $PrC(O)OOC(O)(CH_2)_2CH{=}CHPh$	Phenyl ethylketone	323–338	99.6	12.03	1.96×10^{-3}	73
Butanoyl 5-phenyl-4-pentenoyl-, $PrC(O)OOC(O)(CH_2)_2CH{=}CHPh$	Polycarbonate	310–323	89.5	10.77	3.36×10^{-3}	73
Benzoyl phenoxycarbonyl- $PhC(O)OOC(O)OPh$	Benzene	318–338	132.2	16.55	9.73×10^{-4}	107

Benzoyl 2-(2′-phenyl ethenyl)benzoyl-, 	Chlorobenzene	308–343	76.1	9.09	6.75×10^{-3}	108
Benzoyl 2-(2′-phenyl ethenyl)benzoyl-, 	Methanol	308			9.77×10^{-4}	108
4-Nitrobenzoyl 2-(2′-phenylethenyl)benzoyl-, 	Chlorobenzene	308			8.12×10^{-4}	108

(*continued overleaf*)

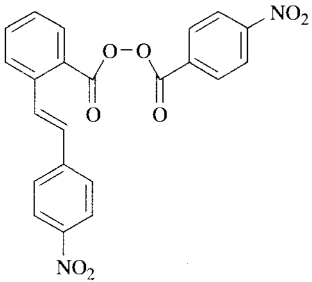
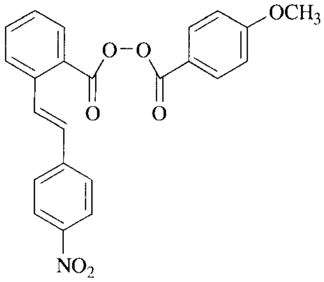
TABLE 5.14 (*continued*)

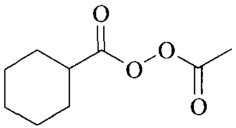
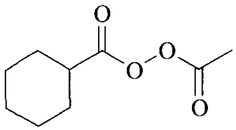
Peroxide	Solvent	T (K)	E (kJ mol^{-1})	log A, A (s^{-1})	k_d, k_i (353K) (s^{-1})	Reference
Benzoyl 2-[2′-(3-nitro phenyl)ethenyl]benzoyl-, 	Chlorobenzene	343			1.82×10^{-4}	108
Benzoyl 2-[2′-(4-nitro phenyl)ethenyl]benzoyl-, 	Chlorobenzene	34			1.20×10^{-4}	108

Benzoyl 2-[2′-(4-nitrophenyl)ethenyl]benzoyl-, 	Tetrahydrofuran	343		6.16×10^{-5}	108
Benzoyl 2-[1′, 2′-di(4-nitrophenyl)ethenyl]benzoyl- 	Chlorobenzene	343		1.55×10^{-3}	108

(*continued overleaf*)

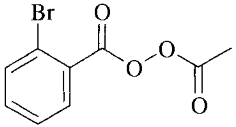
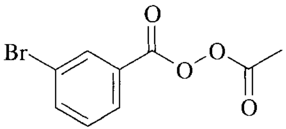
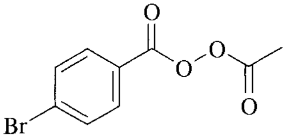
TABLE 5.14 (*continued*)

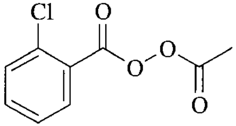
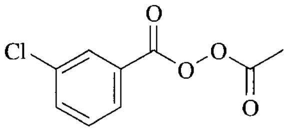
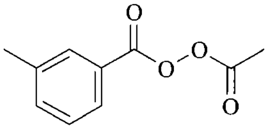
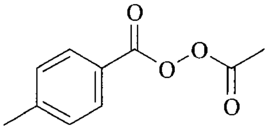
Peroxide	Solvent	T (K)	E (kJ mol^{-1})	log A, A (s^{-1})	k_d, k_i (353K) (s^{-1})	Reference
4-Nitrobenzoyl-2-[2′-(4-nitro phenyl)ethenyl]benzoyl  	Chlorobenzene	343			3.8×10^{-4}	108
4-Methoxybenzoyl-2-[2′-(4-nitro phenyl)ethenyl]benzoyl-,  	Chlorobenzene	343			6.02×10^{-5}	108

		$k_i = 2ek_d$				
Acetyl butanoyl-, $MeC(O)OOC(O)Pr$	Styrene	333–353	111.7	12.08	3.56×10^{-5}	24
Acetyl pentanoyl-, $MeC(O)OOC(O)CH_2Pr$	Styrene	333–353	136.0	15.90	5.97×10^{-5}	24
Acetyl 3-methylbutanoyl-, $MeC(O)OOC(O)CH_2\ CHMe_2$	Styrene	333–353	128.4	14.72	5.25×10^{-5}	24
Acetyl heptanoyl-, $MeC(O)OOC(O)(CH_2)_5Me$	Styrene	333–353	132.2	15.41	7.05×10^{-5}	24
Acetyl cyclohexylcarbonyl- 	Styrene	333–343	77.0	7.56	1.47×10^{-5}	24
Acetyl cyclohexylcarbonyl-, 	Styrene	333–353	77.0	7.23	6.86×10^{-5}	62

(continued overleaf)

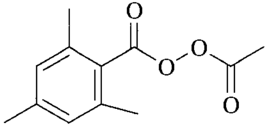
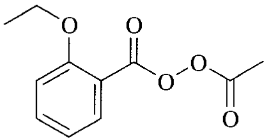
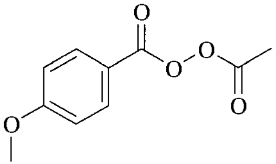
TABLE 5.14 (*continued*)

Peroxide	Solvent	T (K)	E (kJ mol^{-1})	log A, A (s^{-1})	k_d, k_i (353K) (s^{-1})	Reference
Acetyl benzoyl-, MeC(O)OOC(O)Ph	Styrene	333–353	118.8	13.15	3.72×10^{-5}	62
Acetyl benzoyl-, MeC(O)OOC(O)Ph	Styrene	343			1.65×10^{-5}	62
Acetyl 2-bromobenzoyl-, 	Styrene	333–353	107.9	12.0	1.08×10^{-4}	62
Acetyl 3-bromobenzoyl-, 	Styrene	333–353	129.7	14.49	1.99×10^{-5}	62
Acetyl 4-bromobenzoyl-, 	Styrene	333–353	120.5	14.34	3.23×10^{-4}	62

Acetyl 2-chlorobenzoyl-, 	Styrene	333–353	118.4	13.42	7.95×10^{-5}	62
Acetyl 3-chlorobenzoyl-, 	Styrene	333–353	118.8	13.91	2.14×10^{-4}	37
Acetyl 3-methylbenzoyl-, 	Styrene	333–353	128.0	14.62	4.78×10^{-5}	62
Acetyl 4-methylbenzoyl-, 	Styrene	333–353	127.2	14.50	4.77×10^{-5}	62

(*continued overleaf*)

TABLE 5.14 (*continued*)

Peroxide	Solvent	T (K)	E (kJ mol^{-1})	log A, A (s^{-1})	k_d, k_i (353K) (s^{-1})	Reference
Acetyl 2,4,6-trimethylbenzoyl-, 	Styrene	333–353	109.6	12.99	5.92×10^{-4}	62
Acetyl 2-ethoxybenzoyl-, 	Styrene	333–353	118.8	13.86	1.91×10^{-4}	62
Acetyl 4-methoxybenzoyl-, 	Styrene	333–353	127.2	14.67	7.05×10^{-5}	62

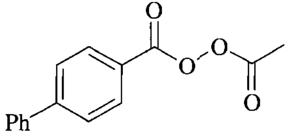
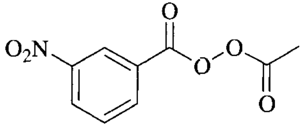
Acetyl 4-phenylbenzoyl-, 	Styrene	333–353	124.3	14.10	5.10×10^{-5}	62
Acetyl 3-nitrobenzoyl-, 	Styrene	333–353	152.7	17.02	2.66×10^{-6}	62
Benzoyl chloroacetyl-, $ClCH_2C(O)OOC(O)Ph$	Styrene	333–353	124.3	14.04	4.44×10^{-5}	62
Benzoyl propanoyl-, EtC(O)OOC(O)Ph	Styrene	333–343	120.1	13.19	2.62×10^{-5}	62
Benzoyl butanoyl-, PrC(O)OOC(O)Ph	Styrene	333–343	125.1	13.94	2.68×10^{-5}	62
Benzoyl 3-methylbutanoyl-, $(Me)_2CHCH_2C(O)OOC(O)Ph$	Styrene	333–353	128.0	14.34	2.51×10^{-5}	62
Benzoyl octanoyl-, $Me(CH_2)_6C(O)OOC(O)Ph$	Styrene	343			2.00×10^{-5}	62
Benzoyl octanoyl-, $Me(CH_2)_6C(O)OOC(O)Ph$	Styrene	343			1.35×10^{-5}	62
Butanoyl propanoyl-, EtC(O)OOC(O)Pr	Styrene	333–353	118.8	14.50	8.34×10^{-4}	109
Pentanoyl propanoyl-, $EtC(O)OOC(O)(CH_2)_3Me$	Styrene	333–343	126.4	15.65	8.84×10^{-4}	109

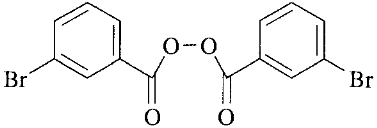
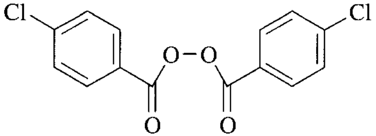
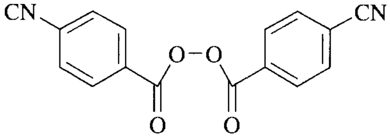
TABLE 5.15 **The Probability *e* of a Radical Pair Escaping the Cage in Diacyl Peroxide Decomposition in Different Solvents**

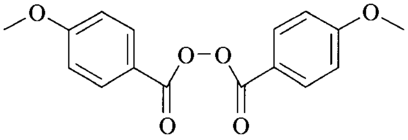
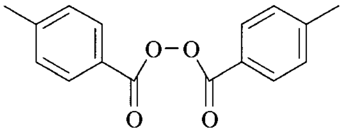
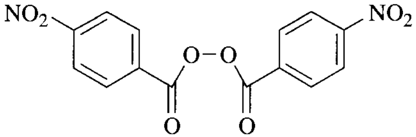
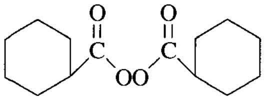
Peroxide	Solvent	*T* (K)	*e*	Reference
Dipropanoyl-, $[EtC(O)O]_2$	Styrene	353	0.70	34
Bis(2-methylpropanoyl)-, $[Me_2CHC(O)O]_2$	Styrene	313	0.25	34
Bis(2-methylpropanoyl)-, $[Me_2CHC(O)O]_2$	Carbon tetrachloride	318	0.49	110
Bis(2-methylpropanoyl)-, $[Me_2CHC(O)O]_2$	Carbon tetrachloride	353	0.80	73
Dibutanoyl-, $[PrC(O)O]_2$	Styrene	353	0.60	34
Dipentanoyl-, $[n\text{-}BuC(O)O]_2$	Styrene	353	0.60	34
Dihexanoyl-, $[Me(CH_2)_4C(O)O]_2$	Ethyl benzene	368	0.64	71
Dihexanoyl-, $[Me(CH_2)_4C(O)O]_2$	Styrene	353	0.60	34
Diheptanoyl-, $[Me(CH_2)_5C(O)O]_2$	Ethyl benzene	368	0.62	71
Diheptanoyl-, $[Me(CH_2)_5C(O)O]_2$	Styrene	353	0.70	34
Dioctanoyl-, $[Me(CH_2)_6C(O)O]_2$	Ethyl benzene	368	0.79	71
Dioctanoyl-, $[Me(CH_2)_6C(O)O]_2$	Styrene	353	0.60	34
Dinonanoyl-, $[Me(CH_2)_7C(O)O]_2$	Ethyl benzene	368	0.73	71

Didecanoyl-, $[Me(CH_2)_8C(O)O]_2$	Ethyl benzene	368	0.66	71
Didecanoyl-, $[Me(CH_2)_8C(O)O]_2$	Styrene	353	0.55	34
Didodecanoyl-, $[Me(CH_2)_{10}C(O)O]_2$	Ethyl benzene	368	0.72	71
Didodecanoyl-, $[Me(CH_2)_{10}C(O)O]_2$	Styrene	353	0.50	34
Dihexadecanoyl-, $[Me(CH_2)_{14}C(O)O]_2$	Ethyl benzene	368	0.57	71
Dihexadecanoyl-, $[Me(CH_2)_{14}C(O)O]_2$	Styrene	353	0.50	34
Dioctadecanoyl-, $[Me(CH_2)_{16}C(O)O]_2$	Ethyl benzene	368	0.64	71
Dioctadecanoyl-, $[Me(CH_2)_{16}C(O)O]_2$	Styrene	353	0.50	34
Bis(4-phenylbutanoyl)-, $[Ph(CH_2)_3C(O)O]_2$	Styrene	353	0.50	34
Bis(5-phenylpentanoyl)-, $[Ph(CH_2)_4C(O)O]_2$	Styrene	353	0.40	34
Dibenzoyl-, $[PhC(O)O]_2$	Carbon tetrachloride	346	0.82	73
Dibenzoyl-, $[PhC(O)O]_2$	Styrene	363	0.72	111

(continued overleaf)

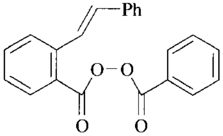
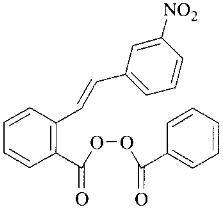
TABLE 5.15 (*continued*)

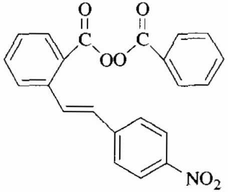
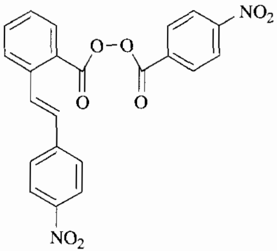
Peroxide	Solvent	T (K)	e	Reference
Bis(3-bromobenzoyl)-, 	Styrene	363	0.47	111
Bis(4-chlorobenzoyl)-, 	Styrene	363	0.77	111
Bis(4-cyanobenzoyl)-, 	Styrene	363	0.34	111

Bis(4-methoxybenzoyl)-,	Styrene	363	0.80	111
				
Bis(4-methylbenzoyl)-,	Styrene	363	0.73	111
				
Bis(4-nitrobenzoyl)-,	Styrene	363	0.87	111
				
Dicyclohexylcarbonyl-,	Benzene	303–358	4.31exp (−8.7/RT)	87
				

(continued overleaf)

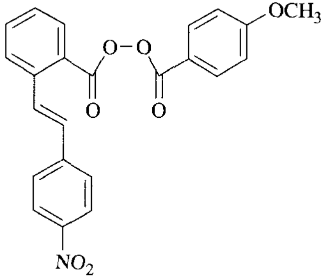
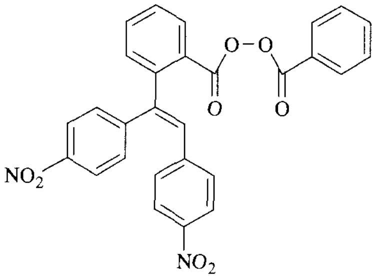
TABLE 5.15 (*continued*)

Peroxide	Solvent	T (K)	e	Reference
Benzoyl 2-(2′-phenylethenyl)benzoyl-,  	Chlorobenzene	343	0.11	108
Benzoyl 2-(2′-(3-nitrophenylethenyl)benzoyl-,  	Chlorobenzene	343	0.15	108

Benzoyl 2-[2′-(4-nitrophenyl)ethenyl]benzoyl- 	Chlorobenzene	343	0.39	108
4-Nitrobenzoyl 2-[2′-(4-nitrophenyl)ethenyl] benzoyl-, 	Chlorobenzene	343	0.34	108

(*continued overleaf*)

TABLE 5.15 ***(continued)***

Peroxide	Solvent	T (K)	e	Reference
4-Methoxybenzoyl 2-[2′-nitrophenyl)ethenyl]benzoyl-, 	Chlorobenzene	343	0.41	108
Benzoyl 2-[1′, 2′-di(4-nitrophenyl)ethyl]benzoyl- 	Chlorobenzene	343	0.13	108

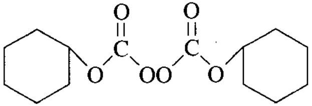
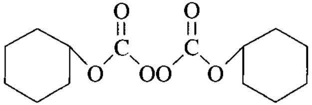
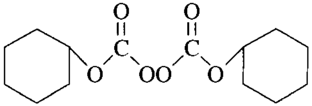
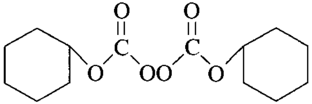
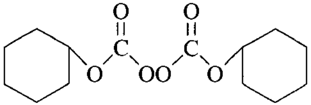
Dicyclohexylperoxydicarbonate, 	Chlorobenzene	348	0.20	106
Dicyclohexylperoxydicarbonate, 	Cyclohexanone	348	0.34	105
Dicyclohexylperoxydicarbonate, 	Ethyl benzene	353–333	3.04exp $(-4.2/RT)$	106
Dicyclohexylperoxydicarbonate, 	Heptane	348	0.50	106
Dicyclohexylperoxydicarbonate, 	Ethyl acetate	348	0.28	105

TABLE 5.16 Synthetic Methods of Production of Peroxy Esters $R^1C(O)OOR$[a]

Reaction	Reactants	Catalyst
$RC(O)Cl + R^1OOMgCl \rightarrow RC(O)OOR^1 + MgCl_2$	$RC(O)Cl$, $R^1OOMgCl$	
$RC(O)X + R^1OOH \rightarrow RC(O)OOR^1 + HX$	$RC(O)X$, R^1OOH[b]	Pyridine, NaOH or other bases
$(RCO)_2O + R^1OOH \rightarrow RC(O)OOR^1 + RCOOH$	$(RCO)_2O$, R^1OOH	Mineral acids, carbonic acids, alkalis
$RC(O)OH + R^1OOH \rightarrow RC(O)OOR^1 + H_2O$	$RC(O)OH$, R^1OOH add. Na_2SO_4, $MgSO_4$, B_2O_3	Mineral acids
$R-N{=}C{=}O + R^1OOH \rightarrow RNHC(O)OOR^1$	$R-N{=}C{=}O$, R^1OOH	Pyridine, triethylamine
$RCH{=}C{=}O + R^1OOH \rightarrow RCH_2C(O)OOR^1$	$RCH{=}C{=}O$, R^1OOH	

[a] See Refs. 1–3.

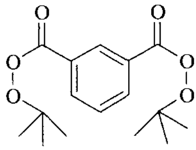
[b] X = Halogen.

TABLE 5.17 Physical Properties of Select Peroxy Esters[a]

Peroxide	MW	BP (K)	MP (K)	Density ($kg\,m^{-3}$)	n_D^{293}
Acetyl 1,1-dimethylethyl-, $MeC(O)OOCMe_3$	144.17	322–324		941.5	1.405
Benzoyl 1,1-dimethylethyl-, $PhC(O)OOCMe_3$	194.23	348–350		1021	1.5007
1,1-Dimethylethyl 2-methylpropanoyl-, $Me_2CHC(O)OOCMe_3$	172.23	300–301		913.2	1.409
1,1-Dimethylethyl hexanoyl-, $Me_3(CH_2)_4C(O)O\ OCMe_3$	200.28			903.4	1.4250
1,1-Dimethylethyl dodecanoyl-, $Me(CH_2)_{10}C(O)O\ OCMe_3$	284.44	281–282		890.3	1.4398
1,1-Dimethylethyl octadecanoyl-, $Me(CH_2)_{16}C(O)O\ OCMe_3$	386.60		311.7 312.3		1.4386 (313 K)

[a] See Ref. 6.

TABLE 5.18 Peroxy Ester Trade Names

Peroxide	Trade Name	Company
Acetyl 1,1-dimethylethyl-, $MeC(O)OOCMe_3$	Luperox 7M50	Elf atochem
	Perbutyl A	Nippon Oil & Fats Co
	Trigonox F	Akzo
Benzoyl 1,1-dimethylethyl-, $PhC(O)OOCMe_3$	Luperox P	Elf atochem
	Peroximon P	Elf atochem
	Perbutyl Z	Nippon Oil & Fats Co
	Trigonox C	Akzo
	Interox TBPB	Interox
Diperoxide, bis(1,1-dimethylethyl) 1,3-benzenedicarbonyl-, 	Perbutyl IF	Nippon Oil & Fats Co
Diperoxide, butyl 4,4-bis(1,1-dimethylethyldioxy)pentanoyl, $(Me_3COO)_2MeCCH_2CH_2C(O)OOBu$	Perhexa V	Nippon Oil & Fats Co
	Trigonox 17	Akzo
Diperoxide, dibenzoyl 1,1,4,4-tetramethyltetramethylene-, $PhC(O)OOCMe_2(CH_2)_2CMe_2OOC(O)Ph$	Luperox 118	Elf atochem
	Peroxymon 118	Elf atochem
	Iterox DHPBZ-75-W	Interox
1,1-Dimethylethyl allyloxycarbonyl-, $CH_2{=}CHCHOC(O)OOCMe_3$	Peromer AC	Nippon Oil & Fats Co
1,1-Dimethylethyl diethylacetyl-, $Et_2CHC(O)OOCMe_3$	Trigonox 27	Akzo
1,1-Dimethylethyl 2-ethylhexanoyl-, $Me(CH_2)_3CHEtC(O)OOCMe_3$	Luperox 26	Elf atochem
	Peroximon 26	Elf atochem
	Perbutyl O	Nippon Oil & Fats Co
	Trigonox 21	Akzo
	Interox TBPEH	Interox
1,1-Dimethylethyl 2-ethylhexyloxycarbonyl-, $Me(CH_2)_3CHEtCH_2OC(O)OOCMe_3$	Luperox TBEC	Elf atochem
1,1-Dimethylethyl 2,2-dimethylpropanoyl-,	Luperox 11 M75	Elf atochem
$Me_3CC(O)OOCMe_3$	Perbut PO	Nippon Oil & Fats Co
	Trigonox 25	Akzo
	Interox TBPPI	Interox
1,1-Dimethylbutyl 3,3-dimethylbutanoyl-, $Me_3CCH_2C(O)OOCMe_2Pr$	Perhexyl NH	Nippon Oil & Fats Co

(*continued overleaf*)

TABLE 5.18 ***(continued)***

Peroxide	Trade Name	Company
1,1-Dimethylbutyl 3,3-dimethylpropanoyl-, $EtMe_2CCH_2C(O)OOCMe_2Pr$	Perhexyl PV	Nippon Oil & Fats Co
1,1-Dimethylethyl 3,3-dimethylbutanoyl-, $Me_3CCH_2C(O)OOCMe_3$	Perbut NH	Nippon Oil & Fats Co
1,1-Dimethylethyl 2,2-dimethyloctanoyl-, $Me(CH_2)_5CMe_2C(O)OOCMe_3$	Luperox 10	Elf atochem
	Perbut ND	Nippon Oil & Fats Co
	Interox TBPND-75-AL	Interox
1,1-Dimethylethyl dodecanoyl-, $Me(CH_2)_{10}C(O)OOCMe_3$	Perbutyl L	Nippon Oil & Fats Co
1,1-Dimethylethyldioxy maleic acid, $Me_3COOC(O)CH{=}CHC(O)OH$	Perbut MA	Nippon Oil & Fats Co
	Interox TBPM-50-P	Interox
1,1-Dimethylethyl 1-methylethyloxycarbonyl-, $Me_2CHOC(O)OOCMe_3$	Luperox TBICM 75	Elf atochem
	Perbut I	Nippon Oil & Fats Co
	Trigonox BPIC	Akzo
1,1-Dimethylethyl 2-methylpropanoyl-, $Me_2CHC(O)OOCMe_3$	Luperox 80M75	Elf atochem
	Perbutyl IB	Nippon Oil & Fats Co
	Trigonox 41-C75	Akzo
1,1-Dimethylpropyl 2,2-dimethylpropanoyl-, $Me_3CC(O)OOCEtMe_2$	Luperox 554M75	Elf atochem
1,1-Dimethylpropyl 3-ethylhexanoyl-, $Me(CH_2)_3CHEtCH_2C(O)OOCEtMe_2$	Luperox 575	Elf atochem
1,1-Dimethylpropyl 2-ethylhexyloxycarbonyl-, $Me(CH_2)_3CHEtCH_2OC(O)OOCEtMe_2$	Luperox TAEC	Elf atochem
1,1-Dimethylpropyl 2,2-dimethyloctanoyl-, $EtCMe_2OOC(O)CMe_2(CH_2)_5Me$	Luperox 540 M75	Elf atochem
1,1-Dimethylethyl 3,5,5-trimethylhexanoyl-, $Me_3CCH_2CHMeCH_2C(O)OOCMe_3$	Luperox 270	Elf atochem
	Peroximon 270	Elf atochem
	Perbut 355	Nippon Oil & Fats Co
	Trigonox 42	Akzo
	Interox TBPIN	Interox
1,1-Dimethyl-3-hydroxybutyl 7,7-dimethyloctanoyl-, $Me_3C(CH_2)_5C(O)OOCMe_2CH_2C(OH)Me$	Luperox 610MD	Elf atochem
1-Methyl-1-phenylethyl 3,3-dimethylbutanoyl-, $Me_3CCH_2C(O)OOCMe_2Ph$	Percumyl NH	Nippon Oil & Fats Co
1-Methyl-1-phenylethyl 7,7-dimethyloctanoyl-,	Luperox 188 M70	Elf atochem

TABLE 5.18 (*continued*)

Peroxide	Trade Name	Company
$Me_3C(CH_2)_5C(O)OOCMe_2Ph$	Percumyl ND Interox CUPND-75-AL	Nippon Oil & Fats Co Interox
1-Methyl-1-phenylethyl octanoyl-, $Me(CH_2)_6C(O)OOCMe_2Ph$	Percumyl O	Nippon Oil & Fats Co

The individual polarographic characteristic of an analyzed compound is the potential $E_{1/2}$ at which the current strength is equal to 50% of its maximum. The mixed-solvent benzene/methanol or benzene/ethanol is used. The amount of reduced perester is proportional to the maximum strength of the electric current at perester concentration in solution <0.01 mol/L. The values of $E_{1/2}$ for some peresters [$RC(O)OOCMe_3$] in a benzene/ethanol solution (1 : 1 V/V) at [LiCl] = 0.3 mol L^{-1} are the following:[7]

R	$CH_2{=}CH$	$MeCH{=}CH$	$Me(CH_2)_4$	Ph	$2\text{-}MeC_6H_4$	$4\text{-}MeC_6H_4$
$E_{1/2}$ (V)	−1.02	−0.97	−1.08	−0.89	−0.97	−0.96

Chromatography and MS are used for identification and analysis of peresters.[7] NMR spectroscopy as well as UV and IR spectroscopy are used for perester identification. The valence frequencies of perester bonds (ν, cm^{-1}) have the following values according to IR spectra:[7]

Bond	$Me(CH_2)_nC(O)OCMe_3$, CCl_4	$PhC(O)OOCMe_3$, CCl_4
C=O	1778	1758
C(O)−O	1136	1237
C−O	1190	1190

5.2.2 Thermochemistry of Peroxy Esters

The enthalpies of formation of diacyl peroxides are collected in Table 5.7. The value of the increment of formation enthalpy of an acyl peroxide group is $\Delta H[(O){-}O{-}C(O)] = -90.6$ kJ mol^{-1} (gas phase), $\Delta H[(O){-}O{-}C(O)(C)] = -206.0.1$ kJ mol^{-1} (liquid phase), and $\Delta H[(O){-}O{-}C(O)(C)] = -237.6$ kJ mol^{-1} (solid phase).[20] The value of the increment of formation enthalpy for the alkyl peroxide group $\Delta H[(O){=}O{=}C)] = -19.2$ kJ mol^{-1} (gas phase), $\Delta H[(O){-}O{-}C] = -28.14$ kJ mol^{-1} (liquid phase), and $\Delta H[(O){-}O{-}(C)] =$

−34.91 kJ mol^{-1} (solid phase).[20] The O−O bond dissociation energies in peroxy esters $RC(O)OOCMe_3$ are equal.

R	Me	Et	Bu	*cyclo*-$C_6H_{11}O$	Ph
D(O-O) (kJ mol^{-1})	149.5	149.5	149.5	150.0	141.4

The values for the formation enthalpies of peroxy esters are collected in Table 5.19.

5.2.3 Decomposition of Peroxy Esters

Three different mechanisms of peroxy esters homolytic decay are known (see Chapter 1).

1. Peresters decompose by splitting of the weakest O−O bond with formation of alkoxyl and acyloxyl radicals. As long as the forming acyloxyl radical is unstable, there occurs a cascade of cage reactions with formation of different cage recombination products.

$$Me_3C(O)OOR \rightarrow [Me_3CO_2^{\bullet} + RO^{\bullet}]$$

$$[Me_3CO_2{}^{\bullet} + RO^{\bullet}] \rightarrow Me_3C(O)OOR$$

$$[Me_3CO_2{}^{\bullet} + RO^{\bullet}] \rightarrow Me_3CO_2{}^{\bullet} + RO^{\bullet}$$

$$[CH_3CO_2{}^{\bullet} + RO^{\bullet}] \rightarrow [C^{\bullet}H_3 + RO^{\bullet}] + CO_2$$

$$[C^{\bullet}H_3 + RO^{\bullet}] \rightarrow C^{\bullet}H_3 + RO^{\bullet}$$

$$[C^{\bullet}H_3 + RO^{\bullet}] \rightarrow CH_3OR$$

2. Many peresters are decomposed by the concerted fragmentation mechanism with simultaneous splitting of O−O and C−C(O) bonds. This concerted fragmentation mechanism predominates for peresters with sufficiently weak C−C(O) bond. For these peresters, the activation energy of decomposition is lower and the rate constant of decomposition is sufficiently higher than for peresters that decompose with the O−O bond splitting. For detailed information about this perester decomposition mechanism, see Chapter 1.

$$PhCH_2C(O)OOR \rightarrow [PhC^{\bullet}H_2 + CO_2 + RO^{\bullet}]$$

$$[PhC^{\bullet}H_2 + CO_2 + RO^{\bullet}] \rightarrow PhCH_2OR + CO_2$$

$$[PhC^{\bullet}H_2 + CO_2 + RO^{\bullet}] \rightarrow PhC^{\bullet}H_2 + CO_2 + RO^{\bullet}$$

3. Some ortho-substituted benzoyl peresters are decomposed by a decomposition mechanism with anchimeric assistance (see Chapter 1). This perester

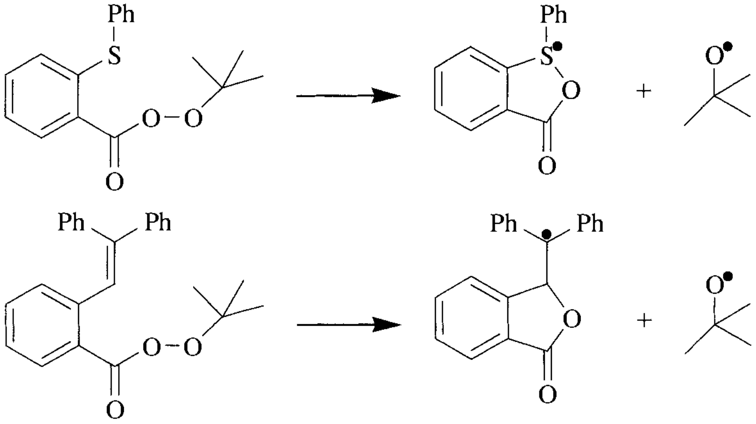
TABLE 5.19 The Enthalpies (ΔH_f^0) of Peroxy Ester Formation in Gas and Condensed Phases

Peroxide	Phase	$-\Delta H_f^0$ (kJ mol^{-1})	Reference
1,1-Dimethylethyl decanoyl-, $Me(CH_2)_8C(O)OOCMe_3$	Liquid	668,3	113
1,1-Dimethylethyl dodecanoyl-, $Me(CH_2)_{10}C(O)OOCMe_3$	Liquid	738.5	113
1,1-Dimethylethyl tetradecanoyl-, $Me(CH_2)_{12}C(O)OOCMe_3$	Liquid	795.8	113
1,1-Dimethylethyl 2,2-dimethylpropanoyl-, $Me_3CC(O)OOCMe_3$	Gas	516.2	114
1,1-Dimethylethyl 2,2-dimethylbutanoyl-, $EtCMe_2C(O)OOCMe_3$	Gas	553.1	114
1,1-Dimethylethyl methoxyacetyl-, $MeOCH_2C(O)OOCMe_3$	Gas	562.4	114
1,1-Dimethylethyl methylmethoxyacetyl-, $MeOCH(CH_3)C(O)OOCMe_3$	Gas	605.0	114
1,1-Dimethylethyl ethoxyacetyl-, $EtOCH_2C(O)OOCMe_3$	Gas	598.0	114
1,1-Dimethylethyl (1-methylethoxy)acetyl-, $Me_2CHOCH_2C(O)OOCMe_3$	Gas	633.9	114
Benzyloxyacetyl 1,1-dimethylethyl-, $PhCH_2OCH_2C(O)OOCMe_3$	Gas	455.8	114
2-Butenoyl 1,1-dimethylethyl-, $MeCH{=}CHC(O)OOCMe_3$	Liquid	417.0	115
1,1-Dimethylethyl 3-methoxycarbonyl-2-propenoyl-, $MeOC(O)CH{=}CHC(O)OOCMe_3$	Liquid	746.8	115
3-Allyloxycarbonylpropanoyl 1,1-dimethylethyl-, $CH_2{=}CHCH_2OC(O)CH_2CH_2C(O)OOCMe_3$	Liquid	818.0	115
3-Allyloxycarbonyl-2-propenoyl 1,1-dimethylethyl-, $CH_2{=}CHCH_2OC(O)CH{=}CHC(O)OOCMe_3$	Liquid	673.2	115
1,1-Dimethylethyl 3-pentenoyl-, $MeCH{=}CHCH_2C(O)OOCMe_3$	Gas	382.0	114
1,1-Dimethylethyl 4-phenyl-3-butenoyl-, $PhCH{=}CHCH_2C(O)OOCMe_3$	Gas	253.0	114
1,1-Dimethylethyl 3-pentynoyl-, $MeC{\equiv}CCH_2C(O)OOCMe_3$	Gas	222.7	114

TABLE 5.19 (*continued*)

Peroxide	Phase	$-\Delta H_f^0$ (kJ mol^{-1})	Reference
1,1-Dimethylethyl 2-methyl-3-pentynoyl-, $MeC{\equiv}CCH(Me)C(O)OOCMe_3$	Gas	252.3	114
1,1-Dimethylethyl 4-phenyl-3-butynoyl-, $PhC{\equiv}CCH_2C(O)OOCMe_3$	Gas	81.8	114
1,1-Dimethylethyl 2-methyl-4-phenyl-3-butynoyl-, $PhC{\equiv}CCH(Me)C(O)OOCMe_3$	Gas	111.3	114
Benzoyl 1,1-dimethylethyl-, $PhC(O)OOCMe_3$	Gas Liquid	300.0 368.2	116
1,1-Dimethylethyl phenylacetyl-, $PhCH_2C(O)OOCMe_3$	Gas	320.4	114
Benzoyl 1-methyl-1-phenylethyl-, $PhC(O)OOC(CH_3)_2Ph$	Liquid	231	117

decomposition proceeds by splitting of the O—O bond with simultaneous addition of formed oxyl-radical to an atom of ortho substituent with formation of an intermediate radical, for example,



The rate constants of anchimerically assisted decomposition of peresters are higher than that of O—O bond splitting.

For data on the cage effect of perester decomposition, see Chapter 2. The yield of cage reactions products increases with increasing viscosity of the solvent. The values of the rate constants of perester decomposition (k_d) and initiation ($k_i = 2ek_d$) are collected in Tables 5.20 and 5.21.

TABLE 5.20 The Rate Constants of the Decomposition of Peroxy Esters RC(O)OOCMe$_3$ in Different Solvents

Peroxide	Solvent	T (K)	E (kJ mol^{-1})	log A, A (s^{-1})	k_d, k_i (383 K) (s^{-1})	Reference
		k_d				
Acetyl 1,1-dimethylethyl-, MeC(O)OOCMe$_3$	Chlorobenzene	353–373	161.9	17.81	5.37×10^{-5}	118
Acetyl 1,1-dimethylethyl-, MeC(O)OOCMe$_3$	Ethylbenzene	358–383	161.5	17.79	5.82×10^{-5}	71
Acetyl 1,1-dimethylethyl-, MeC(O)OOCMe$_3$	Undecane	373–403	133.5	14.10	7.82×10^{-5}	119
1,1-Dimethylethyl propanoyl-, EtC(O)OOCMe$_3$	Benzene	343–363	146.0	15.68	5.87×10^{-5}	120
1,1-Dimethylethyl-2-methylpropanoyl-, Me$_2$CHC(O)OOCMe$_3$	Benzene	343–363	130.5	14.67	7.45×10^{-4}	120
1,1-Dimethylethyl-2-methylpropanoyl-, Me$_2$CHC(O)OOCMe$_3$	Chlorobenzene	363–383	143.5	15.50	8.50×10^{-5}	121
1,1-Dimethylethyl-2-methylpropanoyl-, Me$_2$CHC(O)OOCMe$_3$	Cumene	363–383	136.0	14.37	6.64×10^{-5}	121
1,1-Dimethylethyl-2-methylpropanoyl-, Me$_2$CHC(O)OOCMe$_3$	Ethylbenzene	358–383	123.8	13.42	3.44×10^{-4}	71

(*continued overleaf*)

TABLE 5.20 (*continued*)

Peroxide	Solvent	T (K)	E (kJ mol^{-1})	log A, A (s^{-1})	k_d, k_i (383 K) (s^{-1})	Reference
1,1-Dimethylethyl-2,2-dimethylpropanoyl-, $Me_3CC(O)OOCMe_3$	Chlorobenzene	331–361	125.5	15.30	1.68×10^{-2}	80
1,1-Dimethylethyl-2,2-dimethylpropanoyl-, $Me_3CC(O)OOCMe_3$	Cumene	338–358	118.0	14.01	8.26×10^{-3}	122
1,1-Dimethylethyl-2,2-dimethylpropanoyl-, $Me_3CC(O)OOCMe_3$	Ethylbenzene	358–383	122.2	14.62	9.00×10^{-3}	123
1,1-Dimethylethyl-2,2-dimethylpropanoyl-, $Me_3CC(O)OOCMe_3$	Cumene	318–338	109.2	12.56	4.65×10^{-3}	124
1,1-Dimethylethyl- butanoyl-, $PrC(O)OOCMe_3$	Styrene/carbon tetrachloride	368–383	125.5	12.90	6.08×10^{-5}	71
1,1-Dimethylethyl-3-methylbutanoyl-, $Me_2CHCH_2C(O)OOCMe_3$	Ethylbenzene	318–338	164.0	18.61	1.75×10^{-4}	123
1,1-Dimethylethyl-2,2-diethylbutanoyl-, $Et_3CC(O)OOCMe_3$	Cumene	318–338	105.9	12.51	1.17×10^{-4}	124
1,1-Dimethylethyl pentanoyl-, $Me(CH_2)_3C(O)OOCMe_3$	Ethylbenzene	358–383	165.7	18.54	8.75×10^{-5}	72
1,1-Dimethylethyl-2,2-dimethylpentanoyl-, $Me(CH_2)_2C(Me)_2C(O)OOCMe_3$	Cumene	318–338	107.9	11.59	7.49×10^{-4}	124

1,1-Dimethylethyl hexanoyl-, $Me(CH_2)_4C(O)OOCMe_3$	Acetic acid	383			1.00×10^{-4}	125
1,1-Dimethylethyl hexanoyl-, $Me(CH_2)_4C(O)OOCMe_3$	Butyric acid	383			5.37×10^{-5}	125
1,1-Dimethylethyl hexanoyl-, $Me(CH_2)_4C(O)OOCMe_3$	Chlorobenzene	383			8.32×10^{-5}	125
1,1-Dimethylethyl hexanoyl-, $Me(CH_2)_4C(O)OOCMe_3$	1-Chloro-propionic acid	383			8.13×10^{-5}	125
1,1-Dimethylethyl hexanoyl-, $Me(CH_2)_5C(O)OOCMe_3$	1-Chloro-1- methylpropionic acid	383			4.57×10^{-4}	125
1,1-Dimethylethyl hexanoyl-, $Me(CH_2)_5C(O)OOCMe_3$	Diphenyl ether	383			6.38×10^{-5}	125
1,1-Dimethylethyl hexanoyl-, $Me(CH_2)_5C(O)OOCMe_3$	Nitrobenzene	373–403	150.6	16.37	6.78×10^{-5}	125
1,1-Dimethylethyl hexanoyl-, $Me(CH_2)_5C(O)OOCMe_3$	Propionic acid	383			5.37×10^{-5}	125
1,1-Dimethylethyl hexanoyl-, $Me(CH_2)_5C(O)OOCMe_3$	Undecane	373–403	148.5	16.25	9.94×10^{-5}	119
1,1-Dimethylethyl octanoyl-, $Me(CH_2)_6C(O)OOCMe_3$	Ethylbenzene	358–383	165.7	18.53	8.55×10^{-5}	71
1,1-Dimethylethyl decanoyl-, $Me(CH_2)_8C(O)OOCMe_3$	Ethylbenzene	368–383	165.7	18.55	8.95×10^{-5}	71
1,1-Dimethylethyl dodecanoyl-, $Me(CH_2)_{10}C(O)OOCMe_3$	Chlorobenzene	383			9.00×10^{-5}	109

(*continued overleaf*)

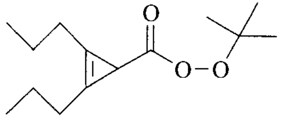
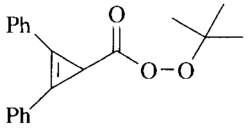
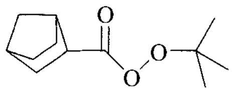
TABLE 5.20 (*continued*)

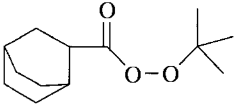
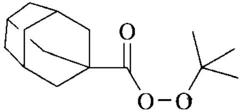
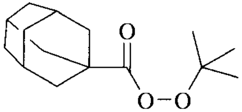
Peroxide	Solvent	T (K)	E (kJ mol^{-1})	log A, A (s^{-1})	k_d, k_i (383 K) (s^{-1})	Reference
1,1-Dimethylethyl dodecanoyl -, $Me(CH_2)_{10}C(O)OOCMe_3$	Ethylbenzene	368–383	165.3	18.49	8.84×10^{-5}	71
1,1-Dimethylethyl tetradecanoyl-, $Me(CH_2)_{12}C(O)OOCMe_3$	Acetic acid	383			1.00×10^{-4}	109
1,1-Dimethylethyl tetradecanoyl-, $Me(CH_2)_{12}C(O)OOCMe_3$	Butyric acid	383–403	146.9	15.77	5.44×10^{-5}	125
1,1-Dimethylethyl tetradecanoyl-, $Me(CH_2)_{12}C(O)OOCMe_3$	2-Chloro-propionic acid	383–404	134.7	14.30	8.50×10^{-5}	125
1,1-Dimethylethyl tetradecanoyl-, $Me(CH_2)_{12}C(O)OOCMe_3$	2-Chloro-2-methyl propionic acid	383			4.46×10^{-4}	123
1,1-Dimethylethyl tetradecanoyl-, $Me(CH_2)_{12}C(O)OOCMe_3$	Chlorobenzene	383			8.7×10^{-5}	125
1,1-Dimethylethyl tetradecanoyl-, $Me(CH_2)_{12}C(O)OOCMe_3$	Diphenyl ether	383			6.45×10^{-5}	125
1,1-Dimethylethyl tetradecanoyl-, $Me(CH_2)_{12}C(O)OOCMe_3$	Nitrobenzene	383			6.38×10^{-5}	125
1,1-Dimethylethyl tetradecanoyl-, $Me(CH_2)_{12}C(O)OOCMe_3$	Propionic acid	383			5.49×10^{-5}	125
1,1-Dimethylethyl hexadecanoyl-, $Me(CH_2)_{14}C(O)OOCMe_3$	Chlorobenzene	383			8.51×10^{-5}	125
1,1-Dimethylethyl hexadecanoyl-, $Me(CH_2)_{14}C(O)OOCMe_3$	Ethylbenzene	368–383	166.5	18.69	9.61×10^{-5}	71

1,1-Dimethylethyl propenoyl-, $CH_2{=}CHC(O)OOCMe_3$	Benzene	353			1.33 × 10^{-6}	126
1,1-Dimethylethyl propenoyl-, $CH_2{=}CHC(O)OOCMe_3$	Benzene	363–383	86.2	7.49	5.42 × 10^{-5}	127
1,1-Dimethylethyl propenoyl-, $CH_2{=}CHC(O)OOCMe_3$	Benzene	353			1.33 × 10^{-6}	127
1,1-Dimethylethyl 2-methyl-propenoyl-, $CH_2{=}CMeC(O)OOCMe_3$	Benzene	363–383	137.0	14.98	1.98 × 10^{-4}	127
3-Butenoyl 1,1-dimethylethyl-, $MeCH{=}CH\ CH_2C(O)OOCMe_3$	*p*-Cymene	333	118.8		2.92 × 10^{-5}	128
1,1-Dimethylethyl 4-phenyl-3-butenoyl-, $PhCH{=}CHCH_2C(O)O\ OCMe_3$	*p*-Cymene	333	115.0		1.16 × 10^{-4}	128
3-Butynoyl 1,1-dimethylethyl-, $MeCH{\equiv}CCH_2C(O)OOCMe_3$	*p*-Cymene	333	124.0		3.72 × 10^{-6}	128
1,1-Dimethylethyl-4-phenyl-3-butynoyl-, $PhCH{\equiv}CCH_2C(O)OOCMe_3$	*p*-Cymene	333	122.4		7.72 × 10^{-6}	128
1,1-Dimethylethyl-2-methyl-3-pentynoyl-, $MeCH{\equiv}CCHMeC(O)OOCMe_3$	*p*-Cymene	333	116.5		6.55 × 10^{-5}	128

(*continued overleaf*)

TABLE 5.20 (*continued*)

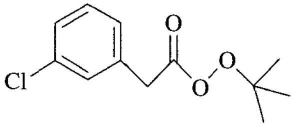
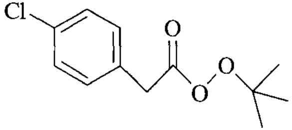
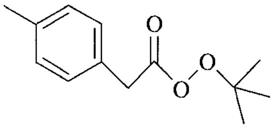
Peroxide	Solvent	T (K)	E (kJ mol^{-1})	log A, A (s^{-1})	k_d, k_i (383 K) (s^{-1})	Reference
1,1-Dimethylethyl 2-methyl-4-phenyl-3-butynoyl-, $PhCH{\equiv}CCHMeC(O)OOCMe_3$	*p*-Cymene	333	115.2		1.09×10^{-4}	128
1,1-Dimethylethyl (2,3-dipropyl)-2-cyclopropenylcarbonyl-, 	Chlorobenzene	313–333	105.9	14.37	8.45×10^{-1}	129
1,1-Dimethylethyl (2,3-diphenyl)-2-cyclopropenylcarbonyl-, 	Chlorobenzene	313–333	101.7	13.76	7.76×10^{-1}	129
1,1-Dimethylethyl-2-bicyclo[2.2.1]heptylcarbonyl-, 	Cumene	318–338	157.7	16.16	4.50×10^{-6}	124

1,1-Dimethylethyl 2-bicyclo[2.2.2]octylcarbonyl-, 	Cumene	318–338	121.8	13.70	1.23×10^{-3}	124
1-Adamantylcarbonyl-1,1-dimethylethyl-, 	Cumene	318–338	118.0	14.12	1.06×10^{-2}	124
1-Adamantylcarbonyl-1,1-dimethylethyl-, 	Cumene	338–358	119.2	14.29	1.08×10^{-2}	123

(*continued overleaf*)

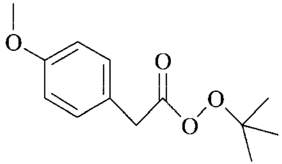
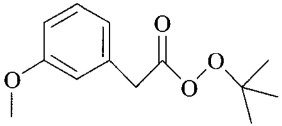
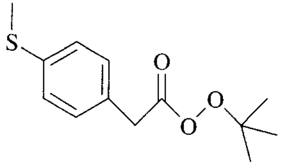
TABLE 5.20 (*continued*)

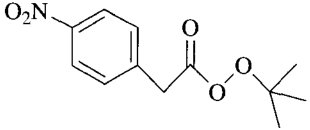
Peroxide	Solvent	T (K)	E (kJ mol^{-1})	log A, A (s^{-1})	k_d, k_i (383 K) (s^{-1})	Reference
1,1-Dimethylethyl methoxyacetyl-, $MeOCH_2C(O)OOCMe_3$	Benzene	313–333	102.9	13.39	2.27×10^{-1}	130
1,1-Dimethylethyl methoxyacetyl-, $MeOCH_2C(O)OOCMe_3$	Benzene	313			2.18×10^{-4}	131
1,1-Dimethylethyl ethoxyacetyl-, $EtOCH_2C(O)OOCMe_3$	Benzene	313			2.95×10^{-4}	131
1,1-Dimethylethyl-1-methylethoxyacetyl-, $Me_2CHOCHC(O)OOCMe_3$	Benzene	313			4.79×10^{-4}	131
1,1-Dimethylethyl butoxyacetyl-, $BuOCH_2C(O)OOCMe_3$	Benzene	313–333	94.6	12.30	2.50×10^{-1}	130
1,1-Dimethylethyl-3-methyl-4-oxapentanoyl-, $MeOCH(Me)CH_2C(O)OOCMe_3$	Benzene	313–333	141.0	15.20	9.34×10^{-5}	130
1,1-Dimethylethyl phenylacetyl-, $PhCH_2C(O)OOCMe_3$	Chlorobenzene	331–361	117.5	13.34	2.07×10^{-3}	122
1,1-Dimethylethyl phenylacetyl-, $PhCH_2C(O)OOCMe_3$	Chlorobenzene	353–373	123.0	14.15	2.37×10^{-3}	118
1,1-Dimethylethyl phenylacetyl-, $PhCH_2C(O)OOCMe_3$	Ethylbenzene	308–358	118.0	13.37	1.89×10^{-3}	71

1,1-Dimethylethyl phenylacetyl-, $PhCH_2C(O)OOCMe_3$	Toluene	353–373	116.7	13.30	2.42×10^{-3}	122
(3-Chlorophenyl)acetyl- 1,1-dimethylethyl-, 	Toluene	353–373	123.0	13.81	1.08×10^{-3}	122
(4-Chlorophenyl)acetyl- 1,1-dimethylethyl-, 	Toluene	353–373	117.2	13.30	2.07×10^{-3}	122
1,1-Dimethylethyl- (4-methylphenyl)acetyl-, 	Toluene	343–363	110.9	12.2	1.19×10^{-3}	122

(continued overleaf)

TABLE 5.20 (*continued*)

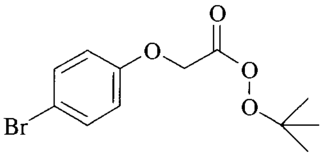
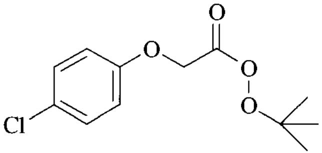
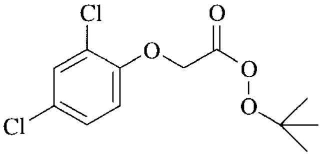
Peroxide	Solvent	T (K)	E (kJ mol^{-1})	log A, A (s^{-1})	k_d, k_i (383 K) (s^{-1})	Reference
1,1-Dimethylethyl-(4-methoxyphenyl)acetyl-, 	Toluene	329–353	105.4	12.86	3.06×10^{-2}	122
1,1-Dimethylethyl-(3-methoxyphenyl)acetyl-, 	Toluene	353–373	122.2	14.02	2.26×10^{-3}	122
1,1-Dimethylethyl-(4-methylthiophenyl)acetyl-, 	Ethylbenzene	363.6			1.07×10^{-3}	132

1,1-Dimethylethyl-(4-nitrophenyl)acetyl-, 	Toluene	353–373	124.7	13.83	6.66×10^{-4}	122
1,1-Dimethylethyl-dimethylphenylacetyl-, $Ph(Me)_2CC(O)OOCMe_3$	Chlorobenzene	313–333	112.7	14.57	1.58×10^{-1}	118
1,1-Dimethylethyl diphenylacetyl-, $Ph_2CHC(O)COOCMe_3$	Chlorobenzene	353–373	104.6	13.08	6.52×10^{-2}	118
1,1-Dimethylethyl diphenylacetyl-, $Ph_2CHC(O)COOCMe_3$	Chlorobenzene	313–333	104.6	13.05	6.09×10^{-2}	118
1,1-Dimethylethyl diphenylacetyl-, $Ph_2CHC(O)COOCMe_3$	Cumene	313–343	107.1	13.31	5.05×10^{-2}	121
1,1-Dimethylethyl-methyldiphenylacetyl-, $MePh_2CC(O)OOCMe_3$	Chlorobenzene	313–333	106.3	14.02	3.33×10^{-1}	118

(continued overleaf)

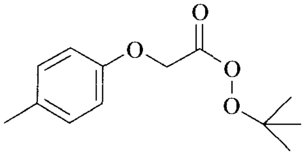
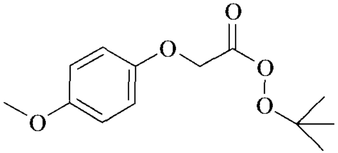
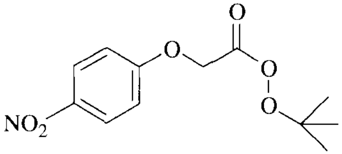
TABLE 5.20 (*continued*)

Peroxide	Solvent	T (K)	E (kJ mol^{-1})	log A, A (s^{-1})	k_d, k_i (383 K) (s^{-1})	Reference
1,1-Dimethylethyl triphenylacetyl-, $Ph_3CC(O)OOCMe_3$	Cumene	299–318	103.3	14.36	1.80	133
1,1-Dimethylethyl-3-phenylpropanoyl-, $PhCH_2CH_2C(O)OOCMe_3$	Ethylbenzene	368–383	147.3	15.89	6.33×10^{-5}	71
1,1-Dimethylethyl-3-phenylpropanoyl-, $PhCH_2CH_2C(O)OOCMe_3$	Chlorobenzene	382–395	149.8	16.23	6.31×10^{-5}	134
1,1-Dimethylethyl 4-phenylbutanoyl-, $Ph(CH_2)_3C(O)OOCMe_3$	Ethylbenzene	368–383	145.2	15.70	7.90×10^{-5}	71
1,1-Dimethylethyl 4-phenylbutanoyl-, $Ph(CH_2)_3C(O)OOCMe_3$	Chlorobenzene	382–395	154.0	16.84	6.88×10^{-5}	134
1,1-Dimethylethyl phenoxyacetyl-, $PhOCH_2C(O)OOCMe_3$	Benzene	313–333	111.3	13.66	3.03×10^{-2}	130
1,1-Dimethylethyl phenoxyacetyl-, $PhOCH_2C(O)OOCMe_3$	Benzene	343.5			4.36×10^{-4}	131

1,1-Dimethylethyl- 4-bromophenoxyacetyl-, 	Benzene	343.5		2.57×10^{-4}	131
1,1-Dimethylethyl- 4-chlorophenoxyacetyl-, 	Benzene	343.5		2.88×10^{-4}	131
1,1-Dimethylethyl- 2,4-dichlorophenoxyacetyl-, 	Benzene	343.5		1.41×10^{-5}	131

(continued overleaf)

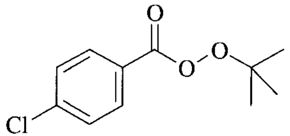
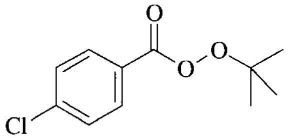
TABLE 5.20 (*continued*)

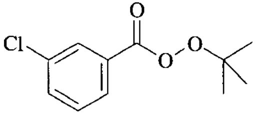
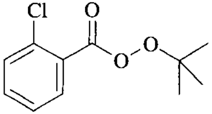
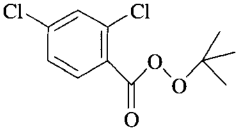
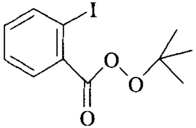
Peroxide	Solvent	T (K)	E (kJ mol^{-1})	log A, A (s^{-1})	k_d, k_i (383 K) (s^{-1})	Reference
1,1-Dimethylethyl- 4-methylphenoxyacetyl-, 	Benzene	343.5			7.24×10^{-4}	131
1,1-Dimethylethyl- 4-methoxyphenoxyacetyl-, 	Benzene	343.5			1.45×10^{-3}	124
1,1-Dimethylethyl- 4-nitrophenoxyacetyl-, 	Benzene	343.5			6.76×10^{-5}	131

1,1-Dimethylethyl-methylphenoxyacetyl-, $Me(PhO)CHC(O)OOCMe_3$	Benzene	313–333	94.6	12.54	4.35×10^{-1}	130
1,1-Dimethylethyl-dimethylphenoxyacetyl-, $Me_2(PhO)CC(O)OOCMe_3$	Benzene	313–333	86.2	11.75	9.86×10^{-1}	130
1,1-Dimethylethyl-3-phenoxypropanoyl-, $PhO(CH_2)_2C(O)OOCMe_3$	Benzene	313–333	156.5	15.56	1.65×10^{-6}	130
1,1-Dimethylethyl-4-phenoxybutanoyl-, $PhO(CH_2)_3C(O)OOCMe_3$	Benzene	313–333	141.0	15.33	1.26×10^{-4}	130
1,1-Dimethylethyl benzyloxyacetyl-, $PhCH_2OCH_2C(O)OOCMe_3$	Benzene	313			1.32×10^{-4}	131
1,1-Dimethylethyl benzylthioacetyl-, $PhCH_2SCH_2C(O)OOCMe_3$	Benzene	313			2.63×10^{-5}	131
1,1-Dimethylethyl chlorocarbonyl-, $ClC(O)OOCMe_3$	Cumene	333–353	124.3	15.54	3.87×10^{-2}	135
1,1-Dimethylethyl chloroacetyl-, $ClCH_2C(O)OOCMe_3$	Ethylbenzene	358–383	149.4	15.88	3.20×10^{-5}	71
1,1-Dimethylethyl trichloroacetyl-, $Cl_3CC(O)OOCMe_3$	Chlorobenzene	358–383	126.8	14.75	2.86×10^{-3}	71
2-Bromohexanoyl 1,1-dimethylethyl-, $Me(CH_2)_3CHBrC(O)OOCMe_3$	Ethylbenzene	358–383	151.9	16.96	1.75×10^{-4}	71

(*continued overleaf*)

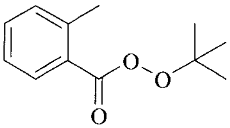
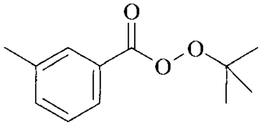
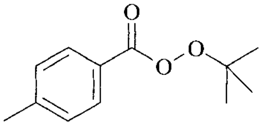
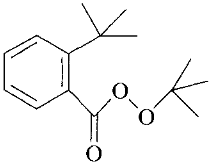
TABLE 5.20 (*continued*)

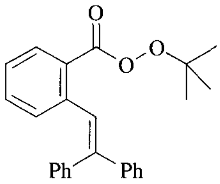
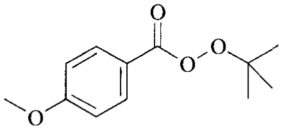
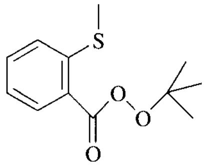
Peroxide	Solvent	T (K)	E (kJ mol^{-1})	log A, A (s^{-1})	k_d, k_i (383 K) (s^{-1})	Reference
Benzoyl 1,1-dimethylethyl-, $PhC(O)OOCMe_3$	4-Chlorotoluene	333–363	143.5	16.11	3.46×10^{-4}	136
Benzoyl 1,1-dimethylethyl-, $PhC(O)OOCMe_3$	Diphenyl ether	373–403	156.9	16.85	2.83×10^{-5}	137
Benzoyl 1,1-dimethylethyl-, $PhC(O)OOCMe_3$	Ethylbenzene	368–383	144.8	15.36	4.09×10^{-5}	71
Benzoyl 1,1-dimethylethyl-, $PhC(O)OOCMe_3$	Undecane	373–403	138.9	14.58	4.33×10^{-5}	138
4-Chlorobenzoyl 1,1-dimethylethyl-, 	Diphenyl ether	373–403	164.4	17.66	1.73×10^{-5}	137
4-Chlorobenzoyl 1,1-dimethylethyl-, 	Undecane	363–403	146.4	15.54	3.75×10^{-5}	119

3-Chlorobenzoyl 1,1-dimethylethyl-, 	Undecane	363–403	136.8	14.26	4.01×10^{-5}	119
2-Chlorobenzoyl 1,1-dimethylethyl-, 	Undecane	363–403	136.0	14.40	7.12×10^{-5}	119
2,4-Dichlorobenzoyl-1,1-dimethylethyl-, 	Undecane	363–403	135.1	14.23	6.38×10^{-5}	119
1,1-Dimethylethyl 2-iodobenzoyl-, 	Chlorobenzene	358–392	120.1	13.13	5.63×10^{-4}	139

(*continued overleaf*)

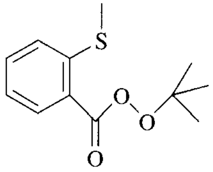
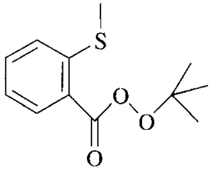
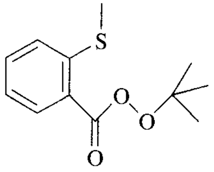
TABLE 5.20 (*continued*)

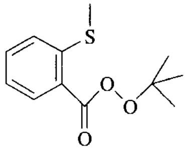
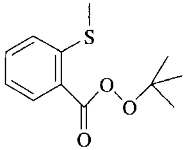
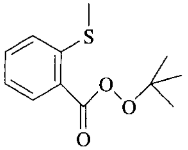
Peroxide	Solvent	T (K)	E (kJ mol^{-1})	log A, A (s^{-1})	k_d, k_i (383 K) (s^{-1})	Reference
1,1-Dimethylethyl 2-methylbenzoyl-, 	Undecane	383–393	136.4	15.17	3.69×10^{-4}	119
1,1-Dimethylethyl 3-methylbenzoyl-, 	Undecane	383			5.01×10^{-5}	119
1,1-Dimethylethyl 4-methylbenzoyl-, 	Undecane	383			4.79×10^{-5}	119
1,1-Dimethylethyl-2-(1′,1′-dimethylethyl)benzoyl-, 	Chlorobenzene	373–409	146.0	16.6	4.88×10^{-4}	139

1,1-Dimethylethyl- 2-(2′, 2′-diphenylethenyl)benzoyl-, 	Undecane	363–392	113.0	12.24	6.75×10^{-4}	140
1,1-Dimethylethyl- 4-methoxybenzoyl-, 	Diphenyl ether	373–403	149.8	16.00	3.72×10^{-5}	137
1,1-Dimethylethyl- 2-methylthiobenzoyl-, 	Acetone	298–313	96.2	12.16	1.09×10^{-1}	139

(*continued overleaf*)

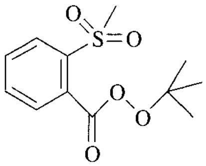
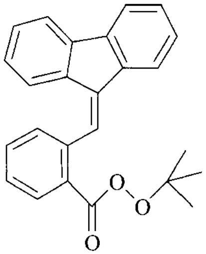
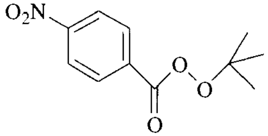
TABLE 5.20 (*continued*)

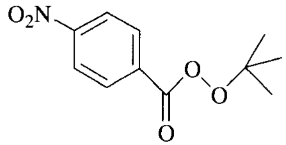
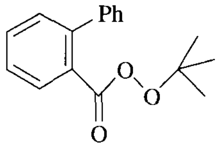
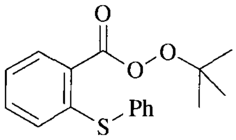
Peroxide	Solvent	T (K)	E (kJ mol^{-1})	log A, A (s^{-1})	k_d, k_i (383 K) (s^{-1})	Reference
1,1-Dimethylethyl-2-methylthiobenzoyl-, 	Acetonitrile	298–313	86.6	11.19	2.39×10^{-1}	139
1,1-Dimethylethyl-2-methylthiobenzoyl-, 	*tert*-Butanol	298–313	93.7	12.16	2.41×10^{-1}	139
1,1-Dimethylethyl-2-methylthiobenzoyl-, 	Chlorobenzene	308–343	97.5	12.15	7.13×10^{-2}	141

1,1-Dimethylethyl- 2-methylthiobenzoyl-, 	Cyclohexane	298–313	100.4	11.5	6.72×10^{-4}	139
1,1-Dimethylethyl- 2-methylthiobenzoyl-, 	Nitrobenzene	313			8.81×10^{-5}	139
1,1-Dimethylethyl- 2-methylthiobenzoyl-, 	Tetrahydrofuran	313			2.02×10^{-5}	139

(continued overleaf)

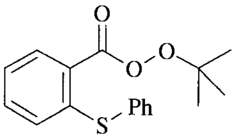
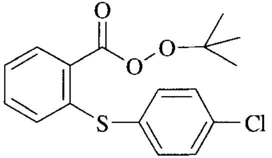
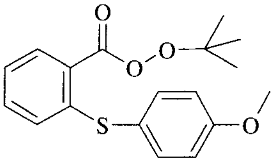
TABLE 5.20 (*continued*)

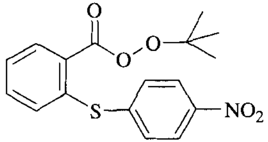
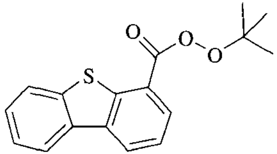
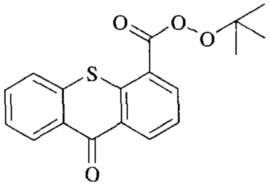
Peroxide	Solvent	T (K)	E (kJ mol^{-1})	log A, A (s^{-1})	k_d, k_i (383 K) (s^{-1})	Reference
1,1-Dimethylethyl-2-methylsulfonylbenzoyl-, 	Chlorobenzene	378–423	161.9	17.19	1.29×10^{-5}	139
1,1-Dimethylethyl [2-(9-fluorenylidene)methyl]benzoyl-, 	Undecane	363			2.45×10^{-3}	140
1,1-Dimethylethyl 4-nitrobenzoyl-, 	Undecane	373–403	146.4	15.36	2.48×10^{-5}	119

1,1-Dimethylethyl 4-nitrobenzoyl-,  	Diphenyl ether	373–404	172.8	18.82	1.79×10^{-5}	137
1,1-Dimethylethyl 2-phenylbenzoyl-,  	Cumene	383–403	152.7	16.77	8.80×10^{-5}	142
1,1-Dimethylethyl-2-phenylthiobenzoyl-,  	Chlorobenzene	372–393	99.2	10.08	3.55×10^{-4}	143

(*continued overleaf*)

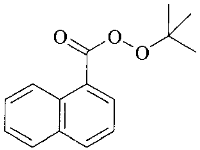
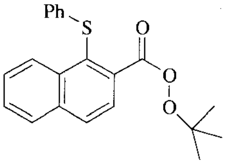
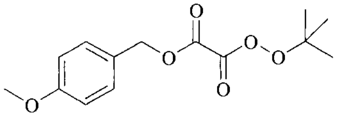
TABLE 5.20 (*continued*)

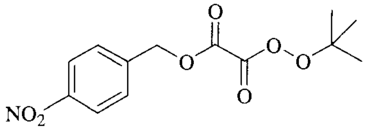
Peroxide	Solvent	T (K)	E (kJ mol^{-1})	log A, A (s^{-1})	k_d, k_i (383 K) (s^{-1})	Reference
1,1-Dimethylethyl-2-phenylthiobenzoyl-, 	Chlorobenzene	313–343	99.2	12.52	9.80×10^{-2}	141
1,1-Dimethylethyl-2-(4-chlorophenylthio)benzoyl-, 	Chlorobenzene	313–343	96.2	11.68	3.63×10^{-2}	139
1,1-Dimethylethyl-2-(4-methoxyphenylthio)benzoyl-, 	Chlorobenzene	307–338	87.4	10.98	1.15×10^{-1}	139

1,1-Dimethylethyl- 2-(4-nitrophenylthio)benzoyl-,  	Chlorobenzene	333–357	94.6	10.84	8.68×10^{-3}	139
1,1-Dimethylethyl- 4-dibenzo[b,d]thiophenoyl-,  	Chlorobenzene	378–408	131.0	13.56	4.94×10^{-5}	139
1,1-Dimethylethyl 4-thioxanthonoyl-,  	Chlorobenzene	393–408	159.4	17.46	5.26×10^{-5}	139

(continued overleaf)

TABLE 5.20 (*continued*)

Peroxide	Solvent	T (K)	E (kJ mol^{-1})	log A, A (s^{-1})	k_d, k_i (383 K) (s^{-1})	Reference
1,1-Dimethylethyl 1-naphthoyl-, 	Chlorobenzene	383			8.70×10^{-5}	143
1,1-Dimethylethyl-1-phenylthio-2-naphthoyl-, 	Chlorobenzene	323–353	102.1	15.54	41.3	143
1,1-Dimethylethyl phenoxyoxalyl-, $PhOC(O)C(O)OOCMe_3$	Benzene	318–338	115.1	14.56	7.29×10^{-2}	144
1,1-Dimethylethyl benzyloxyoxalyl-, $PhCH_2OC(O)C(O)OOCMe_3$	Benzene	318–338	113.8	14.26	5.49×10^{-2}	144
1,1-Dimethylethyl-4-methoxybenzyloxyoxalyl-, 	Benzene	318–338	112.1	14.28	9.81×10^{-2}	144

1,1-Dimethylethyl- 4-nitrobenzyloxyoxalyl-,	Benzene	318–338	119.2	14.71	2.84×10^{-2}	144
						
1,1-Dimethylethyl- 2,5,8-trioxanonanoyl-, $Me(OCH_2CH_2)_2OC(O)OOCMe_3$	Chlorobenzene	383–413	107.2	10.34	5.25×10^{-5}	145
1,1-Dimethylethyl- 2,5,8-trioxanonanoyl-, $Me(OCH_2CH_2)_2OC(O)OOCMe_3$	Chlorobenzene	393			1.44×10^{-4}	146
1,1-Dimethylethyl- 2,5,8-trioxanonanoyl-, $Me(OCH_2CH_2)_2OC(O)OOCMe_3$	Cumene	383–413	97.1	8.89	4.44×10^{-5}	145
1,1-Dimethylethyl- 2,5,8-trioxanonanoyl-, $Me(OCH_2CH_2)_2OC(O)OOCMe_3$	Cumene	393–413			9.40×10^{-4}	146
1,1-Dimethylethyl- 2,5,8-trioxa-9-phenylnonanoyl-, $PhCH_2(OCH_2CH_2)_2OC(O)OOCMe_3$	Chlorobenzene	383–413	110.9	10.76	4.22×10^{-5}	145
1,1-Dimethylethyl- 2,5,8-trioxa-9-phenylnonanoyl-, $PhCH_2(OCH_2CH_2)_2OC(O)OOCMe_3$	Chlorobenzene	403			2.93×10^{-4}	146

(*continued overleaf*)

TABLE 5.20 (*continued*)

Peroxide	Solvent	T (K)	E (kJ mol^{-1})	log A, A (s^{-1})	k_d, k_i (383 K) (s^{-1})	Reference
1,1-Dimethylethyl-2,5,8-trioxa-9-phenylnonanoyl-, $PhCH_2(OCH_2CH_2)_2OC(O)OOCMe_3$	Cumene	383–413	114.3	11.16	3.73×10^{-5}	145
1,1-Dimethylethyl 3,6-dimethyl-2,5,8-trioxa-9-phenylnonanoyl-, $PhCH_2[OCH_2CH(Me)]_2O$-$C(O)OOCMe_3$	Chlorobenzene	383–413	115.1	11.43	5.40×10^{-5}	145
1,1-Dimethylethyl 3,6-dimethyl-2,5,8-trioxa-9-phenylnonanoyl-, $PhCH_2[OCH_2CH(Me)]_2O$ $C(O)OOCMe_3$	Chlorobenzene	403			3.12×10^{-4}	146
		$k_i = 2ek_d$				
Acetyl 1,1-dimethylethyl-, $MeC(O)OOCMe_3$	Styrene	346–368	160.7	17.63	5.17×10^{-5}	34
1,1-Dimethylethyl propanoyl-, $EtC(O)OOCMe_3$	Cumene	373–403	153.4	16.97	1.12×10^{-4}	84
1,1-Dimethylethyl 2-methylpropanoyl-, $Me_2CHC(O)OOCMe_3$	Styrene	358–383	125.5	13.74	4.21×10^{-4}	71
1,1-Dimethylethyl 2,2-dimethylpropanoyl-, $Me_3CC(O)OOCMe_3$	Styrene	358–383	100.4	11.33	4.34×10^{-3}	122
1,1-Dimethylethyl butanoyl-, $PrC(O)OOCMe_3$	Cumene	373–403	143.5	15.62	1.12×10^{-4}	84

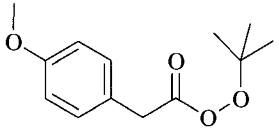
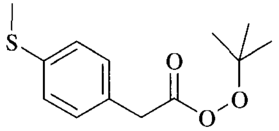
1,1-Dimethylethyl butanoyl-, PrC(O)OOCMe$_3$	Decane	373–403	125.9	12.32	1.41×10^{-5}	84
1,1-Dimethylethyl pentanoyl-, Me(CH$_2$)$_3$C(O)OOCMe$_3$	Styrene	358–383	154.8	17.32	1.62×10^{-4}	71
1,1-Dimethylethyl octanoyl-, Me(CH$_2$)$_6$C(O)OOCMe$_3$	Styrene	358–383	153.1	17.20	2.08×10^{-5}	71
Benzoyl 1,1-dimethylethyl-, PhC(O)OOCMe$_3$	Styrene/chlorobenzene	368–383	150.6	16.04	3.17×10^{-5}	71
1,1-Dimethylethyl-(4-methoxyphenyl)acetyl-, 	Toluene	329			1.29×10^{-3}	132
1,1-Dimethylethyl-(4-methylthiophenyl)acetyl-, 	Toluene	329			7.24×10^{-3}	132

TABLE 5.21 The Probability *e* of a Radical Pair Going Out of the Cage in Perester Decomposition in Different Solvents

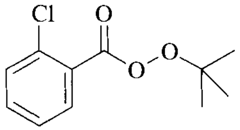
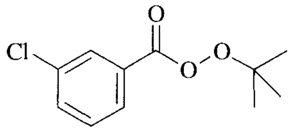
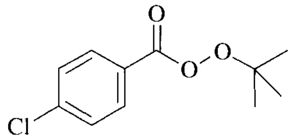
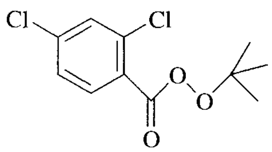
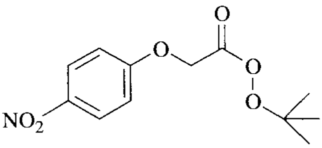
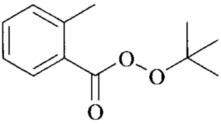
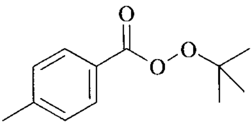
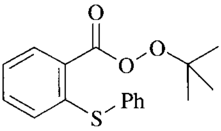
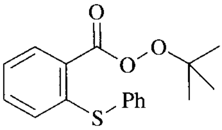
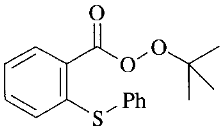
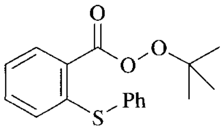
Peroxide	Solvent	T (K)	e	Reference
Acetyl 1,1-dimethylethyl-, $Me_3COOC(O)Me$	Ethyl benzene	368	0.90	71
Acetyl 1,1-dimethylethyl-, $Me_3COOC(O)Me$	Undecane	383	0.49	96
1,1-Dimethylethyl pentanoyl-, $Me_3COOC(O)(CH_2)_3Me$	Ethylbenzene	368	0.90	71
1,1-Dimethylethyl hexanoyl-, $Me_3COOC(O)(CH_2)_4Me$	Ethylbenzene	368	0.90	71
1,1-Dimethylethyl hexanoyl-, $Me_3COOC(O)(CH_2)_4Me$	Undecane	383	0.66	138
1,1-Dimethylethyl 2-methylpropanoyl-, $Me_3COOC(O)CHMe_2$	Ethylbenzene	368	0.70	71
1,1-Dimethyl 2,2-dimethylpropanoyl-, $Me_3COOC(O)CMe_3$	Ethylbenzene	368	0.20	71
2-Chlorobenzoyl 1,1-dimethylethyl-, 	Undecane	383	0.94	139
3-Chlorobenzoyl 1,1-dimethylethyl-, 	Undecane	383	0.67	138
4-Chlorobenzoyl 1,1-dimethylethyl-, 	Undecane	383	0.57	138
2,4-Dichlorobenzoyl 1,1-dimethylethyl-, 	Undecane	383	0.98	138

TABLE 5.21 (*continued*)

Peroxide	Solvent	T (K)	e	Reference
1,1-Dimethylethyl 4-nitrobenzoyl-, 	Undecane	383	0.95	138
1,1-Dimethylethyl 2-methylbenzoyl-, 	Undecane	383	0.73	138
1,1-Dimethylethyl 4-methylbenzoyl-, 	Undecane	383	0.61	138
1,1-Dimethylethyl 2-phenylthiobenzoyl-, 	Acetone	298	0.15	139
1,1-Dimethylethyl 2-phenylthiobenzoyl-, 	Acetonitrile	298	0.33	139
1,1-Dimethylethyl 2-phenylthiobenzoyl-, 	*tert*-Butanol	298	0.15	139
1,1-Dimethylethyl 2-phenylthiobenzoyl-, 	Cyclohexane	298	0.17	139

(*continued overleaf*)

TABLE 5.21 (*continued*)

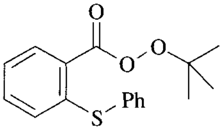
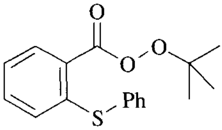
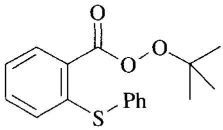
Peroxide	Solvent	T (K)	e	Reference
1,1-Dimethylethyl 2-phenylthiobenzoyl-, 	Ethanol	298	0.26	139
1,1-Dimethylethyl 2-phenylthiobenzoyl-, 	Isopropanol	298	0.20	139
1,1-Dimethylethyl 2-phenylthiobenzoyl-, 	Undecane	298	0.17	139

TABLE 5.22 **The Enthalpies (ΔH_f^0) of Polyperoxides Formation in Gas and Condensed Phases**

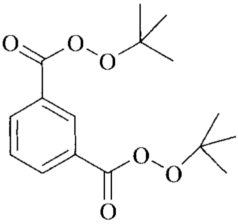
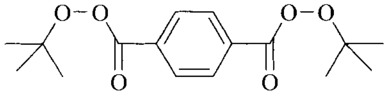
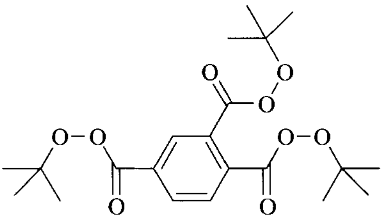
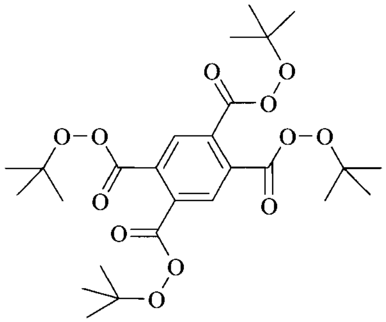
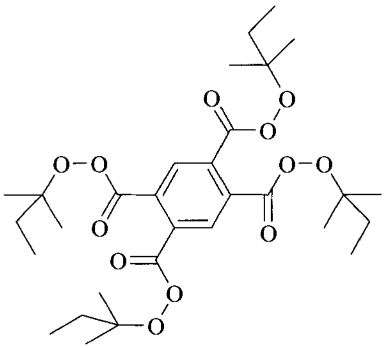
Polyperoxide	Phase	$-\Delta H_f^0$ (kJ mol^{-1})	Reference
Diperoxide, bis(1,1-dimethylethyl) 1,3-benzenedicarbonyl,	Gas	649.6	113
	Solid	783.0	
Diperoxide, bis(1,1-dimethylethyl) 1,4-benzenedicarbonyl, 	Solid	784.0	113

TABLE 5.22 (*continued*)

Polyperoxide	Phase	$-\Delta H_f^0$ (kJ mol^{-1})	Reference
Triperoxide, tris(1,1-dimethylethyl) 1,2,4-benzenetricarbonyl, 	Solid	1169.0	113
Tetraperoxide, tetra(1,1-dimethylethyl) 1,2,4,5-benzenetetracarbonyl, 	Solid	1532.0	147
Tetraperoxide, tetra(1,1-dimethylpropyl) 1,2,4,5-benzenetetracarbonyl, 	Solid	1761.9	147
Diperoxide, bis(1,1-dimethylethyl) 2,4-hexadienedioyl, $Me_3COOC(O)CH{=}CHCH{=}CHC(O)OOCMe_3$	Solid	778.0	148

(*continued overleaf*)

TABLE 5.22 (*continued*)

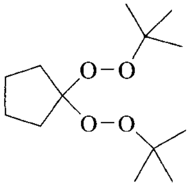
Polyperoxide	Phase	$-\Delta H_f^0$ (kJ mol^{-1})	Reference
Diperoxide, diacetyl hexanedioyl, $\mathrm{MeC(O)OOC(O)(CH_2)_4C(O)OOC(O)Me}$	Solid	1174.0	149
Diperoxide, decanedioyl diacetyl, $\mathrm{MeC(O)OOC(O)(CH_2)_8C(O)OOC(O)Me}$	Solid	1288.5	149
Diperoxide, decanedioyl dipropanoyl, $\mathrm{EtC(O)OOC(O)(CH_2)_8C(O)OOC(O)Et}$	Solid	1344.0	149
Diperoxide, dihexanoyl hexanedioyl, $\mathrm{Me(CH_2)_4C(O)OOC(O)(CH_2)_4\text{-}C(O)OOC(O)(CH_2)_4Me}$	Solid	1403.9	149
Diperoxide, butanedioyl didecanoyl, $\mathrm{Me(CH_2)_8C(O)OOC(O)CH_2\text{-}CH_2C(O)OOC(O)(CH_2)_8Me}$	Solid	1574.7	149
Diperoxide, didecanoyl pentanedioyl, $\mathrm{Me(CH_2)_8C(O)(CH_2)_3C(O)\text{-}OOC(O)(CH_2)_8Me}$	Solid	1590.2	149
Diperoxide, didecanoyl hexanedioyl, $\mathrm{Me(CH_2)_8C(O)OOC(O)(CH_2)_4\text{-}C(O)OOC(O)(CH_2)^8Me}$	Solid	1641.9	149
Diperoxide, decanedioyl didecanoyl, $\mathrm{Me(CH_2)_8C(O)OOC(O)(CH_2)_8\text{-}C(O)OOC(O)(CH_2)_8Me}$	Solid	1748.7	149
Diperoxide, bis(1,1-dimethylethyl)	Gas	656.3	150
1,1,4,4-tetramethyltetramethylene, $\mathrm{Me_3COOCMe_2(CH_2)_2CMe_2OOCMe_3}$	Liquid	725.2	151
Diperoxide, bis(1,1-dimethylethyl) cyclopentylidene,	Gas	482.2	152
	Liquid	549.9	
Diperoxide, bis(1,1-dimethylethyl) 1,3-dimethyl-1-butylidene,	Gas	706.6	152
$\mathrm{[Me_3COO]_2C(Me)CH_2CHMe_2}$	Liquid	771.2	
Diperoxide, bis(1,1-dimethylethyl) 1-methyl-1-propylidene,	Gas	553.6	152
$\mathrm{[Me_3COO]_2C(Me)Et}$	Liquid	612.0	

TABLE 5.23 The Rate Constants for the Decomposition of Polyperoxides in Different Solvents

Diperoxide	Solvent	T (K)	E (kJ mol^{-1})	log A, A (s^{-1})	k_{d1}, k_{d2}, k_i (353 K) (s^{-1})	Reference
		k_{d1}, k_{d2}				
Bis(1,1-dimethylethyl) ethanedioyl-, $[Me_3COOC(O)]_2$	Benzene	308–328	110.9	14.65	1.74×10^{-2}	153
					1.74×10^{-2}	153
Bis(1,1-dimethylethyl) dimethylpropanedioyl-, Me_3CO $OC(O)CMe_2C(O)OOCMe_3$	Cumene	352.5–373	125.5	14.42	7.07×10^{-5}	154
					7.07×10^{-5}	154
Dibenzoyl 2-methylenepropanedioyl-, $PhC(O)OOC(O)CH$ $(=CH_2)C(O)OOC(O)Ph$	Benzene	333–358	83.7	9.50	1.30×10^{-3}	155
	Carbon tetrachloride		115.1	12.84	6.44×10^{-5}	155
	Chlorobenzene					
Bis(1,1-dimethylethyl) phenylpropanedioyl-, Me_3CO $OC(O)CHPhC(O)OOCMe_3$	Cumene	343–363	128.4	15.58	3.81×10^{-4}	156
					3.81×10^{-4}	156
Bis(1,1-dimethylethyl) diphenylpropanedioyl-, $Me_3COOC(O)CPh_2C(O)O$ $OCMe_3$	Cumene	323–343	110.5	14.30	8.90×10^{-3}	121
					8.90×10^{-3}	121

(*continued overleaf*)

TABLE 5.23 (*continued*)

Diperoxide	Solvent	T (K)	E (kJ mol^{-1})	log A, A (s^{-1})	k_{d1}, k_{d2}, k_i (353 K) (s^{-1})	Reference
Butanedioyl dibenzoyl-, $PhC(O)OOC(O)(CH_2)_2$-$C(O)OOC(O)Ph$	Benzene	343–358	125.5	13.97	2.69×10^{-5}	155
	Carbon tetrachloride				2.69×10^{-5}	155
	Chlorobenzene					
Dibenzoyl 2-methylbutanedioyl-, $PhC(O)OOC(O)CH_2$-$CHMeC(O)OOC(O)Ph$	Benzene	343–358	82.8	9.06	6.43×10^{-4}	155
	Carbon tetrachloride		116.3	12.83	4.18×10^{-5}	155
	Chlorobenzene					
Chlorobutanedioyl dibenzoyl-, $PhC(O)OOC(O)CH_2$-$CHClC(O)OOC(O)Ph$	Benzene	333–358	82.8	8.93	4.76×10^{-4}	155
	Carbon tetrachloride		115.1	12.60	3.70×10^{-5}	155
	Chlorobenzene					
Bromobutanedioyl dibenzoyl-, $PhC(O)OOC(O)CH_2$-$CHBrC(O)OOC(O)Ph$	Benzene	343–358	88.3	9.40	2.16×10^{-4}	155
	Carbon tetrachloride		114.2	12.41	3.24×10^{-5}	155
	Chlorobenzene					
Dioctanoyl methylbutanedioyl-, $Me(CH_2)_6C(O)OOC(O)$-$CH_2CHMeC(O)$-$O\ OC(O)(CH_2)_6Me$	Benzene	343–358	96.2	11.43	1.57×10^{-3}	155
	Carbon tetrachloride		130.9	15.68	2.04×10^{-4}	155
	Chlorobenzene					

Dioctanoyl methylenebutanedioyl-, $Me(CH_2)_6C(O)OOC(O)CH_2$-$C(=CH_2)C(O)OOC(O)$-$(CH_2)_6Me$	Benzene	343–358	92.9	10.68	8.58×10^{-4}	155
	Carbon tetrachloride		127.6	14.90	1.04×10^{-4}	155
	Chlorobenzene					
Dioctanoyl chlorobutanedioyl-, $Me(CH_2)_6C(O)OOC(O)$-$CH_2CH(Cl)C(O)$-$OOC(O)(CH_2)_6Me$	Benzene	343–358	95.4	10.82	5.05×10^{-4}	155
	Carbon tetrachloride		126.4	14.66	9.04×10^{-5}	155
	Chlorobenzene					
Bromobutanedioyl dioctanoyl-, $Me(CH_2)_6C(O)OOC(O)$-$CH_2CH(Br)C(O)$-$OOC(O)(CH_2)_6Me$	Benzene	343–358	96.6	10.94	4.43×10^{-4}	155
	Carbon tetrachloride					
	Chlorobenzene		126.4	14.55	7.02×10^{-5}	155

(*continued overleaf*)

TABLE 5.23 (*continued*)

Diperoxide	Solvent	T (K)	E (kJ mol^{-1})	log A, A (s^{-1})	k_{d1}, k_{d2}, k_i (353 K) (s^{-1})	Reference
Bis(1,1-dimethylethyl)	Ethylbenzene	378–398	158.9	17.26	5.59×10^{-7}	157
pentanedioyl-,			158.9	17.26	5.59×10^{-7}	157
$Me_3C(O)OOC(O)$						
$-(CH_2)_3C(O)OOCMe_3$						
Bis(1,1-dimethylethyl)	Ethylbenzene	378–388	113.0	11.89	1.48×10^{-5}	157
2-methylenepentanedioyl-,			140.2	14.63	7.66×10^{-7}	157
$Me_3COOC(O)CH$-						
$(=CH_2)(CH_2)_2C(O)OOCMe_3$						
Bis(1,1-dimethylethyl)	Ethylbenzene	378–398	83.7	7.61	1.68×10^{-5}	157
2-chloropentanedioyl-,			125.5	12.71	1.38×10^{-6}	157
$Me_3COOC(O)CHCl$-						
$(CH_2)_2C(O)OOCMe_3$						
2-Bromopentanedioyl	Benzene	343–358	92.9	10.46	5.17×10^{-4}	155
dibenzoyl-,						
$PhC(O)OOC(O)(CH_2)_2$-	Carbon		112.1	12.35	5.79×10^{-5}	155
$CHClC(O)OOC(O)Ph$	tetrachloride					
	Chlorobenzene					
2-Bromopentanedioyl	Benzene	343–358	97.9	11.24	5.67×10^{-4}	155
dioctanoyl-,						
$Me(CH_2)_6C(O)OOC(O)$-	Carbon		126.4	14.81	1.28×10^{-4}	155
$(CH_2)_2CH(Br)C$-	tetrachloride					
$(O)OOC(O)(CH_2)_6Me$	Chlorobenzene					

Dibenzoyl hexanedioyl-, $PhC(O)OOC(O)(CH_2)_4$-$C(O)OOC(O)Ph$	Styrene	343			2.28×10^{-5}	158
					2.28×10^{-5}	158
Dibenzoyl hexanedioyl-, $PhC(O)OOC(O)(CH_2)_4$-$C(O)OOC(O)Ph$	Styrene	338–363	140.0	16.68	9.21×10^{-5}	158
			140.0	16.68	9.21×10^{-5}	158
Bis(1,1-dimethylethyl) 2-bromohexanedioyl-, $Me_3COOC(O)CHBr$-$(CH_2)_3C(O)OOCMe_3$	Ethylbenzene	383–398	125.5	13.14	3.71×10^{-6}	157
			159.1	17.36	6.57×10^{-7}	157
2-Bromohexanedioyl dibenzoyl-, $PhC(O)OOC(O)(CH_2)_3$-$CHBrC(O)OOC(O)Ph$	Benzene	343–358	91.6	10.50	8.83×10^{-4}	155
	Carbon tetrachloride		112.1	12.44	7.12×10^{-5}	155
	Chlorobenzene					
2-Bromohexanedioyl dioctanoyl-, $Me(CH_2)_6C(O)OOC(O)$-$(CH_2)_3CH(Br)C(O)$-$OOC(O)(CH_2)_6Me$	Benzene	343–358	96.7	11.45	1.38×10^{-3}	155
	Carbon tetrachloride		122.6	14.24	1.26×10^{-4}	155
	Chlorobenzene					
Bis(1,1-dimethylethyl) 2-bromoheptanedioyl-, $Me_3COOC(O)CHBr$-$(CH_2)_4C(O)OOCMe_3$	Ethylbenzene	383–398	125.5	13.16	3.89×10^{-6}	156
			150.6	16.20	8.23×10^{-7}	156

(*continued overleaf*)

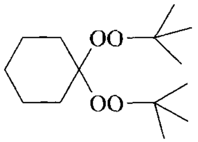
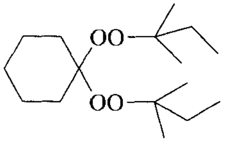
TABLE 5.23 *(continued)*

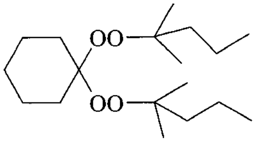
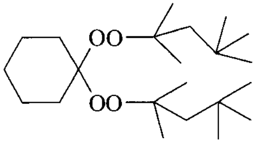
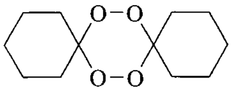
Diperoxide	Solvent	T (K)	E (kJ mol^{-1})	log A, A (s^{-1})	k_{d1}, k_{d2}, k_i (353 K) (s^{-1})	Reference
2-Bromoheptanedioyl dibenzoyl-, PhC(O)OOC(O)-(CH$_2$)$_4$CHBrC(O)OOC(O)Ph	Benzene	343–358	91.6	10.71	1.77×10^{-3}	155
	Carbon tetrachloride		113.0	12.74	1.04×10^{-4}	155
	Chlorobenzene					
2-Bromoheptanedioyl dioctanoyl-, Me(CH$_2$)$_6$C(O)OOC-(O)(CH$_2$)$_4$CH(Br)-C(O)OOC(O)(CH$_2$)$_6$Me	Benzene	343–358	99.2	11.95	1.86×10^{-3}	155
	Carbon tetrachloride		132.6	15.93	2.04×10^{-4}	155
	Chlorobenzene					
Bis(1,1-dimethylethyl) octanedioyl-, Me$_3$C(O)-O OC(O)(CH$_2$)$_6$C(O)-OOCMe$_3$	Styrene	378–398	150.6	16.47	1.53×10^{-6}	157
			150.6	16.47	1.53×10^{-6}	157
Bis(1,1-dimethylethyl) nonanedioyl-, Me$_3$C(O)-OOC(O)(CH$_2$)$_7$-C(O)OOCMe$_3$	Ethylbenzene	378–398	159.0	17.59	1.16×10^{-6}	157
			159.0	17.59	1.16×10^{-6}	157

2-Bromononanedioyl dibenzoyl-, $PhC(O)OOC(O)(CH_2)_6$-CHBrC(O)OOC(O)Ph	Benzene	343–358	87.9	10.08	1.18×10^{-3}	155
	Carbon tetrachloride		110.9	12.49	1.20×10^{-4}	155
	Chlorobenzene					
2-Bromononanedioyl dioctanoyl-, $Me(CH_2)_6C(O)OOC(O)$-$(CH_2)_6CH(Br)$-$C(O)OOC(O)(CH_2)_6Me$	Benzene	343–358	99.6	12.02	1.91×10^{-3}	155
	Carbon tetrachloride		129.7	15.50	2.03×10^{-4}	155
	Chlorobenzene					
Bis(1,1-dimethylethyl) decanedioyl-, $Me_3C(O)OOC(O)$ $(CH_2)_8C(O)OOCMe_3$	Ethylbenzene	378–398	154.8	17.02	1.30×10^{-6}	157
			154.8	17.02	1.30×10^{-6}	157
2-Bromodecanedioyl dibenzoyl-, $PhC(O)OOC(O)$-$(CH_2)_7CH(Br)$-C(O)OOC(O)Ph	Benzene	343–358	87.9	10.08	1.18×10^{-3}	155
	Carbon tetrachloride		110.9	12.51	1.26×10^{-4}	155
	Chlorobenzene					

(*continued overleaf*)

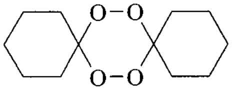
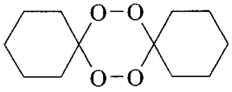
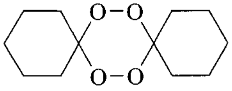
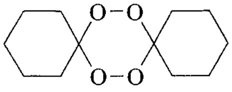
TABLE 5.23 (*continued*)

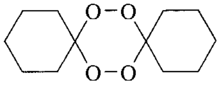
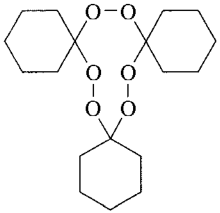
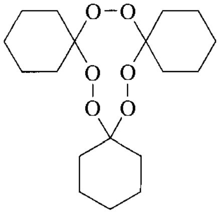
Diperoxide	Solvent	T (K)	E (kJ mol^{-1})	log A, A (s^{-1})	k_{d1}, k_{d2}, k_i (353 K) (s^{-1})	Reference
Bis(1,1-dimethylethyl) undecanedioyl-, $Me_3C(O)OOC$-$(O)(CH_2)_9$ $C(O)OOCMe_3$	Ethylbenzene	378–398	154.8	16.97	1.16×10^{-6}	157
			154.8	16.97	1.16×10^{-6}	157
Bis(1,1-dimethylethyl) cyclohexylidene-,	Decane	363–403	141.4	15.39	2.93×10^{-6}	159
			141.4	15.39	2.93×10^{-6}	159
Bis(1,1-dimethylpropyl) cyclohexylidene-,	Cumene	353–383	143.4	15.94	5.26×10^{-6}	160
						

Bis(1,1-dimethylbutyl) cyclohexylidene-, 	Cumene	353–383	143.96	16.03	5.27×10^{-6}	160
Di(1,1,3,3-tetramethylbutyl) cyclohexylidene-, 	Cumene	353–383	140.2	15.95	1.60×10^{-5}	160
Dicyclohexylidene-, 	Benzene	381–423	149.6	14.70	3.66×10^{-8}	161

(continued overleaf)

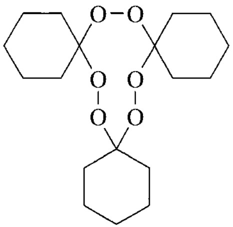
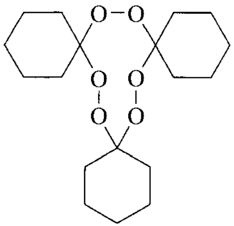
TABLE 5.23 (*continued*)

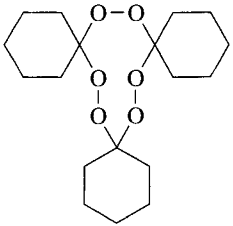
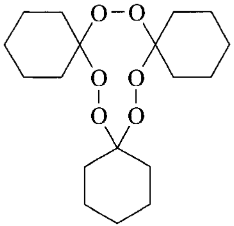
Diperoxide	Solvent	T (K)	E (kJ mol^{-1})	log A, A (s^{-1})	k_{d1}, k_{d2}, k_i (353 K) (s^{-1})	Reference
Dicyclohexylidene-, 	Benzene	381–433	144.8	14.35	8.39×10^{-8}	162
Dicyclohexylidene-, 	Chloroethane	422–438	154.2	15.24	2.65×10^{-8}	163
Dicyclohexylidene-, 	Ethyl acetate	422–438	163.7	16.31	1.22×10^{-8}	163
Dicyclohexylidene-, 	Phenyl acetate	422–438	156.4	15.58	2.74×10^{-8}	163

Dicyclohexylidene-, 	Toluene	422–438	171.6	17.18	6.14×10^{-9}	163
Triperoxide						
Tricyclohexylidene-, 	Cyclohexane	413–428	152.5	14.0	2.72×10^{-9}	163
Tricyclohexylidene-, 	Hexane	413–423	173.6	17.61	8.36×10^{-9}	163

(continued overleaf)

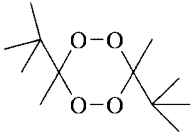
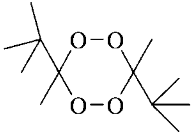
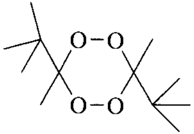
TABLE 5.23 (*continued*)

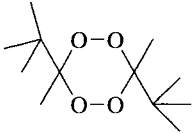
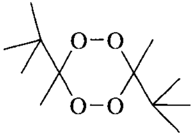
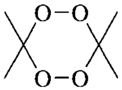
Triperoxide	Solvent	T (K)	E (kJ mol^{-1})	log A, A (s^{-1})	k_{d1}, k_{d2}, k_i (353 K) (s^{-1})	Reference
Tricyclohexylidene-, 	Decane	413–418	150.6	14.69	2.54×10^{-8}	163
Tricyclohexylidene-, 	Toluene	413–423	182.9	19.04	9.46×10^{-9}	163

Tricyclohexylidene-, 	Benzene	413–423	190.3	20.03	7.43×10^{-9}	163
Tricyclohexylidene-, 	Acetone	413–423	140.5	13.98	1.55×10^{-7}	163

(*continued overleaf*)

TABLE 5.23 (*continued*)

Diperoxide	Solvent	T (K)	E (kJ mol^{-1})	log A, A (s^{-1})	k_{d1}, k_{d2}, k_{i} (353 K) (s^{-1})	Reference
1,2,4,5-Tetraoxane 3,6-(1,1-dimethylethyl)- 3,6-dimethyl-, 	Benzene	393–433	128.3	12.61	4.22×10^{-7}	161
3,6-(1,1-dimethylethyl)- 3,6-dimethyl-, 	Acetonitrile	403–433	150.0	14.0	6.37×10^{-9}	161
3,6-(1,1-dimethylethyl)- 3,6-dimethyl-, 	Octane	383–433	154.5	15.83	9.30×10^{-8}	161

3,6-(1,1-dimethylethyl)-3,6-dimethyl-, 	Acetic acid	373–413	136.3	13.85	4.80×10^{-7}	161
3,6-(1,1-dimethylethyl)-3,6-dimethyl-, 	Benzene	393–433	128.0	12.61	4.67×10^{-7}	161
3,3,6,6-tetramethyl-, 	Benzene	408–418	153.1	13.39	5.44×10^{-10}	164

(continued overleaf)

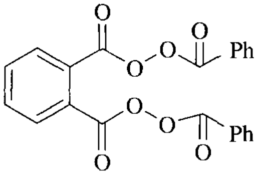
TABLE 5.23 (*continued*)

Diperoxide	Solvent	T (K)	E (kJ mol^{-1})	log A, A (s^{-1})	k_{d1}, k_{d2}, k_i (353 K) (s^{-1})	Reference
Silane						
Vinyltris(5,5-dimethyl-1,3,4-trioxahexyl)-, CH_2=$CHSi[OCH_2OOCMe_3]_3$	Cumene	383–413	124.9	13.04	3.62×10^{-6}	165
Vinyltris(2,6,6-trimethyl-1,4,5-trioxaheptyl)-, CH_2=CH-$Si[OCHMeCH_2O$-$OCMe_3]_3$	Benzene	393–423	124.7	12.32	7.38×10^{-7}	165
Vinyltris(6,6-dimethyl-1,4,5-trioxaheptyl)-, CH_2=CH-$Si[O(CH_2)_2OOCMe_3]_3$	Benzene	403–423	130.6	12.91	3.85×10^{-7}	165
Methyltris(2,6,6-trimethyl-1,4,5-trioxaheptyl)-, $MeSi[OCHMeCH_2OOCMe_3]_3$	Benzene	403–423	133.1	13.35	4.52×10^{-7}	165
Methyltris(6,6-dimethyl-1,4,5-trioxaheptyl)-, $MeSi[O(CH)_2OOCMe_3]_3$	Benzene	403–423	130.6	12.88	3.59×10^{-7}	165
Diphenyldi(2,6,6-trimethyl-1,4,5-trioxaheptyl)-, $Ph_2Si[OCHMeCH_2OOCMe_3]_2$	Benzene	393–423	125.9	12.42	6.17×10^{-7}	165

Dimethyldi[(2,6,6-trimethyl-1,4,5-trioxaheptyl)-, $MeSi[OCHMeCH_2OOCMe_3]_2$		393–423	125.6	12.36	5.95×10^{-7}	165
		$k_i = 2ek_d$				
Diperoxide						
Bis(1,1-dimethylethyl) butanedioyl-, $Me_3COOC(O)(CH_2)_2C(O)OOCMe_3$	Styrene	368–378	107.1	9.53	4.81×10^{-7}	71
Bis(1,1-dimethylethyl) pentanedioyl-, $Me_3COOC(O)-CH_2)_3COOCMe_3$	Styrene	368–378	123.8	12.11	6.18×10^{-7}	71
Bis(1,1-dimethylethyl) hexanedioyl-, $Me_3COOC(O)(CH_2)_4-C(O)OOCMe_3$	Styrene	368–378	121.3	12.11	1.45×10^{-6}	71
Dibenzoyl hexanedioyl-, $PhC(O)OOC(O)(CH_2)_4-C(O)OOC(O)Ph$	Styrene	343			7.06×10^{-6}	27

(*continued overleaf*)

TABLE 5.23 (*continued*)

Diperoxide	Solvent	T (K)	E (kJ mol^{-1})	log A, A (s^{-1})	k_{d1}, k_{d2}, k_i (353 K) (s^{-1})	Reference
Bis(1,1-dimethylethyl) heptanedioyl-, $Me_3COOC(O)$-$(CH_2)_5C(O)OOCMe_3$	Styrene	368–378	141.0	14.83	9.25×10^{-7}	71
Bis(1,1-dimethylethyl) nonanedioyl-, $Me_3COOC(O)$-$(CH_2)_7C(O)OOCMe_3$	Styrene	368–378	154.0	16.81	1.05×10^{-6}	71
Bis(1,1-dimethylethyl) decanedioyl-, $Me_3COOC(O)$-$(CH_2)_8C(O)OOCMe_3$	Styrene	368–378	164.0	18.0	5.40×10^{-7}	71
Dibenzoyl-1,2-benzene-dicarbonyl-, 	Styrene	343			8.0×10^{-6}	27

Bis(1,1-dimethylethyl) propylidene-, $Me_3COOCHEtOOCMe_3$	Styrene	353–363	143.5	15.61	2.38×10^{-6}	166
Bis(1,1-dimethylethyl) ethylidene-, $(Me_3COO)_2CHMe$	Styrene	353–373	163.6	17.98	5.92×10^{-7}	167
Bis(1,1-dimethylethyl) methylethylidene-, $(Me_3COO)_2CMe_2$	Styrene	353–373	157.7	17.46	1.33×10^{-6}	167
Bis(1,1-dimethylethyl) 1-butylidene-, $(Me_3COO)_2CHCH_2Et$	Styrene	353–373	146.9	16.12	2.42×10^{-6}	167
Bis(1,1-dimethylethyl) 1-methylpropylidene-, $(Me_3COO)_2C(Me)Et$	Styrene	353–373	145.2	16.0	3.27×10^{-6}	167
Bis(1,1-dimethylethyl) 2-methylpropylidene-, $(Me_3COO)_2CHCHMe_2$	Styrene	353–373	143.5	15.88	4.43×10^{-6}	167
Bis(1,1-dimethylethyl) 1-ethylpropylidene-, $(Me_3COO)_2CEt_2$	Styrene	353–373	134.3	14.55	4.76×10^{-6}	167

(*continued overleaf*)

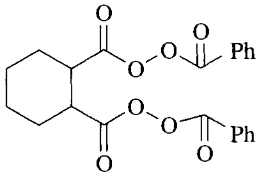
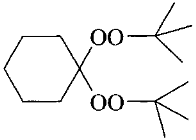
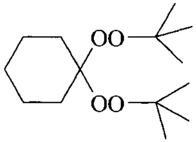
TABLE 5.23 *(continued)*

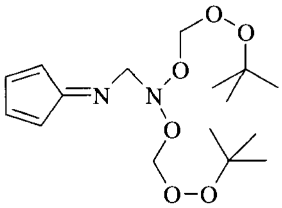
Diperoxide	Solvent	T (K)	E (kJ mol^{-1})	log A, A (s^{-1})	k_{d1}, k_{d2}, k_{i} (353 K) (s^{-1})	Reference
Bis(1,1-dimethylpropyl) methylene-, $[Me_2(Et)COO]_2CH_2$	Styrene	353–373	143.5	15.32	1.22×10^{-6}	167
Bis(1,1-dimethylpropyl) ethylidene-, $[Me_2(Et)COO]_2CHMe$	Styrene	353–373	142.3	15.24	1.53×10^{-6}	167
Bis(1,1-dimethylpropyl) 1-methylethylidene-, $[Me_2(Et)COO]_2CMe_2$	Styrene	353–373	129.7	13.56	2.33×10^{-6}	159
Bis(1,1-dimethylpropyl) 1-methylpropylidene-, $[Me_2(Et)COO]_2CMe(Et)$	Styrene	353–373	130.1	13.88	4.26×10^{-6}	167
Bis(1,1-dimethylpropyl) 1-ethylpropylidene-, $[Me_2(Et)COO]_2CEt_2$	Styrene	353–373	129.7	13.99	6.28×10^{-6}	167
Bis(1-methyl-1-ethylpropyl) 1-methylethylidene-, $Me_2C[OOC(Et)_2Me]_2$	Chlorobenzene	379.6	117.2	12.18	6.88×10^{-6}	167

Bis(1-methyl-1-ethylpropyl) 1-methylethylidene-, $Me_2C[OOC(Et)_2Me]_2$	Pentanol	364.5	119.2	13.35	4.15×10^{-5}	167
Bis(1-methyl-1-ethylpropyl) 1-methylethylidene-, $Me_2C[OOC(Et)_2Me]_2$	Acetic acid	359.8	104.2	12.13	5.15×10^{-4}	167
Bis(1,1-dimethylethyl) 1,2-dimethylpropylidene-, $Me(Me_2CH)C[OOCMe_3]_2$	Tetradecane	409	128.4	12.60	3.99×10^{-7}	167
Bis(1,1-dimethylethyl) 1,2-dimethylpropylidene-, $Me(Me_2CH)C[OOCMe_3]_2$	Chlorobenzene	379.6	102.5	10.34	1.49×10^{-5}	168
Bis(1,1-dimethylethyl) 1,2-dimethylpropylidene-, $Me(Me_2CH)C[OOCMe_3]_2$	Pentanol	367.5	96.2	9.95	5.19×10^{-5}	168
Bis(1,1-dimethylethyl) 1,2-dimethylpropylidene-, $Me(Me_2CH)C[OOCMe_3]_2$	Acetic acid	359.8			9.54×10^{-4}	168

(*continued overleaf*)

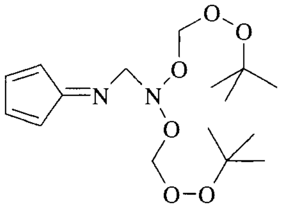
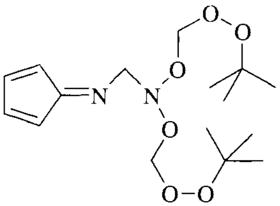
TABLE 5.23 (*continued*)

Diperoxide	Solvent	T (K)	E (kJ mol^{-1})	log A, A (s^{-1})	k_{d1}, k_{d2}, k_i (353 K) (s^{-1})	Reference
Dibenzoyl 1,2-cyclohexane-dicarbonyl-, 	Styrene	343			7.90×10^{-6}	27
Bis(1,1-dimethylethyl) cyclohexylidene-, 	Chlorobenzene	379.6	131.0	13.52	1.37×10^{-6}	168
Bis(1,1-dimethylethyl) cyclohexylidene-, 	Acetic acid	359.8			7.24×10^{-4}	168

Bis(1-methyl-1-ethylpropyl) phenylmethylene-, $PhCH(OOCEt_2Me)_2$	Tetradecane	356.5	84.5	8.41	8.06×10^{-5}	168
Bis(1-methyl-1-ethylpropyl) phenylmethylene-, $PhCH(OOCEt_2Me)_2$	Chlorobenzene	379.6	96.2	9.24	1.01×10^{-5}	168
Bis(1-methyl-1-ethylpropyl) phenylmethylene-, $PhCH(OOCEt_2Me)_2$	Pentanol	367.5	69.9	6.35	1.02×10^{-4}	168
Bis(1-methyl-1-ethylpropyl) phenylmethylene-, $PhCH(OOCEt_2Me)_2$	Acetic acid	359.8	65.3	6.07	2.56×10^{-4}	168
cyclo-2,4-Pentadienylidenaminomethyl- di(5,5-dimethyl-1,3,4-trioxahexyl)amine-, 	Tetradecane	405	67.8		2.13×10^{-4}	168

(*continued overleaf*)

TABLE 5.23 (*continued*)

Diperoxide	Solvent	T (K)	E (kJ mol^{-1})	log A, A (s^{-1})	k_{d1}, k_{d2}, k_i (353 K) (s^{-1})	Reference
cyclo-2,4-Pentadienylidenaminomethyl-di(5,5-dimethyl-1,3,4-trioxahexyl)amine-, 	Chlorobenzene	379.6	75.3	6.55	2.56×10^{-5}	168
cyclo-2,4-Pentadienylidenaminomethyl-di(5,5-dimethyl-1,3,4-trioxahexyl)amine-, 	Pentanol	367.5	69.0	6.16	8.91×10^{-5}	168

Silane						
Dimethyldi(5-ethyl-5-methyl-1,3,4,-trioxaheptyl)-, $Me_2Si[OCH_2OOCMe(Et)_2]_2$	Tetradecane	356.5	73.2	7.16	2.13×10^{-4}	168
Dimethyldi(5-ethyl-5-methyl-1,3,4-trioxaheptyl)-, $Me_2Si[OCH_2OOCMe(Et)_2]_2$	Chlorobenzene	379.6	87.7	8.23	1.79×10^{-5}	168
Dimethyldi(5-ethyl-5-methyl-1,3,4-trioxaheptyl)-, $Me_2Si[OCH_2OOCMe(Et)_2]_2$	Acetic acid	359.8			5.37×10^{-4}	168

TABLE 5.24 Synthetic Methods for Production of Organometallic Peroxides

Reaction	Reactants	Catalyst	References
$R_{4-n}SiCl_n + nCR'R''R'''OOH \rightarrow$ $R_{4-n}Si(OOC\ R'R''R''')_n + nHCl$	$R_{4-n}SiCl_n$ (R is alkyl, aryl), $CR'R''R'''OOH$ (R′, R″, R‴ is alkyl or aryl)	Pyridine, NH_3 or NR_3	169–173
$R_{4-n}SiCl_n + nMe_3COOR'OH \rightarrow$ $R_{4-n}Si(OR'OOCMe_3)_n + nHCl$	$R_{4-n}SiCl_n$(R is alkyl or aryl), $Me_3OOR'OH$ $[R' = -CH_2-, -CH_2CH_2-, -CH_2CH(Me)-, -CH_2CH_2C(Me_2)-]$	Pyridine, NH_3, or NR_3	174–177
$R_3B + O_2 \rightarrow R_2BOOR$	R_3B (R is alkyl)		178–182
$R_3B + 2O_2 \rightarrow RB(OOR)_2$	Dioxygen		
$BCl_3 + 3ROOH \rightarrow (ROO)_3B + 3HCl$	BCl_3, ROOH(R is alkyl)		183
$(RO)_2BCl + R'OONa \rightarrow$ $(RO)_2BOOR' + NaCl$	$(RO)_2BCl$ (R is alkyl) R′OONa(R′ is alkyl or cumyl)		184
$R_2P(O)Cl + R'OOH\ (R'OONa) \rightarrow$ $R_2P(O)OOR' + HCl(NaCl)$	$R_2P(O)Cl$ (R is alkyl, alkoxyl, or aryl), R′OOH, (R′ is alkyl)	Pyridine	185–188

TABLE 5.25 Physical Properties of Selected Organometallic Peroxides[a]

Peroxide	MW	mp (K)	Density ($kg\,m^{-3}$)	n_D^{293}
1,1-Diphenylethyl trimethylsilyl-, $Me_3SiOOCPh_2Me$	286.139			1.5330
Trimethylsilyl triphenylmethyl-, $Me_3SiOOCPh_3$	348.155	334–335		
Trimethylsilyl triphenylsilyl-, $Me_3SiOOSiPh_3$	364.131	339–340		
Butoxydi(1,1-dimethylethyldioxy)borane, $Me(CH_2)_3OB(OOCMe_3)_2$	261.198		928	1.416
Dibutoxy(1,1-dimethylethyldioxy)borane, $[Me(CH_2)_3O]_2BOOCMe_3$	245.203		877	1.4101
Dibutoxy(1-methyl-1-phenylethyldioxy)borane, $[Me(CH_2)_3O]_2BOOCMe_2Ph$	307.219		975	1.4707
(1,1-Dimethylethyloxy)diethylphosphate, $(EtO)_2P(O)OOCMe_3$	226.097		1045	1.4195
(1,1-Dimethylethyloxy)diethylphosphonate, $(EtO)EtP(O)OOCMe_3$	210.102		1001	1.4288
(1,1-Dimethylethyldioxy)-phenylethylphosphonate, $(EtO)PhP(O)OOCMe_3$	258.102		1052	1.4852

[a] See Refs. 189–192.

TABLE 5.26 The Enthalpies (ΔH_f°) of Organometallic Peroxide Formation in the Gas and Condensed Phase

Peroxide	Phase	$-\Delta H_f^\circ$ ($kJ\,mol^{-1}$)	Reference
1,1-Dimethylethyl trimethylsilyl-, $Me_3COOSiMe_3$	Liquid	484	193
1,1-Dimethylethyl trimethylsilyl-, $Me_3COOSiMe_3$	Gas	477.5	194
	Liquid	514.1	
1,1-Dimethylethyl trimethylsilyl-, $Me_3COOSiMe_3$	Gas	483.6	5
Bis(1,1-dimethylethyldioxy)methyl-trimethylsilyl-, $[Me_3COO]_2CHOOSiMe_3$	Gas	752.4	194
	Liquid	809.5	
1,1-Diethylpropyl triethylgermyl-, $Et_3COOGeEt_3$	Liquid	460.7	193
Bis(triethylgermyl)-, $Et_3GeOOGeEt_3$	Liquid	575.0	193
1,1-Dimethylethyl triethylgermyl-, $Me_3COOGeEt_3$	Gas	460.2	5
1,1-Dimethylethyl triethylstannyl-, $Me_3COOSnEt_3$	Liquid	371.2	193
1-Methyl-1-phenylethyl triethylstannyl-, $PhMe_2COOSnEt_3$	Liquid	229.0	193

TABLE 5.27 The Rate Constants for the Decomposition of Organometallic Peroxides

Peroxide	Solvent	T (K)	E (kJ mol^{-1})	log A, A (s^{-1})	k_d, k_i (450 K) (s^{-1})	Reference
		k_d				
Silane						
(1,1-Dimethylethyldioxy) trimethyl-, $Me_3COOSiMe_3$	Anisole	433–483	159.8	14.00	2.83×10^{-5}	192
(1,1-Dimethylethyldioxy) trimethyl-, $Me_3COOSiMe_3$	Chlorobenzene	466.2			2.75×10^{-4}	195
(1,1-Dimethylethyldioxy) trimethyl-, $Me_3COOSiMe_3$	1,1-Dimethyl ethylbenzene	465.8			1.09×10^{-4}	195
(1,1-Dimethylethyldioxy) trimethyl-, $Me_3COOSiMe_3$	Heptane	476–456	172.4	15.04	1.07×10^{-5}	195
(1,1-Dimethylethyldioxy) trimethyl-, $Me_3COOSiMe_3$	Isooctane	456.5	172.4	15.04	1.07×10^{-5}	195
(1,1-Dimethylethyldioxy) trimethyl-, $Me_3COOSiMe_3$	1-Octane	456.4–476.4	177.0	15.59	1.11×10^{-5}	195
(1,1-Dimethylethyldioxy) trimethyl-, $Me_3COOSiMe_3$	Tetralin	466.9			1.05×10^{-4}	195

(1-Methyl-1-phenylethyldioxy) trimethyl-, $Me_3SiOOCMe_2Ph$	Anisole	433–483	166.5	14.9	3.74×10^{-5}	192
(1,1-Diphenylethyldioxy) trimethyl-, $Me_3SiOOCMePh_2$	Anisole	433–483	161.5	14.6	7.14×10^{-5}	192
(Triphenylmethyldioxy) trimethyl-, $Me_3SiOOCPh_3$	Anisole	433–483	161.1	15.1	2.51×10^{-4}	192
(Triphenylmethyldioxy) trimethyl-, $Me_3SiOOCPh_3$	Cumene	433–463	175.7	16.6	1.60×10^{-4}	192
(Triphenylmethyldioxy) trimethyl-, $Me_3SiOOCPh_3$	Dioxane	433–463	175.7	16.8	2.54×10^{-4}	192
(Triphenylmethyldioxy) trimethyl-, $Me_3SiOOCPh_3$	Nonane	433–463	163.2	15.1	1.43×10^{-4}	192
(Triphenylmethyldioxy) trimethyl-, $Me_3SiOOCPh_3$	Toluene	433–463	161.9	15.0	1.61×10^{-4}	192
(1-Methyl-1-phenylethyldioxy) triphenyl-, $Ph_3SiOOCMe_2Ph$	Anisole	423–463	167.4	15.5	1.17×10^{-4}	192
Bis(1,1-dimethylethyldioxy) dimethyl-, $Me_2Si[OOCMe_3]_2$	Anisole	383–483	149.0	13.5	1.60×10^{-4}	192

(continued overleaf)

TABLE 5.27 (*continued*)

Peroxide	Solvent	T (K)	E (kJ mol^{-1})	log A, A (s^{-1})	k_d, k_i (450 K) (s^{-1})	Reference
Tris[1,1-dimethylethyldioxy] methyl-, $MeSi[OOCMe_3]_3$	Anisole	383–483	133.1	12.6	1.41×10^{-3}	192
Tetra(1,1-dimethylethyldioxy)-, $Si[OOCMe_3]_4$	Anisole	383–483	97.9	9.6	1.72×10^{-2}	192
Tetra(1,1-dimethylethyldioxy)-, $Si[OOCMe_3]_4$	Cumene	383–483	102.9	10.2	1.80×10^{-2}	192
Dimethyl(1,1-dimethylethyl dioxy)(methacryloyloxy-2-propyloxy)-, $Me_2Si(OOCMe_3)(OCHMeCH_2O C(O)CMe{=}CH_2)$	Benzene	443–473	118.3	9.84	1.28×10^{-4}	196
Dimethyl(1,1-dimethylethyl dioxymethyloxy) (methacryloyloxyethyloxy)-, $Me_2Si(OCH_2OOCMe_3)$-$(OCH_2CH_2OC(O)CMe{=}CH_2)$	Benzene	383–413	132.9	14.06	4.30×10^{-2}	196
Dimethyl(1,1-dimethylethyldioxymethyloxy) (methacryloyloxyethyloxy)-, $Me_2Si(OCH_2OOCMe_3)$ $(OCH_2CH_2OC(O)CMe{=}CH_2)$	Decane	383–413	143.4	15.34	4.95×10^{-2}	196

(1,1-Dimethylethyldioxy) (diacryloyloxyethyloxy)vinyl-, $CH_2=CHSi(OOCMe_3)(OCH_2CH_2OC(O)CH=CH_2)_2$	Benzene	403–443	73.5	5.96	2.68×10^{-3}	196
(1,1-Dimethylethyldioxy) (diacryloyloxyethyloxy)vinyl-, $CH_2=CHSi(OOCMe_3)(OCH_2CH_2OC(O)CH=CH_2)_2$	Decane	403–443	102.3	8.94	1.16×10^{-3}	196
(1,1-Dimethylethyldioxy) (dimeth acryloyloxyethyloxy)vinyl-, $CH_2=CHSi(OOCMe_3)(OCH_2CH_2OC(O)CMe=CH_2)_2$	Benzene	413–443	79.3	6.58	2.37×10^{-3}	196
(1,1-Dimethylethyldioxy) (dimethacryloyloxy-2-propyloxy)vinyl-, $CH_2=CHSi(OOCMe_3)(OCHMeCH_2OC(O)CMe=CH_2)_2$	Benzene	403–433	87.8	7.73	3.46×10^{-3}	196

(continued overleaf)

TABLE 5.27 (*continued*)

Peroxide	Solvent	T (K)	E (kJ mol^{-1})	log A, A (s^{-1})	k_d, k_i (450 K) (s^{-1})	Reference
Tris(1,1-dimethylethyldioxy) (methacryloyloxyethyloxy)-, $CH_2{=}CMeC(O)OCH_2CH_2OSi(OOCMe_3)_3$	Benzene	433–473	113.1	9.41	1.91×10^{-4}	196
(Acryloyloxyethyloxy)dimethyl (1,1-dimethylethyldioxy)-, $Me_2Si(OOCMe_3)OCH_2CH_2OC(O)CH{=}CH_2$	Benzene	443–473	120.1	10.4	2.88×10^{-4}	196
Dimethyl(1,1-dimethylethyldioxy) (methacryloyloxyethyloxy)-, $Me_2Si(OOCMe_3)(OCH_2CH_2OC(O)CMe{=}CH_2)$	Benzene	453–473	127.4	10.84	1.13×10^{-4}	196
Dimethyl(1,1-dimethylethyldioxy) (methacryloyloxyethyloxy)-, $Me_2Si(OOCMe_3)(OCH_2CH_2OC(O)CMe{=}CH_2)$	Decane	453–473	107.3	8.20	5.56×10^{-5}	196
Disiloxane						
1,3-Di(1,1-dimethylethyldioxy) 1,1,3,3-tetramethyl-, $Me_3COOSiMe_2OSiMe_2OOCMe_3$	Cumene	443–503	155.6	13.1	1.09×10^{-5}	192
1,3-Di(1-phenyl-1-methylethyldioxy) 1,1,3,3-tetramethyl-, $PhCMe_2OOSiMe_2OSiMe_2OOCMe_2Ph$	Cumene	443–503	169.5	14.9	1.68×10^{-5}	192

1,3-Di(1,1-dimethylethyldioxy) 1,1,3,3-tetraphenyl-, $Me_3COOSiPh_2OSiPh_2OOCMe_3$	Cumene	443–503	136.8	11.7	6.62×10^{-5}	192
1,3-Di(1-phenyl-1-methylethyldioxy) 1,1,3,3-tetraphenyl-, $PhCMe_2OOSiPh_2OSiPh_2O\ OCMe_2Ph$	Cumene	443–503	147.2	13.2	1.30×10^{-4}	192
Germane						
1,1-Dimethylethyldioxy(triethyl)-, $Et_3GeOOCMe_3$	Cyclohexene	443–483	119.7	9.6	5.08×10^{-5}	197
1,1-Dimethylethyldioxy(triethyl)-, $Et_3GeOOCMe_3$	1,1-Diphenyl ethylene	443–483	111.7	8.7	5.43×10^{-5}	197
1,1-Dimethylethyldioxy(triethyl)-, $Et_3GeOOCMe_3$	Nonane	443–483	146.4	12.3	2.03×10^{-5}	197
1,1-Dimethylethyldioxy(triethyl)-, $Et_3GeOOCMe_3$	α-Methylstyrene	443–483	164.8	14.3	1.48×10^{-5}	197
Bis(1,1-dimethylethyldioxy)diethyl-, $Et_2Ge(OOCMe_3)_2$	Anisole	443–483	117.6	9.88	1.70×10^{-4}	198
Bis(1,1-dimethylethyldioxy)diethyl-, $Et_2Ge(OOCMe_3)_2$	Cumene	443–483	117.6	9.41	5.74×10^{-5}	198
Germanoxane						
1,1,3,3-Tetraethyl-1,3-(1,1-dimethylethyldioxy)-, $[Me_3COOGe(Et_2)]O_2$	Anisole	443–483	132.6	11.75	2.28×10^{-4}	198

(*continued overleaf*)

TABLE 5.27 (*continued*)

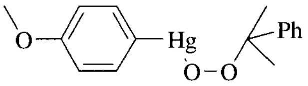
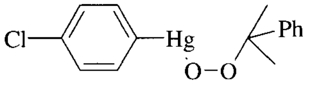
Peroxide	Solvent	T (K)	E (kJ mol^{-1})	log A, A (s^{-1})	k_d, k_i (450 K) (s^{-1})	Reference
1,1,3,3-Tetraethyl-1,3-(1,1-dimethylethyldioxy)-, $[Me_3COOGe(Et_2)]O_2$	Cumene	443–483	121.6	10.1	9.67×10^{-5}	198
Stannane						
1-Methyl-1-phenyldioxy(triethyl)-, $Et_3SnOOCMe_2Ph$	Cyclohexene	433–463	96.7	8.8	3.76×10^{-3}	197
1-Methyl-1-phenyldioxy(triethyl)-, $Et_3SnOOCMe_2Ph$	Nonane	433–463	134.3	12.7	1.29×10^{-3}	197
1-Methyl-1-phenyldioxy(triethyl)-, $Et_3SnOOCMe_2Ph$	α-Methylstyrene	433–463	110.9	10.2	2.12×10^{-3}	197
1,1-Dimethylethyldioxy(triethyl)-, $Et_3SnOOCMe_3$	Cyclohexene	403–443	93.7	7.7	6.66×10^{-4}	197
1,1-Dimethylethyldioxy(triethyl)-, $Et_3SnOOCMe_3$	1,1-Diphenyl ethylene	403–443	85.8	7.3	2.19×10^{-3}	197
1,1-Dimethylethyldioxy(triethyl)-, $Et_3SnOOCMe_3$	Heptene-1	403–443	103.8	8.5	2.82×10^{-4}	197
1,1-Dimethylethyldioxy(triethyl)-, $Et_3SnOOCMe_3$	α-Methylstyrene	403–443	100.0	8.4	6.20×10^{-4}	197
Borane						
Tris-(1,1-dimethylethyldioxy)-, $B[OOCMe]_3$	Nonane	443–463	136.4	12.35	3.29×10^{-4}	199
Diethoxy(1,1-dimethylethyldioxy)-, $(EtO)_2BOOCMe_3$	Nonane	373–403	131.4	11.69	2.74×10^{-4}	190

Di(1,1-dimethylethyldioxy)propoxy-, $PrOB(OOCMe_3)_2$	Nonane	373–403	136.0	11.97	1.53×10^{-4}	190
(Butyldioxy)dibutoxy-, $(n\text{-}BuO)_2BOOBu\text{-}n$	Nonane	403–443	71.1	5.14	7.71×10^{-4}	200
Dibutoxy(1-methyl-1-phenylethyldioxy)-, $(n\text{-}BuO)_2BOOCMe_2Ph$	Nonane	403–443	90.8	7.55	1.02×10^{-3}	200
Dibutoxy(1,1-dimethyl ethyldioxy)-, $(n\text{-}BuO)_2BOOCMe_3$	Nonane	403–443	109.6	9.23	3.22×10^{-4}	200
Bis(dipropoxy)borane peroxide-, $(PrO)_2BOOB(OPr)_2$	Nonane	373–403	117.2	11.00	2.49×10^{-3}	190
Aluminium						
Diethoxy(1,1-dimethylethyldioxy)-, $(EtO)_2AlOOCMe_3$	Carbon tetrachloride	333–353	71.1	7.13	5.73×10^{-2}	201
Diethoxy(1,1-dimethylethyldioxy)-, $(EtO)_2AlOOCMe_3$	Ethylbenzene	333–353	58.6	4.8	9.95×10^{-3}	201

(*continued overleaf*)

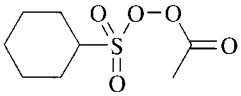
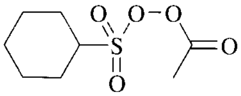
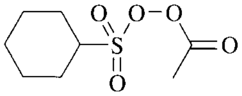
TABLE 5.27 (*continued*)

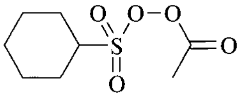
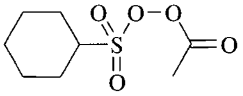
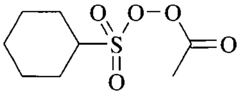
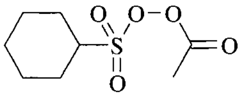
Peroxide	Solvent	T (K)	E (kJ mol^{-1})	log A, A (s^{-1})	k_d, k_i (450 K) (s^{-1})	Reference
Diethoxy(1,1-dimethylethyldioxy)-, $(EtO)_2AlOOCMe_3$	Styrene	333–353	83.7	8.95	1.71×10^{-1}	201
Gallium						
Dimethyl(methyldioxy)-, $Me_2GaOOMe$	Nonane	393–423	101.3	12.15	2.46	202
Dimethyl(1,1-dimethylethyldioxy)-, $Me_2GaOOCMe_3$	Nonane	393–423	140.6	14.72	2.51×10^{-2}	202
Indium						
Dimethyl(methyldioxy)-, $Me_2InOOMe$	Nonane	393–423	65.3	6.46	7.59×10^{-2}	202
Dimethyl(1,1-dimethylethyldioxy)-, $Me_2InOOCMe_3$	Nonane	393–423	112.5	12.04	9.58×10^{-2}	202
Tallium						
Diphenyl(1-methyl-1-phenylethyldioxy)-, $Ph_2TlOOCMe_2Ph$	Toluene	363–413	145.2	14.3	2.79×10^{-3}	203
Diphenyl(1,1-dimethylethyldioxy)-, $Ph_2TlOOCMe_3$	Toluene	363–413	169.5	17.5	6.69×10^{-4}	203
Mercury						
Ethyl(1-methyl-1-phenylethyldioxy)-, $EtHgOOCMe_2Ph$	Toluene	383–393	73.2	6.50	1.21×10^{-2}	204

1-Methyl-1-phenylethyldioxy(1-methylethyl)-, $Me_2CHHgOOCMe_2Ph$	Nonane	383–393	83.7	7.98	1.84×10^{-2}	204
Benzyl(1-methyl-1-phenylethyldioxy)-, $PhCH_2HgOOCMe_2Ph$	Toluene	383–393	104.6	11.02	7.56×10^{-2}	205
(1-Methyl-1-phenylethyldioxy)phenyl-, $PhHgOOCMe_2Ph$	Toluene	383–393	111.7	11.62	4.51×10^{-2}	205
4-Methoxyphenyl(1-methyl-1-phenylethyldioxy)-,	Toluene	383–393	99.2	9.93	2.60×10^{-2}	205
						
4-Chlorophenyl(1-methyl-1-phenylethyldioxy)-,	Toluene	383–393	121.3	11.50	2.63×10^{-2}	205
						
(1,1-Dimethylethyldioxy)ethyl-, $EtHgOOCMe_3$	Toluene	373–393	94.6	9.18	1.58×10^{-2}	205
Bis(1-methyl-1-phenylethyldioxy)-, $PhCMe_2OOHgOOCMe_2Ph$	Toluene	373–393	105.9	11.49	1.57×10^{-1}	205
Lithium						
1,1-Dimethylethyldioxy-, Me_3COOLi	Heptane	353	85.4	7.4	9.90×10^{-6}	206

(continued overleaf)

TABLE 5.27 (*continued*)

Peroxide	Solvent	T (K)	E (kJ mol^{-1})	log A, A (s^{-1})	k_d, k_i (450 K) (s^{-1})	Reference
1,1-Dimethylethyldioxy-, Me_3COOLi	Heptane/ p-xylene	353	77.4	6.5	1.17×10^{-5}	206
1,1-Dimethylethyldioxy-, Me_3COOLi	Heptane/ propylbenzene	353			9.4×10^{-6}	206
1,1-Dimethylethyldioxy-, Me_3COOLi	Heptane/ cumene	353			8.8×10^{-6}	206
1,1-Dimethylethyldioxy-, Me_3COOLi	Heptane/ ethylbenzene	353			9.6×10^{-6}	206
Peroxide						
Acetyl cyclohexylsulfonyl-, 	Acetonitrile	313–333	126.0	15.80	14.90	207
Acetyl cyclohexylsulfonyl-, 	Benzene	313–343	114.0	14.50	18.51	207
Acetyl cyclohexylsulfonyl-, 	Carbon tetrachloride	313–333	127.0	16.50	57.33	207

Acetyl cyclohexylsulfonyl-,	Cumene	313–393	115.0	14.70	22.46	207
						
Acetyl cyclohexylsulfonyl-,	Decane	303–333	93.0	13.20	2.54×10^2	207
						
Acetyl cyclohexylsulfonyl-,	Ethanol	313–333	103.0	12.50	3.50	207
						
Acetyl cyclohexylsulfonyl-,	Ethylbenzene	313–343	104.0	13.10	10.67	207
						

(*continued overleaf*)

TABLE 5.27 (*continued*)

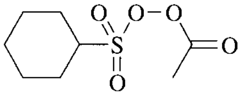
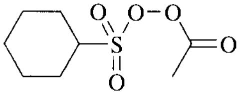
Peroxide	Solvent	T (K)	E (kJ mol^{-1})	log A, A (s^{-1})	k_d, k_i (450 K) (s^{-1})	Reference
Acetyl cyclohexylsulfonyl-, 	Isopropyl alcohol	313–343	113.0	14.00	7.65	207
1,1-Dimethylethyl 1,1-dimethylethylthio-, $Me_3CSOOCMe_3$	2-Methylbutane	230–212	34.0	6.60	4.50×10^2	208
Acetyl cyclohexylsulfonyl-, 	Toluene	313–343	108.0	13.80	18.36	207
(1,1-Dimethylethyldioxy)diethylphosphate, $(Et)_2P(O)OOCMe_3$	Nonane	403–423	121.3	11.02	8.71×10^{-4}	188,209
		$k_i = 2ek_d$				
Silane,bis(1,1-dimethylethyl dioxy)dimethyl-, $Me_2Si[OOCMe_3]_2$	Tetravalerate pentaerythritol	443–473	135.1	11.6	7.93×10^{-5}	192

TABLE 5.28 The Rate Constants for the Decomposition of Peroxides Containing Halogen Atoms

Peroxide	Solvent	T (K)	E (kJ mol^{-1})	log A, A (s^{-1})	k_d(343 K) (s^{-1})	References
1,1-Dimethylethyl (2-oxo-3-oxapentyl)hydroxy (1,1,2,2-tetrafluorethyl)methyl-, $CF_2HCF_2C(OOCMe_3)(OH)$ $CH_2C(O)Oet$	Chlorobenzene	343–363	139.7	18.00	5.31×10^{-4}	210
1,1-Dimethylethyl (2-oxo-3-oxapentyl)hydroxy(1,1,2,2,3,3,4,4-octafluorobutyl)methyl-, $CF_2H(CF_2)_3C(OOCMe_3)(OH)$ $CH_2C(O)OEt$	Chlorobenzene	343–363	125.9	16.1	8.46×10^{-4}	210
1,1-Dimethylethyl (2-oxo-3-oxapentyl)hydroxy (trifluoromethyl)methyl-, $CF_3C(OOCMe_3)(OH)$ $CH_2C(O)OEt$	Chlorobenzene	343–363	124.3	15.8	7.43×10^{-4}	210
1,1-Dimethylethyl (1-chloro-2-oxo-3-oxapentyl)hydroxy(1,1,2,2,3,3,4,4-octafluorobutyl)methyl-, $CF_2H(CF_2)_3C(OOCMe_3)(OH)CH$ $ClC(O)OEt$	Chlorobenzene	343–363	123.0	15.5	5.87×10^{-4}	210

(continued overleaf)

TABLE 5.28 (*continued*)

Peroxide	Solvent	T (K)	E (kJ mol^{-1})	log A, A (s^{-1})	k_d(343 K) (s^{-1})	References
1,1-Dimethylethyl (1,1-dibromo-2-oxo-3-oxapentyl) hydroxy(1,1,2,2,3,3,4,4-octafluorobutyl)methyl-, $CF_2H(CF_2)_3C(OOCMe_3)(OH)CBr_2C(O)OEt$	Chlorobenzene	343–363	97.5	11.8	8.96×10^{-4}	210
1,1-Dimethylethyl perfluorbutanoyl-, $CF_3(CF_2)_2C(O)OOCMe_3$	Benzene/ pyridine	338	111.6	12.6	2.25×10^{-5}	211, 212
1,1-Dimethylethyl perfluorbutanoyl-, $CF_3(CF_2)_2C(O)OOCMe_3$	Toluene/ pyridine	338	92.3	9.6	2.16×10^{-5}	211, 212
1,1-Dimethylethyl perfluorbutanoyl-, $CF_3(CF_2)_2C(O)OOCMe_3$	Octane/ pyridine	338	139.6	15.1	3.04×10^{-7}	211, 212
Diperfluoracetyl-, $CF_3C(O)OOC(O)CF_3$	Genetron 113	358	110.9	13.4	1.65×10^{-3}	213
Diperfluoracetyl-, $CF_3C(O)OOC(O)CF_3$	Heptane	298–338	113.0	15.1	7.79×10^{-3}	214
Diperfluoropropanoyl-, $CF_3CF_2C(O)OOC(O)CF_2CF_3$	Heptane	298–338	118.8	17.5	0.26	214

Diperfluorbutanoyl-, $CF_3(CF_2)_2C(O)OOC(O)(CF_2)_2CF_3$	Heptane	298–338	92.0	12.8	6.16×10^{-2}	214
Diperfluorbutanoyl-, $CF_3(CF_2)_2C(O)OOC(O)(CF_2)_2CF_3$	Genetron 113	303–328	102.9	13.7	1.07×10^{-2}	215
Diperfluoroctanoyl-, $CF_3(CF_2)_6C(O)OOC(O)(CF_2)_6CF_3$	Genetron 113	303–328	100.9	13.4	1.08×10^{-2}	215
Bis(2,2,3,3-tetrafluoro propanoyl)-, $CF_2HCF_2C(O)OOC(O)CF_2CF_2H$	Genetron 113	303–358	89.2	12.0	2.61×10^{-2}	215
Bis(2,2,3,3,4,4,5,5-octafluoro pentanoyl)-, $H(CF_2)_4C(O)OOC(O)(CF_2)_4H$	Genetron 113	303–328	103.4	13.9	1.42×10^{-2}	215
Bis(2,2,3,3,4,4,5,5,6,6,7,7-dodecafluoroctanoyl)-, $CF_2H(CF_2)_5C(O)OOC(O)(CF_2)_5CF_2H$	Genetron 113	303–328	103.4	13.9	1.42×10^{-2}	215
Bis(trifluoromethylacetyl)-, $CF_3CH_2C(O)OOC(O)CH_2CF_3$	Heptane	338–368	121.3	13.4	8.47×10^{-6}	216

(continued overleaf)

TABLE 5.28 (*continued*)

Peroxide	Solvent	T (K)	E (kJ mol^{-1})	log A, A (s^{-1})	k_d(343 K) (s^{-1})	References
Bis(2-trifluoromethyl-3,3,3-fluoropropanoyl)-, $(CF_3)_2CHC(O)O$ $OC(O)CH(CF_3)_2$	Heptane	338–368	117.6	12.9	9.80×10^{-6}	216
Bis(2,2-difluoropropanoyl)-, $MeCF_2C(O)OOC(O)CF_2Me$	Heptane	278–303	91.2	13.0	0.13	217
Bis(2-chlorobutanoyl)-, $MeCH_2CHClC(O)O$ $OC(O)CHClCH_2Me$	Chlorobenzene	333			2.05×10^{-3}	218
Bis(2-bromobutanoyl)-, $MeCH_2CHBrC(O)O$ $OC(O)CHBrCH_2Me$	Chlorobenzene	333			1.60×10^{-3}	218
Bis(2,2-dichloropropanoyl)-, $MeCCl_2C(O)OOC(O)CCl_2Me$	Chlorobenzene	333			2.58×10^{-3}	218

5.3 DECOMPOSITION OF POLYATOMIC PEROXIDES

Polyatomic peroxides contain two or more peroxide groups with different reactivities. They are used for radical initiation at different temperatures. This method is used to synthesize graft-polymers. Synthetic methods of polyperoxide production are the same as for the synthesis of monoatomic peroxides (see Chapters 4 and 5). Enthalpies of polyperoxide formation are collected in Table 5.22. For rate constants for the decomposition of peroxide groups in polyperoxides see Table 5.23.

5.4 ORGANOMETALLIC PEROXIDES

Methods of synthesis for organometallic peroxides depend on the nature of the metal. They are different for boron-, phosphorous-, and silicon-containing peroxides (see Table 5.24). Physical properties of selected peroxides are collected in Table 5.25. For formation enthalpies of organometallic peroxides see Table 5.26. Rate constants of decomposition of organometallic peroxides are collected in Table 5.27 and haloid-containing peroxides are in Table 5.28.

REFERENCES

1. A. G. Davis, *Organic Peroxides*, Butterwork, London, 1961.
2. *Organic Peroxides*, D. Swern (Ed.), John Wiley & Sons, Inc., New York, 1970.
3. V. L. Antonovskii, *Organic Peroxides as Initiators* (Russian), Khimiya, Moscow, 1972.
4. E. G. E. Hawkins, *Organic Peroxides*, Spon Van Nostrand, New York LTD, London, 1961.
5. S. Patai, *The Chemistry Peroxides*, John Wiley & Sons, Inc., New York, 1983.
6. *Data Base: Properties of Organic Compound. Personal Edition*, CRC Press, Boca Raton, FL, 1996.
7. V. L. Antonovskii and M. M. Buzlanova, *Analytical Chemistry of Organic Peroxides* (Russian), Khimiya, Moscow, 1978.
8. C. Wagner, R. Smith, and D. Peters, *Anal. Chem.* **19**, 976 (1947).
9. K. Nozaki, *Ind. Eng. Chem., Analyt. Ed.* **18**, 583 (1949).
10. C. G. Swain, W. H. Stickmayer, and J. T. Clarke, *J. Am. Chem. Soc.* **72**, 5426 (1950).
11. V. L. Antonovskii, *Vestnik Nizhegorodskogo Gosudarstvennogo Universiteta, Organicheskie and Elementoorganicheskie Peroxides* (Russian), Izdatelstvo Nizhegorodskogo Universiteta, Nizhnii Novgorod, Russia, 1996, p. 3.
12. N. Karch, E. T. Koh, Whitsel, and J. M. McBride, *J. Am. Chem. Soc.* **97**, 6729 (1975).
13. M. Sax and R. K. McMollan, *Acta Crystallogr.* **22**, 281 (1967).
14. A. Yu. Kosnikov, V. L. Antonovskii, and S. V. Lindeman, *Izv. AN SSSR, Ser. Khim.* 937 (1985).
15. J. S. Gougontas and K. H. Chang, *Cryst. Struct. Comm.* **8**, 977 (1979).

16. D. W. Walter and J. M. McBride, *J. Am. Chem. Soc.* **103**, 7074 (1981).
17. A. Yu. Kosnikov, V. L. Antonovskii, and S. V. Lindeman, *Kristallografiya* **33**, 875 (1988).
18. V. L. Antonovskii, *Progress in Chemistry of Organic Peroxides* (Russian), TsNIITEneftekhim, Moscow, 1992.
19. E. S. Domalsky and E. D. Hearing, *J. Phys. Chem. Ref. Data* **22**, 805 (1993).
20. Yu. Ya Van-Chin-Syan and N. S. Kachurina, *Vestnik Nizhegorodskogo Gosudarstvennogo Universiteta, Organic and Elementoorganic Peroxides* (Russian), Izdatelstvo Nizhegorodskogo Universiteta, Nizhnii Novgorod, Russia, 1996, p. 29.
21. A. Remboum and M. Szwarc, *J. Am. Chem. Soc.* **76**, 5975 (1954).
22. M. Levy, M. Steinberg, and M. Szwarc, *J. Am. Chem. Soc.* **76**, 5978 (1954).
23. M. J. Shine, J. A. Waters, and D. M. Hoffman, *J. Am. Chem. Soc.* **85**, 3613 (1963).
24. F. G. Edwards and F. R. Mayo, *J. Am. Chem. Soc.* **72**, 1265 (1950).
25. S. D. Ross and M. A. Fineman, *J. Am. Chem. Soc.* **73**, 2176 (1951).
26. O. J. Walker and G. L. E. Wold, *J. Chem. Soc.* 1132 (1937).
27. W. Cooper, *J. Chem. Soc.* 3106 (1951).
28. K. Nozaki and P. D. Bartlett, *J. Am. Chem. Soc.* **68**, 1686 (1946).
29. P. F. Hartman, H. G. Sellers, and D. Turnbull, *J. Am. Chem. Soc.* **69**, 2416 (1947).
30. Kh. S. Bagdasaryan and R. I. Milutinskaya, *Zh. Fiz. Khim.* **27**, 420 (1953).
31. H. C. Bailey and G. W. Godin, *Trans. Faraday Soc.* **52**, 68 (1956).
32. W. R. Foster and G. H. Williams, *J. Chem. Soc.* 2862 (1962).
33. C. G. Swein, W. H. Stockmayer, and J. T. Clarke, *J. Am. Chem. Soc.* **72**, 5426 (1950).
34. B. I. Galibey, *Study of Acyl Peroxides as Initiators of Radical Polymerisation*, Ph.D. Thesis (Russian), Odessa State University, Odessa, USSR, 1965.
35. A. T. Blomquist and A. J. Buselli, *J. Am. Chem. Soc.* **73**, 3883 (1951).
36. R. V. Pankevich and V. S. Dutka, *Kinet. Katal.* **33**, 1087 (1992).
37. K. Nozaki and P. D. Bartlett, *J. Am. Chem. Soc.* **68**, 2377 (1946).
38. H. C. Haaz, *J. Polym. Sci.* **55**, 33 (1961).
39. R. Rado and M. Lazar, *J. Polym. Sci.* **45**, 257 (1960).
40. R. Rado and M. Lazar, *Vysokomol. Soedin.* **3**, 310 (1961).
41. H. C. Haaz, *J. Polym. Sci.* **39**, 493 (1959).
42. R. Rado and M. Lazar, *J. Polym. Sci.* **62**, 5167 (1962).
43. L. N. Guseva, Yu. A. Mikheev, and D. Ya. Toptygin, *Vysokomol. Soedin. A*, **20**, 2006 (1978).
44. L. S. Rogova, L. N. Guseva, Yu. A. Mikheev, and D. Ya. Toptygin, *Vysokomol. Soedin. A*, **21**, 1373 (1979).
45. R. Rado and D. Shimunkova, *Vysokomol. Soedin.* **3**, 1271 (1961).
46. O. A. Ledneva, Yu. A. Mikheev, and D. Ya. Toptygin, *Izv. AN SSSR, Ser. Khim.* 66 (1977).
47. A. P. Mar'in and Yu. A. Shlyapnikov, *Dokl. AN SSSR* **215**, 1160 (1974).
48. J. C. W. Chien and D. S. Wang, *Macromolecules*, **8**, 920 (1975).
49. R. Rado, D. Shimunkova, and L. Malak. *Vysokomol. Soedin.* **4**, 304 (1962).

50. G. G. Makarov, L. M. Postnikov, G. B. Pariysky, Yu. A. Mikheev, and D. Ya. Toptygin, *Vysokomol. Soedin. A*, **20**, 25567 (1978).
51. G. G. Makarov, L. M. Postnikov, G. B. Pariysky, Yu. A. Mikheev, and D. Ya. Toptygin, *Vysokomol. Soedin. A*, **22**, 314 (1980).
52. A. V. Tobolsky, P. M. Norling, N. H. Frick, and H. Ju, *J. Am. Chem. Soc.* **86**, 3925 (1964).
53. R. Rado, F. Szocs, M. Vinkovicova, and J. Placek, *Chem. Zvesti* **27**, 796 (1973).
54. R. Rado, *Chem. Zvesti* **19**, 46 (1965).
55. L. Matisova-Rychla', J. Rychly', and M. Lazar, *Europ. Polym. J.* **8**, 655 (1972).
56. E. G. Atovmyan and A. F. Lukovnikov, *Kinet. Katal.* **5**, 1340 (1970).
57. E. T. Denisov, *Izv. AN SSSR, Ser. Khim.* 812 (1960).
58. C. E. H. Bawn and S. F. Mellish, *Trans. Faraday Soc.* **47**, 1216 (1951).
59. J. C. McGowan and T. Powell, *J. Chem. Soc.* 238 (1960).
60. I. S. Voloshanovskii, Yu. N. Anisimov, and S. S. Ivanchev, *Zh. Obshch. Khim.* **43**, 354 (1973).
61. Yu. A. Oldekop and G. S. Bylina, *Vysokomol. Soedin., Ser. A*, **6**, 1617 (1964).
62. S. C. NG and K. K. Chee, *J. Polym. Sci: Polym. Chem. Ed.* **20**, 409 (1982).
63. Yu. B. Shilov and E. T. Denisov, *Vysokomol. Soedin., Ser. A*, **19**, 1244 (1977).
64. A. P. Griva and E. T. Denisov, *Kinet. Katal.* **17**, 1465 (1976).
65. A. I. Rakhimov, E. P. Androsyuk, S. V. Shelyazhenko, and L. M. Yagypol'sky, *Zh. Obshch. Khim.* **17**, 1652 (1981).
66. F. D. Greene, G. R. Van Norman, J. C. Cantrill, and R. D. Gilliom., *J. Org. Chem.* **25**, 1790 (1960).
67. J. E. Leffler, R. D. Faulkner, and C. C. Petropoulos., *J. Am. Chem. Soc.* **80**, 5435 (1958).
68. W. Honsberg and J. E. Leffler, *J. Org. Chem.* **26**, 733 (1961).
69. A. V. Tobolsky and B. Baysal., *J. Pol. Sci.* **11**, 471 (1953).
70. A. Rembaum and M. Szwarc, *J. Chem. Phys.* **23**, 909 (1955).
71. S. S. Ivanchev, *Physico-chemical Study of Organic Peroxides as Initiators of Radical Polymerisation*, Doctor Diss. Thesis (Russian), Odessa State University, Odessa, USSR, 1968.
72. V. I. Galibey, S. G. Erigova, S. S. Ivanchev, and A. I. Yurzhenko, *Ukrain. Khim. Zh.* **33**, 191 (1967).
73. R. C. Lamb, J. G. Pacifici, and P. W. Ayers, *J. Am. Chem. Soc.* **87**, 3928 (1956).
74. Z. M. Koval', *Chemiluminescence in the Reactions of Peroxyl Radicals*, Ph.D. Thesis (Russian), L'vov Polytech. Institute, L'vov, USSR, 1990.
75. G. A. Razuvaev and Z. M. Terman, *Zh. Obshch. Khim.* **30**, 2387 (1960).
76. J. E. Leffler and A. F. Wilson, *J. Org. Chem.* **25**, 424 (1960).
77. R. C. Lamb, F. F. Roger, G. D. Dean, and F. W. Voight, *J. Am. Chem. Soc.* **84**, 2635 (1962).
78. N. Muramoto, T. Ochiai, O. Simamura, and M. Yoahida. *Chem. Commun.*, 717 (1968).
79. G. Greig and J. C. J. Thynne, *Trans. Faraday Soc.* **63**, 2196 (1967).
80. H. Hart and D. P. Wyman, *J. Am. Chem. Soc.* **81**, 4891 (1959).

81. H. H. Lau and H. Hart, *J. Am. Chem. Soc.* **86**, 914 (1964).
82. K. Fujimori, Y. Hirose, and S. Oae, *J. Chem. Soc. Perkin Trans.2*, 405 (1996).
83. I. S. Voloshanovskii and S. S. Ivanchev, *Zh. Obshch. Khim.* **44**, 892 (1974).
84. G. N. Supichenko, *Kinetics and mechanism of thermo and photodecay of substituted peroxides in the liquid phase*, Ph.D. Thesis (Russian), Institute of General Inorg. Chem., Minsk, Belorussia, 1998.
85. L. E. Redington, *J. Pol. Sci.* **3**, 503 (1946).
86. A. P. Griva, L. N. Denisova, and E. T. Denisov, *Zh. Fiz. Khim.* **59**, 2944 (1985).
87. R. C. Lamb and J. G. Pacifici, *J. Am. Chem. Soc.* **86**, 914 (1964).
88. F. Strain, W. E. Bissinger, W. R. Dial, H. Rudolf, B. J. De Witt, H. C. Stevens, and J. H. Langston, *J. Am. Chem. Soc.* **72**, 1254 (1950).
89. P. A. Carpentier, J. M. DeSimone, and G. W. Roberts, *Chem. Eng. Sci.* **55**, 5341 (2000).
90. V. M. Zhulin, T. V. Lipovich, and V. L. Khim, *Izv. AN SSSR, Ser. Khim.* 1516 (1988).
91. L. M. Terman, V. N. Sedel'nikova, and N. M. Kublanova, *Zh. Obshch. Khim.* **53**, 838 (1983).
92. Z. S. Kartasheva and O. T. Kasaikina, *Izv. AN SSSR, Ser. Khim.* 48 (1991).
93. V. I. Arulin, L. I. Efimov, and V. P. Zubov, *Vysokomol. Soedin., Ser. B.* **17**, 420 (1975).
94. N. S. Dmitrieva, L. G. Kochkina, S. G. Malkevich, A. I. Vasil'eva, and S. G. Lyubetsky, *Vysokomol. Soedin., Ser. B*, **13**, 776 (1971).
95. G. A. Razuvaev, L. M. Terman, V. N. Tarunina, and E. S. Klimov, *Zh. Org. Khim.* **13**, 1879 (1977).
96. E. G. Atovmyan and A. F. Lukovnikov, *Kinet. Katal.* **12**, 890 (1971).
97. Yu. I. Ovchinikova, V. A. Fomin, A. I. D'ýachkov, and V. S. Etlis, *Zh. Obshch. Khim.* **51**, 2335 (1981).
98. G. A. Razuvaev, L. M. Terman, and D. M. Yanovskii, *Zh. Org. Khim.* **1**, 274 (1965).
99. V. A. Fomin, *Vestnik Nizhegorodskogo Universiteta*, Nizhniy Novgorod, 88 (1996).
100. V. A. Fomin, V. S. Etlis, and F. D. Nozrina, *Zh. Org. Khim.* **18**, 32 (1982).
101. V. S. Etlis and N. N. Trofimov, *Zh. Org. Khim.* **5**, 1024 (1969).
102. V. A. Fomin, V. P. Lichterov, and V. S. Etlis, *Zh. Org. Khim.* **6**, 2236 (1970).
103. O. S. Yanovskaya, V. P. Lichterov, and V. S. Etlis, *Zh. Org. Khim.* **6**, 1409 (1970).
104. A. I. Kirilov, A. D. Mol'kov, and L. F. Ivanova, *Vysokomol. Soedin. B*, **16**, 741 (1974).
105. E. T. Denisov, *Izv. AN SSSR, Ser. Khim.* 2037 (1963).
106. Z. I. Kulitskii, L. M. Terman, V. F. Tsepalov, and V. Ya. Shlyapintokh, *Izv. AN SSSR, Ser. Khim.* 253 (1963).
107. V. A. Dodonov and W. A. Waters, *J. Chem. Soc.* 2459 (1965).
108. T. W. Koenig and J. C. Martin, *J. Org. Chem.* **29**, 1520 (1964).
109. G. S. Bylina, A. P. El'nitskii, and Yu. A. Oldekop, *Vysokomol. Soedin.* **8**, 1386 (1966).
110. N. M. Beileryan, F. O. Karapetyan, and O. A. Chaltykyan, *Dokl. AN Armyan. SSR* **43**, 108 (1966).

111. K. F. O. Driscoll and P. J. Wite, *J. Pol. Sci. A*, **3**, 283 (1965).
112. L. S. Silbert and D. Swern, *Anal. Chem.* **30**, 385 (1958).
113. H. A. Swain, L. S. Silbert, and J. C. Miller, *J. Am. Chem. Soc.* **86**, 2562 (1984).
114. T. S. Pokidova and E. T. Denisov, *Kinet. Katal.* **42**, 805 (2001).
115. I. D. Zaykin, *Zh. Fiz. Khim.* **51**, 1130 (1977).
116. Yu. Ya. Van-Chin-Syan, V. N. Dibrivny, and V. A. Fedorova, in *Thesis Dokl. III Vsesoyuznoy Konferenzii po Thermodinamike Organicheskich Soedineniy* (Russian), Gor'kiy, Russia, 1982, p. 9.
117. E. G. Kiparisova and I. B. Rabinovich, *Dokl. AN SSSR* **199**, 1075 (1971).
118. P. D. Barlett and R. R. Hiatt, *J. Am. Chem. Soc.* **80**, 1398 (1958).
119. V. L. Antonovskii, L. D. Bezborodova, and M. E. Yasel'man, *Zh. Fiz. Khim.* **43**, 2286 (1969).
120. V. A. Puchin, T. I. Inrgenko, O. E. Boisan, and L. M. Aparovich, *Ukr. Khim. Zh.* **33**, 478 (1967).
121. P. D. Bartlett and L. B. Gortler, *J. Am. Chem. Soc.* **85**, 1864 (1963).
122. J. P. Lorand, S. D. Chodroff, and R. W. Wallace, *J. Am. Chem. Soc.* **90**, 5266 (1968).
123. P. D. Bartlett and D. M. Simons, *J. Am. Chem. Soc.* **82**, 1753 (1960).
124. R. C. Ford and R. E. Franklin, *J. Am. Chem. Soc.* **90**, 5267 (1967).
125. M. Trachtman and J. G. Miller, *J. Am. Chem. Soc.* **84**, 4828 (1962).
126. V. A. Puchin, *The Study of Nonsaturated Organic Peroxides as Polymer Modificators*, Doctor Diss. Thesis (Russian), Odessa State University, Odessa, USSR, 1969.
127. G. A. Nosaev and D. N. Romantzeva, *Vysokomol. Soedin.* **8**, 16 (1966).
128. M. M. Martin and E. B. Sanders, *J. Am. Chem. Soc.* **89**, 3777 (1967).
129. C. Ruchardt and H. Schwarser, *Chem. Ber.* **99**, 1871, 1878, 1891 (1966).
130. D. R. Dixon and A. Pajaczkowski, *Chem. Commun.* 337 (1966).
131. C. Ruchardt, H. Bock and I. Ruchardt, *Angew. Chem.* **78**, 268 (1966).
132. C. Ruchardt and H. Bock, *Chem. Ber.* **100**, 654 (1967).
133. J. P. Lorand and P. D. Bartlett, *J. Am. Chem. Soc.* **88**, 3294 (1966).
134. M. M. Martin, *J. Am. Chem. Soc.* **84**, 1986 (1962).
135. P. D. Bartlett and H. Minato, *J. Am. Chem. Soc.* **85**, 1858 (1963).
136. A. V. Tobolsky and R. E. Mesrobian, *Organic Peroxides*, Wiley-Interscience, New York, 1954.
137. A. T. Blomquist and I. A. Berstein, *J. Am. Chem. Soc.* **73**, 5546 (1951).
138. V. L. Antonovskii, L. D. Bezborodova, and M. E. Yasel'man, *Zh. Fiz. Khim.* **43**, 2286 (1961).
139. D. L. Tuleen, W. G. Bentrude, and J. C. Martin, *J. Am. Chem. Soc.* **85**, 1936 (1963).
140. J. W. Koenig and J. C. Martin, *J. Org. Chem.* **29**, 1520 (1964).
141. W. G. Bentrude and J. C. Martin, *J. Am. Chem. Soc.* **84**, 1561 (1962).
142. H. Minato, H. Matsuzaki, and K. Miwa, *Bull. Chem. Soc. Japan* **41**, 249 (1968).
143. T. H. Fisher and J. C. Martin, *J. Am. Chem. Soc.* **88**, 3382 (1966).
144. P. D. Bartlett and R. E. Pinkock, *J. Am. Chem. Soc.* **82**, 1769 (1960).
145. V. A. Fomin, B. S. Etlis, Z. I. Aleksandrova, and H. H. Ivanova, *Zh. Org. Khim.* **20**, 282 (1984).

146. V. A. Fomin, Yu. I. Ovchinikova, and F. D. Nozrina, *Zh. Obshch. Khim.* **58**, 1384 (1988).

147. Yu. Ya. Van-Chin-Syan, V. N. Dibravny, and V. A. Donchak, *Izv. Vuzov, Ser. Khim. i Khim. Technologiya* N. 12, 1573 (1981).

148. T. N. Dolbneva, M. I. Domogray, and Yu. Ya. Van-Chin-Syan, in *Khimiya, tekhnologiya veschestv i ich primenenie* (Russian), Visshaya Shkola, L'vov, Russia, 1982, p. 9.

149. V. F. Korotyuk, V. S. Dutka, and S. K. Chyuchmarev, *Dep. Ukr. NIINII*, Kiev, N. 731–733 (1983).

150. H. A. Swain, Kwan Chin-Yin, and Sung Ho-Nan, *J. Chem. Phys.* **84**, 1347 (1980).

151. Yu. Ya. Van-Chin-Syan, Yu. P. Pavlovskii, and N. S. Kachurina, *Zh. Fiz. Khim.* **64**, 553 (1990).

152. N. Passadakis, Yu. Ya. Van-Chin-Syan, and V. L. Antonovskii, in *Thesis. Dokl. VI Vsesoyuznoy Konferenzii po Thermodinamike Organicheskikh Soedineniy* (Russian), Minsk, Russia, 1990, p. 25.

153. P. D. Bartlett, E. P. Benzing, and R. E. Pinkock, *J. Am. Chem. Soc.* **82**, 1762 (1960).

154. L. B. Gortler and M. D. Saltzman, *J. Org. Chem.* **31**, 3821 (1966).

155. A. I. Prisyazhnyuk and S. S. Ivanchev, *Zh. Org. Khim.* **5**, 1172 (1969).

156. L. M. Bobroff, L. B. Gortler, D. J. Sahn, and H. Wiland, *J. Org. Chem.* **31**, 2678 (1966).

157. E. G. Erigova, A. I. Prisyazhnyuk, and S. S. Ivanchev, *Zh. Obshch. Khim.* **38**, 2416 (1968).

158. P. V. Pankevich and V. S. Dutka, *Kinet. Katal.* **33**, 1087 (1992).

159. V. L. Antonovskii and L. D. Bezborodova, *Zh. Fiz. Khim.* **44**, 1224 (1970).

160. K. Matsuyama, T. Sugiura, and Y. Minoshima, *J. Org. Chem.* **60**, 5520 (1995).

161. L. F. R. Cafferata, G. N. Eyler, E. L. Svartman, A. I. Canizo, and E. Alvares, *J. Org. Chem.* **56**, 411 (1991).

162. L. F. R. Cafferata, G. N. Eyler, E. L. Svartman, A. I. Canizo, and E. J. Borkowski, *J. Org. Chem.* **55**, 1058 (1990).

163. J. R. Sanderson and P. R. Story, *J. Org. Chem.* **29**, 3464 (1974).

164. L. F. R. Cafferata, G. N. Eyler, and M. F. Mirifico, *J. Org. Chem.* **49**, 2107 (1984).

165. V. A. Fomin, V. S. Etlis, and I. V. Petrukhin, *Zh. Obshch. Khim.* **53**, 812 (1983).

166. V. D. Enal'ev and V. V. Zaytseva, *Vysokomol. Soedin.* **7**, 275 (1965).

167. V. V. Zaytseva, A. I. Yurzhenko, and V. D. Enal'ev, *Zh. Org. Khim.* **4**, 1402 (1968).

168. A. A. Turovskii, *The Study of Dependence between Thermodynamic Characteristics of Reactants and Transition State of Free Radical Reactions*, Ph.D. Thesis (Russian), L'vov State University, L'vov, USSR, 1968.

169. V. A. Yablokov, A. P. Tarabarina, and D. A. Kreknin, *Zh. Obshch. Khim.* **40**, 2255 (1970).

170. K. L. Berry, *U. S. Pat.* 2,692,887 (1954).

171. W. Hahn and L. Metzinger, *Makromolek. Chem.* **21**, 113 (1956).

172. E. Buncel and A. G. Davis, *J. Chem. Soc.* 1550 (1958).

173. T. I. Yurzhenko and A. K. Litkovetz, *Dokl. AN SSSR*, **136**, 1361 (1961), *Dokl. AN SSSR*, **142**, 1315 (1962).

174. K. A. Moiseichuk, *Dokl. AN SSSR*, 195 (1970).

175. G. S. Akimova and M. P. Grinblat, *Zh. Obshch. Khim.* **43**, 1199 (1973).

176. V. A. Fomin, T. I. Padbil, V. S. Etlis, and B. P. Shtarkman, *Vysokomol. Soedin., Ser. B*, **22**, 330 (1980).

177. V. A. Fomin, V. S. Etlis, and I. V. Pervuchin, *Zh. Obshch. Khim.* **53**, 812 (1983).

178. M. H. Abraham and A. G. Davis, *J. Chem. Soc.* 429 (1959).

179. A. G. Davis and D. G. Hare, *J. Chem. Soc.* 438 (1959).

180. A. G. Davis, D. G. Hare, and O. B. Khan, *J. Chem. Soc.* 112 (1963).

181. A. G. Davis, D. G. Hare, and R. F. Whihe, *J. Chem. Soc.* 341 (1961).

182. A. G. Davis and B. P. Roberts, *J. Chem. Soc.* 17 (1967).

183. A. G. Davis and R. B. Moodie, *J. Chem. Soc.* 2372 (1958).

184. V. A. Shushunov, V. P. Maslennikov, and G. P. Gerbert, *Dokl. AN SSSR*, **199**, 373 (1971).

185. A. Rieche, G. Hilgetag, and G. Schramm, *Chem. Ber.* **95**, 381 (1961).

186. J. B. Harrison and O. Mageli, *U. S. Pat.* 2,960,526 (1960).

187. T. I. Yurzhenko and B. I. Kaspruk, *Dokl. AN SSSR* **168**, 113 (1966).

188. V. P. Maslennikov, V. P. Sergeeva, and V. A. Shushunov, *Dokl. AN SSSR* **209**, 1109 (1973).

189. A. P. Tarabarina, *Reactivity of Organoelement Peroxides of IV Group Elements*, Ph.D. Thesis (Russian), Gor'kiy State University, Gor'kiy, USSR, 1972.

190. V. P. Maslennikov, *Organic Peroxides of Elements of II–V Groups of Periodic System*, Doctor Diss. Thesis (Russian), Moscow State University, Moscow, 1976.

191. G. P. Gerbert, *The Study of Bororganic Peroxides*, Ph.D. Thesis (Russian), Gor'kiy State University, Gor'kiy, USSR, 1971.

192. V. A. Yablokov, *Isomerisation of Organic and Organoelement Peroxides of IV Group Elements*, Doctor Diss. Thesis (Russian), Leningrad Technol. Institute, Leningrad, USSR, 1976.

193. I. B. Rabinovich, E. G. Kiparisova, and Yu. A. Aleksandrov, *Dokl. AN SSSR*, **200**, 1116 (1971).

194. Yu. Ya. Van-Chin-Syan, T. N. Dolbneva, and A. V. Litkovets, *Thermodynamika: Mezhvuzovsky sbornik* (Russian), GGU, Gor'kiy, USSR, 1979, p. 94.

195. R. R. Hiatt, *Can. J. Chem.* **42**, 985 (1964).

196. V. A. Fomin and I. V. Petrukhin, *Zh. Obshch. Khim.* **67**, 621 (1997).

197. Yu. A. Aleksandrov, V. V. Gorbatov, V. G. Tsvetkov, and N. V. Yablokova, *Dokl. AN SSSR*, **234**, 826 (1977).

198. N. V. Yablokova, N. G. Sluchevskaya, A. V. Tomadze, A. V. Ganyushkin, V. A. Yablokov, and Yu. A. Aleksandrov, in *Thesis. Dokl. VI Vsesoyuznnoy Konferenzii po Khim. Org. Perekisnych Soedin.* (Russian), Donezk, USSR, 1976, p. 58.

199. G. P. Gerbert, V. P. Maslennikov, and B. A. Shushunov, *Zh. Obshch. Khim.* **49**, 131 (1970).

200. V. P. Maslennikov, G. P. Gerbert, G. F. Chodarev, and V. A. Shushunov, *Zh. Obshch. Khim.* **41**, 592 (1971).

201. Yu. N. Anisimov and S. S. Ivanchev, *Zh. Obsch. Khim.* **41**, 2248 (1978).

202. N. V. Chikinova, G. I. Makin, and Yu. A. Aleksandrov, in *Thesis. Dokl. VI Vsesoyuznnoy Konferenzii po Khim. Org. Perekisnych Soedin* (Russian), Donezk, USSR, 1976, p. 123.

203. Yu. A. Aleksandrov, A. N. Bryuchanov, V. P. Maslennikov, and I. V. Spirina., *Zh. Obsch. Khim.* **45**, 2347 (1975).

204. V. I. Buzulukov, V. P. Maslennikov, V. F. Chodalev, and Yu. A. Aleksandrov, *Zh. Obsch. Khim.* **44**, 2549 (1974).

205. Yu. A. Aleksandrov, *Liquid-Phase Autoxidation of Elemento-organic Compounds* (Russian), Nauka, Moscow, 1978, p. 65.

206. V. M. Shekunova, N. A. Sokolov, and Yu. A. Aleksandrov, *Zh. Obshch. Khim.* **54**, 1163 (1984).

207. R. N. Zaripov, R. L. Safiullin, E. I. Yanbasarova, R. R. Muslukhov, and V. D. Komissarov, *Izv. AN, Ser. Khim.* 1049 (1995).

208. B. Mile, C. C. Rowlands, P. D. Sillman, and A. J. Holmes, *J. Chem. Soc., Perkin. Trans. 2*, 2141 (1993).

209. V. P. Maslennikov, V. P. Sergeeva, A. F. Shushunova, and T. N. Shuvalova, *Kinet. Katal.* **15**, 38 (1974).

210. A. I. Rakhimov, V. V. Chapurkin, A. I. Valdman, V. I. Saloutin, K. I. Pashkevich, S. L. Kokorin, and Z. E. Skryabina, *Izv. AN, Ser. Khim.* 1647 (1990).

211. P. D. Bartlett and R. R. Hiatt, *J. Am. Chem. Soc.* **80**, 1398 (1958).

212. P. D. Bartlett and D. M. Simons, *J. Am. Chem. Soc.* **82**, 1753 (1960).

213. C. Zhao, R. Zhou, H. Pan, X. Jin, Y. Qu, C. Wu, and X. Jiang, *J. Org. Chem.* **47**, 2009 (1982).

214. V. A. Novikov, V. P. Sass, L. S. Ivanova, and L. F. Sokolov, *Vysokomol. Soedin., Ser. A*, **17**, 1235 (1975).

215. H. Sawada, M. Nakayama, M. Yoshida, and T. Yoshida, *J. Fluorine Chem.* **46**, 423 (1990).

216. M. V. Zhuravlev, V. P. Sass, and S. V. Sokolov, *Zh. Org. Khim.* **19**, 44 (1983).

217. M. V. Zhuravlev, A. I. Burmakov, F. A. Bloshchitsa, V. P. Sass, and S. V. Sokolov, *Zh. Org. Khim.* **18**, 1825 (1982).

218. R. I. Kibal'nikova, *The Synthesis of Diacyl Peroxides and their Reactions with Halogens*, Ph.D. Thesis (Russian), Gor'kiy State University, Gor'kiy, USSR, 1972.

Handbook of Free Radical Initiators. E.T. Denisov, T.G. Denisova, T.S. Pokidova
Copyright © 2003 John Wiley & Sons, Inc.
ISBN: 0-471-20753-5

6

ORGANIC POLYOXIDES

6.1 DIALKYL TRIOXIDES

Dialkyl trioxides are formed as intermediates by the low-temperature oxidation of organic compounds with ozone.[1,2] They are also formed as intermediates in the liquid-phase oxidation of hydrocarbons with tertiary C—H bond as the result of the recombination of tertiary peroxyl radicals.[3]

$$RO_2^{\bullet} + RO_2^{\bullet} \Leftrightarrow ROOOOR$$

$$ROOOOR \rightarrow 2RO^{\bullet} + O_2$$

$$RO^{\bullet} + RO_2^{\bullet} \rightarrow ROOOR$$

Their formation was observed at temperatures from 190 to 240 K.[4]

6.1.1 Synthesis

Dialkyl trioxides are thermally unstable and can be obtained at temperatures as low as 190–240 K. The following synthetic methods are known.

1. Decomposition of hydroperoxides, ROOH, in reactions with heavy metals ions or iodozylbenzene proceed according to the following reactions:[5,6]

$$ROOH + Fe^{2+} \rightarrow RO^{\bullet} + HO^{\bullet} + Fe^{3+}$$

$$RO^{\bullet} + ROOH \rightarrow ROH + RO_2^{\bullet}$$

$$HO^{\bullet} + ROOH \rightarrow H_2O + RO_2^{\bullet}$$

$$RO^{\bullet} + RO_2^{\bullet} \rightarrow ROOOR$$

2. Reaction of ROOH or ROONa (ROOK) with ozone in CH_2Cl_2 or $CFCl_3$ at low temperature:[5,7-11]

$$Me_3COOX + O_3 \rightarrow XO_3^{\bullet} + Me_3COO^{\bullet}$$

$$Me_3COO^{\bullet} + O_3 \rightarrow Me_3CO^{\bullet} + 2O_2$$

$$Me_3COO^{\bullet} + Me_3CO^{\bullet} \rightarrow Me_3COOOCMe_3$$

3. Photolysis of hydroperoxides and azo compounds at low temperature.[3,12-15]
4. Reaction of ROOH with lead tetraacetate (CH_2Cl_2, 200 K).[5]

6.1.2 Thermochemistry of Trioxides

Dissociation energy of the O—O bond in dialkyl trioxides was calculated by quantum chemical methods MNDO and AM1.[16] The results of these calculations are presented in Table 6.1. Enthalpies of trioxides formation are presented in Table 6.2. Increments of $\Delta H\text{O}-(\text{O})_2 = 46.4 \pm 4.2$ kJ mol^{-1} for the additive scheme of ΔH calculations.[17,18] Bond dissociation energy $D(\text{R}^1-\text{OOOR}^2) =$ 266 kJ mol^{-1} is the same for different alkyl substituents R^1 and R^2, $D(\text{R}^1-\text{O}_3) =$ 230 kJ mol^{-1}.[16]

6.1.3 Decay of Trioxides

For the rate constants and activation energies of decay for different ROOOR see Table 6.3. The yield of free radicals (*e*) at alkyl trioxide decomposition depends on the solvent and temperature and is close to unity (Table 6.4). Products of ROOOR decomposition depend on the solvent. The decay of ROOOR in nonhydrogen solvents (CCl_4, $CFCl_3$, etc.) leads to the formation of O_2 and ROOR

TABLE 6.1 Dissociation Energies for the O—O Bond in Trioxides ($\text{R}^1\text{O}-\text{OOR}^2$) Calculated by the MNDO and AM1 Quantum Chemical Methods[a]

Substituent		D(O—O) (kJ mol^{-1})		Substituent		D(O—O) (kJ mol^{-1})	
R^1	R^2	MNDO	AM1	R^1	R^2	MMDO	AM1
H	H	104.6	105.4	Et	H	90.8	87.9
H	Me	111.3	106.3	Et	Me	96.2	88.7
H	Et	109.2	101.7	Et	Et	95.0	84.1
H	Me_3C	104.2	93.7	Et	Me_3C	89.5	75.7
Me	H	86.6	78.7	Me_3C	H	80.7	92.5
Me	Me	92.9	79.5	Me_3C	Me	87.0	92.9
Me	Et	91.2	75.3	Me_3C	Et	84.9	88.3
Me	Me_3C	85.8	66.9	Me_3C	Me_3C	77.0	79.9

[a] See Ref. 16.

TABLE 6.2 The Enthalpies ΔH^0 of Polyoxide $R^1O_xR^2$ Formation (x = 3, 4)[a]

Substituent		$-\Delta H^0$ (kJ mol^{-1})	
R^1	R^2	R^1OOOR^2	R^1OOOOR^2
H	H	51.0	−0.4
Me	H	50.6	2.9
Et	H	87.0	37.7
Me_3C	H	166.1	121.3
Me	Me	50.2	5.9
Et	Me	86.6	39.7
Me_3C	Me	164.4	123.8
Et	Et	123.0	73.6
Me_3C	Et	200.8	157.7
Me_3C	Me_3C	279.5	241.8

[a] See Ref. 17.

TABLE 6.3 The Rate Constants and Activation Energies for the Decay of Dialkyl Trioxides ROOOR[a]

R−	Solvent	k (273 K) (s^{-1})	E (kJ mol^{-1})	log A, A (s^{-1})	Method
Me_3C-	CH_2Cl_2	7.1×10^{-3}	87.0	14.5	CL
Me_3C-	$CFCl_3$	3.2×10^{-3}	90.4	14.8	AFR
Me_3C-	CCl_4	6.0×10^{-4}			CL
Me_3C-	PhOPh	1.9×10^{-3}			CL
Me_3C-	PhCl	3.0×10^{-3}			CL
Me_3C-	MeCN	5.2×10^{-3}			CL
Me_3C-	$MeNO_2$	9.7×10^{-3}			CL
Me_3C-	CF_3COOH	9.5×10^{-2}			CL
Me_2EtC-	CH_2Cl_2	6.8×10^{-3}	80.3	13.2	CL
$PhMe_2C-$	CH_2Cl_2	7.9×10^{-3}	92.0	15.5	CL
Adamantyl-	CH_2Cl_2	3.9×10^{-2}	75.3	13.0	CL

[a] See Refs. 5, 16, 19–22.

TABLE 6.4 The Yield of Free Radicals (e) in $Me_3COOOCMe_3$ Decomposition[a]

Solvent	T (K)	e
$CFCl_3$	265.5	0.94
CH_2Cl_2	252	1.02
CH_2Cl_2	262.5	0.86
CH_2Cl_2	273	0.84
CH_2Cl_2	278.5	0.86

[a] See Ref. 16.

as the products of the reaction of $RO^\bullet$ and $RO_2^\bullet$ radicals. The decay of ROOOR in hydrogen-containing solvents is accompanied by the formation of ROH, O_2, singlet O_2, and products of oxidation of the solvent. The induced decomposition of trioxides is observed at sufficiently high (5×10^{-3} mol L^{-1} and higher) concentrations of trioxide.[23]

6.2 HYDROTRIOXIDES

6.2.1 Synthesis

Hydrotrioxides were supposed to be intermediates in the ozonolysis of aldehydes,[23] ethers,[24] alcohols,[25] silanes,[26] and other compounds.[27–30] This hypothesis was seen by Murray and colleagues in the NMR study of benzaldehyde and 2-methyltetrahydrofuran ozonolysis.[31,32] Hydrotrioxides of different compounds were synthesized by the ozonolysis of ethers,[31–33] acetals,[35–39] alcohols,[33,34,40–42] ketones,[43] hydrocarbons,[44–46] and silanes.[47–50] Hydrotrioxides are synthesized by bubbling of a $O_3{-}O_2$ or $O_3{-}N_2$ mixture through a liquid reactant or its solution at low temperature (200–250 K). The amount of formed ROOOH is analyzed by NMR spectroscopy. Ozone reacts with the hydrotrioxide formed. As a result, the higher its concentration, the higher the yield of ROOOH. For example, the yield extrapolated to $t = 0$ is equal to 0.45 (2-methoxypropane, 195 K,[33] 0.51 (1,1-diethoxyethane, 195 K,[39] 0.90 (propyl alcohol, 183 K).[42]

6.2.2 Structure and Spectrum of Hydrotrioxides

Hydrotrioxides are unstable at room temperatures. The structure of ROOOH was studied by quantum chemical semiempirical and nonempirical methods.[49,51–63] The results of quantum chemical calculations are given in Tables 6.5 and 6.6.

TABLE 6.5 Results for the Quantum Chemical Estimation of the Structural Parameters of HOOOH: Interatomic Distances (r), Valence (θ) and Torsion (φ) Angles, and General Energy (E_{total})

Basis	r(HO) × 10^{10} (m)	r(OO) × 10^{10} (m)	θ(HOO) (°)	θ(OOO) (°)	φ (°)	E_{total} (hartree)	Reference
RHF/STO-3G	1.002	1.392	102.5	105.9	84.2	−222.58049	59
RHF/4-31G	0.959	1.437	103.6	106.0	83.5	−225.21862	59
RHF/6-31G	0.958	1.432	104.1	106.5	83.9	−225.44304	49
RHF/6-31G*	0.953	1.373	103.2	107.2	80.1	−225.53362	59
RHF/6-31G**	0.949	1.373	103.5	107.4	80.8	−225.54584	61
MP2/4-31G	0.992	1.539	99.6	104.4	78.3	−225.62077	59
MP2/6-31G*	0.980	1.442	100.3	106.1	78.5	−226.09075	59
MP2/6-31 + +G*	0.982	1.445	100.8	106.4	79.6	−226.10273	62
MP2/6-31G**	0.972	1.441	100.2	106.2	78.7	−226.11275	61

TABLE 6.6 Results for the Quantum Chemical Estimation of the Structural Parameters of ROOOH: Interatomic Distances (r), Valence (θ) and Torsion (φ) Angles and General Energy (E_{total})[a]

ROOOH	MeOOH			SiH_3OOH
Basis	RHF/STO-3G	RHF/4-31G	RHF/6-31G	RHF/6-31G
$r(X-O) \times 10^{10}$ (m)	1.453	1.438	1.439	1.771
$r(XO-O) \times 10^{10}$ (m)	1.396	1.436	1.430	1.441
$r(O-OH) \times 10^{10}$ (m)	1.392	1.440	1.433	1.429
$r(O-H) \times 10^{10}$ (m)	1.003	0.958	0.957	0.958
θ(OOH) (°)	102.4	103.4	103.9	103.9
θ(OOO) (°)	105.9	106.1	106.5	106.2
θ(XOO) (°)	106.5	107.7	108.1	109.6
φ(HXOO) (°)	179.1	179.0	179.0	180.2
φ(XOOO) (°)	87.8	85.8	86.0	84.1
φ(OOOH) (°)	83.5	82.4	82.6	79.3
E_{total}/(hartree)	−261.16718	−264.18963	−264.45417	−515.49701

[a] See Ref. 63.

The UV spectrum of HOOOH is close to that of H_2O_2. Maximum absorption is observed at $\lambda = 240$ nm, the molar absorption coefficient $\varepsilon = 100$ L mol^{-1} cm^{-1}.[16] Since ROOOH contains the hydrogen atom, its NMR spectrum exhibits proton absorption of the hydrotrioxide group with a chemical shift of 13 m.d. relative to the signal of tetramethyl silane Me_4Si.[31–36,38–50]

The NMR spectrum for the hydrotrioxides of alcohols has two peaks of proton absorption.[16] This is the result of two different cyclic conformations due to the formation of the intramolecular hydrogen bond: one conformation is the result of hydrogen-bond formation between the hydroxyl group and the oxygen of the peroxide group [C—O—H ··· O(H)—O—O], and the other is the hydrogen bond of the type [O—O—O—H ··· O(H)—C]. The rate constant of the transition from one conformation to another for the hydrotrioxide $Me_2C(OH)OOOH$ was estimated as $k = 1.07 \times 10^3 \exp(-645/T) = 78$ s^{-1} (250 K, solvent EtOH/EtOEt = 1 : 3.7 V/V).[16] Along with the intramolecular hydrogen bond, hydrotrioxides form intermolecular associates via hydrogen bonding. The energy of hydrogen bonding depends on the associate configuration and varies for MeOOOH from 20 to 38 kJ mol^{-1} (quantum chemical calculation).[16] The most stable dimer has an atomic cycle of eight.

6.2.3 Thermochemistry

Dissociation energies of O—H and O—O bonds in alkyl hydrotrioxides virtually do not depend on the alkyl substituent. These BDEs are collected in Table 6.7. Enthalpies of hydrotrioxides formation were calculated on the basis of the data in Table 6.7. The enthalpies of formation were calculated

TABLE 6.7 The Bond Dissociation Energies of Hydrotrioxides Calculated by Quantum Chemical Methods

Bond	D (kJ mol^{-1})	Reference	Bond	D (kJ mol^{-1})	Reference
ROOO−H	334.7 ± 3.3	16	HOO−OMe	82.6 ± 4.0	66
ROOO−H	338.9 ± 4.2	63	HOO−OEt	89.3 ± 1.8	66
HOOO−H	345.6 ± 5.0	64	HOO−OCMe$_3$	86.6 ± 5.8	66
HOO−OH	105.0 ± 2.0	65	ROOO−R	266.1 ± 5.0	66
MeOO−OH	108.8 ± 2.5	65	$^{\bullet}$OOO−H	296.2	66
EtOO−OH	105.4 ± 3.8	65	$^{\bullet}$OOO−R	230.1 ± 3.3	66
Me$_3$COO−OH	98.9 ± 5.2	65			

to be the following: −51.0 kJ mol^{-1} (HOOOH), −50.6 kJ mol^{-1} (MeOOOH), −87.0 kJ mol^{-1} (EtOOOH), and −166.1 kJ mol^{-1} (Me$_3$COOOH).[16]

Hydrotrioxide, HOOOH, exists in two forms: anti and sin. The anti configuration is more stable, the difference in enthalpies according to the quantum chemical calculation varies from 14.5 to 20 kJ mol^{-1}.[59]

6.2.4 Decomposition of Hydrotrioxides

Some stable products of hydrotrioxides decomposition are alcohols, esters, acids, and ketones. For example, stable products of cumyl hydrotrioxide, PhMe$_2$COOOH, that decay into CD$_3$COCD$_3$ are cumyl alcohol, PhMe$_2$COH (yield 80–90%), and acetophenone (yield 10–20%).[45] Information about the products of decomposition for different hydrotrioxides is available from Refs. 32,34,38,49.

The decay of hydrotrioxides is accompanied by free radicals generation, which was evidenced by the EPR method[45] and EPR in combination with spin trapping.[34,37,39] Singlet dioxygen, $^1O_2$, is produced in hydrotrioxides decomposition. The yield of $^1O_2$ depends on the structure of hydrotrioxide, temperature, and solvent (see Table 6.8). Chemiluminescence accompanies ROOOH decay. Chemiluminescence is observed in the visible and IR spectral regions. The first is the result of emission from the triplet state of ketone formed in the peroxyl radical disproportionation. The second is due to the formation of singlet dioxygen. Chemiluminescence is widely used for the kinetic study of hydrotrioxides decomposition. The rate constants of decay for several hydrotrioxides are collected in Table 6.9 and free radical yields ($e = k_i/2k_d$) are presented in Table 6.10.

The mechanism of hydrotrioxide decomposition in solvent YH includes the following elementary steps:[16]

$$\mathrm{ROOOH} \rightarrow \mathrm{ROH} + {}^1\mathrm{O}_2$$

$$\mathrm{ROOOH} \rightarrow [\mathrm{RO}^{\bullet} + {}^{\bullet}\mathrm{OOH}]$$

$$[RO^\bullet + {}^\bullet OOH] \rightarrow ROH + {}^1O_2$$

$$[RO^\bullet + {}^\bullet OOH] \rightarrow RO^\bullet + HOO^\bullet$$

$$RO^\bullet + ROOOH \rightarrow ROH + ROOO^\bullet$$

$$RO^\bullet + YH \rightarrow ROH + Y^\bullet$$

$$Y^\bullet + O_2 \rightarrow YO_2{}^\bullet$$

$$ROOO^\bullet \rightarrow RO^\bullet + O_2$$

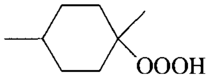
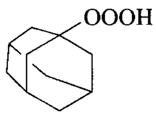
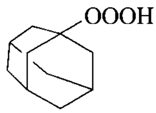
$$YO_2{}^\bullet + YO_2{}^\bullet \rightarrow {>}C{=}O^* + \text{Products}$$

According to this scheme, decay of ROOOH obeys the first-order kinetic law:

$$\ln([ROOOH]/[ROOOH]_0) = -k_{obs}t \qquad (6.1)$$

where $k_{obs} = (a + b[ROOOH]/[YH])$, which depends on the concentrations of ROOOH and YH.

TABLE 6.8 The Yield of Singlet Dioxygen [ϕ ($^1O_2$)] at Hydrotrioxide Decomposition[a]

Hydrotrioxide	Solvent	T (K)	ϕ ($^1O_2$) (%)
1,1-Dimethylpropyl-, $EtMe_2COOOH$	Dichloromethane	285	5.2
1,4-Dimethylcyclohexyl-,  	Dichloromethane	288	15.0
Adamantyl-,  	Dichloromethane	270	7.2
Adamantyl-,  	Dichloromethane	285	6.4
Triphenylmethyl-, Ph_3COOOH	Dichloromethane	278	2.6
Hydroxymethyl-, $CH_2(OH)OOOH$	Dichloromethane	279	2.5

(*continued overleaf*)

TABLE 6.8 (*continued*)

Hydrotrioxide	Solvent	T (K)	ϕ ($^1O_2$) (%)
1-Methylethyl-, $Me_2CHOOOH$	Dichloromethane	281	8.0
1-Methyl 2-propoxyethyl-, Me_2CHOMe_2COOOH	Dichloromethane	279	5.0
1,1-Diethoxyethyl-, $(EtO)_2MeCOOOH$	Dichloromethane	280	19.0
1-Hydroxyethyl-, MeCH(OH)OOOH	Dichloromethane	257	15.4
1-Hydroxyethyl-, MeCH(OH)OOOH	Dichloromethane	290	11.8
1-Hydroxyethyl-, MeCH(OH)OOOH	Trichlorofluoromethane	278	18.1
1-Hydroxyethyl-, MeCH(OH)OOOH	Carbon tetrachloride	278	10.1
1-Hydroxyethyl-, MeCH(OH)OOOH	Benzene	278	8.0
1-Hydroxyethyl-, MeCH(OH)OOOH	Toluene	278	13.0
1-Hydroxyethyl-, MeCH(OH)OOOH	Benzyl alcohol	278	1.6
1-Hydroxyethyl-, MeCH(OH)OOOH	Acetone	278	14.6
1-Hydroxyethyl-, MeCH(OH)OOOH	Acetonitrile	278	12.7

[a] See Refs. 39 and 67.

TABLE 6.9 The Rate Constants for the Decay of Hydrotrioxides Measured by Chemiluminescence

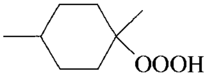
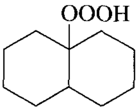
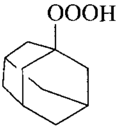
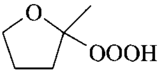
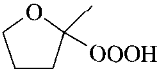
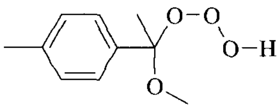
Hydrotrioxide	Solvent	E (kJ mol^{-1})	log A, A (s^{-1})	k (250 K) (s^{-1})	Reference
Hydrotrioxide, HOOOH	Acetone, perdeuterated	54.4	7.7	2.16×10^{-4}	68
Hydrotrioxide, HOOOH	Methyl acetate	52.3	7.5	3.74×10^{-4}	68
1,1-Dimethylpropyl-, $EtMe_2COOOH$	Dichloromethane	77.8	11.5	1.76×10^{-5}	16
1,4-Dimethylcyclohexyl-, 	Dichloromethane	49.8	7.0	3.94×10^{-4}	16

TABLE 6.9 (*continued*)

Hydrotrioxide	Solvent	E (kJ mol^{-1})	log A, A (s^{-1})	k (250 K) (s^{-1})	Reference
(E)-Decalyl-, 	Dichloromethane	62.8	9.2	1.20×10^{-4}	16
Adamantyl-, 	Dichloromethane	62.8	9.5	2.39×10^{-4}	16
Triphenylmethyl-, Ph_3COOOH	Dichloromethane	55.6	9.0	2.42×10^{-3}	16
Benzoyl-, PhC(O)OOOH	Diethyl ether	68.6	11.1	5.85×10^{-4}	31
Benzoyl-, PhC(O)OOOH	Benzaldehyde	44.8	5.4	1.10×10^{-4}	31
Benzoyl-, PhC(O)OOOH	Diethyl ether	72.0	10.0	9.05×10^{-6}	69
Tetrahydrofuran, 2-hydrotrioxy-2-methyl-, 	Tetrahydrofuran	33.6	4.1	1.20×10^{-3}	32
Tetrahydrofuran, 2-hydrotrioxy-2-methyl-, 	Diethyl ether	72.8	11.7	3.09×10^{-4}	32
1-Methoxy-1-methylethyl-, $Me_2(MeO)COOOH$	2-Methoxy-propane	69.4	11.5	1.00×10^{-3}	32
1-Methoxy-1-phenylethyl-, MePh(MeO)COOOH	Acetone	83.3	16.0	3.94×10^{-2}	34
1-Methoxy-1-phenylethyl-, MePh(MeO)COOOH	Ethyl acetate	75.3	14.2	2.93×10^{-2}	34
1-Methoxy-1-phenylethyl-, MePh(MeO)COOOH	Diethyl ether	63.2	12.9	0.50	34
1-Ethoxy-1-phenylethyl-, MePhC(OEt)OOOH	Diethyl ether	64.4	12.3	6.99×10^{-2}	34
1-Methoxy-1-(4-methylphenyl)ethyl-, 	Acetone	73.6	13.8	2.64×10^{-2}	34

(*continued overleaf*)

TABLE 6.9 (*continued*)

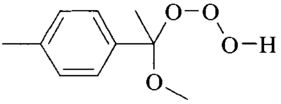
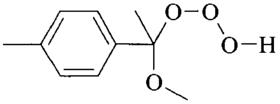
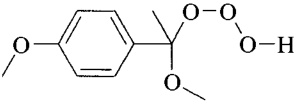
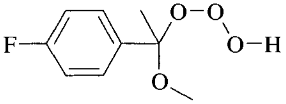
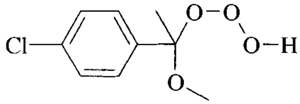
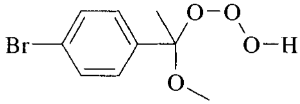
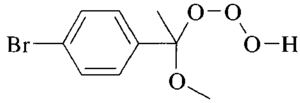
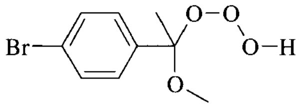
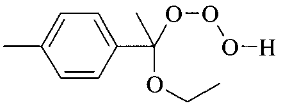
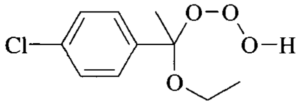
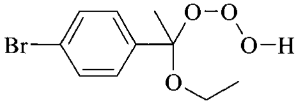
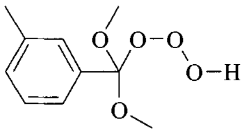
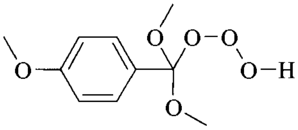
Hydrotrioxide	Solvent	E (kJ mol^{-1})	log A, A (s^{-1})	k (250 K) (s^{-1})	Reference
1-Methoxy-1-(4-methylphenyl)ethyl-, 	Ethyl acetate	64.0	11.8	2.68×10^{-2}	34
1-Methoxy-1-(4-methylphenyl)ethyl-, 	Diethyl ether	78.7	16.4	0.90	34
1-Methoxy-1-(4-methoxyphenyl)ethyl-, 	Diethyl ether	66.9	13.7	0.53	34
1-Methoxy-1-(4-fluorophenyl)ethyl-, 	Diethyl ether	64.8	13.2	0.46	34
1-Methoxy-1-(4-chlorophenyl)ethyl-, 	Diethyl ether	70.3	14.8	1.29	34
1-Methoxy-1-(4-bromophenyl)ethyl-, 	Acetone	85.3	16.8	9.50×10^{-2}	34
1-Methoxy-1-(4-bromophenyl)ethyl-, 	Ethyl acetate	61.9	11.5	3.69×10^{-2}	34

TABLE 6.9 (***continued***)

Hydrotrioxide	Solvent	E (kJ mol^{-1})	log A, A (s^{-1})	k (250 K) (s^{-1})	Reference
1-Methoxy-1-(4-bromophenyl)ethyl-,  	Diethyl ether	70.7	14.7	0.85	34
1-Ethoxy-1-(4-methylphenyl)ethyl-  	Diethyl ether	61.1	11.6	6.82×10^{-2}	34
1-Ethoxy-1-(4-chlorophenyl)ethyl-  	Diethyl ether	80.3	16.4	0.42	34
1-Ethoxy-1-(4-bromophenyl)ethyl-  	Diethyl ether	73.6	14.8	0.26	34
1,1-Dimethoxyethyl-, $(MeO)_2MeCOOOH$	Diethyl ether	67.4	11.8	5.22×10^{-3}	36
1,1-Dimethoxyethyl-, $(MeO)_2MeCOOOH$	1,1-Dimethoxyethane	69.4	11.5	1.00×10^{-4}	32
Dimethoxyphenylmethyl-, $(MeO)_2PhCOOOH$	Diethyl ether	79.5	15.9	0.19	36
Dimethoxy(3-methylphenyl)methyl-,  	Diethyl ether	89.5	17.8	0.13	36
Dimethoxy(4-methoxyphenyl)methyl-,  	Diethyl ether	72.0	13.7	0.45	36

(*continued overleaf*)

TABLE 6.9 (*continued*)

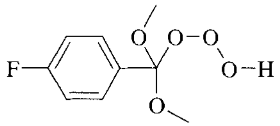
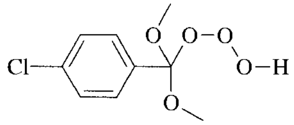
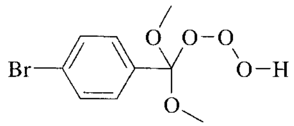
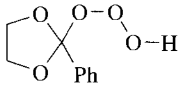
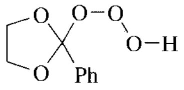
Hydrotrioxide	Solvent	E (kJ mol^{-1})	log A, A (s^{-1})	k (250 K) (s^{-1})	Reference
Dimethoxy(4-fluorophenyl)methyl-, 	Diethyl ether	81.6	16.4	0.22	36
Dimethoxy(4-chlorophenyl)methyl-, 	Diethyl ether	77.0	15.4	0.20	36
Dimethoxy(4-bromophenyl)methyl-, 	Diethyl ether	105.0	21.6	0.46	36
1,1-Diethoxyethyl-, Me(EtO)$_2$COOOH	1,1-Diethoxyethane	60.7	11.1	2.62×10^{-2}	36
1,1-Diethoxyethyl-, Me(EtO)$_2$COOOH	Diethyl ether	55.2	9.8	1.85×10^{-2}	36
1,1-Diethoxyphenylmethyl-, (EtO)$_2$PhCOOOH	Diethyl ether	82.8	16.7	0.25	36
1,3-Dioxolane, 2-hydrotrioxy-2-phenyl-, 	Diethyl ether	66.5	13.1	0.16	36
1,3-Dioxolane, 2-hydrotrioxy-2-phenyl-, 	Dichloromethane	85.8	16.6	4.71×10^{-2}	36
1-Hydroxyethyl-, MeC(OH)OOOH	Ethanol	29.3	3.1	9.51×10^{-4}	41
1-Hydroxyethyl-, MeC(OH)OOOH	Dichloromethane	52.7	8.1	1.23×10^{-3}	16
1-Hydroxypropyl-, EtCH(OH)OOOH	Propanol	71.1	12.6	5.55×10^{-3}	41
1-Hydroxy-1-methylethyl-, Me$_2$C(OH)OOOH	2-Propanol	56.1	7.9	1.51×10^{-4}	41
1-Hydroxy-1-methylethyl-, Me$_2$C(OH)OOOH	Trichloromethane	74.5	11.9	2.16×10^{-4}	41
1-Hydroxy-1-methylethyl-, Me$_2$C(OH)OOOH	Carbon tetrachloride	42.7	6.4	3.01×10^{-3}	41

TABLE 6.9 (*continued*)

Hydrotrioxide	Solvent	E (kJ mol^{-1})	log A, A (s^{-1})	k (250 K) (s^{-1})	Reference
1-Hydroxy-1-methylethyl-, $Me_2C(OH)OOOH$	Hexane	46.9	6.2	2.52×10^{-4}	41
1-Hydroxy-1-methylethyl-, $Me_2C(OH)OOOH$	Acetonitrile	7.2	0.16	4.53×10^{-2}	41
1-Hydroxy-1-methylethyl-, $Me_2C(OH)OOOH$	Diethyl ether	70.3	10.3	4.09×10^{-5}	41
1,2-Dihydroxy-1-methylethyl-, $Me(CH_2OH)C(OH)OOOH$	2-Propanol	59.8	9.7	1.61×10^{-3}	41
1-Hydroxy-1-methylpropyl-, $EtMeC(OH)OOOH$	2-Butanol	44.8	6.9	3.46×10^{-3}	42
1,2-Dihydroxy-1-methylpropyl-, $MeCH(OH)C(OH)(OOOH)Me$	Dichloromethane	56.1	9.7	9.52×10^{-3}	42
1,3-Dihydroxy-1-methylbutyl-, $MeCH(OH)CH_2C(OH)(OOOH)Me$	Dichloromethane	25.1	3.1	7.17×10^{-3}	42
1-Hydroxy-1-phenylethyl-, $MePhC(OH)OOOH$	Diethyl ether	70.3	13.3	4.09×10^{-2}	34
1-Hydroxy-1-phenylethyl-, $MePhC(OH)OOOH$	Acetone	70.7	13.4	4.25×10^{-2}	34
1-Hydroxy-1-phenylethyl-, $MePhC(OH)OOOH$	Ethyl acetate	71.1	13.6	5.55×10^{-2}	34
1-Methyl-1-phenylethyl-, $PhMe_2COOOH$	Acetone, perdeuterated	66.9	10.4	2.14×10^{-4}	45
Tributylsilyl-, $Bu_3SiOOOH$	Tributylsilane	25.1	6.8	35.9	48
Dimethylphenylsilyl-, $PhMe_2SiOOOH$	Acetone	52.7	8.2	1.55×10^{-3}	48

Hydrotrioxides possess the week O—O bond and react with free radicals. These reactions are very difficult to study due to the high instability of hydrotrioxides. The rate constants of different free radical reactions with 1,1-dimethylethyl hydrotrioxide were calculated by the intersecting parabola model of reaction (IPM) method (see Chapter 9) and the results of these calculations are presented in Table 6.11.

TABLE 6.10 The Rate Constant and Yield ($e = k_i/2k_d$) of Free Radical Generation in Hydrotrioxides Decay in Different Solvents[a]

Hydrotrioxide	Solvent	T (K)	$k_i \times 10^5$ (s^{-1})	e
benzoyl-, $PhC(O)OOOH$	Benzaldehyde	253	1.90	6.5×10^{-2}
benzoyl-, $PhC(O)OOOH$	Benzaldehyde	273	15.7	0.12

(*continued overleaf*)

TABLE 6.10 (*continued*)

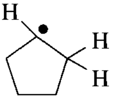
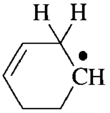
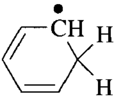
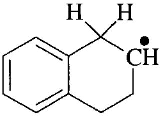
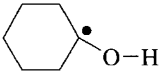
Hydrotrioxide	Solvent	T (K)	$k_i \times 10^5$ (s^{-1})	e
1,1,2-trimethylpropyl-, Me_2CHMe_2COOOH	Diisopropylether	273	0.125	3.5×10^{-5}
1,1-diethoxyethyl-, $(EtO)_2MeCOOOH$	Ethane, 1,1-diethoxy-	228	1.26	3.0×10^{-3}
1-hydroxy-1-methylethyl-, $Me_2C(OH)OOOH$	2-Propanol	263	2.10	1.7×10^{-2}
1-hydroxy-1-methylethyl-, $Me_2C(OH)OOOH$	2-Propanol	273	5.75	2.0×10^{-2}
1-hydroxy-1-methylethyl-, $Me_2C(OH)OOOH$	Trichloromethane	273	13.2	1.7×10^{-2}
1-hydroxy-1-methylethyl-, $Me_2C(OH)OOOH$	Hexane	273	1.65	4.0×10^{-3}
1-hydroxy-1-methylethyl-, $Me_2C(OH)OOOH$	Diethylether	273	0.60	4.0×10^{-3}
1-hydroxy-1-methylethyl-, $Me_2C(OH)OOOH$	Acetonitrile	273	1.19	2.0×10^{-4}

[a] See Refs. 39 and 67.

TABLE 6.11 Rate Constants of Free Radical Reactions with Me_3COOOH Calculated by the IPM Method[a]

$R^{\bullet}$	ΔH_e (kJ mol^{-1})	E (kJ mol^{-1})	log A, A (L mol^{-1} s^{-1})	k (250 K) (L mol^{-1} s^{-1})
$R^{\bullet} + HOOOCMe_3 \rightarrow ROH + Me_3COO^{\bullet}$				
$C^{\bullet}H_3$	−290.4	14.6	9.00	8.90×10^5
$CH_3C^{\bullet}H_2$	−295.4	13.8	9.00	1.31×10^6
$Me_2C^{\bullet}H$	−305.4	12.2	9.00	2.82×10^6
$Me_3C^{\bullet}$	−302.4	12.7	9.00	2.22×10^6
$CH_2{=}C^{\bullet}H$	−385.8	4.2	9.00	1.33×10^8
$CH_2{=}CHC^{\bullet}H_2$	−244.4	23.3	9.30	2.70×10^4
$C_6H_5^{\bullet}$	−377.4	2.9	9.00	2.48×10^8
$PhC^{\bullet}H_2$	−249.4	22.2	9.00	2.30×10^4
$RCH{-}HC^{\bullet}H_2 + HOOOCMe_3 \rightarrow RCH{=}CH_2 + H_2O + Me_3COO^{\bullet}$				
$C^{\bullet}H_2CH_2{-}H$	−263.7	24.3	8.85	5.93×10^3

TABLE 6.11 (*continued*)

$R^{\bullet}$	ΔH_e (kJ mol^{-1})	E (kJ mol^{-1})	log A, A (L mol^{-1} s^{-1})	k (250 K) (L mol^{-1} s^{-1})
$MeCH-HC^{\bullet}H_2$	−265.4	21.6	8.70	1.54×10^4
$Me_2C-HC^{\bullet}H_2$	−272.5	19.9	8.41	1.78×10^4
$EtC^{\bullet}HMe_2C-H$	−275.4	19.3	8.42	2.44×10^4
	−262.3	22.1	8.99	2.37×10^4
$HC^{\bullet}=CH-H$	−258.4	23.0	8.68	7.49×10^3
$CH_2=CH(C-H)HC^{\bullet}H_2$	−279.7	18.4	8.73	7.68×10^4
$CH_2=CHC-HMeC^{\bullet}H_2$	−288	16.7	8.45	9.14×10^4
$CH_2=CHC-HMeC^{\bullet}HMe$	−289.9	16.3	8.45	1.11×10^5
	−266.0	21.3	8.70	1.78×10^4
	−322.5	10.1	8.86	5.62×10^6
$PhCH-HC^{\bullet}H_2$	−271.7	20.1	8.71	3.24×10^4
	−284.8	17.3	8.74	1.33×10^5
$RC^{\bullet}HNH_2 + HOOOCMe_3 \rightarrow RCH{=}NH + H_2O + Me_3COO^{\bullet}$				
$C^{\bullet}H_2NH-H$	−256.4	21.4	8.70	1.67×10^4
$MeC^{\bullet}HNH-H$	−263.3	18.8	8.72	6.21×10^4
$MeN-HC^{\bullet}Me_2$	−268.5	17.3	8.74	1.35×10^5
$PhC^{\bullet}HNH-H$	−252.9	16.7	8.75	1.84×10^4
$R^1R^2C^{\bullet}OH + HOOOCMe_3 \rightarrow R^1R^2\ C{=}O + H_2O + Me_3COO^{\bullet}$				
$H_2C^{\bullet}O-H$	−289.6	19.7	8.41	1.98×10^4
$MeHC^{\bullet}O-H$	−295.2	17.1	8.44	7.38×10^4
$Me_2C^{\bullet}O-H$	−299.3	15.6	8.46	1.61×10^5
$Me_2CHC^{\bullet}HO-H$	−306.3	15.0	8.47	2.20×10^5
	−287.8	17.8	8.43	5.22×10^4

---

[a] See Chapter 9 for the calculation equations: (9.13), (9.15), and (9.16).

6.3 TETROXIDES

Tetroxides are formed as intermediates during trioxide decomposition due to the recombination of the peroxyl radicals formed:[16]

$$\mathrm{ROOOR} \rightarrow \mathrm{RO_2}^{\bullet} + \mathrm{RO}^{\bullet}$$

$$\mathrm{RO_2}^{\bullet} + \mathrm{RO_2}^{\bullet} \rightarrow \mathrm{ROOOOR}$$

They are formed in autoxidized hydrocarbons bearing tertiary C—H bonds as intermediates of peroxyl radical recombination:[70,71]

$$\mathrm{RO_2}^{\bullet} + \mathrm{RO_2}^{\bullet} \rightarrow \mathrm{ROOOOR}$$

6.3.1 Peroxyl Radical–Tetroxide Equilibrium

The equilibrium between *tert*-butyl peroxyl radicals and *tert*-butyl tetroxide was first demonstrated by Bartlett and Guaraldi[3] for peroxyl radicals generated by the irradiation of bis(1,1-di-methylethyl) peroxycarbonate in CH_2Cl_2 at 77 K and oxidation of 1,1-di-methylethyl hydroperoxide with lead tetraacetate at 183 K in CH_2Cl_2. A series of studies of this equilibrium were performed later using ESR technique (see Table 6.12). It is seen that the enthalpy of tetroxide decomposition ranges from 30 to 48 kJ mol^{-1}.

TABLE 6.12 The Enthalpies and Entropies of Equilibrium for ROOOOR ⇔ $2RO_2^{\bullet}$

R—	Solvent	ΔH^0 (kJ mol^{-1})	ΔS^0 (J mol^{-1} K^{-1})	K (200 K) (mol L^{-1})	Reference
Me_3C—	Dichloromethane	46.6	222	0.27	3
Me_3C—	Dichlorodifluoromethane	35.1	136	8.6×10^{-3}	13
Me_3C—	2-Methylbutane	35.1	125	2.3×10^{-3}	13
$EtMe_2C$—	2-Methylbutane	37.2	151	1.5×10^{-2}	72
$EtMe_2C$—	Dichlorodifluoromethane	31.4	121	1.3×10^{-2}	13
$MeEt_2C$—	2-Methylbutane	40.6	184	0.10	72
Me_2CH—	Dichlorodifluoromethane	33.5	105	5.4×10^{-4}	73
Me_2CH—	Cyclopropane	33.0	63	4.7×10^{-6}	74
Me_2CD—	Dichlorodifluoromethane	33.5	138	2.9×10^{-2}	73
$PrMe_2C$—	2-Methylpentane	37.2	163	6.3×10^{-2}	72
Me_2CHMe_2C—	2,3-Dimethylbutane	34.3	142	3.9×10^{-2}	72
Me_2CHMe_2C—	2-Methylbutane	36.0	138	6.4×10^{-3}	13
Me_3CMe_2C—	2,2,3-Trimethylbutane	36.4	159	6.3×10^{-2}	72
$Me_3CCH_2Me_2C$—	Dichlorodifluoromethane	32.6	130	1.9×10^{-2}	13
cyclo-[$(CH_2)_4CH$—]	Dichlorodifluoromethane	31.4	59	7.6×10^{-6}	74
cyclo-[$(CH_2)_4CH$—]	Cyclopropane	31.0	84	1.9×10^{-4}	74
cyclo-[$(CH_2)_5MeC$—]	Dichlorodifluoromethane	29.3	146	0.94	13
cyclo-[$(CH_2)_4MeC$—]	Dichlorodifluoromethane	33.5	125	6.0×10^{-3}	13
$PhMe_2C$—	Cumene	46.9	201	1.8×10^{-2}	72
$PhMe_2C$—	2-Methylbutane	44.3			5
$PhMe_2C$—	Dichlorodifluoromethane	38.5	134	8.8×10^{-4}	13

6.3.2 Decay of Tetroxides

Irreversible decay of tetroxide occurs as the result of the dissociation of the O—OR bond to produce of $RO_3^{\bullet}$ and $RO^{\bullet}$ radicals:

$$\text{ROOOOR} \rightarrow \text{RO}_3^{\bullet} + \text{RO}^{\bullet}$$

The results of the estimation of k_d are collected in Table 6.13.

6.3.3 Thermochemistry of Tetroxides

According to quantum chemical calculations and the experimental findings (see Tables 6.11 and 6.12), the BDEs were found to be the following:[16]

$$\begin{aligned} D(\text{ROO—OOR}) &= 35.0 \pm 2.3\ \text{kJ mol}^{-1} \\ D(\text{ROOO—OH}) &= 105.0 \pm 2.0\ \text{kJ mol}^{-1} \\ D(\text{ROOO—OR}) &= 87.0 \pm 5.8\ \text{kJ mol}^{-1} \\ D(\text{ROOOO—R}) &= 266.1 \pm 5.0\ \text{kJ mol}^{-1} \end{aligned}$$

TABLE 6.13 The Rate Constants and Activation Energies of Tetroxide Decay for ROOOOR → $RO_3^{\bullet}$ + $RO^{\bullet}$

R—	Solvent	E (kJ mol^{-1})	log A, A (s^{-1})	k_d (200 K) (s^{-1})	Reference
$Me_2CH—$	Dichlorodifluoromethane	40.2	10.3	0.63	73
$Me_3C—$	Dichlorodifluoromethane	71.5	16.7	1.06×10^{-2}	3
$Me_3C—$	2-Methylbutane	73.2	16.6	3.04×10^{-3}	3
$Me_2PrC—$	2-Methylpentane	76.1	19.6	0.53	1
$BuCH_2CHMe—$	Heptane	44.8	11.6	0.79	72
$Me_3CMe_2C—$	2,2,3-Trimethylbutane	67.8	17.5	0.21	72
cyclo-$[(CH_2)_4CH—]$	Cyclopentane	41.8	12.3	24.2	3
cyclo-$[(CH_2)_5CH—]$	Cyclohexane	40.6	11.6	9.9	3
$PhMe_2C—$	Cumene	69.0	17.1	0.12	3

TABLE 6.14 The Enthalpies of Formation for Tetroxides[a]

Tetroxide	$-\Delta H^0$ (kJ mol^{-1})	Tetroxide	$-\Delta H^0$ (kJ mol^{-1})
HOOOOH	136.0	EtOOOOMe	156.5
MeOOOOH	131.0	$Me_3COOOOMe$	231.4
EtOOOOH	163.2	EtOOOOEt	192.9
$Me_3COOOOH$	246.0	$Me_3COOOOEt$	265.7
MeOOOOMe	125.5	$Me_3COOOOCMe_3$	349.0

[a] See Ref. 16.

For the enthalpies of formation of tetroxides calculated by the increment methods,[18] see Table 6.14.

REFERENCES

1. *The Chemistry of Peroxides*, S. Patai (Ed.), John Wiley & Sons, Inc., Chichester, U.K., 1983.
2. *Organic Polyoxides*, W. Ando (Ed.), John Wiley & Sons, Inc., New York, 1992.
3. P. D. Bartlett and G. Guaraldi, *J. Am. Chem. Soc.* **89**, 4799 (1967).
4. S. W. Benson, *J. Am. Chem. Soc.* **86**, 3922 (1964).
5. P. D. Bartlett and P. Gunther, *J. Am. Chem. Soc.* **88**, 3288 (1966).
6. N. A. Milas and B. Plesnicar, *J. Am. Chem. Soc.* **90**, 4450 (1968).
7. N. A. Milas and S. M. Djokic, *Chem. Ind.* **9**, 405 (1962).
8. N. A. Milas and S. M. Djokic, *J. Am. Chem. Soc.* **84**, 3098 (1962).
9. P. D. Bartlett and M. Lahav, *Isr. J. Chem.* **10**, 101 (1972).
10. W. A. Pryor and M. E. Kurz, *Tetrahedron Lett.* **697** (1978).
11. M. E. Kurz and W. A. Pryor, *J. Am. Chem. Soc.* **100**, 7953 (1978).
12. T. Mill and R. S. Stringham, *J. Am. Chem. Soc.* **90**, 1062 (1968).
13. K. Adamic, J. A. Howard, and K. U. Ingold, *Can. J. Chem.* **47**, 3803 (1969).
14. J. Bennett, G. Brunton, and R. Summers, *J. Chem. Soc. Perkin Trans.* **2**, 981 (1980).
15. P. Ase, W. Bock, and A. Snelson, *J. Phys. Chem.* **90**, 2099 (1986).
16. S. L. Khursan, *Organic polyoxides*, Doctor Diss. Thesis, (Russian), Institute of Organic Chemistry, Ufa, Russia, 1999.
17. S. L. Khursan and V. V. Shereshovets, *Izv. AN, Ser. Khim.* 2190 (1996).
18. S. W. Benson, *Thermochemical Kinetics*, John Wiley & Sons, Inc., New York, 1976.
19. S. L. Khursan, V. V. Shereshovets, N. M. Shislov, A. F. Khalizov, A. I. Voloshin, and V. D. Komissarov, *React. Kinet. Catal. Letters*, **52**, 249 (1994).
20. S. L. Khursan, V. V. Shereshovets, A. F. Khalizov, A. I. Voloshin, V. D. Komissarov, and V. P. Kazakov, *React. Kinet. Catal. Lett.* **51**, 389 (1993).
21. A. F. Khalizov, S. L. Khursan, and V. V. Shereshovets, *Izv. AN, Ser. Khim.* 61 (1999).
22. S. L. Khursan, A. F. Khalizov, and V. V. Shereshovets, *Izv. AN, Ser. Khim.* 924 (1997).
23. H. M. White and P. S. Bailey, *J. Org. Chem.* **30**, 3037 (1965).
24. C. C. Price and A. L. Tumolo, *J. Am. Chem. Soc.* **86**, 4691 (1964).
25. M. C. Whitting, A. J. Bolt, and J. H. Parish, *Adv. Chem. Ser.* **77**, 4 (1968).
26. J. D. Austin and L. Spialter, *Adv. Chem. Ser.* **77**, 26 (1968).
27. J. F. Batterbee and P. S. Bailey, *J. Org. Chem.* **32**, 3899 (1967).
28. G. A. Hamilton, B. S. Ribner, and T. M. Hellman, *Adv. Chem. Ser.* **77**, 15 (1968).
29. P. Deslongshamps and C. Morean, *Can. J. Chem.* **49**, 2465 (1971).
30. V. V. Shereshovets, S. L. Khursan, V. D. Komissarov, and G. A. Tolstikov, *Russ. Chem. Rev.* **70**, 123 (2001).
31. R. W. Murray, W. C. Lumma, and J. W.-P. Lin, *J. Am. Chem. Soc.* **92**, 3205 (1970).

32. F. E. Stary, D. E. Emge, and R. W. Murray, *J. Am. Chem. Soc.* **98**, 1880 (1976).
33. N. N. Kabal'nova, *Organic hydrotrioxides as precursor of singlet oxygen*, Ph.D. Thesis, (Russian), Institute of Organic Chemistry, Ufa, USSR, 1988.
34. B. Plesnicar, F. Kovac, and M. Schara, *J. Am. Chem. Soc.* **110**, 214 (1988).
35. F. Kovac and B. Plesnicar, *J. Chem. Soc., Chem. Commun.* **122** (1978).
36. F. Kovac and B. Plesnicar, *J. Am. Chem. Soc.* **101**, 2677 (1979).
37. *Oxygen and Oxy-Radicals in Chemistry and Biology*, M. A. Rodgers and E. L. Powers (Eds.), Academic Press, New York, 1981.
38. E. M. Kuramshin, L. G. Kulak, S. S. Zlotskii, and D. L. Rakhmankulov, *Zh. Org. Chem.* **22**, 1986 (1986).
39. V. V. Shereshovets, F. A. Galieva, N. N. Kabalnova, N. M. Shishlov, R. R. Sadykov, V. D. Komissarov, and G. A. Tolstikov, *Izv. AN SSSR, Ser. Khim.* 317 (1986).
40. N. Ya. Shafikov, R. A. Sadykov, V. V. Shereshovets, A. A. Panasenko, and V. D. Komissarov, *Izv. AN SSSR, Ser. Khim.* 1923 (1981).
41. V. V. Shereshovets, F. A. Galieva, and V. D. Komissarov, *Izv. AN SSSR, Ser. Khim.* 304 (1988).
42. N. Ya. Shafikov, *Kinetics, products and mechanism of ethanol ozonolysis*, Ph.D. Thesis, (Russian), Institute of Organic Chemistry, Ufa, USSR, 1985.
43. V. V. Shereshovets, N. N. Kabal'nova, V. D. Komissarov, and G. A. Tolstikov, *Izv. AN SSSR, Ser. Khim.* 1660 (1985).
44. W. A. Pryor, N. Ohto, and D. F. Church, *J. Am. Chem. Soc.* **104**, 5813 (1982).
45. W. A. Pryor, N. Ohto, and D. F. Church, *J. Am. Chem. Soc.* **105**, 3614 (1983).
46. M. Zarth and A. de Meijere, *Chem. Ber.* **118**, 2429 (1985).
47. E. J. Corey, M. M. Mehrotra, and A. U. Khan, *J. Am. Chem. Soc.* **108**, 2472 (1986).
48. B. I. Tarunin, V. N. Tarunina, and Yu. A. Kurskiy, *Zh. Obsh. Khim.* **58**, 1060 (1988).
49. B. Plesnicar, J. Cerkovnik, J. Koller, and F. Kovac, *J. Am. Chem. Soc.* **113**, 4946 (1991).
50. M. Koenig, J. Barrau, and N. Ben Hamida, *J. Organomet. Chem.* **356**, 133 (1988).
51. T. V. Yagodovskaya, D. Yu. Zhogin, and L. I. Nekrasov, *Zh. Fiz. Khim.* **49**, 2683 (1975).
52. G. A. Schembelov, T. V. Yagodovskaya, and L. I. Nekrasov, *Zh. Fiz. Khim.* **50**, 772 (1976).
53. M. P. Khadzhi-Ogly, I. P. Gloriozov, T. V. Yagodovskaya, and L. 1. Nekrasov, *Zh. Fiz. Khim.* **57**, 1910 (1983).
54. L. Radom, W. J. Hehre, and J. A. Pople, *J. Am. Chem. Soc.* **93**, 289 (1971).
55. L. Radom, W. J. Hehre, and J. A. Pople, *J. Am. Chem. Soc.* **94**, 2371 (1972).
56. R. J. Blint and M. D. Newton, *J. Chem. Phys.* **95**, 6220 (1973).
57. B. Plesnicar, S. Kaiser, and A. Azman, *J. Am. Chem. Soc.* **95**, 5476 (1973).
58. B. Plesnicar, D. Kocjan, S. Murovec, and A. Azman, *J. Am. Chem. Soc.* **98**, 3143 (1976).
59. D. Cremer, *J. Chem. Phys.* **69**, 4456 (1978).
60. C. F. Jackels and D. H. Phillips, *J. Chem. Phys.* **84**, 5013 (1986).
61. C. Gonzalez, J. Theisen, L. Zhu, H. B. Schlegel, W. L. Hase, and E. W. Kaiser, *J. Phys. Chem.* **95**, 6784 (1991).

62. J. Koller and B. Plesnicar, *J. Am. Chem. Soc.* **118**, 2470 (1996).
63. J. Koller, M. Hodoscek, and B. Plesnicar, *J. Am. Chem. Soc.* **112**, 2124 (1990).
64. T. P. W. Jungkamp and J. H. Seinfeld, *Chem. Phys. Lett.* **257**, 15 (1996).
65. T. H. Lay and J. W. Bozzelli, *J. Phys. Chem. A*, **101**, 9505 (1997).
66. S. L. Khursan and V. V. Shereshovets, *Izv. AN, Ser. Khim.* 1129 (1996).
67. V. V. Shereshovets, F. A. Galieva, R. A. Sadykov, V. D. Komissarov, and G. A. Tolstikov, *Izv. AN SSSR, Ser. Khim.* 2208 (1989).
68. E. J. Cerkovnik and B. Plesnicar, *J. Am. Chem. Soc.* **115**, 12169 (1993).
69. P. T. Chou, M. L. Martinez, and S. L. Studer, *Chem. Phys. Lett.* **174**, 46 (1990).
70. J. A. Howard, *Adv. Free Radical Chem.* **4**, 49 (1972).
71. *Comprehensive Chemical Kinetics*, C. H. Bamford and C. F. H. Tipper (Eds.), Elsevier, Amsterdam, The Netherlands, Vol. 16, 1980.
72. J. E. Bennett, D. M. Brown, and B. Mile, *Trans. Faraday Soc.* **66**, 397 (1970).
73. E. Furimsky, J. A. Howard, and J. Selwyn, *Can. J. Chem.* **58**, 677 (1980).
74. J. E. Bennett, G. Brunton, J. R. L. Smith, T. M. F. Salmon, and D. J. Waddington, *J. Chem. Soc.,Faraday Trans. I*, **83**, 2421 (1987).

Handbook of Free Radical Initiators. E.T. Denisov, T.G. Denisova, T.S. Pokidova
Copyright © 2003 John Wiley & Sons, Inc.
ISBN: 0-471-20753-5

7

AZO COMPOUNDS

The first azo compounds (sinonime shell diazenes) were synthesized by Thiele and Heuser at the end of the nineteenth century.[1] They found the various experimental and technological applications only in the last 50 to 70 years of the twentieth century. Which made development of their chemistry necessary. Polymer chemistry found an important application for azo compounds to be used as initiators. Azo compounds of different structures can be used over a wide range of temperatures (330–450 K) where they can be conveniently used as initiators.[2–5] They can produce thermo- and photoinitiation of free radicals. Azo compounds of the general structure RMeXCN=NCXMeR are resistant toward induced (chain) decomposition. They do not participate in reactions of chain transfer in polymerization.

7.1 SYNTHESIS AND STRUCTURE OF AZO COMPOUNDS

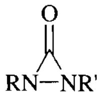
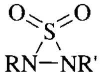
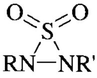
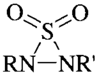
The basic reactant for the synthesis of azo compounds is hydrazine or its derivatives.[6] The main reactions for the synthesis are given in Table 7.1 and the physical properties of selected azo compounds are listed in Table 7.2.

Azo compounds have an N=N double bond and because of the sp^2-hybrid state of the nitrogen atoms they exist in two geometrical isomers, the trans (E) and cis (Z) forms. The high chemical reactivity of the azo linkage is closely related to the nitrogen atom. The main driving force of azo compound decomposition is the extreme differences in BDE between doubly bound nitrogen atoms (~400 kJ mol^{-1}) and two triple bonded atoms (~945 kJ mol^{-1}).[2] The interatomic distances (m) and angles (degrees) in azo compounds are given in Table 7.3.[2,44–53]

TABLE 7.1 Methods of Synthesis of Some Azo Compounds

Reaction	References
Oxidation of 1,2-Dialkylhydrazines	
$2RR^1C=O + NH_2NH_2 \rightarrow RR^1C=NN=CRR^1 + 2H_2O$ $RR^1C=NN=CRR^1 + \text{Reductant} \rightarrow RR^1CHNHNHCHRR^1$ $RR^1CHNHNHCHRR^1 + \text{Oxidant} \rightarrow RR^1CHN=NCHRR^1$ $(R, R^1 = \text{alkyl, aryl; } R = H, \text{ and } R^1 = \text{alkyl or aryl})$	7–10
$RR^1C=NN=CRR^1 + 2HCN \rightarrow RR^1C(CN)NHNHC(CN)RR^1$ $RR^1C(CN)NHNHC(CN)RR^1 + \text{Oxidant} \rightarrow R^1RC(CN)N=NC(CN)RR^1$ $(R, R^1 = \text{alkyl, aryl; } R = H \text{ and } R^1 = \text{alkyl or aryl})$	11
$Me_2C(CN)N=NC(CN)Me_2 + 2MeOH + 2H_2O \rightarrow$ $Me_2C(CO_2Me)N=NC(CO_2Me)Me_2 + 2NH_3$ Catalyst = acid $Me_2C(CO_2Me)N=NC(CO_2Me)Me_2 + LiAlH_4 \rightarrow$ $Me_2C(CH_2OH)N=NC(CH_2OH)Me_2$ $Me_2C(CH_2OH)N=NC(CH_2OH)Me_2 + MeC(O)OC(O)Me \rightarrow$ $Me_2C(CH_2OC(O)Me)N=NC(CH_2OC(O)Me)Me_2$	1,12,13
$Me_2C=NN=CMe_2 + Cl_2 \rightarrow Me_2ClCN=NC(Cl)Me_2$ $Me_2ClCN=NCClMe_2 + 2X^- \rightarrow Me_2XCN=NCXMe_2 + 2Cl^-$ $X = SCN, MeCO_2, MeCOS, PhS, CN, N_3, PhO, Me, MeO, MeS, AlR_3$	14–20
$MeNHNH_2 + PhC(O)Me \rightarrow PhMeC=NNHMe + H_2O$ $PhMeC=NNHMe + \text{Reductant} \rightarrow PhMeCHNHNHMe$ $PhMeCHNHNHMe + \text{Oxidant} \rightarrow PhMeCHN=NMe$	21
$Ph\ NHNH_2 + Ph_2C=O \rightarrow PhNHN=CPh_2 + H_2O$ $PhNHN=CPh_2 + \text{Reductant} \rightarrow PhNHNHCHPh_2$ $PhNHNHCHPh_2 + \text{Oxidant} \rightarrow PhN=NCHPh_2$	22
$RR^1C=NN=CRR^1 + PhMgBr/H_2O \rightarrow R^1RPhCNHN=CRR^1$ $R^1RPhCNHN=CRR^1 + \text{Reductant} \rightarrow R^1RPhCNHNHCHRR^1$ $R^1RPhCNHNHCHRR^1 + \text{Oxidant} \rightarrow R^1RPhCN=NCHRR^1$ $RR^1C=NN=CRR^1 + \text{Reductant} \rightarrow RR^1CHNHN=CRR^1$ $RR^1CHNHN=CRR^1 + (COOH)_2 \cdot 2H_2O \rightarrow$ $RR^1CHNHNH_2 \cdot (COOH)_2 + RR^1C(O)$ $RR^1CHNHNH_2 \cdot (COOH)_2 + 2NaOH \rightarrow$ $RR^1CHNHNH_2 + (COONa)_2 + 2H_2O$ $RR^1CHNHNH_2 + R^2R^3C=O \rightarrow RR^1CHNHN=CR^2R^3 + H_2O$ $RR^1CHNHN=CR^2R^3 + \text{Reductant} \rightarrow RR^1CHNHNHCHR^2R^3$ $RR^1CHNHNHCHR^2R^3 + \text{Oxidant} \rightarrow RR^1CHN=NCHR^2R^3$ $(R, R^1, R^2$ and R^3 are combination of H and alkyl groups.)	23–27
$RC(O)OR + NH_2NH_2 \rightarrow RC(O)NHNH_2 + ROH$ $RC(O)NHNH_2 + RR^1C=O \rightarrow RC(O)NHN=CRR^1 + H_2O$ $RC(O)NHN=CRR^1 + \text{Reductant} \rightarrow RCH_2NHNHCHRR^1$ $RCH_2NHNHCHRR^1 + \text{Oxidant} \rightarrow RCH_2N=NCHRR^1$ $(R, R^1 = \text{alkyl})$	28

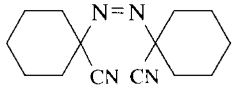
TABLE 7.1 (*continued*)

Reaction	References
Oxidation of Amines	
$2R^1R^2R^3CNH_2 + IF_5(\text{pyridine}) \rightarrow R^1R^2R^3CN{=}NCR^1R^2R^3 + 4HF + IF$ (R^1, R^2, R^3 = alkyl, aryl, cycloalkyl, C≡N)	11,29
Oxidation of Ureas	
$RNHC(O)NHR^1 + 1.Me_3COCl/2.Me_3CO^-K^+ \rightarrow$  $\overset{\overset{O}{\|}}{RN{-}NR'}$  $\overset{\overset{O}{\|}}{RN{-}NR'} + HCl \rightarrow [RNHN(CO_2H)R^1] \rightarrow RNHNHR^1$ $RNHNHR^1 + \text{Oxidant} \rightarrow RN{=}NR^1$ (R, R^1 = alkyl,aryl)	30–32
Oxidation of N,N′-Dialkylsulphamides	
$RNHSO_2NHR + NaOH/NaOCl \rightarrow$  $\overset{O\ S\ O}{RN{-}NR'}$  $\overset{O\ S\ O}{RN{-}NR'} + 2H_2O \rightarrow RNHNHR + H_2SO_4$  $\overset{O\ S\ O}{RN{-}NR'} + \text{Oxidant} \rightarrow RN{=}NR$ (R = alkyl, aryl)	33–40
Other Methods	
$PhN{=}NCMe_2Cl + HNMe_2 \rightarrow PhN{=}NCMe_2NMe_2 + HCl$	41
$Me_2C{=}NNHR + PhN_2Cl \rightarrow PhN{=}NCMe_2N{=}NR + HCl$	42

Azo compounds consume UV light in the 22000–30000-cm^{-1} range. The lowest energy transition is that of the ($n \rightarrow \pi^*$) type, which is the result of a strong interaction between nonbonding and bonding nitrogen orbitals. The characteristics of the UV absorption spectrum of azo compounds are given in Table 7.4.

Irradiation of the (E)- azo compounds leads to isomerization to the (Z)- azo compounds. For example, (E)- dimethyldiazene is transformed into the (Z) isomer with a quantum yield $\Phi = 0.42$ (benzene, 298 K), and

TABLE 7.2 Physical Properties of Selected Azo Compounds[a]

Compound	CAS Registry Number	MW	bp (K)	mp (K)	ρ ($kg\,m^{-3}$)
(E)-Diazene					
Dimethyl-, MeN=NMe	4143-41-3	58.08	274.5	195	743
Bis(trifluoromethyl)-, $F_3CN{=}NCF_3$	372-63-4	166.03	241.4	135	
Dipropyl-, PrN=NPr	821-67-0	114.16	387		
Dibutyl-, BuN=NBu	2159-75-3	142.24	333 (18 Torr)		
Methylphenyl-, MeN=NPh	4406-66-0	120.15	333 (15 Torr)		
Ethylphenyl-, EtN=NPh	935-08-0	134.18	450		962.8
Phenyl(triphenylmethyl)-, $PhN{=}NCPh_3$	981-18-0	348.45		384.0	
2,2′-Azobis[2-methylpropanenitrile], $Me_2C(CN)N{=}NC(CN)Me_2$	78-67-1	140.16			
1,1′-Azobis-[cyclohexanecarbonitrile], 	2094-98-6	244.34		373	

---

[a] See Ref. 43.

(E)-methylethyldiazene is transformed into the (Z) isomer with a quantum yield $\Phi = 0.50$ (water, 298 K).[3]

Due to symmetric configuration the (E)- azo compounds do not have a dipole moment, but the (Z) isomers do. For example, the dipole moment of (Z)-dimethyldiazene is $\mu = 3.2$ D.[3]

7.2 THERMOCHEMISTRY OF AZO COMPOUNDS

The enthalpies of (E)- azo compound formation are presented in Table 7.5. The transformation of the (E) isomer into the (Z) isomer is accompanied by an increase in enthalpy due to formation of a compound with strained configuration. The strain energy varies from 25 to 50 $kJ\,mol^{-1}$.[3]

Diazenes	Methyl-	Ethylmethyl-	1-Bicyclo-[2.2.2]octyl-	1,1,3,3-Tetramethylbutyl-
Strain energy ($kJ\,mol^{-1}$)	24.0	33.5	52.7	44.8

TABLE 7.3 Bond Lengths and Bond Angles (φ) in Azo Compounds

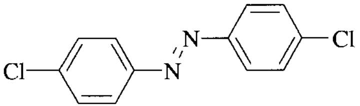
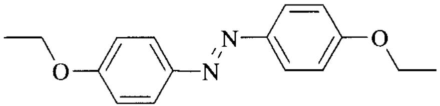
Compound	Bond Length (10^{-10} m)		Bond Angles (φ) (°)	References
Diazene,	N–N	C–N	NNH, NNC, NNF	
dihydro-, (*E*)-HN=NH	1.238		109	45
Difluoro-, (*E*)-FN=NF	1.230	1.396	105.5	46
Difluoro-, (*Z*)-FN=NF	1.214	1.410	114.4	46
Dimethyl-, (*E*)-MeN=NMe	1.254	1.474	111.9	47
Methyltrifluoromethyl-, (*E*)-MeN=NCF$_3$	1.219	1.476 (F$_3$C-N) 1.440 (Me–N)	126.2 (F$_3$CNN) 110.5 (MeNN)	47
Bis(trifluoromethyl)-, (*Z*)-F$_3$CN=NCF$_3$	1.236	1.490	133	47
Diphenyl,- (*E*)-PhN=NPh	1.247	1.434	113.6	48
Diphenyl,- (*Z*)-PhN=NPh	1.253	1.443	121.9	49
Bis(4-chlorophenyl)-, (*E*)-	1.252	1.443	112.6	50
				
Bis(4-ethoxyphenyl)-, (*E*)-	1.255	1.426	114.3	51
				
2,2′-Azobis[2-methylpropanenitrile], (*E*)-Me$_2$C(CN)N=NC(CN)Me$_2$	1.220	1.497	114.5	52,53
2,2′-Azobis[2-ethylbutanenitrile], (*E*)-Et$_2$C(CN)N=NC(CN)Et$_2$	1.218	1.488	114.8	52,53

TABLE 7.4 Absorption Spectrum of Azo Compounds[a]

(E)-Diazene	ν_{max} ($n \rightarrow \pi$) (cm^{-1})	ε (L mol^{-1} cm^{-1})	ν_{max} ($n \rightarrow \sigma^*$) (cm^{-1})	ν_{max} ($\pi \rightarrow \pi^*$) (cm^{-1})
Dimethyl-, (E)- MeN=NMe	29410	5	54000	90000
Diethyl-, (E)- EtN=NEt	28170	10	53000	
Dipropyl-, (E)- PrN=NPr	28090	8	52000	
Dibutyl-, (E)- BuN=NBu	27210	13.5	50000	
Diphenyl-, (E)- PhN=NPh	22600	510		31300
Diphenyl-, (Z)- PhN=NPh	23100	1518		35700

[a] See Ref. 2.

TABLE 7.5 The Formation Enthalpies (ΔH_f^0) of Selected (E)- Azo Compounds in the Gas and Condensed Phases

(E)-Diazene	ΔH_f (cond) (kJ mol^{-1})	ΔH_f^0 (g) (kJ mol^{-1})	References
Butylmethyl-, MeN=NBu	42.5 ± 2.2	78.9 ± 2.2	54
Dipropyl-, PrN=NPr	11.5 ± 3.5	51.3 ± 3.5	55
Bis(1-methylethyl)-, $Me_2CHN{=}NCHMe_2$	−0.3 ± 3.5	35.6 ± 3.6	55
Dibutyl-, BuN=NBu	−40.1 ± 3.8	8.8 ± 3.8	50
Bis(1,1-dimethylethyl)-, $Me_3CN{=}NCMe_3$	−74.7 ± 3.6	−35.6 ± 3.6	55
Bis(1,1-dimethylethyl)-, $Me_3CN{=}NCMe_3$	−75.5 ± 2.7	−36.4 ± 2.8	56
1,1-Dimethylethyl-(1,1,3,3-tetramethylbutyl)-, $Me_3CN{=}NCMe_2CH_2CMe_3$	−172.8 ± 5.4	−119.2 ± 5.4	55
Bis(1,1,3,3-tetramethylbutyl)-, $Me_3CCH_2CMe_2N{=}NCMe_2CH_2CMe_3$	−263.2 ± 9.2	−196.6 ± 9.2	55
2,2′-Asobis[2-methylpropanenitrile], $Me_2C(CN)N{=}NC(CN)Me_2$	228.9		57,58

7.3 DECOMPOSITION OF AZO COMPOUNDS

Decomposition of azo compounds into dinitrogen and two alkyl radicals

$$RN{=}NR \rightarrow R^{\bullet} + N_2 + R^{\bullet}$$

is an endothermic reaction. The activation energy (E) of decomposition is sufficiently higher than the enthalpy of reaction (ΔH).

R (kJ mol^{-1})	Pr	Me$_2$CH	Bu	Me$_3$C
$\Delta H_f(RN_2R)$[a]	51.3	35.6	8.8	−35.6
$\Delta H_f(R^\bullet)$[b]	100.0	90.0	81.0	48.0
ΔH	148.7	144.4	153.2	131.6
E	199.2	171.1	222.5	179.5

[a] See Ref. 54 and 55.
[b] See Ref. 59.

Two mechanisms of azo compound decomposition are discussed extensively in the literature: concerted decomposition with simultaneous dissociation of two C−N bonds

$$RN{=}NR \rightarrow R\cdots N{=}N\cdots R \rightarrow R^\bullet + N_2 + R^\bullet$$

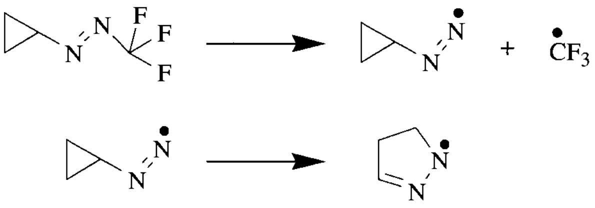
and nonconcerted decomposition with dissociation of one C−N bond succeeded by the fast decomposition of the unstable RN=N$^\bullet$ radical.[2,3,60]

$$RN{=}NR \rightarrow R^\bullet + RN{=}N^\bullet$$

$$RN{=}N^\bullet \rightarrow R^\bullet + N_2$$

The intermediate RN=N$^\bullet$ radicals were not detected by EPR even at low temperatures (70–150 K) in photolysis of azo compounds. Theoretical analysis of the thermal decomposition of azomethane proved that the concerted mechanism of decomposition is energetically preferable.[2] The concerted decomposition of unsymmetrical azo compounds $R^1N{=}NR^2$ should depend on the structure of R^1 as well as R^2 radicals, and therefore the rate constant of $R^1N{=}NR^2$ decomposition $k_d(R^1N_2R^2)$ should differ from $k_d(R^1N_2R^1)$ and $k_d(R^2N_2R^2)$. In the case of the nonconcerted mechanism of azo compound decomposition, one can expect that $k_d(R^1N_2R^2)$ will be close to $k_d(R^2N_2R^2)$, where R^2 radical is more stabilized than R^1, that is, $(D(R^2{-}H) < D(R^1{-}H))$. It is seen that in most cases of $R^1N_2R^2$ decomposition one is faced with cases of $R^1N_2R^2$ decomposition by the concerted mechanism (see Table 7.6). So the concerted mechanism of decomposition is valid for most azo compounds.[2,3,60]

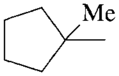
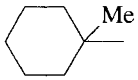
The nonconcerted mechanism of decomposition was seen by Szwarc and co-workers.[61] They studied the photolytic decomposition of cyclopropyltrifluoromethyldiazene in the gas phase and 2,3-dimethylbutane in solution. They found 2-pyrazoline with yield 15–20% among the products. The apparent mechanism follows:



Some other azo compounds that are decomposed by a nonconcerted mechanism are known. It is considered that decomposition of symmetrical azo compounds occurs via a concerted mechanism and some unsymmetrical azo compounds are decomposed by concerted and nonconcerted mechanisms simultaneously. Phenyl-substituted azo compounds are decomposed by a nonconcerted mechanism.[3]

The linear dependence between the activation energy of (E) azo compound RN_2R decomposition and the BDE of the R–H bond [D(R-H)] was established.[3] Rate constants of azo compound decomposition in the gas phase and hydrocarbon solvents are similar (see Table 7.6). The mean value for the rate constant of 2,2′-asobis[2-methylpropanenitrile] (AIBN) decomposition in hydrocarbon and aromatic solutions was recommended to be $k_d = 10^{15} \times \exp(-127.5/RT)\ s^{-1}$.[62] The values of the activation energies and rate constants of azo compound decomposition in the gas and liquid phases is seen in Tables 7.7–7.13.

TABLE 7.6 The Comparison of Decomposition Rate Constants (T = 350 k) of Symmetrical and Unsymmetrical Azo Compounds[a]

R^1	R^2	k_{11} ($R^1N_2R^1$) ($L\,mol^{-1}\,s^{-1}$)	k_{12} ($R^1N_2R^2$) ($L\,mol^{-1}\,s^{-1}$)	log (k_{11}/k_{12})
$CH_2{=}CHCH_2$	Me	9.96×10^{-8}	2.54×10^{-8}	0.59
$CH_2{=}CHCH_2$	Pr	9.96×10^{-8}	3.72×10^{-8}	0.43
$CH_2{=}CHCMe_2$	Me	4.03×10^{-3}	5.20×10^{-7}	3.89
$CH_2{=}CHCMe_2$	Me_2CH	4.03×10^{-3}	8.31×10^{-6}	2.69
$CH_2{=}CHCMe_2$	Me_3C	4.03×10^{-3}	1.11×10^{-4}	1.56
MePhCH	Me	3.00×10^{-6}	2.40×10^{-9}	3.10
MePhCH	Me_2CH	3.00×10^{-6}	4.18×10^{-8}	1.86
Me_2PhC	Me_2CH	1.36×10^{-3}	3.13×10^{-7}	3.64
Me_2PhC		1.36×10^{-3}	1.24×10^{-5}	2.04
Me_2PhC		1.36×10^{-3}	1.31×10^{-5}	2.02
Me_2PhC	$PhCH_2$	1.36×10^{-3}	1.29×10^{-7}	4.02
$Me_2(CN)C$	Me_3C	6.77×10^{-5}	6.31×10^{-6}	1.03
$Me_2(CN)C$	Ph	6.77×10^{-5}	3.29×10^{-10}	5.31
$Me_2(CN)C$	1-Adamantyl	6.77×10^{-5}	7.85×10^{-7}	1.94

[a] See Ref. 3.

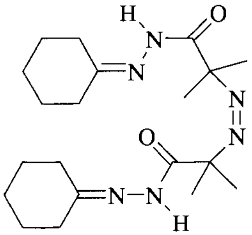
TABLE 7.7 The Rate Constants for Thermal Decay of Symmetrical Alkyl *E*-Azo Compounds in the Gas Phase and Different Solvents

(*E*)-Diazene	Solvent	*T* (K)	*E* (kJ mol^{-1})	log *A*, *A* (s^{-1})	k_d (453 K) (s^{-1})	Reference
Dimethyl-, MeN=NMe	Gas phase	552–600	214.2	16.50	6.33×10^{-9}	63
Dimethyl-, MeN=NMe	Gas phase	563–603	219.7	16.50	1.47×10^{-9}	64
Dimethyl-, MeN=NMe	Gas phase	550–600	219.2	16.50	1.68×10^{-9}	65
Dimethyl-, MeN=NMe	Gas phase	463–603	210.0	15.90	4.85×10^{-9}	66
Dimethyl-, MeN=NMe	Gas phase	502–594	214.2	15.7	1.00×10^{-9}	67
Dimethyl-, MeN=NMe	Gas phase	565–609	219.7	16.55	1.65×10^{-9}	68
Dimethyl-, MeN=NMe	Gas phase	663–723	192.5	14.01	6.51×10^{-9}	69
Dimethyl-, MeN=NMe	Gas phase	663–723	231.8	17.30	3.73×10^{-10}	70
Dimethyl-, MeN=NMe	Gas phase	800–1300	221.7	17.02	2.86×10^{-9}	71
Bis(trideuteriummethyl)-, $D_3CN{=}NCD_3$	Gas phase	529–570	212.1	15.49	1.08×10^{-9}	72
Bis(trifluoromethyl)-, $F_3CN{=}NCF_3$	Gas phase	690–760	202.9	13.95	3.58×10^{-10}	73
Bis(trifluoromethyl)-, $F_3CN{=}NCF_3$	Gas phase	572–634	220.5	15.10	4.73×10^{-11}	74
Bis(trifluoromethyl)-, $F_3CN{=}NCF_3$	Gas phase	600–650	220.9	15.32	7.06×10^{-11}	75
Diethyl-, EtN=NEt	Gas phase	453	202.9	15.7	2.01×10^{-8}	76
Diethyl-, EtN=NEt	Gas phase	453	197.5	15.10	2.12×10^{-8}	77
Diethyl-, EtN=NEt	Gas phase	740–900	207.9	16.40	2.68×10^{-8}	78
Diethyl-, EtN=NEt	Gas phase	553–673	186.2	14.21	5.49×10^{-8}	79
Dipropyl-, PrN=NPr	Gas phase	503–673	191.2	14.60	3.58×10^{-8}	80
Bis(1-methylethyl)-, $Me_2CHN{=}NCHMe_2$	Gas phase	503–673	170.7	13.68	9.93×10^{-7}	80
Bis(1-methylethyl)-, $Me_2CHN{=}NCHMe_2$	Gas phase	523–563	171.1	13.75	1.05×10^{-6}	81
Bis(1-methylethyl)-, $Me_2CHN{=}NCHMe_2$	Gas phase	625–800	200.4	16.60	3.11×10^{-7}	78
Di-2-propenyl-, $CH_2{=}CHCH_2N{=}NCH_2CH{=}CH_2$	Gas phase	453	151.0	15.54	1.34×10^{-2}	82
Dibutyl-, BuN=NBu	Gas phase	596–653	222.5	17.71	1.13×10^{-8}	83

(*continued overleaf*)

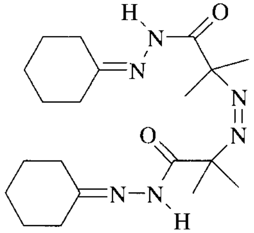
TABLE 7.7 (*continued*)

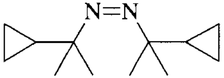
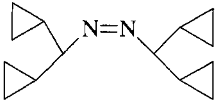
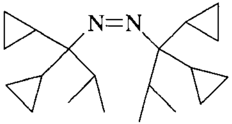
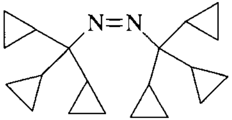
(E)-Diazene	Solvent	T (K)	E (kJ mol^{-1})	log A, A (s^{-1})	k_d (453 K) (s^{-1})	Reference
Bis(1-methylpropyl)-, $EtCHMeN{=}NCHMeEt$	Gas phase	539–618	202.5	17.28	8.52×10^{-7}	83
Bis(2-methylpropyl)-, $Me_2CHCH_2N{=}NCH_2CHMe_2$	Gas phase	539–618	205.0	16.23	3.91×10^{-8}	83
Bis(1,1-dimethylethyl)-, $Me_3CN{=}NCMe_3$	Gas phase	500–700	179.1	16.40	5.60×10^{-5}	78
Bis(1,1-dimethylethyl)-, $Me_3CN{=}NCMe_3$	Gas phase	513–533	176.6	16.30	8.65×10^{-5}	79
Bis(1,1-dimethylethyl)-, $Me_3CN{=}NCMe_3$	Gas phase	493–559	179.9	17.15	2.55×10^{-4}	83
Bis(1,1-dimethylethyl)-, $Me_3CN{=}NCMe_3$	Gas phase	453–493	179.1	16.34	4.88×10^{-5}	84
Bis(1,1-dimethylethyl)-, $Me_3CN{=}NCMe_3$	Diphenylether	438–473	180.3	16.96	1.48×10^{-4}	85
Bis(1,1-dimethylethyl)-, $Me_3CN{=}NCMe_3$	n-$C_{100}H_{202}$	443–473	183.7	17.48	1.99×10^{-4}	86
Bis(1,1-dimethylethyl)-, $Me_3CN{=}NCMe_3$	Hexadecane	453	184.5	17.21	8.63×10^{-5}	87
Bis(1,1-dimethylpropyl)-, $EtCMe_2N{=}NCMe_2Et$	Hexadecane	453	182.0	17.10	1.30×10^{-4}	87
Bis(1,1-dimethylbutyl)-, $EtCH_2CMe_2N{=}NCMe_2CH_2Et$	Hexadecane	453	173.6	16.46	2.77×10^{-4}	87
Bis(1,1,2-trimethylpropyl)-, $Me_2CHCMe_2N{=}NCMe_2CHMe_2$	Ethylbenzene	453			3.06×10^{-4}	88
Bis(1-methyl-1-ethylpropyl)-, $Et_2CMeN{=}NCMeEt_2$	Ethylbenzene	453			1.91×10^{-4}	88
Bis(1,1,3-trimethylbutyl)-, $Me_2CHCH_2CMe_2N{=}NCMe_2CH_2CHMe_2$	Ethylbenzene	453			7.66×10^{-4}	88
Bis(1,1,2,2-tetramethylpropyl)-, $Me_3CCMe_2N{=}NCMe_2CMe_3$	Ethylbenzene	453			5.41×10^{-4}	88
Bis(1,1,2,2-tetramethylpropyl)-, $Me_3CCMe_2N{=}NCMe_2CMe_3$	Toluene	453	174.4	16.92	6.46×10^{-4}	87
Bis(1,1,2,2-tetramethylpropyl)-, $Me_3CCMe_2N{=}NCMe_2CMe_3$	Diphenyl ether	443–473	159.3	15.06	4.92×10^{-4}	89
Bis(1,2-dimethyl-1-ethylpropyl)-, $Me_2CHCMeEtN{=}NCMeEtCHCMe_2$	Ethylbenzene	453			5.46×10^{-4}	88
Bis(1,1-diethylpropyl)-, $Et_3CN{=}NCEt_3$	Ethylbenzene	453			3.72×10^{-4}	88

Bis(1,1,3,3-tetramethylbutyl)- Me$_3$CCH$_2$CMe$_2$N=NCMe$_2$CH$_2$CMe$_3$	Diphenyl ether	403–433	133.5	15.57	1.50	89
Bis(1,1,3,3-tetramethylbutyl)- Me$_3$CCH$_2$CMe$_2$N=NCMe$_2$CH$_2$CMe$_3$	Toluene	453	148.1	15.44	2.31×10^{-2}	87
Bis(1-methyl-1-methoxyethyl)-, MeOCMe$_2$N=NCMe$_2$OMe	Diphenyl ether	423–457	178.3	17.62	1.15×10^{-3}	89
Bis(1-methyl-1-methylthioethyl)-, MeSCMe$_2$N=NCMe$_2$SMe	Diphenyl ether	408–438	84.7	7.92	1.42×10^{-2}	89
Bis(1-methyl-1-methoxycarbonylethyl)-, MeOC(O)CMe$_2$N=NCMe$_2$C(O)OMe	Decalin		122.6	14.1	9.19×10^{-1}	90
Bis(1-acetoxy-1-methylethyl)-, MeC(O)OCMe$_2$N=NCMe$_2$OC(O)Me	Diphenyl ether	463–498	171.1	15.27	3.47×10^{-5}	89
Bis(1-acetylthio-1-methylethyl)-, MeC(O)SCMe$_2$N=NCMe$_2$SC(O)Me	Diphenyl ether	403–432	153.2	15.99	2.11×10^{-2}	89
Bis(1-chloro-1-methylethyl)-, ClCMe$_2$N=NCMe$_2$Cl	Diphenyl ether	448–473	102.2	8.61	6.69×10^{-4}	89
Bis(3,4-diaza-2-oxo-1,1,5-trimethyl-4-hexenyl)-, Me$_2$C=NNHC(O)CMe$_2$N=NCMe$_2$C(O)NHN=CMe$_2$	Isoprene/methanol	453	149.2	12.68	3.00×10^{-5}	91
Bis(3,4-diaza-2-oxo-1,1,5-trimethyl-4-heptenyl)-, MeEtC=NNHC(O)CMe$_2$N=NCMe$_2$C(O)NHN=CMeEt	Isoprene/methanol	453	144.6	12.24	3.70×10^{-5}	91
Bis(4-cyclohexyliden-3,4-diaza-1,1-dimethyl-2-oxobutyl)-, 	Isoprene/methanol	453	121.2	9.68	5.07×10^{-5}	91

(continued overleaf)

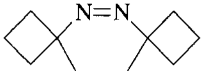
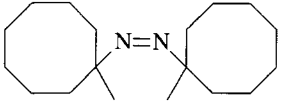
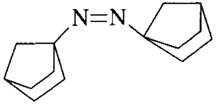
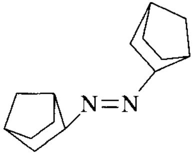
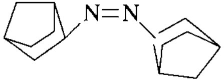
TABLE 7.7 (*continued*)

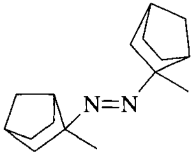
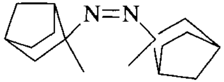
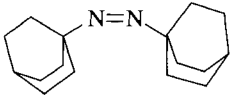
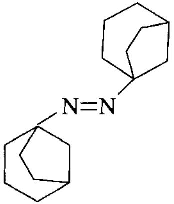
(E)-Diazene	Solvent	T (K)	E (kJ mol^{-1})	log A, A (s^{-1})	k_d (453 K) (s^{-1})	Reference
Bis(4-cyclohexyliden-3,4-diaza-1,1-dimethyl-2-oxobutyl)-, 	Isoprene/acetic acid	453	108.7	8.10	3.68×10^{-5}	91
Bis(1-carbazoyl-1-methylethyl)-, $H_2NNHC(O)CMe_2N{=}NCMe_2C(O)NHNH_2$	Isoprene/methanol	453	127.3	10.35	4.69×10^{-5}	91
Bis(1,1-diethyl-2,2-dimethylpropyl)-, $Me_3CCEt_2N{=}NCEt_2CMe_3$	Ethylbenzene	453			1.09×10^{-2}	88
Bis[1-ethyl-1-(1′-methylethyl)-2-methylpropyl]-, $(Me_2CH)_2CEtN{=}NCEt(CHMe_2)$	Ethylbenzene	453			6.99×10^{-3}	88
Bis(3,3-dimethyl-1,1-diethylbutyl)-, $Me_3CCH_2CEt_2N{=}NCEt_2CH_2CMe_3$	Ethylbenzene	453			3.72×10^{-2}	88
Bis[1,1-di(1′-methylethyl)-2-methylpropyl)]-, $(Me_2CH)_3CN{=}NC(CHMe_2)_3$	Ethylbenzene	453			2.10×10^{-2}	88
Bis(1,1-dimethylnonyl)-, $Me(CH_2)_7CMe_2N{=}NCMe_2(CH_2)_7Me$	Ethylbenzene	453			2.35×10^{-4}	88
Bis(1-butyl-1-ethylpentyl)-, $Bu_2(Et)CN{=}NC(Et)Bu_2$	Ethylbenzene	453			7.4×10^{-4}	88
Bis[1-butyl-1-(1′-methylethyl)pentyl)-, $Bu_2(Me_2CH)CN{=}NC(CHMe_2)Bu_2$	Ethylbenzene	453			1.47×10^{-3}	88

Bis[1-butyl-1-(1′,1′-dimethylethyl)pentyl]-, $Bu_2(Me_3C)CN{=}NC(CMe_3)Bu_2$	Ethylbenzene	453			1.09×10^{-2}	88
Bis[1-(2′, 2′-dimethylpropyl)-1,3,3-trimethylbutyl]-, $(Me_3CCH_2)_2CMeN{=}NCMe(CH_2CMe_3)_2$	Diphenyl ether	373–398	129.3	14.59	4.79×10^{-1}	92
Bis(1-cyclopropyl-1-methylethyl)-, 	Diphenyl ether	418–443	161.9	16.10	2.70×10^{-3}	93
Bis(dicyclopropylmethyl)-, 	Diphenyl ether/ isoquinoline (90:10)%	393–423	152.3	16.42	7.22×10^{-2}	93
Bis(1,1-dicyclopropyl-2-methylpropyl)-, 	Diphenyl ether	393–420	162.3	17.20	3.06×10^{-2}	93
Bis(tricyclopropylmethyl)-, 	Diphenyl ether	378–408	146.9	16.18	1.74×10^{-1}	93

(continued overleaf)

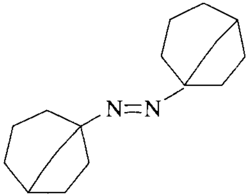
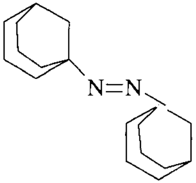
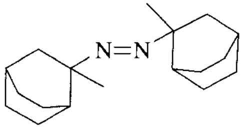
TABLE 7.7 (*continued*)

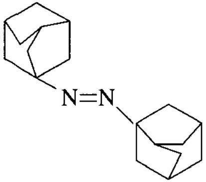
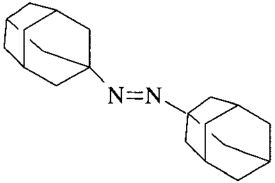
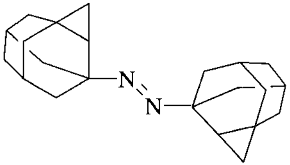
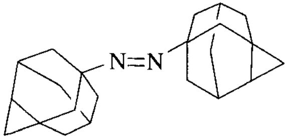
(E)-Diazene	Solvent	T (K)	E (kJ mol^{-1})	log A, A (s^{-1})	k_d (453 K) (s^{-1})	Reference
Bis(1-methylcyclobutyl)-,  	Benzene	453	216.3	18.28	2.18×10^{-7}	31
Bis(1-methylcyclooctyl)-,  	Benzene	453	149.8	15.38	1.28×10^{-2}	31
Bis(1-norbornyl)-,  	Benzene	453	197.9	12.88	1.15×10^{-10}	94
Bis(*exo*-2-norbornyl)-,  	Benzene	473			8.14×10^{-5}	95
Bis(*endo*-2-norbornyl)-,  	Benzene	453	151.9	15.38	7.33×10^{-3}	95

Bis[*exo*-2-(2-methylnorbornyl)]-, 	Benzene	473	3.10×10^{-5}	85
Bis[*endo*-2-(2-methylnorbornyl)]-, 	Benzene	473	2.11×10^{-3}	85
Bis(1-bicyclo[2.2.2]octyl)-, 	Benzene	573	7.60×10^{-5}	94
Bis(1-bicyclo[3.2.1]octyl]-, 	Benzene	573	5.40×10^{-5}	94

(*continued overleaf*)

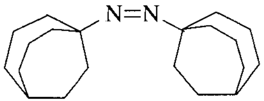
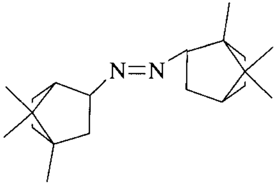
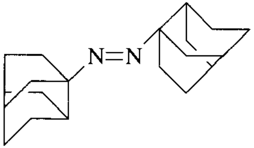
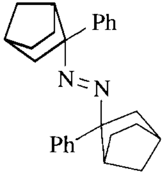
TABLE 7.7 (*continued*)

(E)-Diazene	Solvent	T (K)	E (kJ mol^{-1})	log A, A (s^{-1})	k_d (453 K) (s^{-1})	Reference
Bis(1-bicyclo[3.2.2]nonyl)-, 	Benzene	573	180.3	15.68	0.17	94
Bis(1-bicyclo[3.3.1]nonyl)-, 	Benzene	573			6.88×10^{-4}	94
Bis[2-(2-*endo*-methylbicyclo[2.2.2.]octyl]-, 	Benzene	473			2.43×10^{-3}	95

Bis[3-noradamantyl]-, 	Benzene	453	243.5	16.79	5.16×10^{-12}	94
Bis(1-adamantyl)-, 	Benzene	453	258.6	20.38	3.64×10^{-10}	86
Bis(1-homoadamantyl)-, 	Benzene	453	201.2	16.47	1.86×10^{-7}	94
Bis(3-homoadamantyl)-, 	Benzene	453	186.2	17.37	7.94×10^{-5}	94

(continued overleaf)

TABLE 7.7 *(continued)*

(*E*)-Diazene	Solvent	T (K)	E (kJ mol^{-1})	log A, A (s^{-1})	k_d (453 K) (s^{-1})	Reference
Bis(1-bicyclo[3.3.2]decyl)-,  	Benzene	453	181.2	16.89	9.92×10^{-5}	94
Bis(2-camphyl)-,  	Hexadecane	530–560	183.7	14.63	2.80×10^{-7}	96
Bis(tricyclo[4.4.0.0^{3,8}]decyl)-,  	Benzene	573			4.60×10^{-5}	94
Bis[*endo*-2-(2-phenyl)norbornyl]-,  	Benzene	333			2.91×10^{-2}	3

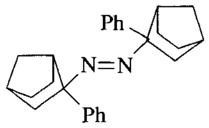
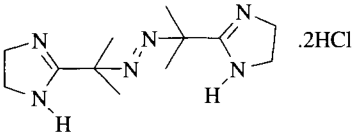
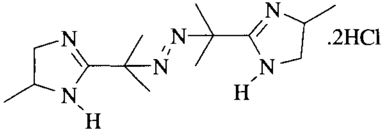
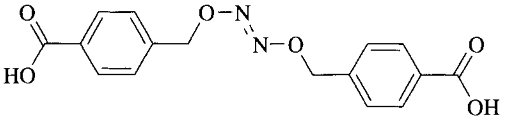
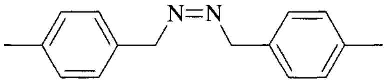
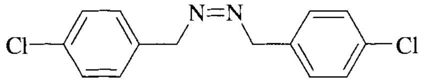
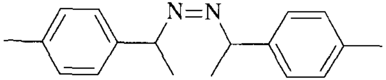
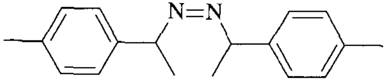
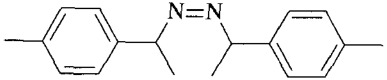
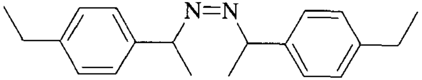
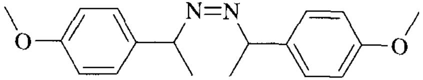
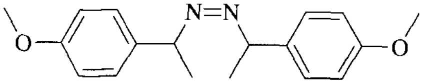
Bis[*exo*-2-(2-phenyl)norbornyl]-,	Benzene	333		6.2×10^{-5}	3
					
2,2′-Azobis[2-methylpropionamidine] dihydrochloride $HN{=}C(NH_2)CMe_2N{=}N\ CMe_2C(NH_2){=}NH.2HCl$	Water, pH 6.20	295		4.82×10^{-5}	97
2,2′-Azobis[2-(imidazolin-2-yl)propane] dihydrochloride	Water, pH 6.25	295		7.5×10^{-6}	97
					
2,2′-Azobis[2-(4-methylimidazolin-2-yl)propane] dihydrochloride	Water, pH 6.25	295		1.6×10^{-5}	97
					
Hyponitrile,					
Bis(1,1-dimethylethyl)-, $Me_3CON{=}NOCMe_3$	Isooctane	318–348	15.07	2.15×10^{-4}	98
Bis(1-methyl-1-phenylethyl)-, $Me_2PhCON{=}NOCMe_2Ph$	Cyclohexane	313–343	15.30	1.37×10^{-3}	99
Bis(4-carboxybenzyl)-,	Water, pH 6.5–8	310		1.41×10^{-4}	100
					

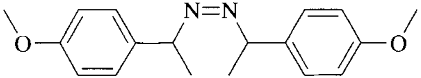
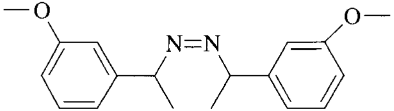
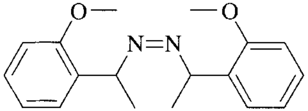
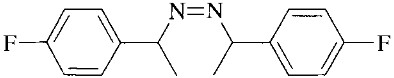
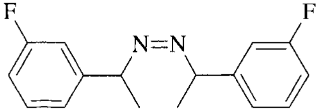
TABLE 7.8 Rate Constants for the Thermal Decay of Symmetrical Aryl-Containing (*E*)-Azo Compounds in Different Solvents

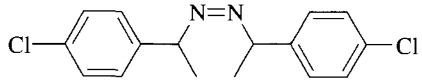
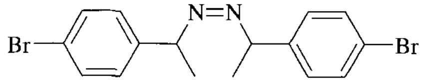
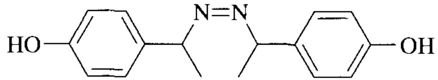
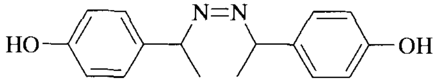
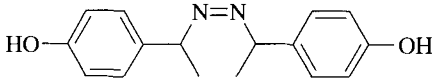
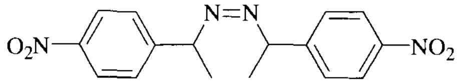
(*E*)-Diazene	Solvent	*T* (K)	*E* (kJ mol^{-1})	log *A*, *A* (s^{-1})	k_d (353 K) (s^{-1})	Reference
Dibenzyl-, $PhCH_2N{=}NCH_2Ph$	Diphenyl ether	408–448	144.8	14.26	6.82×10^{-8}	89
Bis(1-phenylethyl)-, PhCHMeN=NCHMePh	Acetic acid	317–327	117.2	15.06	5.22×10^{-3}	101
Bis(1-phenylethyl)-, PhCHMeN=NCHMePh	*p*-Cymene	358–378	127.2	13.46	4.34×10^{-6}	102
Bis(1-phenylethyl)-, PhCHMeN=NCHMePh	1,2-Dibenzyldioxy ethane	370			3.73×10^{-5}	103
Bis(1-phenylethyl)-, PhCHMeN=NCHMePh	Dibutyl carbynol	370			3.35×10^{-5}	103
Bis(1-phenylethyl)-, PhCHMeN=NCHMePh	Diphenyl methane	370			3.99×10^{-5}	103
Bis(1-phenylethyl)-, PhCHMeN=NCHMePh	Dodecane	370			3.18×10^{-5}	103
Bis(1-phenylethyl), PhCHMeN=NCHMePh	Ethyl benzene	373–383	136.4	14.83	4.43×10^{-6}	7
Bis(1-phenylethyl)-, PhCHMeN=NCHMePh	Ethyl benzene	378			8.95×10^{-5}	104
Bis(1-phenylethyl)-, PhCHMeN=NCHMePh	*N*-Methylpropamid	370			3.71×10^{-5}	103
Bis(1-phenylethyl)-, PhCHMeN=NCHMePh	*N*,*N*-Methylbenzyl aniline	370			4.13×10^{-5}	103
Bis(1-phenylethyl)-, PhCHMeN=NCHMePh	Polycarbonate	370			3.29×10^{-5}	103
Bis(1-phenylethyl)-, PhCHMeN=NCHMePh	Pyridine	317–327	130.0	16.97	5.42×10^{-3}	101
Bis(1-phenylethyl)-, PhCHMeN=NCHMePh	Toluene	317–327	113.0	14.40	4.78×10^{-3}	101
Bis(1-deutero-1-phenylethyl)-, PhCDMeN=NCDMePh	Ethylbenzene	378			7.59×10^{-5}	104
Bis[(4-methylphenyl)methyl]-, 	Diphenyl ether	408–448	145.6	14.44	7.86×10^{-8}	89
Bis[(4-chlorophenyl)methyl]-, 	Diphenyl ether	408–448	150.6	15.16	7.51×10^{-8}	89

Bis[1-(4-methylphenyl)ethyl]-,  	*p*-Cymene	368–378	128.9	13.83	5.71×10^{-6}	102
Bis[1-(4-methylphenyl)ethyl]-,  	Ethyl benzene	373–383	137.7	15.07	4.95×10^{-6}	7
Bis[1-(4-methylphenyl)ethyl]-,  	Toluene	317–327	100.4	12.40	3.50×10^{-3}	101
Bis[1-(4-ethylphenyl)ethyl]-,  	*p*-Cymene	368–378	128.0	13.66	5.24×10^{-6}	102
Bis[1-(4-methoxyphenyl)ethyl]-,  	Diphenyl ether	408–448	146.4	14.63	9.27×10^{-8}	89
Bis[1-(4-methoxyphenyl)ethyl]-,  	Ethyl benzene	373–383	149.8	16.85	4.83×10^{-6}	7

(*continued overleaf*)

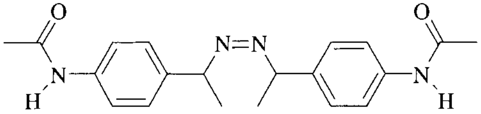
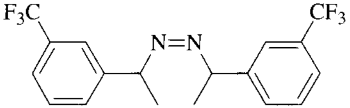
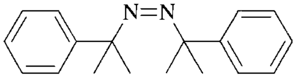
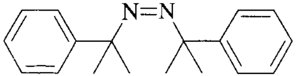
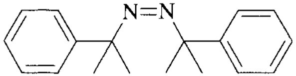
TABLE 7.8 (*continued*)

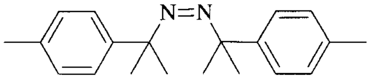
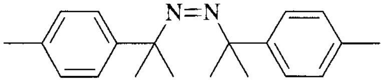
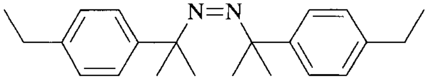
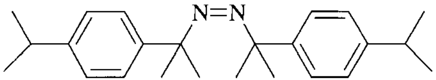
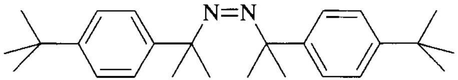
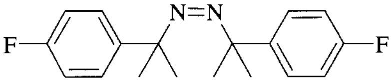
(E)-Diazene	Solvent	T (K)	E (kJ mol^{-1})	log A, A (s^{-1})	k (353 K) (s^{-1})	Reference
Bis[1-(4-methoxyphenyl)ethyl]-, 	*p*-Cymene	368–378	129.7	13.93	5.47×10^{-6}	102
Bis[1-(3-methoxyphenyl)ethyl]-, 	*p*-Cymene	368–378	174.4	19.94	1.36×10^{-6}	102
Bis[1-(2-methoxyphenyl)ethyl]-, 	*p*-Cymene	358–378	135.6	15.02	9.02×10^{-6}	102
Bis[1-(4-fluorophenyl)ethyl]-, 	*p*-Cymene	358–378	149.8	16.59	2.65×10^{-6}	102
Bis[1-(3-fluorophenyl)ethyl]-, 	*p*-Cymene	378			1.12×10^{-4}	102

Bis[1-(4-chlorophenyl)ethyl]-, 	*p*-Cymene	368–378	134.7	15.11	1.51×10^{-5}	102
Bis[1-(4-bromophenyl)ethyl]-, 	Toluene	317–327	117.2	14.74	2.50×10^{-3}	101
Bis[1-(4-hydroxyphenyl)ethyl]-, 	Acetic acid	317–327	133.9	17.56	5.58×10^{-3}	101
Bis[1-(4-hydroxyphenyl)ethyl]-, 	Pyridine	317–327	133.9	17.58	5.84×10^{-3}	101
Bis[1-(4-hydroxyphenyl)ethyl]-, 	Toluene	317–327	121.3	15.63	4.80×10^{-3}	101
Bis[1-(4-nitrophenyl)ethyl]-, 	Toluene	317–327	113.0	13.81	1.23×10^{-3}	101

(continued overleaf)

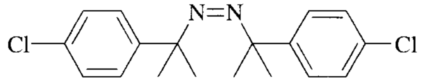
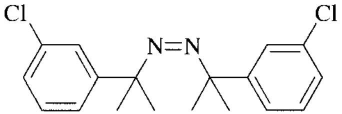
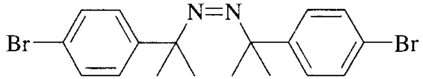
TABLE 7.8 (*continued*)

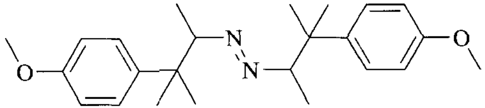
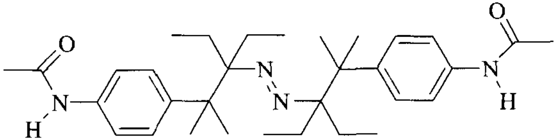
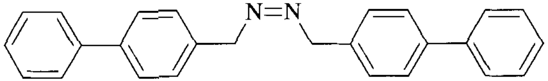
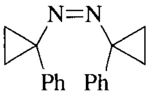
(*E*)-Diazene	Solvent	*T* (K)	*E* (kJ mol^{-1})	log *A*, *A* (s^{-1})	*k* (353 K) (s^{-1})	Reference
Bis[1-(4-*N*-acetamidophenyl)ethyl]-, 	Toluene	317–327	125.5	16.23	4.57×10^{-3}	101
Bis[1-(3-trifluoromethylphenyl)ethyl]-, 	*p*-Cymene	368–378	138.1	15.15	5.19×10^{-6}	102
Bis(1-phenylpropyl)-, PhCHEtN=NCHEtPh	Ethylbenzene	373–383	136.4	14.83	4.43×10^{-6}	7
Bis(diphenylmethyl)-, $Ph_2CHN{=}NCHPh_2$	Toluene	327–337	111.3	13.76	1.95×10^{-3}	105
Bis(1-methyl-1-phenylethyl)-, 	Toluene	313–342	123.8	14.02	5.02×10^{-5}	106
Bis(1-methyl-1-phenylethyl)-, 	Toluene	314–331	122.6	15.35	1.62×10^{-3}	107
Bis(1-methyl-1-phenylethyl)-, 	Ethylbenzene		123.0	15.54	2.18×10^{-3}	85

Bis[1-methyl-1-(4-methylphenyl)ethyl]-, 	Toluene	314–331	120.5	15.22	2.45×10^{-3}	107
Bis[1-methyl-1-(4-methylphenyl)ethyl]-, 	Toluene	314–330	112.1	13.84	1.79×10^{-3}	108
Bis[1-methyl-1-(4-ethylphenyl)ethyl] -, 	Toluene	316–331	108.8	13.13	1.07×10^{-3}	107
Bis[1-methyl-1-(4-(1-methylethyl)phenyl)ethyl]-, 	Toluene	316–331	124.3	15.66	1.85×10^{-3}	107
Bis[1-methyl-1-(4-(1,1-dimethyl ethyl)phenyl)ethyl]-, 	Toluene	316–331	123.4	15.50	1.74×10^{-3}	107
Bis[1-methyl-1-(4-fluorophenyl)ethyl-, 	Toluene	314–330	120.5	15.15	2.09×10^{-3}	108

(*continued overleaf*)

TABLE 7.8 (*continued*)

(E)-Diazene	Solvent	T (K)	E (kJ mol^{-1})	log A, A (s^{-1})	k (353 K) (s^{-1})	Reference
Bis[1-methyl-1-(4-chlorophenyl)ethyl]-,  	Toluene	314–330	116.3	14.68	2.96 × 10^{-3}	108
Bis[1-methyl-1-(3-chlorophenyl)ethyl]-,  	Toluene	314–330	118.0	14.95	3.09 × 10^{-3}	108
Bis[1-methyl-1-(4-bromophenyl)ethyl]-,  	Toluene	316–331	117.6	14.93	3.38 × 10^{-3}	107
Bis(1,2-dimethyl-1-phenyl propyl)-, $Me_2CHCPhMeN{=}NCPhMeCHMe_2$	Ethyl benzene	323			3.52 × 10^{-4}	109
Bis(1,1-dimethyl-2-phenylethyl)-, $PhCH_2CMe_2N{=}NCMe_2CH_2Ph$	Tetralin	353	152.3	14.21	4.72 × 10^{-9}	16
Bis(1-methyl-1-phenoxyethyl)-, $PhOCMe_2N{=}NCMe_2OPh$	Tetralin	353	138.9	12.76	1.61 × 10^{-8}	16
Bis(1-methyl-1-phenylthioethyl)-, $PhSCMe_2N{=}NCMe_2SPh$	Tetralin	353	107.5	10.55	4.40 × 10^{-6}	16
Bis(1,1-dimethyl-3-phenylpropyl)-, $Ph(CH_2)_2CMe_2N{=}NCMe_2(CH_2)_2Ph$	Ethyl benzene	373–383	139.7	15.36	4.88 × 10^{-6}	9
Bis(1,2-dimethyl-2-phenylpropyl)-, $PhCMe_2CHMeN{=}NCHMeCMe_2Ph$	Diphenyl ether	527			1.33 × 10^{-3}	9

Bis[1,2-dimethyl-2-(4-methoxyphenyl)propyl]-,	Diphenyl ether	529			1.35×10^{-3}	7
						
Bis[1,1-diethyl-2-methyl-2-(4′-acetamidophenyl)propyl]-,	Diphenyl ether	529			2.24×10^{-3}	7
						
Bis(1,2-diphenylpropyl)(*meso*)-, $PhMeCHCHPhN{=}NCHPhCHMePh$	Ethyl benzene	370–388	138.5	15.02	3.36×10^{-6}	9
Bis(1,2-diphenylpropyl)(*dl*)-, $PhMeCHCHPhN{=}NCHPhCHMePh$	Ethyl benzene	370–388	138.9	15.12	3.69×10^{-6}	9
Bis(1-butyl-1-phenylpentyl)-, $Bu_2CPhN{=}NCPhBu_2$	Ethyl benzene	323			6.24×10^{-4}	109
Bis(1,3-diphenylpentyl)-, $EtCHPhCH_2CHPhN{=}NCHPhCH_2CHPhEt$	Xylene	392			d5.6×10^{-4}	110
Bis[(4-phenylphenyl)methyl]-,	Diphenyl ether	408–438	140.3	14.05	1.95×10^{-7}	89
						
Bis(diphenylmethyl)-, $Ph_2CHN{=}NCHPh_2$	Toluene	327–337	111.3	13.76	1.95×10^{-3}	105
Bis(1-phenylcyclopropyl)-,	Benzene, Toluene		135.6	12.20	1.37×10^{-8}	111
						

(continued overleaf)

TABLE 7.8 (*continued*)

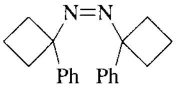
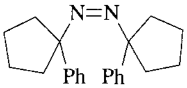
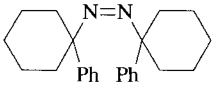
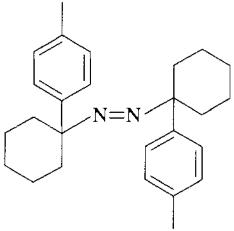
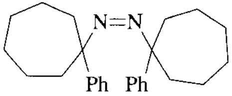
(E)-Diazene	Solvent	T (K)	E (kJ mol^{-1})	log A, A (s^{-1})	k (353 K) (s^{-1})	Reference
Bis(1-phenylcyclobutyl)-, 	Benzene		125.5	14.38	6.45×10^{-5}	111
Bis(1-phenylcyclopentyl)-, 	Benzene		105.4	14.72	1.33×10^{-1}	111
Bis(1-phenylcyclohexyl)-, 	Benzene		128.0	16.39	2.82×10^{-3}	111
Bis[1-(4-methylphenyl)cyclohexyl], 	Benzene		107.9	13.18	1.64×10^{-3}	111
Bis(1-phenylcycloheptyl)-, 	Benzene		100.4	14.36	3.19×10^{-1}	111

TABLE 7.9 Rate Constants of Thermal Decay of AIBN in Different Solvents and in Solid Polymers

Solvent	T (K)	E (kJ mol^{-1})	log A, A (s^{-1})	k_d, k_I (s^{-1})	Reference
		k_d (353 K)			
Acetic acid	355			1.50×10^{-4}	42
Acetic acid	353			1.49×10^{-4}	112
Acrylonitrile	333			1.2×10^{-5}	113
Aniline	353			1.68×10^{-4}	114
Benzene	323–343	127.6	15.11	1.69×10^{-4}	115
Benzene	303–373	128.9	15.19	1.31×10^{-4}	116
Benzene	333			3.16×10^{-5}	114
Benzene	335			1.42×10^{-5}	117
N-Benzyl-*N*-methylaniline	340			3.10×10^{-5}	7
Butanol	340			2.72×10^{-5}	7
Butanol	355			1.55×10^{-4}	118
1-Butylpentanol	345			2.44×10^{-4}	7
Butyric acid	343–373	128.0	15.15	1.62×10^{-4}	90
Carbon tetrachloride	335			1.18×10^{-5}	117
Carbon tetrachloride	350			1.21×10^{-4}	112
Chlorobenzene	335			1.42×10^{-5}	117
Chlorobenzene	338			2.35×10^{-5}	119
Collidine	353			1.68×10^{-4}	120
Cyclohexanol	355			1.43×10^{-4}	118
Cyclohexanone	343–373	138.9	16.79	1.72×10^{-4}	90
Cyclohexanone	355			1.43×10^{-4}	121
Decalin	343–373	139.7	16.84	1.47×10^{-4}	90
Dibenzylglycol	340			3.10×10^{-5}	7
Dibromomethane	343–373	126.4	14.98	1.89×10^{-4}	90
N,*N*-Dimethylaniline	340–345	128.7	15.32	1.89×10^{-4}	7
N,*N*-Dimethylformamide	333			1.07×10^{-5}	113
Diphenylmethane	340–345	133.4	15.97	1.70×10^{-4}	7
Dodecanethiol	353			1.46×10^{-4}	112
1,2-Dichlorobenzene	353			1.45×10^{-4}	120
1,1-Dimethylpropanol	353			1.40×10^{-4}	121
Ethylene glycol	353			1.25×10^{-4}	120
Formamide	343–373	132.6	15.81	1.54×10^{-4}	90
Methyllinoliate	323–363	128.6	15.13	1.26×10^{-4}	122
2-Methylpropanol	353			1.76×10^{-4}	121
N-Methyl propionamide	339–345	133.4	15.97	1.70×10^{-4}	7
Nitrobenzene	335			1.79×10^{-5}	117
Nitrobenzene	353–373	130.1	17.39	1.38×10^{-2}	120
Nitrobutane	355			1.45×10^{-4}	118
Nitromethane	335			1.34×10^{-5}	117
Propylen carbonate	340–345	135.7	16.30	1.66×10^{-4}	7
Tetralin	423	118.8	13.72	1.38×10^{-4}	16
Toluene	343–378	130.1	15.42	1.47×10^{-4}	123
Toluene	338–353	128.1	15.15	1.57×10^{-4}	124
Toluene	353			1.55×10^{-4}	114

(*continued overleaf*)

TABLE 7.9 (*continued*)

Solvent	T (K)	E (kJ mol^{-1})	log A, A (s^{-1})	k_d, k_i (s^{-1})	Reference
Toluene	353			1.66×10^{-4}	121
Undecane	353			1.05×10^{-4}	120
p-Xylene	353	123.0		9.97×10^{-5}	112
p-Xylene	350			5.33×10^{-6}	118
	$k_i = 2ek_d$ *(353 K)*				
Benzene	313–351	123.4	14.25	9.78×10^{-5}	125
Benzene	313–351	128.4	15.00	1.00×10^{-4}	126
Carbone tetrachloride	343–333	127.2	14.60	6.00×10^{-5}	126
Cyclohexanol	338–363	146.4	17.70	1.09×10^{-4}	127
Cyclohexanone	328–353	142.3	17.30	1.75×10^{-4}	128
Cumene	347–370	138.4	15.57	1.23×10^{-5}	129
Cumene	363			4.70×10^{-4}	130
p-Cymene	347–370	150.6	17.24	9.03×10^{-6}	129
Ethylacetate	313–313	128.4	15.12	1.32×10^{-4}	126
Ethylmethacrylate	318–368	137.0	16.68	2.56×10^{-4}	131
Methylmethacrylate	308–373	128.6	15.27	1.74×10^{-4}	131
(1-Methylpropyl)methacrylate	308–373	139.8	16.64	8.99×10^{-5}	131
Nonylmethacrylate	308–373	142.3	16.90	6.98×10^{-5}	131
Styrene	323–343	124.4	15.27	7.28×10^{-4}	132
	Solid Phase				
Polystyrene	333–353	128.0	13.74	6.30×10^{-6}	133
Polystyrene	353			7.80×10^{-5}	134
Polyethylene	335–365	176.0	20.30	1.81×10^{-6}	135
Polypropylene	345–362	154.0	17.71	7.36×10^{-6}	136
Polypropylene	329–364	141.0	15.57	5.08×10^{-6}	137
(*Z*)-1,4-Polyisoprene	353–373	134.0	14.93	1.26×10^{-5}	138

TABLE 7.10 The Probability of Radical Pair Formed from 2,2′-Azobis[2-methylpropanenitrile] (AIBN) Escaping the Cage in Different Solvents

Solvent	T (K)	e	Reference
Acetic acid	338	0.51	139
Acetonitrile	338	0.67	139
Acrylonitrile	323	1.03	140
Benzene	336	0.62	117
Benzene	353	0.44	125
Benzene	338	0.44	139
Benzene + acrylonitrile	333	0.5	141
Benzene + butylacrylate	333	0.5	142
Benzene + chlorovinyl	323	0.74	140
Benzene + 10% ethylacetate	313–343	$2.62 \exp(-4.1/RT)$	143
Benzene + methylacrylate	323	0.72	140

TABLE 7.10 (*continued*)

Solvent	T (K)	e	Reference
Bromobenzene	323	0.50	144
tert-Butanol	323–343	$5.43 \times 10^3 \exp(-26.5/R)$	145
Carbon tetrachloride	336	0.45	117
Chlorobenzene	336	0.57	117
Cyclohexanol	338–363	$4.43 \times 10^2 \exp(-20.8/RT)$	127
Cyclohexanol	323–353	$1.38 \times 10^2 \exp(-17.3/RT)$	145
Cyclohexanon	328–353	$75.2 \exp(-13.9/RT)$	128
n-Decane	328–323	$2.61 \exp(-5.9/RT)$	117
1,1-Dichlorobenzene	338	0.37	139
2,8-Dimethyloctane	333–353	$3.09 \times 10^2 \exp(-17.8/RT)$	146
Dioxane	323	0.51	144
Dioxane	323	0.56	147
Dioxane	323	0.63	147
Dioxane	333	0.61	140
Dioxane	333	0.46	148
Dioxane	333	0.52	149
Dioxane	333	0.64	149
Dioxane	333	0.6	142
Dioxane	333	0.7	142
Dioxane	333	0.5	150
Dioxane	333	0.52	151
Diphenylethane	333	0.42	146
Ethylacetate	313–343	$6.7 \exp(-7.9/RT)$	143
Ethylbenzene	333–353	$14.9 \exp(-8.9/RT)$	146
Ethylmethacrylate	318–363	$5.4 \exp(-6.3/RT)$	131
Isobutylmethacrylate	308–353	$1.78 \times 10^2 \exp(-16.7/RT)$	131
Isopropylbenzene	313–353	$3.29 \exp(-4.9/RT)$	146
Methyllinoliate	323–363	$2.47 \exp(-3.8/RT)$	122
Methylmethacrylate	323	0.56	140
Methylmethacrylate	333	0.52	149
Methylmethacrylate	333	0.50	150
Methylmethacrylate	333	0.43	148
Nitrobenzene	336	0.73	118
Nitrobenzene	336	0.75	118
Nonylmethacrylate	308–353	$1.36 \times 10^2 \exp(-17.6/RT)$	131
Styrene	323	0.70	140
Styrene	323	0.52	144
Styrene	333	0.61	152
Styrene	333	0.48	148
Styrene	333	0.64	149
Styrene	333	0.70	142
Styrene	338	0.40	139
Styrene + butylacrylate	333	0.52	151
Styrene + butylacrylate	333	0.60	142
Styrene + methylmethacrylate	333	0.46	148
Toluene	338	0.44	139
2,2,4-Trimethylpentane	333–353	$12.7 \exp(-9.8/RT)$	148

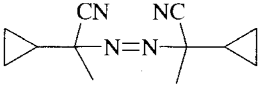
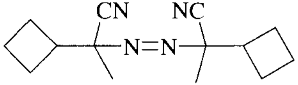
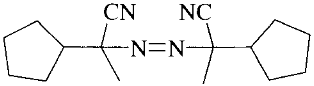
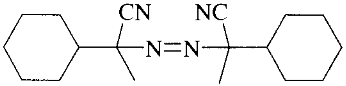
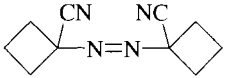
TABLE 7.11 Rate Constants of the Thermal Decay of Symmetrical (*E*)-Azonitriles in Different Solvents

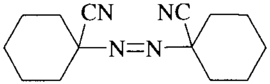
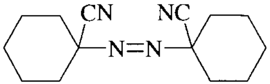
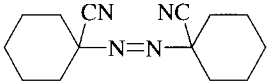
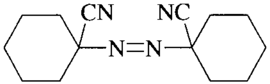
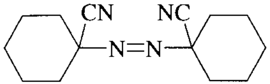
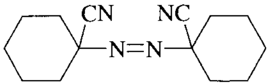
Compound	Solvent	T (K)	E (kJ mol^{-1})	log A, A (s^{-1})	k_d (353 K) (s^{-1})	Reference
2,2-Azobis(2-methylbutanenitrile), EtCMe(CN)N=NCMe(CN)Et	Decaline	340–350	122.6	14.1	9.09×10^{-5}	90
2,2-Azobis(2-methylbutanenitrile), EtCMe(CN)N=NCMe(CN)Et	Diphenyl methane	340–345	130.5	14.54	1.70×10^{-5}	103
2,2-Azobis[2-methylbutanenitrile], EtCMe(CN)N=NCMe(CN)Et	*N*,*N*-Dimethyl aniline	340–345	125.9	14.06	2.69×10^{-5}	103
2,2-Azobis[2-methylbutanenitrile], EtCMe(CN)N=NCMe(CN)Et	Ethyl benzene	343–353	138.1	16.31	7.50×10^{-5}	153
2,2-Azobis[2-methylbutanenitrile], EtCMe(CN)N=NCMe(CN)Et	*N*-Methyl propamide	340–345	133.5	15.96	1.61×10^{-4}	103
2,2-Azobis[2-methylbutanenitrile], EtCMe(CN)N=NCMe(CN)Et	Polycarbonate	340–345	133.1	15.86	1.46×10^{-4}	103
2,2-Azobis[2-methylbutanenitrile], EtCMe(CN)N=NCMe(CN)Et	Toluene	343–353	123.0	14.15	8.90×10^{-5}	121
2,2-Azobis[2-ethylbutanenitrile], $Et_2C(CN)N{=}NC(CN)Et_2$	Nitrobenzene	353–373	143.1	17.1	8.42×10^{-5}	154
2,2-Azobis[2-methylpentanenitrile], PrCMe(CN)N=NCMe(CN)Pr	Toluene	343–353	138.1	16.63	1.57×10^{-4}	121
2,2-Azobis[2,3-dimethylbutanenitrile], $Me_2CHCMe(CN)N{=}NCMe(CN)CHMe_2$	Toluene	343–353	133.9	15.81	9.92×10^{-5}	121
2,2-Azobis[2-ethyl-3-methylbutanenitrile], $Me_2CHCEt(CN)N{=}NCEt(CN)CHMe_2$	Toluene	353.5			1.01×10^{-4}	155
2,2-Azobis[2-(1′-methylethyl)-3-methylbutanenitrile], $(Me_2CH)_2C(CN)N{=}NC(CN)(CHMe_2)_2$	Toluene	353.5			1.26×10^{-4}	155

2,2-Azobis[2-methylhexanenitrile], $BuCMe(CN)N{=}N$ $CMe(CN)Bu$	Toluene	353.2			1.58×10^{-5}	121
2,2-Azobis[2,4-dimethylpentanenitrile], $Me_2CHCH_2CMe(CN)N{=}NCMe(CN)CH_2CHMe_2$	Toluene	343–353	121.3	14.80	7.10×10^{-4}	121
2,2-Azobis[2,4-dimethylpentanenitrile], $Me_2CHCH_2CMe(CN)N{=}NCMe(CN)CH_2CHMe_2$	*p*-Xylene	350			5.75×10^{-4}	112
2,2-Azobis[2-(3′-methylpropyl)-4-methylpentanenitrile)], $(Me_2CHCH_2)_2C(CN)N{=}N$ $C(CN)(CH_2CHMe_2)_2$	Toluene	333–353	126.8	16.48	5.21×10^{-3}	155
2,2-Azobis[2,3,3-trimethylbutanenitrile], $Me_3CCMe(CN)N{=}NCMe(CN)CMe_3$	Toluene	313–323	147.3	17.64	6.98×10^{-5}	155
2,2-Azobis[2,3,3-trimethylbutanenitrile], (diastereomer), $Me_3CCMe(CN)N{=}NCMe(CN)CMe_3$ (diastereomer)	Toluene	313–353	127.2	14.83	1.02×10^{-4}	156
2,2-Azobis[2-methylheptanenitrile], $Me(CH_2)_4CMe(CN)N{=}N$ $CMe(CN)(CH_2)_4Me$	Toluene	353			1.63×10^{-5}	155
2,2-Azobis[2-methylheptanenitrile], $Me(CH_2)_4CMe(CN)N{=}N$ $CMe(CN)(CH_2)_4Me$	*p*-Xylene	343–363	126.4	14.95	1.76×10^{-4}	157
2,2-Azobis[2-trimethylsilyloxypropanenitrile], Me_3SiOC $Me(CN)N{=}NCMe(CN)(OSiMe_3)$	Diphenyl ether	348–368	134.7	15.97	1.09×10^{-4}	158
4,4-Azobis[4-cyanopentanoic acid], $HOC(O)(CH_2)_2CMe(CN)N{=}N$ $CMe(CN)(CH_2)_2C(O)OH$	Dioxane	338–353	132.6	15.77	1.41×10^{-4}	159
2,2-Azobis(5-hydroxypentanenitrile), $HO(CH_2)_3CMe(CN)N{=}N$ $CMe(CN)(CH_2)_3OH$	Dioxane	338–353	133.1	15.85	1.43×10^{-4}	159

(continued overleaf)

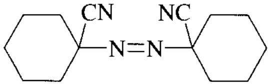
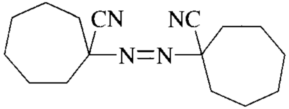
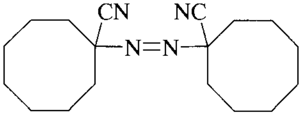
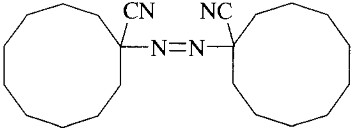
TABLE 7.11 (*continued*)

Compound	Solvent	T (K)	E (kJ mol^{-1})	log A, A (s^{-1})	k_d (353 K) (s^{-1})	Reference
2,2-Azobis[2-cyclopropylpropanenitrile],  	Toluene	353.5			3.31×10^{-3}	160
2,2-Azobis[2-cyclobutylpropanenitrile],  	Toluene	353.5			1.51×10^{-4}	160
2,2-Azobis[2-cyclopentylpropanenitrile],  	Toluene	353.5			1.30×10^{-4}	160
2,2-Azobis[2-cyclohexylpropanenitrile],  	Toluene	353.5			2.27×10^{-4}	160
1,1-Azobis(cyclobutanecarbonitrile),  	Toluene	393–413	134.3	15.11	1.73×10^{-5}	161

1,1-Azobis(cyclohexanecarbonitrile), 	Benzene	353			8.32×10^{-6}	162
1,1-Azobis(cyclohexanecarbonitrile), 	Chlorobenzene	353–373	138.9	15.49	8.64×10^{-6}	163
1,1-Azobis(cyclohexanecarbonitrile), 	Cumene	347–370	138.4	15.57	1.23×10^{-5}	129
1,1-Azobis(cyclohexanecarbonitrile), 	*p*-Cymene	347–370	150.6	17.24	9.03×10^{-6}	129
1,1-Azobis(cyclohexanecarbonitrile), 	Toluene	353–375	148.1	16.70	6.10×10^{-6}	161
1,1-Azobis(cyclohexanecarbonitrile), 	*p*-Xylene	353–373	166.9	19.36	4.61×10^{-6}	157

(*continued overleaf*)

TABLE 7.11 (*continued*)

Compound	Solvent	T (K)	E (kJ mol^{-1})	log A, A (s^{-1})	k_d (353 K) (s^{-1})	Reference
1,1-Azobis(cyclohexanecarbonitrile),  	p-Xylene	350			5.31×10^{-6}	118
1,1-Azobis(cycloheptanecarbonitrile),  	Toluene	322–340	115.1	14.09	1.14×10^{-3}	161
1,1-Azobis(cyclooctanecarbonitrile),  	Toluene	310–323	108.4	13.92	7.58×10^{-3}	161
1,1-Azobis(cyclodecanecarbonitrile),  	Toluene	324–343	117.2	14.60	1.81×10^{-3}	161
2,2-Azobis(2-phenylpropanenitrile), MePh(CN)CN=NC(CN)PhMe	Benzene	353	84.5	12.28	5.98×10^{-1}	90

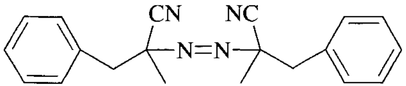
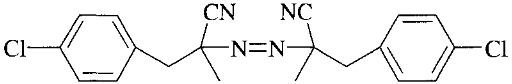
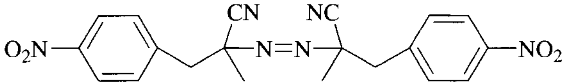
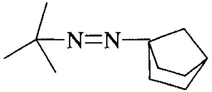
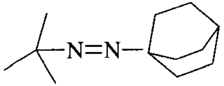
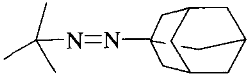
2,2-Azobis[2-methyl-3-phenylpropanenitrile], 	Toluene	353			1.16×10^{-4}	162
2,2-Azobis[2-methyl-3-(4-chlorophenyl)propanenitrile], 	Toluene	353			8.8×10^{-5}	164
2,2-Azobis[2-methyl-3-(4-nitrophenyl)propanenitrile], 	Toluene	353			1.00×10^{-4}	164
2,2-Azobis[2,4-dimethyl-4-phenylpentanenitrile], $PhMe_2CCH_2Me(CN)CN{=}NC(CN)MeCH_2CMe_2Ph$	Benzene	353	95.4	12.28	1.46×10^{-2}	90
4,4-Azobis[4-cyanopentanoic acid], $Me(CN)C(CH_2CH_2COOH)N{=}N$ $C(CH_2CH_2COOH)(CN)Me$	*p*-Xylene	333–353	142.3	16.96	8.01×10^{-5}	157
4,4-Azobis[4-cyanopentanoic acid], $Me(CN)C(CH_2CH_2COOH)N{=}N$ $C(CH_2CH_2COOH)(CN)Me$	Water	288–323	108.8	12.17	1.18×10^{-4}	165

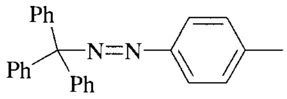
TABLE 7.12 Rate Constants of the Thermal Decay of Unsymmetrical (*E*)-Azo Compounds in the Gas Phase and Different Solvents

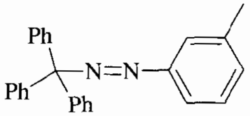
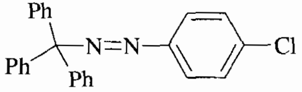
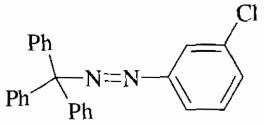
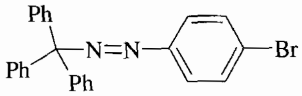
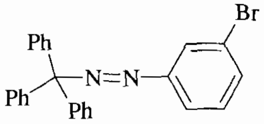
Diazene	Solvent	T (K)	E (kJ mol^{-1})	log A, A (s^{-1})	k_d (353 K) (s^{-1})	Reference
Methyl(1-methylethyl)-, $MeN{=}NCHMe_2$	Gas phase	523–605	198.7	15.45	1.12×10^{-14}	166
Methyl(2-propenyl)-, $MeN{=}NCH_2CH{=}CH_2$	Gas phase	436–455	148.1	14.51	3.94×10^{-8}	167
Methyl(1,1-dimethyl-2-propenyl)-, $MeN{=}NCMe_2CH{=}CH_2$	*p*-Diisopropylbenzene	388–406	151.5	16.32	7.99×10^{-7}	168
Methyl(1-phenylethyl)-, $MeN{=}NCHMePh$	Diphenyl ether/isoquinoline	424–444	136.4	15.55	2.33×10^{-5}	21
Ethyl(1-methylethyl)-, $EtN{=}NCMe_2H$	Gas phase	553–673	206.0	16.6	1.31×10^{-14}	169
Propyl(2-propenyl)-, $PrN{=}NCH_2CH{=}CH_2$	Gas phase	374–399	149.0	14.8	5.65×10^{-8}	167
1-Methylethyl(1,1-dimethyl-2-propenyl)-, $Me_2CHN{=}NCMe_2CH{=}CH_2$	*p*-Diisopropylbenzene	370–388	140.6	16.05	1.76×10^{-5}	168
1-Methylethyl(1-phenylethyl)-, $Me_2CHN{=}NCHMePh$	Diphenyl ether/isoquinoline	416–438	152.7	15.48	7.67×10^{-8}	170
1-Methylethyl(1-methyl-1-phenylethyl)-, $Me_2CHN{=}NCMe_2Ph$	Diphenyl ether/isoquinoline	393–416	153.6	16.43	5.03×10^{-7}	170
1-Ethylpropyl(1-ethyl-1-phenylpropyl), $Et_2CHN{=}NCEt_2Ph$	Diphenyl ether/isoquinoline	393–420	163.2	17.59	2.76×10^{-7}	170
1,3-Dimethylbutyl(1,3-dimethyl-1-phenylbutyl)-, $Me_2CHCH_2CMePhN{=}N$ $CHMeCH_2CHMe_2$	Diphenyl ether/isoquinoline	376–403	147.3	16.53	5.42×10^{-6}	170
1,1-Dimethylethyl(1,1-dimethyl-2-propenyl)-, $Me_3CN{=}NCMe_2CH{=}CH_2$	Gas phase	354–380	124.7	12.73	1.90×10^{-6}	167
1,1-Dimethylethyl(1,1-dimethyl-2-propenyl)-, $Me_3CN{=}NCMe_2CH{=}CH_2$	*p*-Diisopropylbenzene	346–360	115.0	13.28	1.83×10^{-4}	168

1,1-Dimethylethyl[1-methyl-1-(*N*,*N*-dimethylamino)ethyl]-, $Me_3CN{=}NCMe_2NMe_2$	Hexane	385–403	114.2	11.86	9.15×10^{-6}	171
1,1-Dimethylethyl[1-methyl-1-(*N*,*N*-dimethylamino)ethyl]-, $Me_3CN{=}NCMe_2NMe_2$	Hexane	387			2.78×10^{-4}	171
1,1-Dimethylethyl[1-methyl-1-(*N*,*N*-dimethylamino)ethyl]-, $Me_3CN{=}NCMe_2NMe_2$	Methanol	387			1.53×10^{-3}	171
1,1-Dimethylethyl[1-methyl-1-(*N*,*N*-dimethylamino)ethyl]-, $Me_3CN{=}NCMe_2NMe_2$	*N*,*N*-Dimethyl formamide	394			2.82×10^{-4}	171
1-Cyano-1-trimethylsilyloxyethyl(1,1-dimethylethyl)-, $Me_3CN{=}NCMe(CN)(OSiMe_3)$	Toluene	298–312	106.6	14.56	6.11×10^{-2}	158
(1,1-Dimethylethyl)phenyl-, $Me_3CN{=}NPh$	Benzene	573			1.06×10^{-3}	93
(1,1-Dimethylethyl) (1-bicyclo[2.2.1]heptyl)-, 	Benzene		207.1	16.73	1.22×10^{-14}	60
1-Bicyclo[2.2.2.]octyl (1,1-dimethylethyl)-, 	Benzene		198.7	16.73	2.13×10^{-13}	94
1-Adamantyl(1,1-dimethylethyl)-, 	Benzene		192.0	16.45	1.09×10^{-12}	94

(continued overleaf)

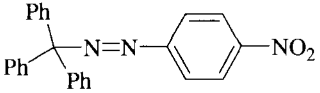
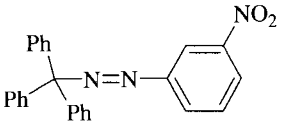
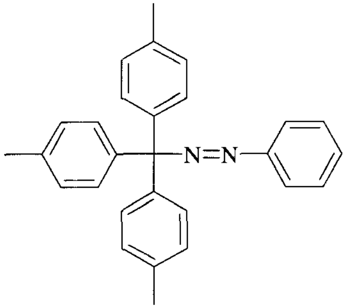
TABLE 7.12 (*continued*)

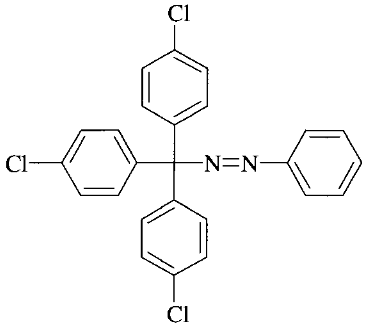
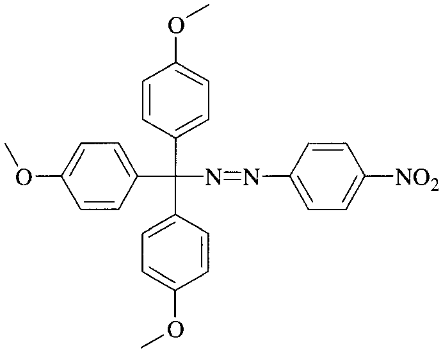
Diazene	Solvent	T (K)	E (kJ mol^{-1})	log A, A (s^{-1})	k_d (353 K) (s^{-1})	Reference
1,1-Dimethylethyl[1,3,3-trimethyl-1-(2′, 2′-dimethylpropyl)butyl]-, $Me_3CN{=}NCMe(CH_2CMe_3)_2$	Diphenyl ether	413–437	144.3	14.62	1.85×10^{-7}	172
1,1-Dimethylethyl(1,3,3-trimethylbutyl)-, $Me_3CN{=}NCMe_2CH_2CMe_3$	Diphenyl ether	428–453	162.3	16.08	1.16×10^{-8}	172
Diphenylmethyl(phenyl)-, $PhN{=}NCHPh_2$	Decaline	397–417	142.3	14.22	1.46×10^{-7}	22
Phenyl(triphenylmethyl)-, $PhN{=}NCPh_3$	Acetic acid	323–338	113.0	14.43	5.12×10^{-3}	173
Phenyl(triphenylmethyl)-, $PhN{=}NCPh_3$	Anizol	298–348	123.0	16.02	6.60×10^{-3}	174
Phenyl(triphenylmethyl)-, $PhN{=}NCPh_3$	Benzene	298–348	114.6	14.65	4.93×10^{-3}	174
Phenyl(triphenylmethyl)-, $PhN{=}NCPh_3$	Butanol	323–338	129.7	17.04	7.05×10^{-3}	173
Phenyl(triphenylmethyl)-, $PhN{=}NCPh_3$	Chlorobenzene	323–338	120.9	15.70	6.46×10^{-3}	174
Phenyl(triphenylmethyl)-, $PhN{=}NCPh_3$	Cyanobenzene	323–338	123.8	16.08	5.77×10^{-3}	174
Phenyl(triphenylmethyl)-, $PhN{=}NCPh_3$	Cyclohexane	323–338	105.0	12.97	2.71×10^{-3}	174
Phenyl(triphenylmethyl)-, $PhN{=}NCPh_3$	Dimethyl malonate	323–338	119.2	15.38	5.52×10^{-3}	174
Phenyl(triphenylmethyl)-, $PhN{=}NCPh_3$	Nitrobenzene	323–338	121.3	15.71	5.77×10^{-3}	125
Phenyl(triphenylmethyl)-, $PhN{=}NCPh_3$	Nitrobenzene	323–338	113.0	14.34	4.16×10^{-3}	173
Phenyl(triphenylmethyl)-, $PhN{=}NCPh_3$	Nitromethane	323–338	117.2	15.04	4.99×10^{-3}	173
Phenyl(triphenylmethyl)-, $PhN{=}NCPh_3$	Toluene	323–338	114.6	14.73	5.92×10^{-3}	173
4-Methylphenyl(triphenylmethyl)-, 	Toluene	323–338	105.4	13.29	4.94×10^{-3}	173

3-Methylphenyl(triphenylmethyl)-, 	Toluene	317–327	122.2	15.94	7.21×10^{-3}	173
4-Chlorophenyl(triphenylmethyl)-, 	Toluene	323–338	114.2	14.34	2.76×10^{-3}	173
3-Chlorophenyl(triphenylmethyl)-, 	Toluene	323–338	124.7	15.95	3.15×10^{-3}	173
4-Bromophenyl(triphenylmethyl)-, 	Toluene	323–338	116.3	14.62	2.58×10^{-3}	173
3-Bromophenyl(triphenylmethyl)-, 	Toluene	317–327	125.1	16.06	3.54×10^{-3}	175

(*continued overleaf*)

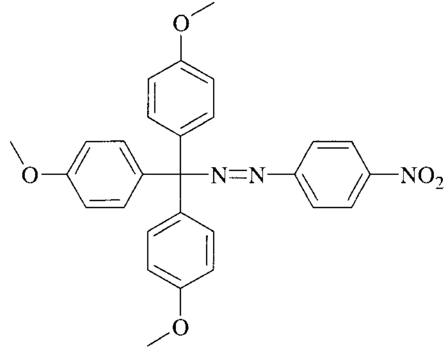
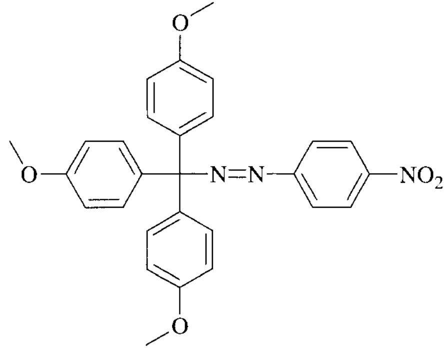
TABLE 7.12 (*continued*)

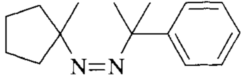
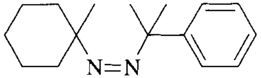
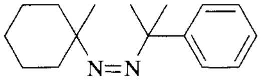
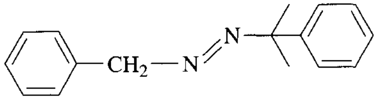
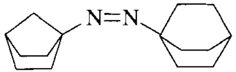
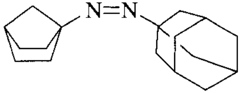
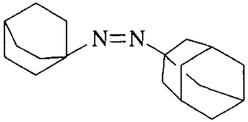
Diazene	Solvent	T (K)	E (kJ mol^{-1})	log A, A (s^{-1})	k_d (353 K) (s^{-1})	Reference
4-Nitrophenyl(triphenylmethyl)-, 	Toluene	323–338	122.6	15.32	1.51×10^{-3}	173
3-Nitrophenyl(triphenylmethyl)-, 	Toluene	317–327	127.6	16.09	1.62×10^{-3}	175
Phenyl[tris(4-methylphenyl)methyl]-, 	Toluene	323–338	115.1	14.80	5.87×10^{-3}	173

Phenyl[tris(4-chlorophenyl)methyl]-, 	Toluene	323–338	108.8	14.23	1.35×10^{-2}	173
4-Nitrophenyl[tris(4-methoxyphenyl)methyl]-, 	Cyanobenzene	327–357	119.5	15.00	2.08×10^{-3}	176

(continued overleaf)

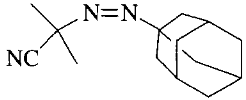
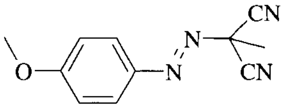
TABLE 7.12 (*continued*)

Diazene	Solvent	T (K)	E (kJ mol^{-1})	log A, A (s^{-1})	k_d (353 K) (s^{-1})	Reference
4-Nitrophenyl[tris(4-methoxyphenyl)methyl]-, 	Decalin	327–357	125.9	15.82	1.55×10^{-3}	176
4-Nitrophenyl[tris(4-methoxyphenyl)methyl]-, 	1,4-Dimetoxy benzene	327–357	128.4	16.30	1.99×10^{-3}	127

1-Methylcyclopentyl(1-methyl-1-phenylethyl)-, 	1,1-Dimethyl ethylbenzene		134.7	15.20	1.85×10^{-5}	31
1-Methyl-cyclohexyl(1-methyl-1-phenylethyl)-, 	Cumene	363			2.00×10	27
1-Methyl-cyclohexyl(1-methyl-1-phenylethyl)-, 	1,1-Dimethyl ethylbenzene		133.9	15.10	1.93×10^{-5}	31
Benzyl(1-methyl-1-phenylethyl)-, 	Cumene		154.0	16.09	2.01×10^{-7}	26
1-Bicyclo[2.2.1]heptyl(1-bicyclo[2.2.2.]octyl)-, 	Benzene	573			1.11×10^{-5}	94
1-Adamantyl(1-bicyclo[2.2.1]heptyl)-, 	Benzene	573			2.80×10^{-5}	94
1-Adamantyl(1-bicyclo[2.2.2]octyl)-, 	Benzene	573			2.51×10^{-4}	94

(continued overleaf)

TABLE 7.12 (*continued*)

Diazene	Solvent	T (K)	E (kJ mol^{-1})	log A, A (s^{-1})	k_d (353 K) (s^{-1})	Reference
Ethoxycarbonyl(1-methyl-1-cyanoethyl)-, EtOC(O)N=NCMe$_2$CN	Decalin		138.1	14.08	4.42×10^{-7}	177
1-Cyano-1-methylethyl(1,1-Dimethylethyl)-, Me$_3$CN=NCMe$_2$CN	Hexadecane		145.6	16.53	9.67×10^{-6}	178
1-Cyano-1,3,3-trimethylbutyl(1,1-dimethylethyl)-, Me$_3$CN=NCMe(CN)CH$_2$CMe$_3$	Decalin		126.4	15.29	3.86×10^{-4}	178
1-Cyano-1-methylethyl (1-methyl-1-methoxyethyl)-, MeOCMe$_2$N=NCMe$_2$CN	Decalin		134.3	16.50	4.24×10^{-4}	179
1-Cyano-1-methylethyl (phenyl)-, PhN=NCMe$_2$CN	Decalin		180.3	17.43	5.63×10^{-10}	177
Adamantyl (1-cyano-1-methylethyl)-, 	Benzene		143.1	15.25	1.19×10^{-6}	178
1,1-Dicyanoethyl (4-methoxyphenyl)-, 	Decane	358	142.0	16.33	2.08×10^{-5}	180

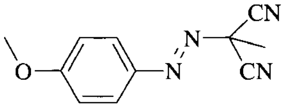
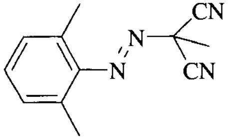
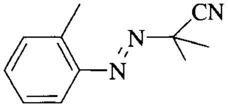
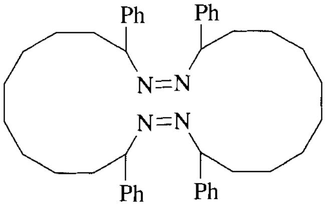
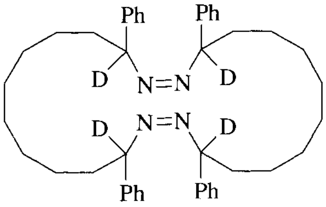
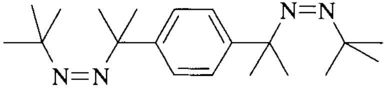
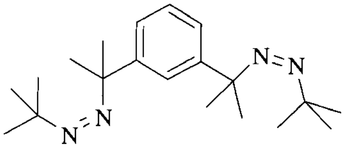
1,1-Dicyanoethyl(4-methoxyphenyl)-, 	1,2-Dichlorobenzene		115.9	12.75	3.98×10^{-5}	181
1,1-Dicyanoethyl(2,6-dimethylphenyl)- 	1,2-Dichlorobenzene		130.5	17.31	9.99×10^{-3}	182
1-Cyano-1-phenylethyl(phenyl)-, PhN=NCMe(CN)Ph	Decalin		135.6	16.22	1.43×10^{-4}	177
1-Cyano-1,3-dimethyl-3-phenylbutyl(phenyl)-, $PhN{=}NCMe(CN)CH_2CMe_2Ph$	Decalin		150.2	16.17	8.80×10^{-7}	177
1-Cyano-1,3-dimethyl-3-phenylbutyl(phenyl)-, $PhN{=}NCMe(CN)CH_2CMe_2Ph$	Decalin		172.8	18.14	3.72×10^{-8}	177
1-Cyano-1-methylethyl(2-methylphenyl)-, 	1,2-Dichlorobenzene	413–453	149.4	13.80	4.93×10^{-9}	182
1-Cyano-3-methylbutyl (1-methyl-1-phenylethyl)-, $Me_2PhCN{=}NC(CN)CH_2CHMe_2$	1,2-Dichlorobenzene	413–453	178.2	18.90	3.40×10^{-8}	182

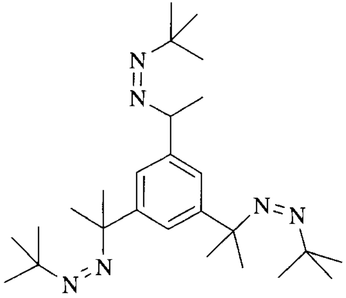
TABLE 7.13 Rate Constants for the Thermal Decay of Polyazo Compounds in Different Solvents

Compound	Solvent	T (K)	E (kJ mol^{-1})	log A, A (s^{-1})	k_d (353 K) (s^{-1})	Reference
Cyclo(3,12,15,24-tetraphenyl-1,2,13,14-tetraazatetracosane),  	Ethylbenzene	386			8.70×10^{-5}	183
Cyclo(3,12,15,24-tetradeuterium-3,12,15,24-tetraphenyl-1,2,13,14-tetraazatetracosane),  	Ethylbenzene	386			7.41×10^{-5}	183

N,*N*′-Bis[(4-(1,1-dimethylethyl-1-azo)-4-cyanopentanoyl)-oxyethyl]azobisformamide, $Me_3CN{=}NCMe(CN)(CH_2)_2C(O)O(CH_2)_2NHC(O)N{=}NC(O)NH(CH_2)_2OC(O)(CH_2)_2CMe(CN)N{=}NCMe_3$	$C_{26}H_{42}N_{10}O_6$	345–365	74.5	6.74	5.20×10^{-5}	184
1,1,2,2-Tetramethyl-1,2-bis(1,1-dimethylethyl-1-azo)ethane-, $Me_3CN{=}NCMe_2CMe_2N{=}NCMe_3$	Toluene	426–447	149.2	13.8	5.28×10^{-9}	185
1,1,2,2-Tetramethyl-1,2-bis(1,1-dimethylethyl-1-azo)ethane, $Me_3CN{=}NCMe_2CMe_2N{=}NCMe_3$	Benzene-d_6	398–417	131.9	12.7	1.52×10^{-7}	185
1,4-Bis[1-methyl-1-(1,1-dimethylethyl-1-azo)ethyl]benzene,  	Benzene	369–398	160.2	18.96	1.80×10^{-5}	186
1,3-Bis[1-methyl-1-(1,1-dimethylethyl-1-azo)ethyl]benzene,  	Benzene	383–402	136.4	15.56	2.38×10^{-5}	186

(*continued overleaf*)

TABLE 7.13 (*continued*)

Compound	Solvent	T (K)	E (kJ mol^{-1})	log A, A (s^{-1})	k_d (353 K) (s^{-1})	Reference
1,3,5-Tris[1-methyl-1-(1,1-di methylethyl-1-azo)ethyl] benzene, 	Benzene	374–398	139.7	15.96	1.94×10^{-5}	186

REFERENCES

1. J. Thiele and K. Heuser, *Ann.* **290**, 1 (1896).
2. O. P. Strausz, J. W. Lown, and H. E. Gunning, in *Comprehensive Chemical Kinetics*, C. H. Bamford and C. F. H. Tipper (Eds.), Elsevier, Amsterdam, The Netherlands, 1972, Vol. 5, p. 566.
3. P. S. Engel, *Chem. Rev.* **80**, 99 (1980).
4. *The Chemistry of Free Radical Polymerisation*, G. Moad and D. H. Solomone (Eds.), Elsevier Science Inc., New York, 1995.
5. G. Moade and D. H. Solomone, *Azo and Peroxy Initiator*, Pergamon Press, Oxford, U.K., Vol. 3, 1989, p. 97.
6. *The Chemistry of the Hydrazo, Azo and Azoxy Groups*, S. Patai (Ed.), John Wiley & Sons, Inc., New York, 1975.
7. S. G. Cohen, S. J. Groszos, and D. B. Sparrow, *J. Am. Chem. Soc.* **72**, 3947 (1950).
8. J. R. Shelton and C. K. Liang, *Synthesis*, 204 (1971).
9. S. F. Scheppele and S. Seltser, *J. Am. Chem. Soc.* **90**, 358 (1968).
10. B. K. Bandlish, Ph. D. Thesis Louisiana State University, New Orleans, LA, 1973.
11. C. G. Overberger, J. P. Anselme, and J. G. Lombardino, *Organic Compounds with Nitrogen-Nitrogen Bonds*, Roland Press, New York, 1966.
12. A. F. Bickel and W. A. Waters, *Rec. Trav. Chim.* **69**, 312 (1950).
13. G. A. Mortimer, *J. Org. Chem.* **30**, 1632 (1965).
14. A. Goldschmidt and B. Acksteiner, *Liebigs Ann. Chem.* **618**, 173 (1958).
15. E. Benzing, *Liebzig Ann. Chem.* **631**, 1 (1960).
16. A. Ohno and Y. Ohnishi, *Tetrahedron Lett.* 4405 (1969).
17. J. W. Timberlake and J. C. Martin, *J. Org. Chem.* **33**, 4054 (1968).
18. J. W. Timberlake and M. L. Hodges, *Tetrahedron Lett.* 4147 (1970).
19. J. W. Timberlake, A. W. Garner, and M. L. Hodges, *Tetrahedron Lett.* 309 (1973).
20. W. Duismann, H. D. Beckhans, and C. Ruchardt, *Tetrahedron Lett.* 265 (1974).
21. S. Seltzer and F. T. Dunne, *J. Am. Chem. Soc.* **87**, 2628 (1965).
22. S. G. Cohen and C. H. Wang, *J. Am. Chem. Soc.* **77**, 3628 (1955).
23. C. G. Overberger and A. V. Digiulio, *J. Am. Chem. Soc.* **80**, 6562 (1958).
24. A. Tsolis, S. G. Mylonakis, M. T. Nieh, and S. Seltzer, *J. Am. Chem. Soc.* **94**, 829 (1972).
25. S. Seltzer, *J. Am. Chem. Soc.* **85**, 14 (1963).
26. K. P. Kopecky and T. Gillan, *Can. J. Chem.* **47**, 2371 (1969).
27. R. C. Neuman and E. S. Alhadeff, *J. Org. Chem.* **35**, 3401 (1970).
28. A. Spialter, D. H. O'Brien, G. L. Untereiner, and W. A. Reusch, *J. Org. Chem.* **30**, 3278 (1965).
29. T. E. Stevens, *J. Org. Chem.* **26**, 2531 (1961).
30. F. D. Greene, J. C. Stowell, and W. R. Bergmark, *J. Org. Chem.* **34**, 2254 (1969).
31. J. Hinz and C. Ruchardt, *Liebigs Ann. Chem.* **765**, 94 (1972).
32. A. Oberlinner and C. Ruchardt, *Tetrahedron Lett.* 4685 (1969).
33. E. Schmitz, *Dreiringe mit Zwei Heteroatomen*, Springer-Verlag, Berlin, 1967, p. 55.

34. R. Ohme and H. Preuschhot, *Liebigs Ann. Chem.* **713**, 74 (1968).
35. R. Ohme, H. Preushhof, and H. U. Heune, *Org. Synth.* **52**, 11 (1972).
36. J. C. Stowell, *J. Org. Chem.* **32**, 2360 (1967).
37. J. W. Timberlake, H. L. Hodges, and K. Betterton, *Synthesis* 632 (1972).
38. P. S. Engel and D. J. Bishop, *J. Am. Chem. Soc.* **94**, 2148 (1972).
39. F. D. Greene and S. S. Hecht, *J. Org. Chem.* **35**, 2482 (1970).
40. C. C. Wamser and P. L. Chang, *J. Am. Chem. Soc.* **95**, 2044 (1973).
41. P. S. Engel and W.-X. Wu, *J. Org. Chem.* **55**, 2720 (1990).
42. P. S. Engel, Ch. Wang, Y.-Q. Chen., Sh. L. He, B. K. Andrews, and R. B. Weisman, *J. Org. Chem.* **59**, 6257 (1994).
43. D. R. Lide and G. W. A. Milne (Eds.), *Properties of Organic Compounds, Personal Edition*, CRC Press, Database, Boca Raton, FL, 1996.
44. D. Lide (Ed.), *Handbook of Chemistry and Physics*, CRC Press, Boca Raton, FL, 1991–1992.
45. A. Trombetti, *Can. J. Pys.* **46**, 1005 (1968).
46. R. K. Bohn and S. H. Bauer, *Inorg. Chem.* **6**, 309 (1967).
47. C. H. Chang, R. F. Porter, and S. H. Bauer, *J. Am. Chem. Soc.* **92**, 5313 (1970).
48. A. B. Jaffe, D. S. Malament, E. P. Slisz, and J. M. McBride, *J. Am. Chem. Soc.* **94**, 8515 (1972).
49. G. Argay and K. Sasva'ri, *Acta Crystallogr. B*, **27**, 1851 (1971).
50. C. J. Brown, *Acta Crystallogr.* **21**, 146 (1966).
51. A. Mostad and C. Romming, *Acta Chem. Scand.* **25**, 3561 (1971).
52. H. Hope and D. Victor, *Acta Crystallogr. B*, **25**, 1849 (1969).
53. J. L. Galigne, *Acta Crystallogr. B*, **26**, 1977 (1970).
54. P. S. Engel, R. L. Montgomery, M. Mansson, R. A. Leckonby, H. L. Foyt, and F. D. Rossini, *J. Chem. Thermodyn.* **10**, 205 (1978).
55. P. S. Engel, R. A. Melaugh, M. Mansson, J. W. Timberlake, A. W. Garner, and F. D. Rossini, *J. Chem. Thermodyn.* **8**, 607 (1976).
56. R. L. Montogomery, P. S. Engel, R. A. Leckonby, F. D. Rossini, M. Mansson, S. Szilagyi, and J. W. Timberlake, *J. Chem. Eng. Data* **23**, 129 (1979).
57. P. S. Engel, J. L. Wood, J. A. Sweet, and J. L. Margrave, *J. Am. Chem. Soc.* **96**, 2381 (1974).
58. W. S. McEwan and M. W. Rigg, *J. Am. Chem. Soc.* **73**, 4725 (1951).
59. W. Tsang, in *Energetics of Free Radicals*, A. Greenberg, and J. Liebman (Eds.), Blackie Academic and Professional, New York, 1996, p. 22.
60. T. Koenig, in *Free Radicals*, J. K. Kochi (Ed.), John Wiley & Sons, Inc., New York, 1973, Vol. 1, p. 113.
61. K. Chakravorty, J. M. Pearson, and M. Szwarc, *J. Phys. Chem.* **73**, 746 (1969).
62. E. T. Denisov, *Liquid-Phase Reaction Rate Constants*, Plenum, New York, 1974.
63. H. C. Ramsperger, *J. Am. Chem. Soc.* **49**, 912 (1927).
64. H. C. Ramsperger, *J. Am. Chem. Soc.* **49**, 1495 (1927).
65. L. S. Kassel, *Kinetics of Homogeneous Gas Reaction*, New York, 1932, p. 196.
66. O. K. Rice and D. V. Stickman, *J. Chem. Phys.* **4**, 242 (1936).

67. C. Steel and A. F. Trotman-Dickenson, *J. Chem. Soc.* **975** (1959).
68. H. A. Taylor and F. P. Jahn, *J. Chem. Phys.* **7**, 470 (1939).
69. M. Page, H. O. Pritchard, and A. F. Trotman-Dickenson, *J. Chem. Soc.* 3878 (1953).
70. W. Forst and O. K. Rice, *139th National Meeting ACS*, St. Louis, MO, 1961.
71. G. Chilts, C. F. Aten, and S. H. Bauer, *J. Phys. Chem.* **66**, 1426 (1966).
72. Ch. Do-Rin and O. K. Rice, *Int. J. Chem. Kinet.* **1**, 171 (1969).
73. D. Clark and H. O. Pritchard, *J. Chem. Soc.* 2136 (1956).
74. E. Leventhal, C. R. Simonds, and C. Steel, *Can. J. Chem.* **40**, 930 (1962).
75. T. H. McGee and C. E. Waring, *J. Phys. Chem.* **73**, 2838 (1969).
76. W. D. Clark, D. F. Swinehart, and R. D. McCoy, *132nd ACS Meeting*, New York, 1957, p. 475.
77. H. S. Sandhu, *J. Phys. Chem.* **72**, 1857 (1968).
78. M. J. Perona, P. C. Beadle, and D. M. Golden, *Int. J. Chem. Kinet.* **5**, 495 (1973).
79. G. Martin and A. J. Maccoll, *J. Chem. Soc., Perkin Trans.* 2, 1887 (1977).
80. G. Geiseler and J. Hoffmann, *J. Phys. Chem.* **57**, 318 (1968).
81. H. C. Ramsperger, *J. Am. Chem. Soc.* **50**, 714 (1928).
82. B. H. Al-Sader and R. J. Crauford, *Can. J. Chem.* **48**, 2745 (1970).
83. A. U. Blackham and N. L. Eatough, *J. Am. Chem. Soc.* **84**, 2922 (1962).
84. J. B. Levy and B. K. W. Copeland, *J. Am. Chem. Soc.* **82**, 5314 (1960).
85. J. C. Martin and J. M. Timberlake, *J. Am. Chem. Soc.* **92**, 978 (1970).
86. M. Prochazka, O. Ruba, and D. Lim, *Coll. Czech. Chem. Commun.* **33**, 3387 (1968).
87. M. Prochazka, *Coll. Czech. Chem. Commun.* **41**, 1557 (1976).
88. W. Duismann and C. Ruchardt, *Tetrahedron Lett.*, 4517 (1974).
89. B. K. Bandlish, A. W. Garner, M. L. Hodges, and J. W. Timberlake, *J. Am. Chem. Soc.* **97**, 5856 (1975).
90. D. Lim, *Coll. Czech. Chem. Commun.* **33**, 1122 (1968).
91. F. Ya. Grishenko, Z. V. Fal'chenko, N. A. Busko, and V. K. Grishchenko, *Vysokomol. Soed. Ser. B*, **32**, 728 (1990).
92. J. W. Timberlake and A. W. Garner, *J. Org. Chem.* **41**, 1666 (1976).
93. J. Hinz, A. Oberlinner, and C. Ruchardt, *Tetrahedron Lett.* 1975 (1973).
94. V. Golzke, F. Groeger, A. Oberlinner, and C. Ruchardt, *Nouv. J. Chim.* **2**, 169 (1978).
95. J. Hinz, *Inaugural Dissertation*, University of Freiburg, Freiburg, Germany, 1971.
96. J. A. Berson, C. L. Olsen, and J. S. Walis, *J. Am. Chem. Soc.* **84**, 3337 (1962).
97. R. U. R. Wahl, L. Zeng, S. A. Madison, R. L. DePinto, and B. J. Shay, *J. Chem. Soc. Perkin Trans. 2*, 2009 (1998).
98. H. Klefer and T. G. Traylor, *Tetrahedron Lett.* 6163 (1966).
99. E. Rizzardo, A. K. Serelis, and D. H. Solomon, *Aust. J. Chem.* **35**, 2013 (1982).
100. K. U. Ingold, T. Paul, M. J. Young, and L. Doiron, *J. Am. Chem. Soc.* **119**, 12364 (1997).
101. S. C. Cohen and Ch. H. Wang, *J. Am. Chem. Soc.* **75**, 5504 (1953).
102. J. R. Shelton and C. K. Liang, *J. Org. Chem.* **38**, 2301 (1973).
103. R. C. Petersen, J. H. Markgraf, and S. D. Ross, *J. Am. Chem. Soc.* **83**, 3819 (1961).

104. S. Selzer, *J. Am. Chem. Soc.* **83**, 2625 (1961).
105. S. G. Cohen and Ch. H. Wang, *J. Am. Chem. Soc.* **77**, 2457 (1955).
106. S. F. Nelsen and P. D. Bartlett, *J. Am. Chem. Soc.* **88**, 137 (1966).
107. J. R. Shelton, Ch. K. Liang, and P. Kovacic, *J. Am. Chem. Soc.* **90**, 354 (1968).
108. P. Kovacic, R. R. Flynn, J. F. Gormih, A. H. Kappelman, and J. R. Shelton, *J. Org. Chem.* **34**, 3312 (1969).
109. W. Duismann and C. Ruchardt, *Chem. Ber.* **106**, 1083 (1973).
110. C. G. Overberger and A. B. Finestone, *J. Am. Chem. Soc.* **78**, 1638 (1956).
111. J. Bonnekessel and C. Ruchardt, *Chem. Ber.* **106**, 2890 (1973).
112. F. M. Lewis and M. S. Matheson, *J. Am. Chem. Soc.* **71**, 747 (1949).
113. J. Szafko, W. Feist, and B. Pabinszafko, *J. Pol. Sci. A., Polym. Chem.* **34**, 613 (1996).
114. D. C. Blackley and H. W. Melville, *Makromol. Chem.* **18/19**, 16 (1956).
115. J. W. Breitenbach and A. Shindler, *Monatsh. Chem.* **83**, 724 (1952).
116. J. P. Van Hook and A. V. Tobolsky. *J. Am. Chem. Soc.* **80**, 779 (1958).
117. G. S. Hammond, J. N. Sen, and C. E. Boser, *J. Am. Chem. Soc.* **74**, 3244 (1955).
118. L. M. Arnett and J. H. Petersen, *J. Am. Chem. Soc.* **74**, 2027 (1952).
119. S. Rummel, H. Hubner, and P. Krumbiegel, *Z. Chem.* **10**, 392 (1967).
120. K. Ziegler and W. Deparade, *Liebzig Ann. Chem.* **567**, 123 (1950).
121. C. G. Overberger, M. T. O' Shaughnessy, and H. Shalit, *J. Am. Chem. Soc.* **71**, 2661 (1949).
122. L. V. Pisemskii, B. L. Psicha, and V. V. Charitonov, *Neftekhimiya* **40**, 123 (2000).
123. M. Talat-Erben and S. Bywater, *J. Am. Chem. Soc.* **77**, 3712 (1955).
124. S. Rummel, H. Hubner, and P. Krumbiege, *Z. Phys. Chem.* **9**, 351 (1967).
125. C. E. H. Bawn and D. Verdin, *Trans. Faraday Soc.* **56**, 815 (1960).
126. C. E. H. Bawn and S. F. Mellish, *Trans. Faraday Soc.* **47**, 1216 (1951).
127. A. L. Aleksandrov, T. I. Sapacheva, and V. F. Shuvalov, *Izv. AN SSSR, Ser. Khim.* 955 (1969).
128. A. L. Aleksandrov and E. T. Denisov, *Kinet. Katal.* **10**, 912 (1969).
129. J. Betts and J. C. Robb, *Trans. Faraday Soc.* **64**, 2402 (1968).
130. Z. I. Kulitskii, L. M. Terman, V. F. Tsepalov, and V. Ya. Shlyapintokh, *Izv. AN SSSR, Ser. Khim.* 253 (1963).
131. S. N. Khanna, S. R. Chatterjee, U. S. Nandi, and S. R. Palit, *Trans. Faraday Soc.* **58**, 1827 (1962).
132. A. V. Tobolsky and B. Baysal, *J. Polym. Sci.* **11**, 471 (1953).
133. O. N. Karpukhin, T. V. Pokholok, and V. Ya. Shlyapintokh, *Vysokomol. Soed., A*, **13**, 22 (1971).
134. A. P. Griva, L. N. Denisova, and E. T. Denisov, *Zh. Fiz. Khim.* **59**, 946 (1985).
135. A. P. Griva, L. N. Denisova, and E. T. Denisov, *Vysokomol. Soed., A*, **19**, 219 (1977).
136. S. L. Shanina, V. A. Roginskii, and V. B. Miller, *Vysokomol. Soed., A*, **18**, 1160 (1976).
137. B. A. Krisyuk, E. N. Ushakov, A. P. Griva, and E. T. Denisov, *Dokl. AN SSSR*, **277**, 630 (1984).
138. V. V. Pchelintsev and E. T. Denisov, *Vysokomol. Soed., A*, **25**, 781 (1983).
139. J. A. Howard and K. U. Ingold, *Can. J. Chem.* **42**, 1044 (1964).

140. L. M. Arnett and J. H. Peterson, *J. Am. Chem. Soc.* **74**, 2031 (1952).
141. J. C. Bevington and D. E. Evans, *Trans. Faraday Soc.* **55**, 1777 (1959).
142. J. H. Bradbury and H. W. Melville, *Proc. R. Soc., London, Ser. A.* **222**, 456 (1954).
143. L. M. Andronov and G. E. Zaikov, *Kinet. Katal.* **8**, 270 (1967).
144. G. Henrici-Olive and S. Olive, *Makromol. Chem.* **58**, 188 (1962).
145. M. S. Chloplyankina, A. L. Buchyachenko, A. G. Vasileva, and M. B. Neiman, *Izv. AN SSSR, Ser. Khim.* 1296 (1965).
146. V. F. Tsepalov and E. M. Kotsuba, *Izv. AN SSSR, Ser. Khim.*, 1220 (1967).
147. H. M. Beyleryan, S. K. Grigoryan, and O. A. Chaltikyan, *Izv. Armyan. AN SSR*, **17**, 245 (1964).
148. J. C. Bevington, H. W. Melville, and R. P. Taylor, *J. Pol. Sci.* **14**, 463 (1954).
149. J. C. Bevington, *Intern. Sympos. Macromol. Chem.* Milan, 3 (1954).
150. G. Ayrey and C. G. Moore, *J. Pol. Sci.* **36**, 41 (1959).
151. J. C. Bevington, J. H. Bradbure, and G. M. Burnett, *J. Pol. Sci.* 12, 469 (1954).
152. J. C. Bevington, *Trans. Faraday. Soc.* **51**, 1392 (1955).
153. W. Duismann and C. Ruchardt, *Chem. Ber.* **111**, 596 (1978).
154. K. Ziegler, V. Deparade, and W. Meys, *Liebigs Ann. Chem.* **567**, 141 (1950).
155. C. G. Overberger, W. F. Hale, M. B. Berenbaum, and A. B. Finestone, *J. Am. Chem. Soc.* **76**, 6185 (1954).
156. C. G. Overberger and M. B. Berenbaum, *J. Am. Chem. Soc.* **73**, 2618 (1951).
157. F. M. Lewis and M. S. Matheson, *J. Am. Chem. Soc.* **71**, 747 (1949).
158. P. S. Engel., C. F. Billera, T. B. Dunn, and D. A. Barry, *J. Org. Chem.* **63**, 9763 (1998).
159. S. P. Verneker, N. D. Ghatge, and P. P. Wadgaokner, *J. Polym. Sci. A-1.* **26**, 953 (1988).
160. C. G. Oberberger and A. Lebovits, *J. Am. Chem. Soc.* **76**, 2722 (1954).
161. C. G. Overberger, H. Biletch, A. B. Finestone, J. Lilker, and J. Herbert, *J. Am. Chem. Soc.* **75**, 2078 (1953).
162. A. F. Barton, J. C. Bevington, and A. Wahid, *Makromol. Chem.* **67**, 195 (1963).
163. Ch.-H. S. Wu, G. S. Hammond, and J. M. Wight, *J. Am. Chem. Soc.* **82**, 5386 (1960).
164. C. G. Overberger and H. J. Biletch, *J. Am. Chem. Soc.* **73**, 4880 (1951).
165. E. A. S. Cavell and A. C. Meeks, *Makromol. Chem.* **108**, 304 (1967).
166. H. C. Ramsperger, *J. Am. Chem. Soc.* **51**, 2134 (1929).
167. R. J. Crawford and K. J. Takagi, *J. Am. Chem. Soc.* **94**, 7406 (1972).
168. P. S. Engel and D. J. Bishop, *J. Am. Chem. Soc.* **97**, 6754 (1975).
169. G. Martin and A. J. Maccol, *J. Chem. Soc., Perkin Trans. 2*, 1887 (1977).
170. C. G. Overberger and A. V. Diguilio, *J. Am. Chem. Soc.* **81**, 2154 (1959).
171. P. S. Engel and W. Wu, *J. Org. Chem.* **55**, 2720 (1990).
172. J. W. Timberlake and A. W. Garner, *J. Org. Chem.* **41**, 1666 (1976).
173. G. L. Davies, D. H. Hey, and G. H. Williams, *J. Chem. Soc.* **79**, 4104 (1957).
174. M. G. Adler and J. E. Leffler, *J. Am. Chem. Soc.* **76**, 1425 (1954).
175. S. Solomon, Ch. H. Wang, and S. G. Cohen, *J. Am. Chem. Soc.* **79**, 4104 (1957).
176. M. D. Cohen, J. E. Leffler, and L. H. Barbato, *J. Am. Chem. Soc.* **76**, 4169 (1954).
177. M. Prochazka, O. Ryba, and D. Lim, *Coll. Czech. Chem. Comm.* **36**, 3650 (1971).

178. M. Prochazka, O. Ryba, and D. Lim, *Coll. Czech. Chem. Comm.* **36**, 2640 (1971).
179. D. S. Malament, *Isr. J. Chem.* **11**, 819 (1973).
180. R. Kerber, O. Nuyken, and R. Steinhausen, *Makromol. Chem.* **175**, 3225 (1974).
181. R. Kerber, O. Nuyken, and V. Pasupathy, *Makromol. Chem.* **170**, 155 (1973).
182. B. W. Brooks, F. S. Dainton, and K. J. Ivin, *Trans. Faraday Soc.* **61**, 1437 (1965).
183. S. G. Mylonakis and S. Seltzer, *J. Am. Chem. Soc.* **90**, 5487 (1968).
184. C. J. Simionescu, A. A. Popa, and M. Pastavanu, *Brt. Polym. J.* **23**, 347 (1990).
185. P. S. Engel, Ch. Wang, Ya. Chen., C. Ruchardt, and H.-D. Beclhaus, *J. Am. Chem. Soc.* **115**, 65 (1993).
186. P. S. Engel, L. Pan, Y. Ying, and B. Alemany, *J. Am. Chem. Soc.* **123**, 3706 (2001).

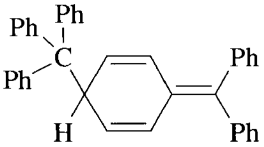
Handbook of Free Radical Initiators. E.T. Denisov, T.G. Denisova, T.S. Pokidova
Copyright © 2003 John Wiley & Sons, Inc.
ISBN: 0-471-20753-5

8

COMPOUNDS WITH WEAK C–C, N–N, C–N, AND N–O BONDS

8.1 POLYPHENYLHYDROCARBONS

The BDE of C–C bonds in hydrocarbons are lower than the BDE of C–H bonds; for example, D(C–H) $= 422$ kJ mol^{-1} and D(C–C) $= 378$ kJ mol^{-1} in ethane. This is why the C–C bond dissociation starts the chain reaction of thermolysis for hydrocarbons.[1] The values of the C–C bond dissociation energies of aliphatic hydrocarbons cover the range of 300–380 kJ mol^{-1} and hydrocarbons are stable at moderate temperatures. However, among olefins and alkylaromatic hydrocarbons we can find compounds that dissociate homolytically under mild conditions (300–400 K). Gomberg was the first to synthesize unstable, hexaphenylethane, Ph_3CCPh_3, which decomposed into two triphenylmethyl radicals at room temperature.[2] The discovery of the free triphenylmethyl radical opened the epoch of free radical chemistry a century ago.[3] Later, it was proved that two triphenylmethyl radicals cannot form hexaphenylethane due to huge steric hindrance. Thus combine with formation of a hydrocarbon with the following quinone structure[4]



Many years later, polyphenylhydrocarbons found their application as initiators of free radical polymerization.[5] Low thermal stability of hydrocarbons with the structure $Me_{3-n}Ph_nCCPh_nMe_{3-n}$ is the result of stabilization of the formed $Me_{3-n}Ph_nC^\bullet$ radical.[6]

$R^\bullet$	$Me_3C^\bullet$	$Me_2PhC^\bullet$	$MePh_2C^\bullet$	$Ph_3C^\bullet$
$D(R-R)/(kJ\,mol^{-1})$	321	151	125	80

The rate constants for the decomposition of polyphenylhydrocarbons into free radicals are seen in Table 8.1.

8.2 SUBSTITUTED HYDRAZINES

The dinitrogen molecule has a very strong N–N bond $D(N{\equiv}N) = 473$ kJ mol^{-1}.[6] The N–N bond in the hydrazine molecule is sufficiently weaker: $D(H_2N-NH_2) = 275$ kJ mol^{-1}. The introduction of the phenyl groups into the hydrazine molecule decreases the BDE of the N–N bond.[6]

Molecule	$N{\equiv}N$	H_2NNH_2	H_2NNHPh	Ph_2NNPh_2
$D(N-N)/kJ\,mol^{-1}$	473	275	219	125

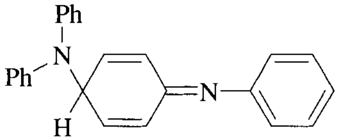
Tetraphenylhydrazine is a very convenient generator of diphenylaminyl radicals at moderate temperatures. The mechanism for the decomposition of tetraphenylhydrazine in solution includes the following steps:

$$Ph_2NNPh_2 \rightarrow [Ph_2N^\bullet + Ph_2N^\bullet]$$

$$[Ph_2N^\bullet + Ph_2N^\bullet] \rightarrow 2Ph_2N^\bullet$$

$$[Ph_2N^\bullet + Ph_2N^\bullet] \rightarrow Ph_2NNPh_2$$

$$[Ph_2N^\bullet + Ph_2N^\bullet] \rightarrow$$

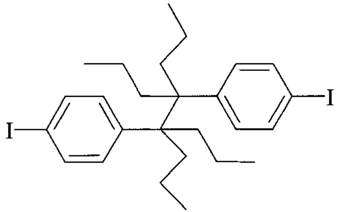
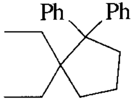


The values for the decomposition rate constants of tetraphenylhydrazine and its analogues are seen in Table 8.2.

The *N*-nitrozoacylarylamines possess a weak N–N bond and is decomposed into free radicals with activation energies close to 100 kJ mol^{-1} (see Table 8.3). The (S)-nitrozothiols have weak S–N bonds that split with formation of an alkylthiyl radical and NO (rate constants for the decomposition are seen in Table 8.3).

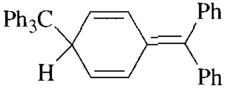
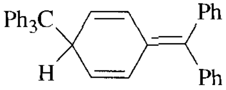
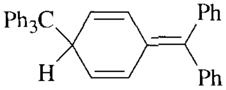
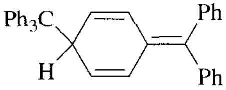
$$RSNO \rightarrow RS^\bullet + NO^\bullet$$

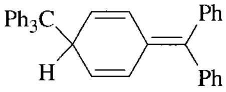
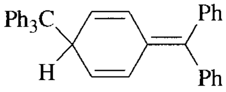
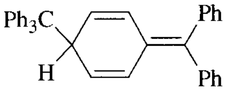
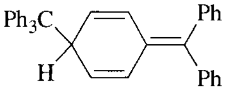
TABLE 8.1 Rate Constants for the Thermal Decay of Polyphenylalkanes

Compound	Solvent	T (K)	E, (kJ mol^{-1})	log A, A (s^{-1})	k_d (350 K) (s^{-1})	Reference
2,2,3,3-Tetraphenylbutane, $MeCPh_2CPh_2Me$	Bromobenzene	337.6			3.72×10^{-4}	7
2,2,3,3-Tetraphenylbutane, $MeCPh_2CPh_2Me$	Chlorobenzene	333–353	125.5	16.13	2.51×10^{-3}	7
2,2,3,3-Tetraphenylbutane, $MeCPh_2CPh_2Me$	Chlorobenzene	333			2.00×10^{-4}	8
2,2,3,3-Tetraphenylbutane, $MeCPh_2CPh_2Me$	2,6-Dichlorobenzene	338			4.07×10^{-4}	7
3,3,4,4-Tetraphenylhexane, $EtPh_2CCPh_2Et$	Toluene	293–323	77.4	9.74	1.54×10^{-2}	9
3,4-Diethyl-3,4-diphenylhexane, $Et_2PhCCPhEt_2$	Chlorobenzene	415.1			3.80×10^{-4}	7
4,5-Diphenyl-4,5-dipropyloctane, $Pr_2PhCCPhPr_2$	Chlorobenzene	383–399	150.6	16.35	7.49×10^{-7}	7
5,6-Dibutyl-5,6-diphenyldecane, $Bu_2PhCCPhBu_2$	Chlorobenzene	384–399	159.0	17.43	5.02×10^{-7}	7
4,5-Di(4′-iodophenyl)-4,5-dipropyloctane, 	Chlorobenzene	373–393	129.7	13.91	3.58×10^{-6}	10
1,1-Diphenyl-2,2-diethylcyclopentane, 	Toluene	293–313	85.8	11.64	6.84×10^{-2}	9

(*continued overleaf*)

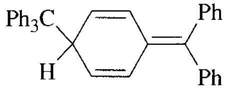
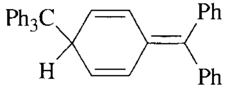
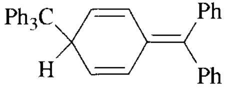
TABLE 8.1 (*continued*)

Compound	Solvent	T (K)	E, (kJ mol^{-1})	log A, A (s^{-1})	k_d (350 K) (s^{-1})	Reference
Diphenyl(4-triphenylmethyl-2,5-cyclohexadien-1-ylidene)methane, 	Aniline	273			3.20×10^{-3}	11
Diphenyl(4-triphenylmethyl-2,5-cyclohexadien-1-ylidene)methane, 	Carbon tetrachloride	283–293	80.3	12.97	9.68	11
Diphenyl(4-triphenylmethyl-2,5-cyclohexadien-1-ylidene)methane, 	2-Chloroethanol	273			2.19×10^{-3}	11
Diphenyl(4-triphenylmethyl-2,5-cyclohexadien-1-ylidene)methane, 	Dibromomethane	273			3.31×10^{-3}	11

Diphenyl(4-triphenylmethyl-2,5-cyclohexadien-1-ylidene)methane, 	Diethyl malonate	273	2.19×10^{-3}	11
Diphenyl(4-triphenylmethyl-2,5-cyclohexadien-1-ylidene)methane, 	*N*,*N*-Diethyl acetamide	273	2.19×10^{-3}	11
Diphenyl(4-triphenylmethyl-2,5-cyclohexadien-1-ylidene)methane, 	*N*,*N*-Dimethyl aniline	273	2.29×10^{-3}	11
Diphenyl(4-triphenylmethyl-2,5-cyclohexadien-1-ylidene)methane, 	Methanol	273	2.88×10^{-3}	11

(*continued overleaf*)

TABLE 8.1 (*continued*)

Compound	Solvent	T (K)	E, (kJ mol^{-1})	log A, A (s^{-1})	k_d (350 K) (s^{-1})	Reference
Diphenyl(4-triphenylmethyl-2,5-cyclohexadien-1-ylidene)methane,  	Nitrobenzene	273			2.51×10^{-3}	11
Diphenyl(4-triphenylmethyl-2,5-cyclohexadien-1-ylidene)methane,  	Pyridine	273			2.19×10^{-3}	11
Diphenyl(4-triphenylmethyl-2,5-cyclohexadien-1-ylidene)methane,  	Toluene	273			2.51×10^{-3}	11

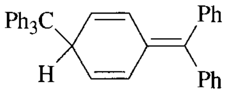
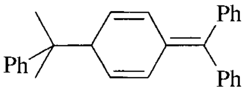
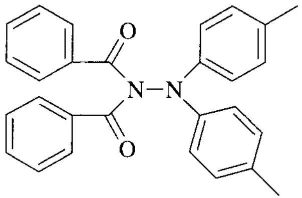
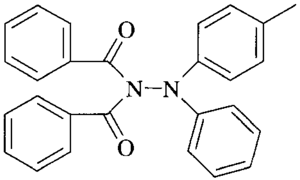
Diphenyl(4-triphenylmethyl-2,5-cyclohexadien-1-ylidene)methane, 	Trichloromethane	273			3.51×10^{-3}	11
Diphenyl[4-(1′-methyl-1-phenylethyl)-2,5-cyclo-hexadien-1-ylidene]methane, 	Hexene	299–313	111.3	15.79	0.151	12
Diacetyl, MeC(O)C(O)Me	Methylethylketone	383–418	148.1	13.46	2.28×10^{-9}	13

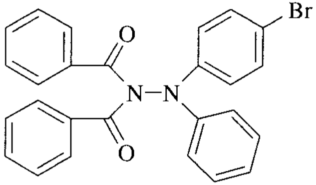
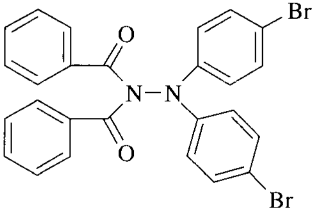
TABLE 8.2 Rate Constants for the Thermal Decay of Hydrazines

Hydrazine	Solvent	T (K)	E, (kJ mol^{-1})	log A, A (s^{-1})	k_d (350 K) (s^{-1})	References
Hydrazine, NH_2NH_2	Gas phase	970–1120	225.9	13.00	1.93×10^{-21}	14
Hydrazine, NH_2NH_2	Gas phase	903–1053	251.0	12.60	1.38×10^{-25}	15
Hydrazine, NH_2NH_2	Gas phase	887–1034	227.6	11.70	5.41×10^{-23}	16,17
Perfluorohydrazine, NF_2NF_2	Gas phase	613–680	81.2	14.98	7.27×10^{2}	18
Methylhydrazine, $MeNHNH_2$	Gas phase	546–862	217.1	13.19	6.17×10^{-20}	16
1,1-Dimethylhydrazine, Me_2NNH_2	Gas phase	709–831	207.5	13.22	1.79×10^{-18}	16
Phehylhydrazine, $PhNHNH_2$	Gas phase	598–710	167.4	11.80	6.56×10^{-14}	17
Tetraphenylhydrazine, Ph_2NNPh_2	Benzene	333–358	117.3	13.76	1.79×10^{-4}	19
Tetraphenylhydrazine, Ph_2NNPh_2	1,2-Dichlorobenzene	348–373	125.5	15.04	2.04×10^{-4}	20
Tetraphenylhydrazine, Ph_2NNPh_2	Chlorobenzene	298.2–383	117.5	13.89	2.26×10^{-4}	21
1,1-Dibenzoyl-2,2-bis(4′-methylphenyl)hydrazine, 	Methylacetate	308–313	62.8	11.01	43.4	22

1,1-Dibenzoyl-2-(4′-methylphenyl)-2-phenylhydrazine, 	Methylacetate	253–233	66.1	11.44	37.6	22
1,1-Dibenzoyl-2,2-diphenylhydrazine, $Ph_2NN(COPh)_2$	Methylacetate	253–233	69.5	11.87	31.5	22

(*continued overleaf*)

TABLE 8.2 (*continued*)

Hydrazine	Solvent	T (K)	E, (kJ mol^{-1})	log A, A (s^{-1})	k_d (350 K) (s^{-1})	References
1,1-Dibenzoyl-2-(4′-bromophenyl)-2-phenylhydrazine,  	Methylacetate	258–243	69.5	11.74	23.3	22
1,1-Dibenzoyl-2,2-bis(4′-bromophenyl)hydrazine,  	Methylacetate	258–233	72.0	12.15	25.4	22

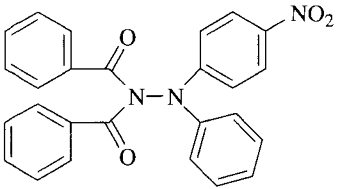
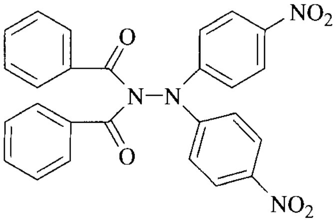
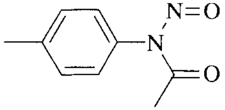
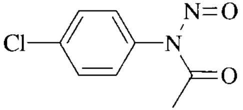
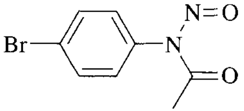
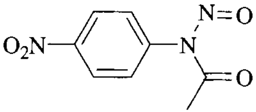
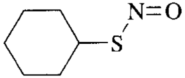
1,1-Dibenzoyl-2-(4′-nitrophenyl)-2-phenylhydrazine, 	Methylacetate	253–243	80.8	12.73	4.69	22
1,1-Dibenzoyl-2,2-bis(4′-nitrophenyl)hydrazine, 	Methylacetate	273–303	90.4	13.80	2.04	22

TABLE 8.3 Rate Constants for the Thermal Decay of *N*-Nitrozo-N-Acylarylamines and (*S*)-Nitrozothiols in Solutions

Compound	Solvent	*T* (K)	*E*, (kJ mol^{-1})	log *A*, *A* (s^{-1})	k_d (350 K) (s^{-1})	Reference
N-Nitrozo-*N*-acylphenylamine, PhN(NO)C(O)Me	Benzene	293–303	95.2	12.87	4.60×10^{-2}	23
N-Nitrozo-*N*-acyl-4-methylphenylamine, 	Benzene	293–303	97.2	13.23	5.30×10^{-2}	23
N-Nitrozo-*N*-acyl-4-chlorophenylamine, 	Benzene	293–303	95.5	12.88	4.24×10^{-2}	23
N-Nitrozo-*N*-acyl-4-bromophenylamine, 	Benzene	293–303	98.9	13.52	5.75×10^{-2}	23

N-Nitrozo-*N*-acyl-4-nitrophenylamine, 	Benzene	293–303	106.9	13.55	3.95 x 10^{-3}	23
(*S*)-Nitrozohexylthiol, $Me(CH_2)_5SNO$	Acetonitrile	333–353	120.9	13.40	2.27 x 10^{-5}	24
(*S*)-Nitrozo-1,1-dimethylpropylthiol, $EtMe_2SNO$	Acetonitrile	343			1.45 x 10^{-4}	24
(*S*)-Nitrozophenylthiol, PhSNO	Acetonitrile	303			1.41 x 10^{-3}	24
(*S*)-Nitrozocyclohexylthiol, 	Acetonitrile	333–353	132.2	15.35	4.17 x 10^{-5}	24

8.3 ALKOXYAMINES

Alkoxyamines, R_2NOR^1, have weak C–O and N–O bonds. They have an important part application in polymer chemistry as the component of "living polymerization" for regulation of the molecular weight of a polymer.[25] Alkoxyamines are formed as products of the chain termination in oxidized polymers when sterically hindered amines (derivatives of 1,1,5,5-tetramethylpiperidine) are used as light stabilizers.[26] The decomposition of R_2NOR^1 in solution or in a polymer consists of the following stages:[25]

$$R_2NOR^1 \rightarrow [R_2NO^\bullet + R^{1\bullet}]$$

$$[R_2NO^\bullet + R^{1\bullet}] \rightarrow R_2NOR^1$$

$$[R_2NO^\bullet + R^{1\bullet}] \rightarrow R_2NOH + \text{Olefin}$$

$$[R_2NO^\bullet + R^{1\bullet}] \rightarrow R_2NO^\bullet + R^{1\bullet}$$

The nitroxyl radical reacts very promptly with any alkyl radical or macroradical in solution. Rate constants for these reactions are seen in Chapter 3. Some nitroxyl radicals participate in the reaction of disproportionation. Rate constants of alkoxyamine decomposition are collected in Table 8.4.

8.4 NITRO COMPOUNDS

Nitro compounds possess a weak C–N bond and their decomposition in the gas phase proceeds via free radical formation.[37,38] The limiting step of nitroalkanes decomposition is their splitting along the C–N bond

$$RNO_2 \rightarrow R^\bullet + {}^\bullet NO_2$$

succeeding by chain reactions induced by alkyl radicals. The following stable products for the gas-phase thermolysis of nitroethane (850 K) were identified (mol %):[39] H_2O (66), CO (48), N_2 (29), NO (34), CH_4 (37), CH_2O (22), C_2H_4 (40), NO_2 (8), C_2H_6 (3).

Polynitro compounds are widely used as explosives. The splitting C–N bond is supposed to be the first step for polynitro compound decomposition, for example,

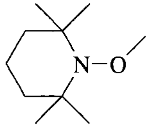
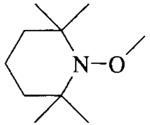
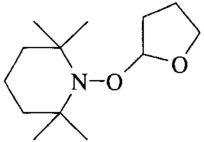
$$(NO_2)_3CNO_2 \rightarrow (NO_2)_3C^\bullet + {}^\bullet NO_2$$

Nitro compounds are not used as initiators of radical polymerization because they act as inhibitors terminating the chains in this reaction with macroradicals.[40]

$$R^\bullet + R^1NO_2 \rightarrow R^1N(O^\bullet)OR$$

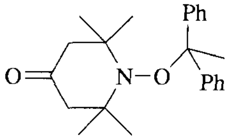
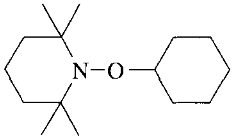
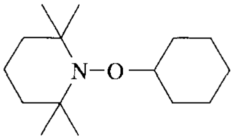
The values for the physical properties and enthalpies of formation for selected nitro compounds are presented in Tables 8.5 and 8.6 and rate constants of their decomposition in the gas and liquid phases are collected in Tables 8.7 and 8.8.

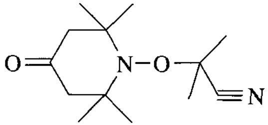
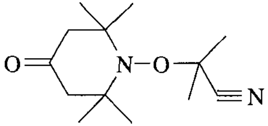
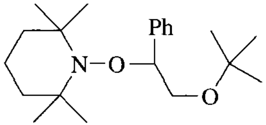
TABLE 8.4 Rate Constant of Thermal Decay of the Related *N*-Alkoxyamines

N-Alkoxyamine	Solvent	*T* (K)	*E*, (kJ mol^{-1})	log *A*, *A* (s^{-1})	k_d (350 K) (s^{-1})	References
(2,2,6,6-Tetramethyl-1-piperidinyloxy)methane,  	Gas phase	503–533	189.5	15.30	1.05×10^{-13}	27
(2,2,6,6-Tetramethyl-1-piperidinyloxy)methane,  	Cyclohexadiene or 9,10-dihydroanthracene	503–533	192.5	15.30	3.72×10^{-14}	27
2-(2′, 2′, 6′, 6′-Tetramethyl-1′-piperidinyloxy)tetrahydrofurane,  	Cyclohexadiene or 9,10-dihydroanthracene	503–533	179.5	14.10	2.05×10^{-13}	27

(continued overleaf)

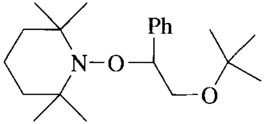
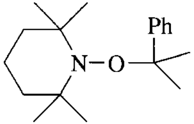
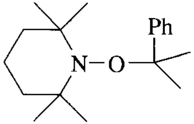
TABLE 8.4 (*continued*)

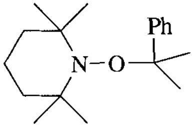
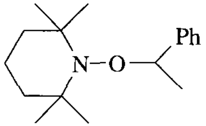
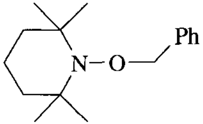
N-Alkoxyamine	Solvent	*T* (K)	*E*, (kJ mol^{-1})	log *A*, *A* (s^{-1})	k_d (350 K) (s^{-1})	References
1-(4′-oxo-2′, 2′, 6′, 6′-tetramethyl-1′-piperidyloxy)-1,1-diphenylethane,  	Chlorobenzene		102.6	14.80	0.31	28
(2,2,6,6-Tetramethyl-1-piperidinyloxy)cyclohexane,  	Cyclohexadiene or 9,10-dihydroanthracene	488–495	171.5	14.10	3.2×10^{-12}	27
(2,2,6,6-Tetramethyl-1-piperidinyloxy)cyclohexane,  	Isooctane		134.0	13.70	5.03×10^{-7}	29

2-Methyl-2-(4′-oxo-2′, 2′, 6′, 6′-tetramethyl-1′-piperidinyloxy)propionitrile, 	Cyclohexane	92.1	9.04	1.97×10^{-5}	28
2-Methyl-2-(4′-oxo-2′, 2′, 6′, 6′-tetramethyl-1′-piperidinyloxy)propionitrile, 	Isooctane	87.0	8.60	4.13×10^{-5}	29
2-(1′, 1′-Dimethylethoxy)-1-phenyl-1-(2′, 2′, 6′, 6′-tetra methyl-1-piperidinyloxy)ethane, 	Toluene	133.2	14.04	1.45×10^{-6}	30

· (*continued overleaf*)

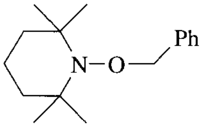
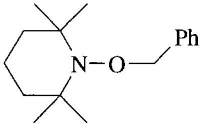
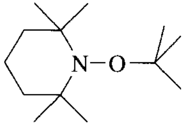
TABLE 8.4 (*continued*)

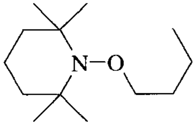
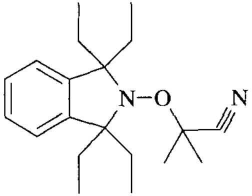
N-Alkoxyamine	Solvent	T (K)	E, (kJ mol^{-1})	log A, A (s^{-1})	k_d (350 K) (s^{-1})	References
2-(1′, 1′-Dimethylethoxy)-1-phenyl-1-(2′, 2′, 6′, 6′-tetra methyl-1′-piperidinyloxy)ethane,  	Toluene		138.8	14.96	1.76×10^{-6}	30,31
2-Phenyl-2-(2′, 2′, 6′, 6′-tetramethyl-1′-piperidinyloxy)propane,  	*tert*-Butylbenzene	343–363	114.4	14.11	1.09×10^{-3}	32
2-phenyl-2-(2′, 2′, 6′, 6′-tetramethyl-1′-piperidinyloxy)propane,  	Cyclohexane		114.0	14.00	9.69×10^{-4}	33

2-Phenyl-2-(2′, 2′, 6′, 6′-tetramethyl-1′-piperidinyloxy)propane, 	Isooctane	121.0	14.90	6.95×10^{-4}	29
1-Phenyl-1-(2′, 2′, 6′, 6′-tetramethyl-1′-piperidinyloxy)ethane, 	Cyclohexane	129.0	13.70	2.81×10^{-6}	33
Phenyl(2,2,6,6-tetramethyl-1-piperidinyloxy)methane, 	*tert*-Butylbenzene	99.0	11.85	1.19×10^{-3}	34

(continued overleaf)

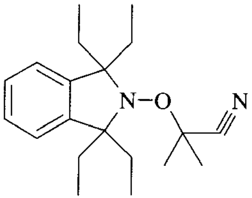
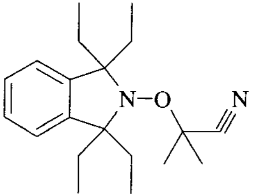
TABLE 8.4 (*continued*)

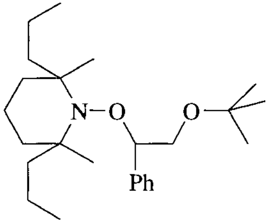
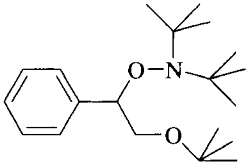
N-Alkoxyamine	Solvent	T (K)	E, (kJ mol^{-1})	log A, A (s^{-1})	k_d (350 K) (s^{-1})	References
Phenyl(2,2,6,6-tetramethyl-1-piperidinyloxy)methane, 	Cyclohexane		137.0	13.60	1.43×10^{-7}	33
Phenyl(2,2,6,6-tetramethyl-1-piperidinyloxy)methane, 	Styrene	396			7.7×10^{-5}	35
2-Methyl-2-(2′, 2′, 6′, 6′-tetramethyl-1′-piperidinyloxy)propane, 	*tert*-Butylbenzene		97.0	10.76	1.92×10^{-4}	34

1-(2′, 2′, 6′, 6′-Tetramethyl-1′-piperidinyloxy)butane, 	*tert*-Butylbenzene		99.0	10.40	4.22×10^{-5}	34
2-Methyl-2-(1′, 1′, 3′, 3′-tetraethyl-2′-benz[c]pirrolidinyloxy)-propionitrile, 	Hexane	333			3.0×10^{-4}	36

(*continued overleaf*)

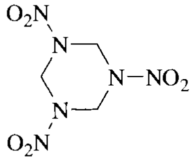
TABLE 8.4 (*continued*)

N-Alkoxyamine	Solvent	T (K)	E, (kJ mol^{-1})	log A, A (s^{-1})	k_d (350 K) (s^{-1})	References
2-Methyl-2-(1′, 1′, 3′, 3′-tetraethyl-2′-benz[c] pirrolidinyloxy)-propionitrile, 	Ethyl acetate	333			3.50×10^{-4}	36
2-Methyl-2-(1′, 1′, 3′, 3′-tetraethyl-2′-benz[c]pirrolidinyloxy)-propionitrile, 	Methanol	333			6.8×10^{-4}	36

2-(1′, 1′-Dimethylethoxy)-1-(2′, 6′-dimethyl-2′, 6′-dipropyl-1′-piperidinyloxy)-1-phenylethane,  	Ethyl acetate	353	2.9×10^{-5}	36
Di(1,1-dimethylethyl)[2-(1′, 1′-dimethylethoxy)-1-phenylethyloxy]amine,  	Ethyl acetate	363	1.65×10^{-4}	36

(continued overleaf)

TABLE 8.5 Physical Properties of Selected Nitro Compounds[a]

Compound	CAS Registry Number	Belstein Registry Number	MW	bp (K)	mp (k)	$\rho^{293\text{ K}}$ (kg m^{-3})	$n_D^{293\text{ K}}$
Nitromethane, $MeNO_2$	75–52–5	1698205	61.04	374.1	244.5	1137.1	
Dinitromethane, $CH_2(NO_2)_2$	625–76–3	1758684	106.04	373	<258		
Tetranitromethane, $C(NO_2)_4$	509–14–8	1795620	196.03	399.1	286.8	1638.0	1.4384
1,1-Dinitroethane, $MeCH(NO_2)_2$	600–40–8	1758537	120.06	458.5		$1349.0^{297\text{ K}}$	1.4322
1,2-Ethanediol, dinitrate, $NO_2OCH_2CH_2ONO_2$	628–96–6	1709055	152.06	471.5	250.7	1491.8	
1,2,3-Propanetriol, trinitrate, $[NO_2OCH_2]_2CHONO_2$	55–63–0	1802063	227.09	491	286.5	1593.1	$1.4786^{285\text{ K}}$
1,3,5-Trinitroperhydro-1,3,5-triazine, 	121–82–4	288466	222.12		478.5	1820	1.820

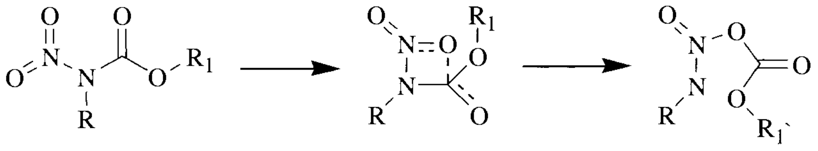
[a] See Ref. 41.

The limiting step for nitroamine decomposition in the gas phase is the dissociation of the N—N bond, which was supposed for dimethylnitroamine decomposition.[37]

$$Me_2NNO_2 \rightarrow Me_2N^{\bullet} + {}^{\bullet}NO_2$$

Evidently, the decomposition of nitroalkanes and nitroamines in nonpolar solvents occurs homolytically, and the formed alkyl and aminyl radicals react with solvent.

The decomposition of *N*-nitroamides are supposed to proceed via molecular mechanism with the formation of the four-centered transition state, namely,[37]



The formed azo compound is unstable and decomposes into free radicals. The values for the rate constants of decomposition for *N*-nitroamines and *N*-nitroamides are in Table 8.9

Difluoroamines possess a weak N—C bond that splits under heating.[37]

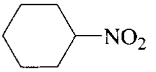
$$RNF_2 \rightarrow R^{\bullet} + {}^{\bullet}NF_2$$

TABLE 8.6 The Formation Enthalpy of Nitro Compounds[a]

Compound	$-\Delta H_f^0$ (kJ mol^{-1}) (solid)	$-\Delta H_f^0$ (kJ mol^{-1}) (liquid)	$-\Delta H_f^0$ (kJ mol^{-1}) (gas)
Nitromethane, $MeNO_2$		119.2	80.8
Dinitromethane, $CH_2(NO_2)_2$		105.4	59.8
Trinitromethane, $CH(NO_2)_3$	48.5	33.1	0.8
Tetranitromethane, $C(NO_2)_4$		−36.8	−77.4
Nitroethane, $MeCH_2NO_2$		141.8	100.4
1,2-Dinitroethane, $NO_2(CH_2)_2NO_2$	178.7	166.1	95.8
1,1-Dinitroethane, $MeCH(NO_2)_2$		166.1	102.1
1,1,1-Trinitroethane, $MeC(NO_2)_3$	108.8	93.3	52.7
Hexanitroethane, $(NO_2)_3CC(NO_2)_3$	−83.7	−96.2	−154.4
1-Nitropropane, $EtCH_2NO_2$		168.6	125.1
2-Nitropropane, $MeCH(NO_2)Me$		181.2	139.7
1,3-Dinitropropane, $NO_2(CH_2)_3NO_2$		207.1	132.2
1,1-Dinitropropane, $EtCH(NO_2)_2$		170.7	119.7
1,1-Dinitropropane, $EtCH(NO_2)_2$		163.2	112.1
2,2-Dinitropropane, $MeC(NO_2)_2Me$	190.4	177.0	129.7
1,1,1-Trinitropropane, $CH_2NO_2CH(NO_2)CH_2NO_2$		120.5	77.0
1,1,1,2,2-Pentanitropropane, $MeC(NO_2)C(NO_2)_3$	56.9	39.7	−33.9
1-Nitrobutane, $BuNO_2$		192.5	143.9
2-Nitrobutane, $EtCH(NO_2)Me$		207.5	162.8
2-Methyl-2-nitropropane, $MeCMe(NO_2)Me$	231.4	218.8	177.8
1,1-Dinitrobutane, $PrCH(NO_2)_2$		196.6	142.7
1,4-Dinitrobutane, $NO_2(CH_2)_4NO_2$	249.4	236.8	161.9
1,1,1,4-Tetranitrobutane, $CH_2NO_2(CH_2)_2C(NO_2)_3$	189.9	179.1	104.2
2-Methyl-1,1,1,3-tetranitropropane, $CH_2NO_2CHMeC(NO_2)_3$	172.0	159.4	83.7

(*continued overleaf*)

TABLE 8.6 (*continued*)

Compound	$-\Delta H_f^0$ (kJ mol^{-1}) (solid)	$-\Delta H_f^0$ (kJ mol^{-1}) (liquid)	$-\Delta H_f^0$ (kJ mol^{-1}) (gas)
1,1,3,3-Tetranitrobutane, $MeC(NO_2)_2CH_2CH(NO_2)_2$	215.9	203.3	120.1
2,2,3,3-Tetranitrobutane, $MeC(NO_2)_2C(NO_2)_2Me$	182.8	164.8	84.5
1,1-Dinitropentane, $BuCH(NO_2)_2$		217.1	159.8
1,1,1-Trinitropentane, $BuC(NO_2)_3$		174.5	121.3
1,1,1,3,5,5,5-Heptanitropentane, $C(NO_2)_3CH_2CH(NO_2)CH_2C(NO_2)_3$	153.6	141.0	38.5
2,3-Dimethyl-2,3-dinitrobutane, $Me_2C(NO_2)C(NO_2)Me_2$	311.7	291.6	222.6
2-Methyl-2,3,3-trinitropentane, $Me_2C(NO_2)C(NO_2)_2Et$	290.4	274.9	197.1
2,2-Dimethyl-1,1,1,4,4-pentanitropentane, $MeC(NO_2)_2CH_2CMe_2C(NO_2)_3$	276.6	261.5	175.3
1-Nitropentane, $BuCH_2NO_2$		215.4	165.1
2-Nitro-2,4,4-trimethylpentane, $Me_3CCH_2CMe_2NO_2$		304.1	249.5
Nitrocyclohexane, 		214.0	159.3

[a] See Refs. 42 and 43.

Rate constants for the decomposition of difluoroamines are presented in Table 8.10.

8.5 NITRATES AND NITRITES

The thermal decomposition of alkyl nitrates is limited and initiated by the cleavage of the O—N bond.

$$RONO_2 \rightarrow RO^{\bullet} + {}^{\bullet}NO_2$$

The BDE of this bond does not depend on the structure of the alkyl substituent and is 155 ± 5 kJ mol^{-1} (see Table 8.11). Gas-phase decomposition of ethyl nitrate > 470 K proceeds as a chain reaction and is accompanied by detonation.[37]

TABLE 8.7 Rate Constants for the Thermal Decay of Nitro Compounds in the Gas Phase

Nitro Compound	T (K)	E, (kJ mol^{-1})	log A, A (s^{-1})	k_d (473 K) (s^{-1})	References
Nitromethane, Me_3NO_2	653–713	224.3	14.60	6.77×10^{-11}	44,45
Nitromethane, Me_3NO_2	623–723	230.9	14.10	3.99×10^{-12}	46
Nitromethane, Me_3NO_2	633–663	230.5	14.34	7.69×10^{-12}	47
Nitromethane, Me_3NO_2	893–1473	244.8	16.21	1.50×10^{-11}	48
Nitrotrichloromethane, CCl_3NO_2	413–443	156.5	15.35	1.17×10^{-2}	49
Nitrotrichloromethane, CCl_3NO_2	441–443	157.6	15.35	8.83×10^{-3}	50
Nitroethane, $EtNO_2$	763–828	232.6	15.90	1.64×10^{-10}	51
Nitropropane, $PrNO_2$	873–1173	244.8	15.36	2.12×10^{-12}	52
2-Nitropropane, Me_2CHNO_2	873–1173	225.9	15.38	2.71×10^{-10}	52
Dichlorodinitromethane, $Cl_2C(NO_2)_2$	383–423	143.5	14.96	0.13	53,54
Dinitrofluoromethane, $FCH(NO_2)_2$	517–537	202.9	16.38	9.41×10^{-7}	55
Difluorodinitromethane, $F_2C(NO_2)_2$	508–543	198.3	15.88	9.58×10^{-7}	56
Chlorodinitrofluoromethane, $FClC(NO_2)_2$	443–487	173.6	15.44	1.86×10^{-4}	57
Bromodinitrofluoromethane, $FBrC(NO_2)_2$	443–483	165.3	15.00	8.80×10^{-4}	57
Dinitrofluoroiodomethane, $FIC(NO_2)_2$	433–470	166.1	15.40	1.14×10^{-3}	57
Trinitromethane, $HC(NO_2)_3$	453–473	177.4	15.46	7.41×10^{-5}	55
Fluorotrinitromethane, $FC(NO_2)_3$	451–509	175.3	15.40	1.10×10^{-4}	56
Chlorotrinitromethane, $ClC(NO_2)_3$	393–438	152.3	15.27	2.83×10^{-2}	53,54
Iodotrinitromethane, $IC(NO_2)_3$	386–423	143.9	14.77	7.57×10^{-2}	53,54
Tetranitromethane, $C(NO_2)_4$	443–596	171.1	17.53	4.32×10^{-2}	58
Tetranitromethane, $C(NO_2)_4$	359–450	161.5	15.70	7.33×10^{-3}	54
1,1-Dinitroethane, $MeCH(NO_2)_2$	470–539	197.1	16.44	4.72×10^{-6}	59
1,1-Dinitro-1-fluoroethane, $MeCF(NO_2)_2$	487–535	195.6	16.70	1.26×10^{-5}	56
1-Bromo-1,1-dinitroethane, $MeCBr(NO_2)_2$	433–463	169.5	15.84	1.32×10^{-3}	60
1,1-Dichloro-1-nitroethane, $MeCCl_2NO_2$	463–508	178.2	15.22	3.48×10^{-5}	60
1,1,1-Trinitroethane, $MeC(NO_2)_3$	433–483	180.7	16.70	5.56×10^{-4}	61
1,2-Difluoro-1,1,2,2-tetranitroethane, $FC(NO_2)_2FC(NO_2)_2$	380–453	176.6	17.40	7.91×10^{-3}	56
Fluoropentanitroethane, $FC(NO_2)_2C(NO_2)_3$	361–413	152.7	16.60	0.55	56
Hexanitroethane, $C(NO_2)_3C(NO_2)_3$	363–403	149.8	16.52	0.95	53,62
1,1-Dichloro-1-nitropropane, $EtCCl_2NO_2$	473–531	178.6	15.15	2.67×10^{-5}	60
1,1-Dinitropropane, $EtCH(NO_2)_2$	488–538	200.8	16.60	2.66×10^{-6}	59
2,2-Dinitropropane, $MeC(NO_2)_2Me$	448–483	211.3	18.20	7.35×10^{-6}	63
1,1,1-Trinitropropane, $EtC(NO_2)_3$	433–473	177.0	16.32	5.94×10^{-4}	61

(*continued overleaf*)

TABLE 8.7 (*continued*)

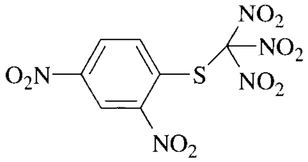
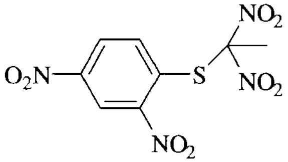
Nitro Compound	T (K)	E, (kJ mol^{-1})	log A, A (s^{-1})	k_d (473 K) (s^{-1})	References
1,1-Dinitrobutane, $PrCH(NO_2)_2$	493–538	201.7	16.70	2.66×10^{-6}	59
1,1,1-Trinitrobutane, $PrC(NO_2)_3$	433–473	182.4	17.22	1.19×10^{-2}	61
1,1,1,3,5,5-Heptanitropentane, $[(NO_2)_3CCH_2]_2CHNO_2$	393–413	148.1	15.08	5.31×10^{-2}	64
3-Fluoro-1,1,1,3,5,5,5-heptanitropentane, $[(NO_2)_3CCH_2]_2CFNO_2$	393–413	146.9	15.42	0.16	64
3-Chloro-1,1,1,3,5,5,5-heptanitropentane, $[(NO_2)_3CCH_2]_3CClNO_2$	393–413	146.0	15.43	0.20	64
3-Bromo-1,1,1,3,5,5,5-heptanitropentane, $[(NO_2)_3CCH_2]_2CBrNO_2$	393–413	143.1	15.15	0.22	64
1,4-Difluoro-1,1,4,4-tetranitrobutane, $F(NO_2)_2CCH_2CH_2CF(NO_2)_2$	423–473	192.5	15.84	3.82×10^{-6}	64
1,5-Difluoro-1,1,3,5,5-pentanitropentane, $[F(NO_2)_2CCH_2]_2CHNO_2$	453–493	172.4	15.0	9.16×10^{-5}	64
1,3,5-Trifluoro-1,1,3,5,5-pentanitropentane, $[F(NO_2)_2CCH_2]_2CFNO_2$	433–473	165.3	14.77	3.28×10^{-4}	64
3-Chloro-1,5-difluoro-1,1,3,5,5-pentanitropentane, $[F(NO_2)_2CCH_2]CClNO_2$	433–473	165.3	15.48	1.68×10^{-3}	64
3-Bromo-1,5-difluoro-1,1,3,5,5-pentanitropentane, $[F(NO_2)_2CCH_2]_2CBrNO_2$	433–473	161.9	15.12	1.74×10^{-3}	64
1,5-Difluoro-1,1,3,3,5,5-hexanitropentane, $[F(NO_2)_2CCH_2]_2C(NO_2)_2$	403–433	151.9	15.22	2.79×10^{-2}	64
Methylthiotrinitromethane, $MeSC(NO_2)_3$	323–353	128.9	15.72	30.58	65
Trinitromethylthiobenzene, $PhSC(NO_2)_3$	353–373	193.7	15.52	1.35×10^{-6}	65
2,4-Dinitro-1-(trinitromethyl)thiobenzene,  	348–363	133.1	15.72	10.51	65
1,1-Dinitro-1-methylthioethane, $MeSC(NO_2)_2Me$	393–423	161.1	17.45	0.46	65
(1,1-Dinitroethyl)thiobenzene, $PhSC(NO_2)_2Me$	393–423	159.8	17.70	1.13	65

TABLE 8.7 (*continued*)

Nitro Compound	T (K)	E, (kJ mol^{-1})	log A, A (s^{-1})	k_d (473 K) (s^{-1})	References
2,4-Dinitro-(1′, 1′-dinitroethyl) thiobenzene, 	393–408	156.9	17.25	0.84	65
1,1-Dinitroethylmethyl sulfone $MeSO_2C(NO_2)_2Me$	433–463	164.4	14.85	4.96×10^{-4}	65
1,1-Dinitroethylphenyl sulfone $PhSO_2C(NO_2)_2Me$	443–468	162.8	14.70	5.27×10^{-4}	65
1,1-Dinitro-4-chloro-1-fluoro-3-oxabutane, $ClCH_2OCH_2C(NO_2)_2F$	483–529	195.8	16.50	7.55×10^{-6}	66
1-Fluoro-1,1,3-trinitropropane, $CH_2(NO_2)CH_2C(NO_2)_2F$	473–508	193.7	16.55	1.44×10^{-5}	66

Nitrites exist as a mixture of two forms: syn and anti. Isomerization of one form into another proceeds intramolecularly. The rate constant of methyl nitrite isomerization[37] is equal to $k = 2.0 \times 10^{13}\exp[-46.4(\text{kJ mol}^{-1})/RT]$ s^{-1}.

The first step of alkylnitrites decomposition is the splitting of the weakest O–N bond.

$$\text{RONO} \rightarrow \text{RO}^{\bullet} + {}^{\bullet}\text{NO}$$

The activation energies of alkylnitrite decomposition does not depend on the structure of R and are close to that of alkylnitrates (see Table 8.12).

8.6 DISULFIDES AND POLYSULFIDES

Disulfides and polysulfides have weak S–S bonds that are cleaved by heating.[124] The more sulfur atoms in the polysulfide the lower is the BDE of the S–S bond.[125]

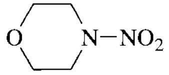
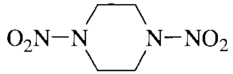
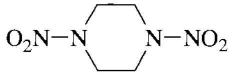
Polysulfide	HSSH	MeSSH	EtSSEt	PhSSPh	HSSSH	HSSSSH
D(S–S)/ kJ mol^{-1}	270	272	277	206	230	190

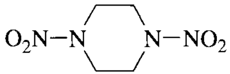
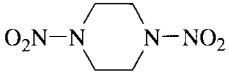
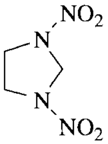
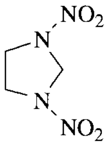
TABLE 8.8 Rate Constants for the Thermal Decay of the Nitro Compounds in the Liquid Phase

Compound	Solvent	T (K)	E, (kJ mol^{-1})	log A, A (s^{-1})	k_d (473 K) (s^{-1})	Reference
Tetranitromethane, $C(NO_2)_4$	Liquid phase	353–383	156.5	15.50	1.65×10^{-2}	67
Tetranitromethane, $C(NO_2)_4$	Tetrachloromethane	358–423	166.1	16.70	2.28×10^{-2}	68
Tetranitromethane, $C(NO_2)_4$	Freon-114B	393–408	172.8	17.17	1.22×10^{-2}	68
Tetranitromethane, $C(NO_2)_4$	Freon-113	373–408	166.9	16.80	2.34×10^{-2}	68
1,1,1,6,6,6-Hexanitro-3,5-oxaheptane, $(NO_2)_3CCH_2$-$OCH_2OCH_2C(NO_2)_3$	Liquid phase	393–458	173.6	16.34	1.48×10^{-3}	69
1,1,1,6,6,6-Hexanitro-3,5-oxaheptane, $(NO_2)_3CCH_2OCH_2$-$OCH_2C(NO_2)_3$	Trinitrotoluene	423–458	173.6	16.34	1.48×10^{-3}	69
1,1,1,7,7,7-Hexanitro-3-oxa-4-oxoheptane, $(NO_2)_3CCH_2CH_2$-$C(O)OCH_2C(NO_2)_3$	Liquid phase	393–448	173.2	16.95	6.66×10^{-3}	69
1,1,1,7,7,7-Hexanitro-3-oxa-4-oxoheptane, $(NO_2)_3CCH_2CH_2$-$C(O)OCH_2C(NO_2)_3$	Trinitrotoluene	413–473	173.2	16.95	6.66×10^{-3}	69

1,1,1-Trinitroethane, $MeC(NO_2)_3$	Liquid phase	373–413	178.2	19.93	1.78	70
Hexanitroethane, $C(NO_2)_3C(NO_2)_3$	Tetrachloromethane	343–393	158.2	18.6	8.51	70
Hexanitroethane, $C(NO_2)_3C(NO_2)_3$	Heptane	343–393	119.2	13.0	0.69	70
Hexanitroethane, $C(NO_2)_3C(NO_2)_3$	Cyclohexane	443–393	87.9	9.1	0.25	70
1,7-Difluoro-3,5-dioxa-1,1,7,7-tetranitroheptane, $[F(NO_2)_2CCH_2O]_2\ CH_2$	Trinitrotoluene	463–513	195.4	16.5	8.35×10^{-6}	69
1,7-Difluoro-3-oxa-4-oxo-1,1,7,7-tetranitroheptane, $F(NO_2)_2CCH_2CH_2\ C(O)OCH_2C(NO_2)_2F$	Liquid phase	463	196.6	16.88	1.48×10^{-5}	69
Chlorotrinitromethane, $ClC(NO_2)_3$	Tetrachloromethane	358–419	159.8	16.5	7.13×10^{-2}	68
Bromotrinitromethane, $BrC(NO_2)_3$	Tetrachloromethane	358–404	141.4	16.6	9.66	68
Iodotrinitromethane, $IC(NO_2)_3$	Liquid phase	358–393	141.4	15.5	0.77	67
1,2-Dichloro-1,1,2,2-tetranitroethane, $ClC(NO_2)_2C(NO_2)_2Cl$	Freon-113	318–358	110.9	16.6	2.26×10^4	70

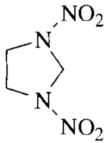
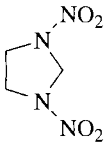
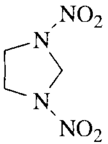
TABLE 8.9 Rate Constants for the Thermal Decay of Nitroamines in the Gas and Liquid Phase

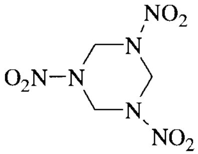
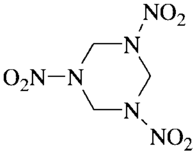
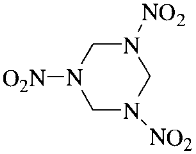
Compound	Solvent	T (K)	E, (kJ mol^{-1})	log A, A (s^{-1})	k_d (473 K) (s^{-1})	Reference
Dimethylnitroamine, Me_2NNO_2	Gas phase		193.3	15.80	2.84×10^{-6}	71
Dimethylnitroamine, Me_2NNO_2	Gas phase	453–513	169.9	14.10	2.18×10^{-5}	72
Dimethylnitroamine, Me_2NNO_2	Gas phase		170.7	14.10	1.78×10^{-5}	73
Dimethylnitroamine, Me_2NNO_2	Gas phase + CH_2O	453–513	162.7	13.70	5.41×10^{-5}	74
Diethylnitroamine, Et_2NNO_2	Gas phase	453–513	174.0	15.10	7.67×10^{-5}	75
Diethylnitroamine, Et_2NNO_2	Gas phase	473–513	176.1	14.80	2.25×10^{-5}	75
Dinitromethylamine, $MeN(NO_2)_2$	Gas phase	323–358	118.0	14.80	58.8	76
Dinitroethylamine, $EtN(NO_2)_2$	Gas phase	323–358	123.8	15.60	84.8	76
Dinitropropylamine, $PrN(NO_2)_2$	Gas phase	323–358	129.3	16.40	1.32×10^{2}	76
Dinitrobutylamine, $BuN(NO_2)_2$	Gas phase	323–358	123.4	15.50	74.6	76
N-Nitromorpholine, 	Gas phase	483–518	162.8	13.60	4.19×10^{-5}	77
1,4-Dinitro-hexahydropyrazine, 	Gas phase	473–513	159.8	13.60	8.98×10^{-5}	78
1,4-Dinitro-hexahydropyrazine, 	Nitrobenzene	498–518	155.2	12.00	7.26×10^{-6}	79

1,4-Dinitro-hexahydropyrazine, 	Liquid phase	489–523	198.3	17.30	2.52×10^{-5}	79
1,4-Dinitro-hexahydropyrazine, 	Trinitrobenzene	503–518	191.6	15.70	3.48×10^{-6}	80
1,3-Dinitrotetrahydro-1,3-diazol, 	Gas phase	443–473	146.4	13.50	2.15×10^{-3}	78
1,3-Dinitrotetrahydro-1,3-diazol, 	Gas phase + NO	443–473	169.0	15.60	8.65×10^{-4}	78

(continued overleaf)

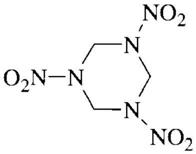
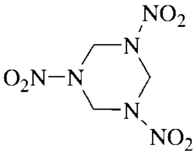
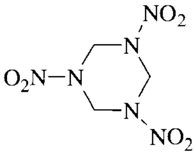
TABLE 8.9 *(continued)*

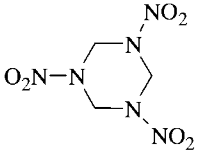
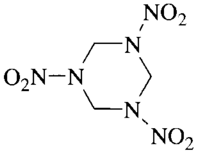
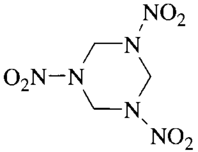
Compound	Solvent	T (K)	E, (kJ mol^{-1})	log A, A (s^{-1})	k_d (473 K) (s^{-1})	Reference
1,3-Dinitrotetrahydro-1,3-diazol, 	Dinitrobenzene	443–483	156.5	13.60	2.08×10^{-4}	79
1,3-Dinitrotetrahydro-1,3-diazol, 	Trinitrobenzene	393–483	158.6	14.00	3.06×10^{-4}	80
1,3-Dinitrotetrahydro-1,3-diazol, 	Liquid phase	408–473	155.2	13.90	5.77×10^{-4}	79

1,3,5-Trinitroperhydro-1,3,5-triazine, 	Gas phase		142.7	13.50	5.51×10^{-3}	81
1,3,5-Trinitroperhydro-1,3,5-triazine, 	Gas phase	443–463	125.5	11.70	6.93×10^{-3}	82
1,3,5-Trinitroperhydro-1,3,5-triazine, 	Gas phase	443–473	146.4	13.50	2.15×10^{-3}	78

(*continued overleaf*)

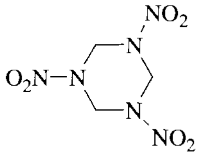
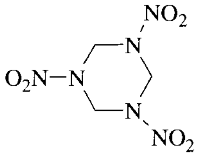
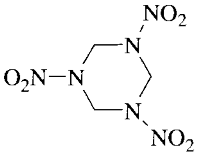
TABLE 8.9 (*continued*)

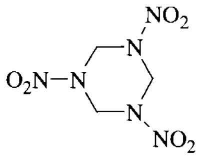
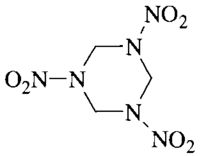
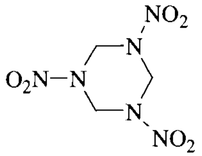
Compound	Solvent	T (K)	E, (kJ mol^{-1})	log A, A (s^{-1})	k_d (473 K) (s^{-1})	Reference
1,3,5-Trinitroperhydro-1,3,5-triazine, 	Gas phase + NO	443–473	169.0	15.60	8.65×10^{-4}	78
1,3,5-Trinitroperhydro-1,3,5-triazine, 	Gas phase		169.0	16.00	2.17×10^{-3}	83
1,3,5-Trinitroperhydro-1,3,5-triazine, 	Trinitrotoluene	468–553	171.5	15.50	3.64×10^{-4}	81

1,3,5-Trinitroperhydro-1,3,5-triazine, 	Dicyclohexylphthalate	474–553	173.6	15.40	1.69×10^{-4}	81
1,3,5-Trinitroperhydro-1,3,5-triazine, 	Dinitrobenzene	433–473	166.1	14.30	9.06×10^{-5}	84
1,3,5-Trinitroperhydro-1,3,5-triazine, 	Trinitrotoluene	439–457	154.4	13.90	7.07×10^{-4}	85

(continued overleaf)

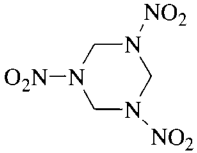
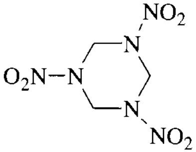
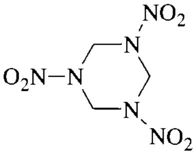
TABLE 8.9 (*continued*)

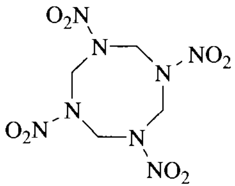
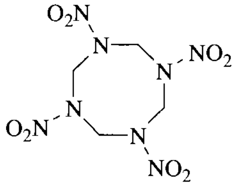
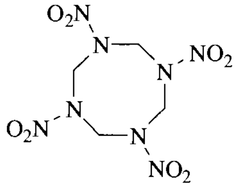
Compound	Solvent	T (K)	E, (kJ mol^{-1})	log A, A (s^{-1})	k_d (473 K) (s^{-1})	Reference
1,3,5-Trinitroperhydro-1,3,5-triazine, 	Benzophenone		158.2	14.50	1.07×10^{-3}	85
1,3,5-Trinitroperhydro-1,3,5-triazine, 	Liquid phase	486–572	198.7	18.50	3.60×10^{-4}	81
1,3,5-Trinitro-1,3,5-hexahydro-1,3,5-triazine, 	Liquid phase	486–572	203.7	19.20	5.07×10^{-4}	86

1,3,5-Trinitroperhydro-1,3,5-triazine, 	Liquid phase		180.3	16.40	3.08×10^{-4}	87
1,3,5-Trinitroperhydro-1,3,5-triazine, 	Liquid phase	477–753	209.6	19.60	2.84×10^{-4}	88
1,3,5-Trinitroperhydro-1,3,5-triazine, 	Liquid phase	478–493	200.0	18.70	4.11×10^{-4}	89

(*continued overleaf*)

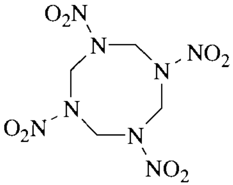
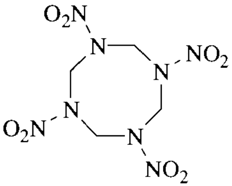
TABLE 8.9 (*continued*)

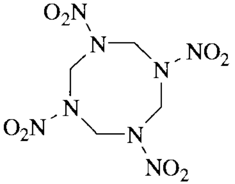
Compound	Solvent	T (K)	E, (kJ mol^{-1})	log A, A (s^{-1})	k_d (473 K) (s^{-1})	Reference
1,3,5-Trinitroperhydro-1,3,5-triazine, 	Liquid phase	423–470	213.0	18.60	1.20×10^{-5}	90
1,3,5-Trinitroperhydro-1,3,5-triazine, 	Liquid phase	423–470	217.6	19.10	1.17×10^{-5}	84
1,3,5-Trinitroperhydro-1,3,5-triazine, 	Liquid phase	413–463	166.5	11.20	6.51×10^{-8}	91

1,3,5,7-Tetranitro-1,3,5,7-tetraazacyclooctane, 	Gas phase	444–488	221.3	20.20	5.77×10^{-5}	82
1,3,5,7-Tetranitro-1,3,5,7-tetraazacyclooctane, 	Gas phase	503–523	133.9	13.20	2.59×10^{-2}	81
1,3,5,7-Tetranitro-1,3,5,7-tetraazacyclooctane, 	Gas phase	478–553	165.3	14.20	8.83×10^{-5}	78

(continued overleaf)

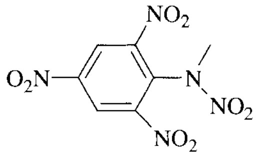
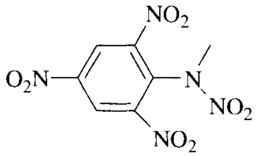
TABLE 8.9 (*continued*)

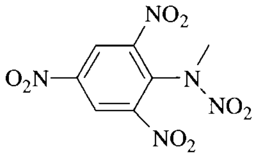
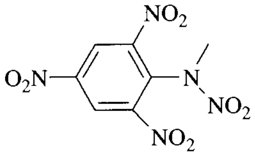
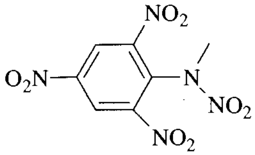
Compound	Solvent	T (K)	E, (kJ mol^{-1})	log A, A (s^{-1})	k_d (473 K) (s^{-1})	Reference
1,3,5,7-Tetranitro-1,3,5,7-tetraazacyclooctane, 	Gas phase		159.0	12.50	8.74×10^{-5}	83
1,3,5,7-Tetranitro-1,3,5,7-tetraazacyclooctane, 	Dinitrobenzene	444–488	187.9	16.00	1.78×10^{-5}	84

1,3,5,7-Tetranitro-1,3,5,7-tetraazacyclooctane, 	Liquid phase	544–587	220.5	19.70	2.24×10^{-5}	81
3-(*N*-Methyl-*N*-nitro)amino-methylpropionate, $MeN(NO_2)CH_2CH_2COOMe$	Dibutyl phthalate	473–503	169.0	13.70	1.09×10^{-5}	92
3-(*N*-Methyl-*N*-nitro) aminopropionitrile, $MeN(NO_2)CH_2CH_2CN$	Dibutyl phthalate	463–503	175.3	14.40	1.10×10^{-5}	92
Methylnitro(2-oxapropyl) amine, $MeN(NO_2)CH_2OMe$	Dibutyl phthalate	463–503	171.1	13.90	1.01×10^{-5}	92
3-(*N*-Methyl-*N*-nitro)amino propionic acid, $MeNNO_2(CH_2)_2COOH$	Dibutyl phthalate	473–503	170.7	14.00	1.41×10^{-5}	92
3-(*N*-Methyl-*N*-nitro)amino propionic acid, $MeNNO_2(CH_2)_2COOH$	Dibutyl phthalate	453–493	167.8	14.70	1.48×10^{-4}	93
4-Aza-4-nitro-1,7-heptanedinitrile, $N(NO_2)(CH_2CH_2CN)_2$	Dibutyl phthalate	483–523	172.8	13.90	6.57×10^{-6}	92

(*continued overleaf*)

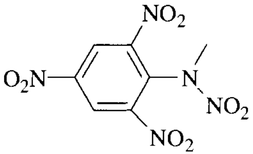
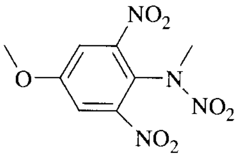
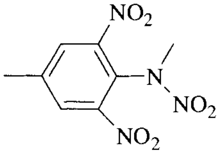
TABLE 8.9 *(continued)*

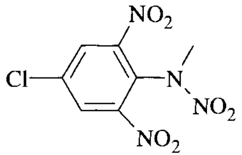
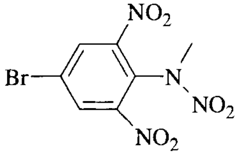
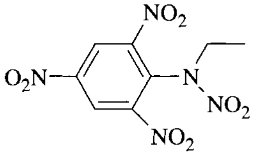
Compound	Solvent	T (K)	E, (kJ mol^{-1})	log A, A (s^{-1})	k_d (473 K) (s^{-1})	Reference
4-Aza-4-nitro-1,7-heptodioic acid, $N(NO_2)(CH_2CH_2COOH)_2$	Dibutyl phthalate	473–513	170.7	14.10	1.78×10^{-5}	92
1,1-Dimethylethyl-(4-nitro-4-aza-1,7-heptodionate), $N(NO_2)[CH_2CH_2C(O)OCMe_3]_2$	Dibutyl phthalate	483–523	170.3	13.70	7.83×10^{-6}	92
Bis(2,2-dinitropropyl) nitroamine, $NNO_2[CH_2C(NO_2)_2Me]_2$	Dinitro benzene	418–443	166.1	15.70	2.28×10^{-3}	94
N-Methyl-*N*-nitro-2,4,6-trinitrobenzenamine, 	Liquid phase	484–533	160.7	15.40	4.50×10^{-3}	95
N-Methyl-*N*-nitro-2,4,6-trinitrobenzenamine, 	Liquid phase	405–437	146.0	12.90	5.98×10^{-4}	96

N-Methyl-*N*-nitro-2,4,6-trinitrobenzenamine,	Liquid phase	404–428	150.6	13.80	1.48×10^{-3}	97
						
N-Methyl-*N*-nitro-2,4,6-trinitrobenzenamine,	Liquid phase	413–433	147.3	13.50	1.71×10^{-3}	95
						
N-Methyl-*N*-nitro-2,4,6-trinitrobenzenamine,	Liquid phase	413–438	167.4	16.00	3.26×10^{-3}	98
						

(*continued overleaf*)

TABLE 8.9 (*continued*)

Compound	Solvent	T (K)	E, (kJ mol^{-1})	log A, A (s^{-1})	k_d (473 K) (s^{-1})	Reference
N-Methyl-*N*-nitro-2,4,6-trinitrobenzenamine,  	Liquid phase	423–448	150.2	13.50	8.19×10^{-4}	92
2,6-Dinitro-4-methoxy-*N*-methyl-*N*-nitrobenzenamine,  	Dimethylbenzene	418–438	134.3	12.40	3.71×10^{-3}	92
2,6-Dinitro-4-methyl-*N*-methyl-*N*-nitrobenzenamine,  	Dimethylbenzene	423–443	143.1	13.40	3.96×10^{-3}	92

4-Chloro-2,6-dinitro-*N*-methyl-*N*-nitrobenzenamine, 	Dimethylbenzene	418–438	141.0	13.10	3.38×10^{-3}	92
4-Bromo-2,6-dinitro-*N*-methyl-*N*-nitrobenzenamine, 	Dimethylbenzene	428–448	141.4	13.40	6.10×10^{-3}	92
N-Ethyl-*N*-nitro-2,4,6-trinitrobenzenamine, 	Dimethylbenzene	417–438	139.3	13.90	3.29×10^{-2}	92

(*continued overleaf*)

TABLE 8.9 (*continued*)

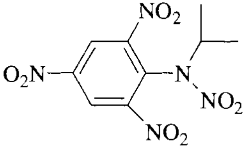
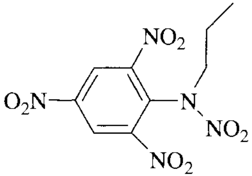
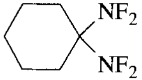
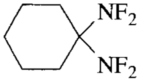
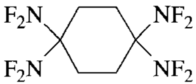
Compound	Solvent	T (K)	E, (kJ mol^{-1})	log A, A (s^{-1})	k_d (473 K) (s^{-1})	Reference
N-(1-Methylethyl)-N-nitro-2,4,6-trinitrobenzenamine,  	Dimethylbenzene	408–428	136.8	13.30	1.56×10^{-2}	92
N-Nitro-N-propyl-2,4,6-trinitrobenzenamine,  	Dimethylbenzene	403–423	140.2	14.20	5.22×10^{-2}	92

TABLE 8.10 Rate Constants for the Thermal Decay of Difluoroamines

Compound	Solvent	T (K)	E, (kJ mol^{-1})	log A, A (s^{-1})	k_d (473 K) (s^{-1})	Reference
1,1-Bis(difluoroamino)-1-methylethane, $Me_2C(NF_2)_2$	Gas phase	493–533	195.8	15.60	9.50×10^{-7}	99
1,1-Bis(difluoroamino)-cyclohexane, 	Gas phase	483–503	200.4	16.42	1.95×10^{-6}	99
1,1-Bis(difluoroamino)-cyclohexane, 	Liquid phase	413–438	196.2	16.15	3.04×10^{-6}	99
1,1,4,4-Tetra(difluoroamino)-cyclohexane, 	Gas phase	483–533	192.9	15.85	3.53×10^{-6}	99

(*continued overleaf*)

TABLE 8.10 (*continued*)

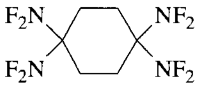
Compound	Solvent	T (K)	E, (kJ mol^{-1})	log A, A (s^{-1})	k_d (473 K) (s^{-1})	Reference
1,1,4,4-Tetra(difluoroamino)-cyclohexane, 	Liquid phase	423–453	197.1	16.00	1.71×10^{-6}	99
Difluorobis(difluoroamino)-methane, $F_2C(NF_2)_2$	Gas phase	645–730	224.7	15.75	8.63×10^{-10}	100
Difluorobis(difluoroamino)-methane, $F_2C(NF_2)_2$	Gas phase	463–733	202.5	16.45	1.22×10^{-6}	100
Fluorotris(difluoroamino)-methane, $FC(NF_2)_3$	Gas phase	498–523	192.0	15.73	3.37×10^{-6}	101
Tetra(difluoroamino)methane, $C(NF_2)_4$	Gas phase	463–733	169.5	16.40	4.81×10^{-3}	100

TABLE 8.11 Rate Constants for the Thermal Decay of Alkyl Nitrates ($RONO_2$) in the Gas and Liquid Phase

Compound	Phase	T (K)	E, (kJ mol^{-1})	log A, A (s^{-1})	k_d (473 K) (s^{-1})	References
Methyl nitrate, $MeONO_2$	Gas		169.5	15.7	9.59×10^{-4}	102–104
Ethyl nitrate, $EtONO_2$	Gas		167.4	16.0	3.27×10^{-3}	102–104
Ethyl nitrate, $EtONO_2$	Gas	453–488	166.9	15.8	2.34×10^{-3}	105
Ethyl nitrate, $EtONO_2$	Gas	434–454	172.4	16.85	6.48×10^{-3}	106
Ethyl nitrate, $EtONO_2$	Gas	448–482	160.0	14.74	1.18×10^{-3}	107
Ethyl nitrate, $EtONO_2$	Liquid		167.4	14.7	1.64×10^{-3}	108
1-Propyl nitrate, $PrONO_2$	Gas		167.4	16.5	1.03×10^{-2}	109
2-Propyl nitrate, Me_2CHONO_2	Gas		169.5	16.5	6.05×10^{-3}	110
2-Methyl-2-propyl nitrate, Me_3CONO_2	Gas		168.2	15.9	2.12×10^{-3}	102
1,2-Ethanediol, dinitrate, $NO_2OCH_2CH_2ONO_2$	Gas		149.4	14.3	6.33×10^{-3}	111
1,2-Ethanediol, dinitrate, $NO_2OCH_2CH_2ONO_2$	Liquid		162.3	14.5	3.78×10^{-4}	108
1,2-Propanediol, dinitrate, $MeCH(ONO_2)CH_2ONO_2$	Liquid		168.6	15.8	1.52×10^{-3}	108
1,3-Propanediol, dinitrate, $NO_2OCH_2CH_2CH_2ONO_2$	Liquid		163.6	14.9	6.82×10^{-4}	108
1,2,3-Propanetriol, trinitrate, $CH(ONO_2)[CH_2ONO_2]_2$	Gas		150.6	15.5	7.40×10^{-2}	112
1,2,3-Propanetriol, trinitrate, $CH(ONO_2)[CH_2ONO_2]_2$	Liquid		164.4	15.4	1.76×10^{-3}	108
1,2,3-Propanetriol, 1,3-dinitrate, $NO_2OCH_2CH(OH)CH_2ONO_2$	Liquid		177.4	16.8	1.62×10^{-3}	108
1,4-Butandiol, dinitrate, $NO_2O(CH_2)_2ONO_2$	Liquid		163.2	15.1	1.19×10^{-3}	108
2,3-Butanediol, dinitrate, $MeCH(ONO_2)CH(ONO_2)Me$	Liquid		174.1	16.7	2.98×10^{-3}	110

The values for enthalpies and entropies of selected disulfate formation are in Table 8.13.

Polysulfides are used for regulation of polymer weight through performing the "living polymerization" with reversible addition[127,128]

$$RS^{\bullet} + R^1CH_2C^{\bullet}HX \Leftrightarrow R^1CH_2CH(SR)X$$

Alkyl disulfides are decomposed with dissociation of the S—S (main homolysis) and C—S bonds (side homolytic reaction).[124] Besides homolytic splitting, the

TABLE 8.12 Rate Constants of Thermal Decay of the Alkylnitrites in the Gas Phase

Nitrite	T (K)	E, (kJ mol^{-1})	log A, A (s^{-1})	k_d (473 K) (s^{-1})	Reference
Methyl-, MeONO	463–513	152.3	13.20	2.41×10^{-4}	113
Methyl-, MeONO	483–513	151.0	13.10	2.66×10^{-4}	114
Methyl-, MeONO	453–513	153.1	13.00	1.24×10^{-4}	115
Methyl-, MeONO	780–1000	142.2	12.90	1.57×10^{-3}	116
Ethyl-, EtONO	463–513	157.7	14.14	5.31×10^{-4}	117
Ethyl-, EtONO	484–505	156.1	14.14	7.97×10^{-4}	118
Ethyl-, EtONO	435–475	156.9	13.79	2.91×10^{-4}	119
Ethyl-, EtONO	473–503	153.5	13.66	5.12×10^{-4}	120
Propyl-, PrONO	~500	154.8	14.44	2.21×10^{-3}	118
Propyl-, PrONO	473–503	145.2	13.20	1.46×10^{-3}	121
Propyl-, PrONO	443–483	157.5	14.44	1.11×10^{-3}	122
1-Methylethyl-, Me_2CHONO	443–483	157.5	14.44	1.11×10^{-3}	123
1-Methylethyl-, Me_2CHONO	~500	154.8	14.10	1.01×10^{-3}	120
Butyl-, BuONO	~500	154.8	14.48	2.43×10^{-3}	120
Butyl-, BuONO	475–512	151.5	13.66	8.51×10^{-4}	121

TABLE 8.13 The Enthalpies and Entropies of Formation of Disulfides.[a]

Disulfide	$-\Delta H_f^0$ (kJ mol^{-1}) (gas)	$-\Delta H_f^0$ (kJ mol^{-1}) (liquid)	$-\Delta S^0$ (J mol^{-1} K^{-1}) (gas)
Methyl-, MeSSMe	24.3	62.6	336.7
Ethyl-, EtSSEt	74.5	120.1	414.6
Propyl-, PrSSPr	117.2	171.5	494.7
Methylethyl-, $Me_2CHSSCHMe_2$	133.9	188.2	475.5
Butyl-, BuSSBu	159.0	222.9	572.1
Dimethylethyl-, $Me_3CSSCMe_3$	200.8	255.2	500.2
Phenyl-, PhSSPh	−242.7	−148.5	478.6
Phenyldisulfone, $PhSO_2SO_2Ph$	481.3	643.2	

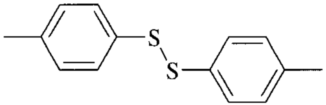
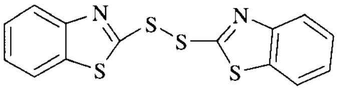
[a] See Ref. 126.

molecular mechanism was for dimethyldisulfide decomposition.[124]

$$Me_3SSMe_3 \rightarrow Me_3SH + Me_2S$$

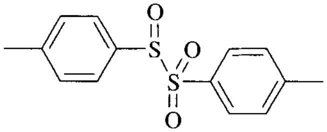
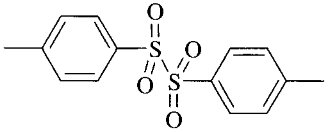
Polysulfides are decomposed with cleavage of the S–S bond. The thermal decomposition of dimethyl trisulfide at 353 K results in the formation of disulfide

TABLE 8.14 Rate Constants of Thermal Decay of Sulfur-Containing Compounds in the Gas Phase

Compound	Solvent	T (K)	E, (kJ mol^{-1})	log A, A (s^{-1})	k_d (350 K) (s^{-1})	Reference
Dimethyl disulfide, MeSSMe	Gas	589–646	188.3	13.30	1.58×10^{-15}	129
Dimethyl tetrasulfide, MeSSSSMe	Gas		153.1	17.98	1.35×10^{-5}	130
Tetramethyltiuram disulfide, $Me_2NC(S)SSC(S)NMe_2$	Toluene	373			5.5×10^{-6}	131
Benzylmethyl sulfide, $PhCH_2$ SMe	Gas	818–844	215.5	13.48	2.08×10^{-19}	132
p-Tolyl disulfide, 	Toluene	373			2.0×10^{-8}	133
Benzothiazolyl disulfide, 	Toluene	373			8.3×10^{-6}	131
Diphenyl thiosulfinate, PhS(O)SPh	Benzene	373	141.2	15.73	9.0×10^{-5}	134

(*continued overleaf*)

TABLE 8.14 (*continued*)

Compound	Solvent	T (K)	E, (kJ mol^{-1})	log A, A (s^{-1})	k_d (350 K) (s^{-1})	Reference
Di-*p*-tolylsulfinyl sulfone, 	Dioxane	373	112.4	14.94	1.46×10^{-2}	135
Di-*p*-tolyl disulfone, 	Diglyme	373	168.0	16.04	9.28×10^{-10}	136
3-Methylsulfonyl-1-propene, $CH_2{=}CHCH_2SO_2Me$	Gas	633–733	199.6	14.10	2.05×10^{-16}	137
Benzylmethyl sulfone, $MeSO_2CH_2Ph$	Gas	660–750	214.4	14.52	3.33×10^{-18}	137

and tetrasulfide due to the following reactions:[124]

$$\text{MeSSSMe} \rightarrow \text{MeSS}^\bullet + \text{MeS}^\bullet$$
$$\text{MeSS}^\bullet + \text{MeSS}^\bullet \rightarrow \text{MeSSSSMe}$$
$$\text{MeS}^\bullet + \text{MeS}^\bullet \rightarrow \text{MeSSMe}$$

The tri-, penta-, and hexasulfides were found as the products of methyltetrasulfide decomposition; and no dimethyl disulfide was found as a product. This means that the cleavage of MeSSSSMe occurs via a homolytic reaction:

$$\text{MeSSSSMe} \rightarrow 2\text{MeSS}^\bullet$$

The rate constant for the decomposition is equal to $k = 9.55 \times 10^{17}\exp[-153.1\ (\text{kJ mol}^{-1})/RT]\ \text{s}^{-1}$ (Table 8.14). The thermal stability of polysulfides decreases with an increase in the number of sulfur atoms in the polysulfide linkage. Data on the decay of polysulfides are collected in Table 8.14.

8.7 ORGANOMETALLIC COMPOUNDS

Organometallic compounds, such as GeR_4, SnR_4, PbR_4, HgR_2, and so on, have relatively weak metal–carbon bonds and are dissociated with free radical formation.[138] Tetramethyl tin and its thermolysis played a crucial role in the origin of radical chemistry. Panneth's experiments with tin mirrors were the first experimental evidences for free radicals as labile intermediates in different gas-phase reactions.[139] For the enthalpies of organometallic compound formation see Table 8.15. Rate constants of organometallic decomposition with homolytic scission of a C–metal bond are collected in Table 8.16.

TABLE 8.15 Enthalpy of Formation for Organometallic Compounds[a]

Compound	$-\Delta H_f^0$ (kJ mol^{-1}) (gas)	Compound	$-\Delta H_f^0$ (kJ mol^{-1}) (gas)
Diethylmercury, $HgEt_2$	66.5	Trimethylgallium, $GlMe_3$	−28.03
Dipropylmercury, $HgPr_2$	17.6	Tetraethylgermane, $GeEt_4$	−146.4
Di(1-methylethyl)mercury, $Hg(CHMe_2)_2$	36.4	Tetraethyllead, $PbEt_4$	96.2
Dibutylmercury, $HgBu_2$	−24.3	Trimethylarsine, $AsMe_3$	15.5
Dimethylcadmium, $CdMe_2$	105.4	Trimethylantimony, $SbMe_3$	26.8
Dimethylzinc, $ZnMe_2$	54.4	Trimethylbismuth, $BiMe_3$	−122.2

[a] See Ref. 138.

TABLE 8.16 Rate Constants for the Thermal Decay of Organometallic Compounds in the Gas Phase

Compound	T (K)	E, (kJ mol^{-1})	log A, A (s^{-1})	k_d (473 K) (s^{-1})	Reference
Diethylmercury, $HgEt_2$	593–643	173.6	14.1	8.49×10^{-6}	140
Diethylmercury, $HgEt_2$	593–690	177.8	14.1	2.92×10^{-6}	141
Diethylmercury, $HgEt_2$		194.6	15.5	1.02×10^{-6}	138
Dipropylmercury, $HgPr_2$	605–677	197.1	15.5	5.42×10^{-7}	142
Dipropylmercury, $HgPr_2$		197.1	15.5	5.42×10^{-7}	138
Di(1-methylethyl)mercury, $Hg(CHMe_2)_2$	502–714	169.0	16.2	3.45×10^{-3}	143
Di(1-methylethyl)mercury, $Hg(CHMe_2)_2$	513–575	170.3	16.4	3.92×10^{-3}	144
Di(1-methylethyl)mercury, $Hg(CHMe_2)_2$	443–503	113.0	11.0	3.32×10^{-2}	144
Di(1-methylethyl)mercury, $Hg(CHMe_2)_2$		170.3	16.4	3.92×10^{-3}	138
Dibutylmercury, $HgBu_2$	617–686	200.0	15.8	5.17×10^{-7}	144
Dibutylmercury, $HgBu_2$		200.0	15.8	5.17×10^{-7}	138
Dimethylcadmium, $CdMe_2$	743–800	204.2	13.4	7.08×10^{-10}	145
Dimethylcadmium, $CdMe_2$	742–844	191.6	11.9	5.51×10^{-10}	146
Dimethylcadmium, $CdMe_2$	531.0	182.0	13.0	7.97×10^{-8}	147
Dimethylcadmium, $CdMe_2$		227.6	15.0	7.34×10^{-11}	138
Dimethylzinc, $ZnMe_2$	843–1000	197.5	11.25	2.75×10^{-11}	148
Trimethylindium, $InMe_3$	550–781	197.5	15.7	7.76×10^{-7}	149
Trimethylindium, $InMe_3$	550–781	197.5	15.7	7.76×10^{-7}	138
Trimethylthallium, Me_3Tl	458–591	114.6	10.8	1.39×10^{-2}	150
Tetraethylsilane, $SiEt_4$	793–873	211.3	15.8	2.92×10^{-8}	151
Tetrapropylsilane, $SiPr_4$	793–843	192.5	14.14	7.62×10^{-8}	151
Hexamethyldisilane, $Me_3SiSiMe_3$	940–1020	207.2	12.2	2.08×10^{-11}	152
Tetraethylgermane, $GeEt_4$	693–723	213.4	14.23	4.61×10^{-10}	153
Tetraethyllead, $PbEt_4$	506–548	154.8	12.6	3.2×10^{-5}	154
Tetraethyllead, $PbEt_4$	518–548	154.4	12.1	1.12×10^{-5}	155
Trimethylbismuth, $BiMe_3$	619–857	184.1	14.0	4.67×10^{-7}	156

REFERENCES

1. K. J. Laidler and L. F. Loucks, in *Comprehensive Chemical Kinetics*, C. H. Bamford and C. F. H. Tipper (Eds.), Elsevier, Amsterdam, The Netherlands, 1972, Vol. 5, p. 1.
2. M. Gomberg, *J. Am. Chem. Soc.* **20**, 757 (1900).
3. *Proceedings of Conference Gomberg 2000*, University of Michigan, Ann Arbor, MI, 2000.
4. J. M. McBide, *Tetrahedron*, **30**, 2009 (1974).

5. R. Houwink and A. J. Staverman, *Chemie und Technologie der Kunststoffe*, Akademische Verlagsgesellschaft, Leipzig, Germany, 1962.
6. D. Lide (ed.), *Handbook of Chemistry and Physics*, CRC Press, Boca Raton, FL, 1992.
7. K. Ziegler and W. Deparade, *Liebige. Ann. Chem.* **567**, 123 (1950).
8. L. R. Mahoney, *J. Am. Chem. Soc.* **88**, 3035 (1966).
9. E. Borsig, M. Lazar, and M. Capla, *Coll. Czech. Chem. Comm.* **32**, 4289 (1967).
10. K. Ziegler, W. Deparade, and H. Kuhlhorn. *Liebige. Ann. Chem.* **567**, 151 (1950).
11. K. Ziegler, P. Orth, and K. Weber, *Liebigs Ann. Chem.* **504**, 131 (1933).
12. S. F. Nelsen and P. D. Bartlett, *J. Am. Chem. Soc.* **88**, 137 (1966).
13. G. E. Zaikov, Z. K. Mayzus, and N. M. Emanuel, *Dokl. AN SSSR*, **140**, 405 (1961).
14. E. T. McHale, B. E. Knox, and H. B. Palmer, *10th International Symposium on Combustion*, Butterworths Publication, London, 1965, p. 341.
15. M. Szwarc, *J. Chem. Phys.* **17**, 505 (1949).
16. J. A. Kerr, R. C. Sekhar, and A. F. Trotman-Dickenson, *J. Chem. Soc.* 3217 (1963).
17. J. A. Kerr, A. F. Trotman-Dickenson, and M. Wolter, *J. Chem. Soc.* 3584 (1964).
18. L. M. Brown and B. de B. Darwent, *J. Chem. Phys.* **42**, 2158 (1965).
19. F. Tyudesh and M. Azori. *Acta Chim. Acad. Sci. Hung.* **34**, 61 (1962).
20. C. K. Cain and F. Y. Wiselogle, *J. Am. Chem. Soc.* **62**, 1163 (1940).
21. V. T. Varlamov, *Kinet. Katal.* **42**, 862 (2001).
22. W. K. Wilmarth and N. Schwartsz, *J. Am. Chem. Soc.* **77**, 4551 (1955).
23. D. H. Hey, J. S. Webb, and G. H. Williams, *J. Chem. Soc.* 4657 (1952).
24. M. D. Bartberger, J. D. Mannion, S. C. Powell, J. S. Stamler, K. N. Houk, and E. J. Toone, *J. Am. Chem. Soc.* **123**, 8868 (2001).
25. T. Fukuda, A. Goto, and K. Ohno, *Macromol. Rapid Commun.* **21**, 151 (2000).
26. E. T. Denisov and T. G. Denisova, *Handbook of Antioxidants*, CRC Press, Boca Raton, FL, 2000.
27. M. V. Ciriano, H. -G. Korth, B. W. Van Scheppingen, and P. Mulder, *J. Am. Chem. Soc.* **121**, 6375 (1999).
28. D. W. Grattan, D. J. Carlsson, J. A. Howard, and P. M. Wiles, *Can. J. Chem.* **57**, 2834 (1979).
29. C. Neri, S. Costanzi, R. Farris, and V. Malatesta, *13 International Conference on Advances in the Stabilization and Degradation of Polymers*, Lucern, Switzerland, 1991.
30. S. A. F. Bon, G. Chambard, and A. L. German, *Macromolecules* **32**, 8269 (1999).
31. S. A. F. Bon, G. Chambard, F. A. C. Bergman, E. H. H. Snellen, B. Klumperman, and A. L. German, *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **38**(1), 748 (1997).
32. T. Kothe, S. Marque, R. Martschke, M. Popov, and H. Fisher, *J. Chem. Soc. Perkin Trans. 2*, 1555 (1998).
33. W. G. Shene, S. T. Belt, T. J. Connolly, P. Hahn, and J. C. Scaiano, *Macromolecules* **31**, 9103 (1998).
34. P. Slipa, L. Greei, P. Carloni, and E. Damiani, *Polym. Degrad. Stab.* **55**, 323 (1997).

35. C. J. Hawker, G. G. Barelay, A. Orellana, J. Dao, and W. Devonport, *Macromolecules* **29**, 5245 (1966).
36. G. Moad and E. Rizzardo, *Macromolecules* **28**, 8722 (1995).
37. O. P. Strausz, J. W. Lown, and H. E. Gunnig, in *Comprehensive Chemical Kinetics*, C. H. Bamford and C. F. H. Tipper (Eds.), Elsevier, Amsterdam, The Netherlands, 1972, Vol. 5, p. 566.
38. G. B. Manelis, G. M. Nazin, Yu. I. Rubtsov, and V. A. Strunin, *Thermodecomposition and Combustion of Explosives and Powders* (Russian), Nauka, Moscow, 1996.
39. P. Gray, A. D. Yoffe, and L. Rosselaar, *Trans. Faraday Soc.* **51**, 1489 (1955).
40. E. T. Denisov and V. V. Azatyan, *Inhibition of Chain Reactions*, Gordon and Breach, London 2000.
41. D. R. Lide and G. W. A. Milne (Eds.), *Data Base: Properties of Organic Compounds. Personal Edition*, CRC Press, Boca Raton FL, 1996.
42. Yu. A. Lebedev, E. A. Miroshnichenko, and Yu. K. Knobel, *Thermochemistry of Nitrocompounds* (Russian), Nauka, Moscow, 1970.
43. S. P. Verevkin, *Thermochimica Acta* **307**, 17 (1997).
44. T. L. Cottrell and T. J. Reid, *J. Chem. Phys.* **18**, 1306 (1950).
45. T. L. Cottrell, T. E. Graham, and T. J. Reid, *Trans. Faraday Soc.* **47**, 584 (1951).
46. C. G. Grawforth and D. J. Waddington, *Trans. Faraday Soc.* **65**, 1336 (1969).
47. V. V. Dubikhin, G. M. Nazin, and G. B. Manelis, *Izv. AN SSSR, Ser. Khim.* 1339 (1971).
48. K. Glenzer and J. Trol, *Helv. Chim. Acta* **55**, 2884 (1972).
49. V. V. Dubikhin, G. M. Nazin, and G. B. Manelis, *Izv. AN SSSR, Ser. Khim.* 1338 (1971).
50. E. W. R. Stiecie and W. M. F. Smith, *J. Chem. Phys.* **6**, 145 (1938).
51. K. Glenzer and J. Troe, *Helv. Chim. Acta* **56**, 577 (1973).
52. K. Glenzer and J. Troe, *Helv. Chim. Acta* **56**, 1691 (1973).
53. G. M. Nazin, G. B. Manelis, and F. I. Dubovitskii, *Dokl. AN SSSR*, **177**, 1387 (1967).
54. G. M. Nazin, G. B. Manelis, and G. N. Nechiporenko, and F. I. Dubovitskii, *Comb. Flame* **12**, 102 (1968).
55. G. M. Nazin, G. B. Manelis, and F. I. Dubovitskii, *Izv. AN SSSR, Ser. Khim.* 1035 (1969).
56. G. M. Nazin, G. B. Manelis, and F. I. Dubovitskii, *Izv. AN SSSR, Ser. Khim.* 2631 (1968).
57. G. M. Nazin, G. B. Manelis, and F. I. Dubovitskii, *Izv. AN SSSR, Ser. Khim.* 2801 (1968).
58. J. M. Sullivan and A. E. Axworthy, *J. Phys. Chem.* **70**, 3366 (1966).
59. G. M. Nazin, G. B. Manelis, and F. I. Dubovitskii, *Izv. AN SSSR, Ser. Khim.* 2629 (1968).
60. G. M. Nazin, G. B. Manelis, and F. I. Dubovitskii, *Izv. AN SSSR, Ser. Khim.* 1239 (1971).
61. G. M. Nazin, G. B. Manelis, and F. I. Dubovitskii, *Izv. AN SSSR, Ser. Khim.* 389 (1968).
62. G. M. Nazin, G. B. Manelis, and F. I. Dubovitskii, *Dokl. AN SSSR*, **177**, 1127 (1967).

63. J. M. Flournoy, *J. Chem. Phys.* **36**, 1107 (1962).
64. V. N. Grebennikov, V. G. Prokudin, and G. M. Nazin, *Izv. AN SSSR, Ser. Khim.* 2822 (1984).
65. V. N. Grebennikov, V. E. Erashko, and G. M. Nazin, *Izv. AN SSSR, Ser. Khim.* 310 (1977).
66. V. N. Grebennikov and G. M. Nazin, *Izv. AN SSSR. Ser. Khim.* 1635 (1978).
67. G. M. Nazin, G. B. Manelis, and F. I. Dubovitskii, *Izv. AN SSSR. Ser. Khim.* 2628 (1968).
68. H. P. Marshall, F. G. Borgardt, and P. Noble, *J. Phys. Chem.* **69**, 25 (1965).
69. B. G. Matveev, L. D. Nazina, G. M. Nazin, D. A. Nesterenko, and L. T. Eremenko, *Izv. RAN. Ser. Khim.* 2455 (1998).
70. H. P. Marshall, F. G. Borgardt, and P. Noble, *J. Phys. Chem.* **72**, 1513 (1968).
71. R. Shaw and F. E. Walter, *J. Phys. Chem.* **181**, 2572 (1977).
72. J. M. Flournoy, *J. Chem. Phys.* **36**, 1106 (1962).
73. B. L. Korsunskii and F. I. Dubovitskii, *Dokl. AN SSSR*, **155**, 402 (1964).
74. B. L. Korsunskii, F. I. Dubovitskii, and G. V. Sitonina, *Dokl. AN SSSR*, **174**, 1126 (1967).
75. B. L. Korsunskii, F. I. Dubovitskii, and E. A. Shurigin, *Izv. AN SSSR, Ser. Khim.* 1452 (1967).
76. B. L. Korsunskii, G. V. Sitonina, and B. S. Fedorov, *Izv. AN SSSR, Ser. Khim.* 790 (1989).
77. F. I. Dubovitskii and B. L. Korsunskii, *Usp. Khimii*, **50**, 1828 (1981).
78. Ya. M. Burov and G. M. Nazin, *Kinet. Katal.* **23**, 12 (1982).
79. G. V. Sitonina, B. L. Korsunskii, and N. F. Pyatakov, *Izv. AN SSSSR, Ser. Khim.* 311 (1979).
80. B. A. Lur'e and V. N. Ivachov, *Chemical Physics of Condensed Explosive Compounds* (Russian), Khimiya, Moscow, 1979, p. 12.
81. A. I. B. Robertson, *Trans. Faraday Soc.* **45**, 85 (1949).
82. M. S. Belyaeva, G. K. Klimenko, L. T. Babaitseva, and P. N. Stolyarov, *Chemical Physics of Combustion and Explosion: Kinetics of Chemical Reactions* (Russian), BICP AN SSSR, Chernogolovka, USSR, 1977, p. 47.
83. Yu. Ya. Maksimov, V. N. Apalkoba, O. V. Braverman, and A. I. Solov'ev, *Zh. Fiz. Khim.* **59**, 342, (1985).
84. Yu. Ya. Maksimov, *Theory of Explosive Compounds* (Russian), Vysshaya Shkola, Moscow, 1967, p. 73.
85. J. Wildy, *Symp. on chemical problems connected with the stability of explosives*, Stockholm, Sweden, 1967, p. 51.
86. F. C. Rouch and A. J. Fanelli, *J. Phys. Chem.* **73**, 1604 (1969).
87. R. N. Rogers and G. W. Daub, *J. Anal. Chem.* **45**, 596 (1973).
88. R. N. Rogers and L. S. Smith, *Thermochim. Acta* **1**, 1 (1970).
89. Y. Oyumi, *Prop. Explos. Pyrotech.* **13**, 41 (1988).
90. K. K. Andreev, *Decomposition and Combustion of Explosive Compounds* (Russian), Nauka, Moscow, 1966, p. 67.
91. Yu. M. Burov and G. M. Nazin, *Khim. Fiz.* **3**, 1126 (1984).

92. R. S. Stepanov, V. N. Shan'ko, I. P. Medvetskaya, and V. M. Gorodetskaya, *Chemical Physics of Combustion and Explosion: Kinetics of Chemical Reactions* (Russian), BICP AN SSSR, Chernogolovka, USSR, 1977, p. 56.
93. V. N. Shanko and R. S. Stepanov, *Fiz. Khim.* (Krasnoyarsk), **1**, 190 (1974).
94. B. L. Korsunskii, L. Ya Kiseleva, V. I. Ramushev, and F. I. Dubovitskii, *Izv. AN SSSR, Ser. Khim.* 1778 (1974).
95. A. J. B. Robertson and A. Yoffe, *Nature (London)*, **161**, 806 (1948).
96. M. A. Cook and M. T. Abegg, *Ind. Eng. Chem.* **48**, 1090 (1956).
97. F. I. Dubovitskii, Yu. I. Rubtsov, and G. B. Manelis, *Izv. Akad. Nauk. O. Khim. N.* 1764 (1960).
98. F. I. Dubovitskii, G. B. Manelis, and L. P. Smirnov, *Zh. Fiz. Khim.* **35**, 521 (1961).
99. A. V. Fokin, V. N. Grebennikov, and G. M. Nazin, *Dokl. AN SSSR*, **382**, 735 (1993).
100. J. M. Sullivan, A. E. Axworthy, and T. J. Hauser, *J. Phys. Chem.* **74**, 2611 (1970).
101. E. W. Neuvar, *Industr. And Eng. Chem. Prod. Res. Develop.* **28**, 319 (1969).
102. L. Batt and R. T. Milne, *Int. J. Chem. Kinet.* **8**, 59 (1976).
103. L. Batt and R. T. Milne, *Int. J. Chem. Kinet.* **9**, 549 (1977).
104. L. Batt and R. T. Milne, *Int. J. Chem. Kinet.* **9**, 567 (1977).
105. G. K. Adams and C. E. H. Bawn, *Trans. Faraday Soc.* **45**, 494 (1949).
106. J. Levy, *J. Am. Chem. Soc.* **76**, 3254 (1954).
107. F. H. Pollard, H. S. B. Marshall, and A. E. Pedler, *Trans. Faraday Soc.* **52**, 59 (1956).
108. A. F. Afanasiev, B. A. Lur'e, and B. S. Svetlov, in *Theory of Explosive Compounds* (Russian), Vysshaya Shkola, Moscow, 1967, p. 63.
109. G. D. Mendenhall, D. M. Golden, and S. W. Benson, *Int. J. Chem. Kinet.* **7**, 725 (1974).
110. J. Jullien, J. M. Pechine, and M. A. Sadek, *Prop. Explos. Pyrotech.* **8**, 99 (1983).
111. K. K. Andreev, A. P. Glazkova, N. D. Maurina, and B. S. Svetlov, *Zh. Fiz. Khim.* **32**, 1726 (1958).
112. C. E. Waring and G. Krasins, *J. Phys. Chem.* **74**, 999 (1970).
113. E. W. R. Steacie and G. T. Shaw, *Proc. Roy. Soc. A London, Ser.*, **146**, 388 (1934).
114. E. W. R. Steacie and D. S. Calder, *J. Chem. Phys.* **4**, 96 (1936).
115. L. Phillips, *J. Chem. Soc.* 3082 (1961).
116. I. S. Zaslonko, S. M. Kogarko, E. V. Mozzhuchin, Yu. P. Petrov, and A. A. Borisov, *Kinet. Katal.* **11**, 296 (1970).
117. E. W. R. Steacie and G. T. Shaw, *J. Chem. Phys.* **2**, 345 (1934).
118. E. W. R. Steacie and S. Katz, *J. Chem. Phys.* **5**, 125 (1936).
119. J. B. Levy, *J. Am. Chem. Soc.* **78**, 1780 (1956).
120. F. Marta and L. Seres, *Acta Univ. Szeged., Acta Phys. Chem.* **12**, 35 (1966).
121. M. F. Nagiev, Z. G. Petrova, and A. I. Sultanova, *Dokl. AN SSSR*, **109**, 573 (1956).
122. E. W. R. Steacie and G. T. Shaw, *J. Chem. Phys.* **3**, 344 (1935).
123. E. W. R. Steacie and G. T. Shaw, *Proc. Roy. Soc. A*, **151**, 685 (1935).
124. O. P. Strausz, H. E. Gunning, and J. W. Lown, in *Comprehensive Chemical Kinetics*, C. H. Bamford and C. F. H. Tipper (Eds.), Elsevier, Amsterdam, The Netherlands, 1972, Vol. 5, p. 697.

125. D. A. Armstrong, in *S-centered Radicals*, Z. B. Alfassi (Ed.), John Wiley & Sons, Inc., New York, 1999.

126. S. G. Lias, J. F. Liebman, R. D. Levin, and S. A. Kafafi, *NIST Standard Reference Database*, 19A, NIST Positive Ion Energetics, Version 2.0, NIST, Gaithersburg, MD, 1993.

127. D. H. Solomon, *The Chemistry of Free Radical Polymerization*, Pergamon Press, Oxford, U.K., 1995.

128. O. Ito, in *General Aspects of the Chemistry of Radicals*, Z. B. Alfassi (Ed.), John Wiley & Sons, Inc., Chichester, U.K., 1999 p. 209.

129. J. A. Coope and W. A. Bryce, *Can. J. Chem.* **32**, 768 (1954).

130. I. Kende, T. L. Pickering, and A. V. Tobolsky, *J. Am. Chem. Soc.* **87**, 5582 (1965).

131. R. E. Davis and C. Perrin, *J. Am. Chem. Soc.* **82**, 1590 (1960).

132. E. H. Braye, A. H. Sehon, and B. B. Darwent, *J. Am. Chem. Soc.* **77**, 5282 (1955).

133. J. L. Kice, in *Free Radicals*, J. K. Kochi (Ed.), John Wiley & Sons, Inc., New York, 1973, Vol. 2, p. 711.

134. P. Koch, E. Cuiffarin, and A. Fava, *J. Am. Chem. Soc.* **92**, 5971 (1970).

135. J. L. Kice and N. E. Pavlowski, *J. Am. Chem. Soc.* **86**, 4898 (1964).

136. J. L. Kice and N. A. Favstritsky, *J. Org. Chem.* **35**, 114 (1970).

137. W. K. Busfield and K. J. Ivin, *Trans. Faraday Soc.* **57**, 1044 (1961).

138. S. Benson and H. E. O'Neal, *Kinetic Data on Gas Phase Unimolecular Reactions*, National Bureau of Standards, Washington, D.C., 1970.

139. F. Panneth and W. Hofeditz, *Ber. Deutsh. Chem. Ges.* **62**, 135 (1929).

140. B. G. Gowenlock, J. C. Polanyi and E. Warhurst, *Proc. Roy. Soc., London Ser, A.* **218**, 269 (1953).

141. H. V. Carter, E. I. Chapell, and E. Warhurst, *J. Chem. Soc.* 106 (1956).

142. H. T. J. Chilton and B. G. Gowenlock, *Trans. Faraday Soc.* **50**, 824 (1954).

143. H. T. J. Chilton and B. G. Gowenlock, *Trans. Faraday Soc.* **49**, 1451 (1953).

144. B. H. M. Billinge and B. G. Gowenlock, *Trans. Faraday Soc.* **59**, 690 (1963).

145. M. Krech and S. J. Price, *Can. J. Chem.* **43**, 1929 (1965).

146. A. T. C. H. Tan and A. H. Sehon, *Can. J. Chem.* **46**, 191 (1968).

147. C. M. Laurie and R. H. Long, *Trans. Faraday Soc.* **53**, 1431 (1957).

148. S. J. W. Price and A. F. Trotman-Dickenson, *Trans. Faraday Soc.* **53**, 1208 (1957).

149. M. G. Jacko and S. J. W. Price, *Can. J. Chem.* **42**, 1198 (1964).

150. M. G. Jacko and S. J. W. Price, *Can. J. Chem.* **43**, 1961 (1965).

151. C. E. Waring, *Trans. Faraday Soc.* **36**, 1142 (1940).

152. J. A. Connor, R. N. Haszeldine, G. J. Leigh, and R. D. Sedgwick, *J. Chem. Soc., A*, 768 (1967).

153. R. L. Geddes and E. Mack, *J. Am. Chem. Soc.* **52**, 4372 (1930).

154. G. L. Pratt and J. H. Purnell, *Trans. Faraday. Soc.* **60**, 519 (1964).

155. J. A. Leermakers, *J. Am. Chem. Soc.* **55**, 4508 (1933).

156. S. J. W. Price and A. F. Trotman-Dickenson, *Trans. Faraday Soc.* **54**, 1630 (1958).

Handbook of Free Radical Initiators. E.T. Denisov, T.G. Denisova, T.S. Pokidova
Copyright © 2003 John Wiley & Sons, Inc.
ISBN: 0-471-20753-5

PART II

BIMOLECULAR REACTIONS OF FREE RADICAL GENERATION

Handbook of Free Radical Initiators. E.T. Denisov, T.G. Denisova, T.S. Pokidova
Copyright © 2003 John Wiley & Sons, Inc.
ISBN: 0-471-20753-5

9

PARABOLIC MODEL OF BIMOLECULAR HOMOLYTIC REACTION

9.1 INTRODUCTION

Initiators that decompose into free radicals are widely used in technology, synthesis, and the experimental study for the initiation of free radical reactions. Along with this, different bimolecular reactions play an important role in the initiation of chain reactions.[1,2] For example, the study of chain autoinitiation in oxidized hydrocarbons helped to open a great variety of bimolecular reactions for free radical generation.[3–7]

$$\mathrm{ROOH + ROOH \rightarrow RO_2^{\bullet} + H_2O + RO^{\bullet}}$$

$$\mathrm{ROOH + CH_2{=}CHR^1 \rightarrow RO^{\bullet} + HOCH_2C^{\bullet}HR^1}$$

$$\mathrm{ROOH + R^1OH \rightarrow RO^{\bullet} + H_2O + R^1O^{\bullet}}$$

$$\mathrm{ROOH + O{=}CR^1R^2 \Leftrightarrow ROOC(OH)R^1R^2}$$

$$\mathrm{ROOC(OH)R^1R^2 \rightarrow RO^{\bullet} + R^1R^2C(O^{\bullet})OH}$$

$$\mathrm{ROOH + HY \rightarrow RO^{\bullet} + H_2O + Y^{\bullet}}$$

These bimolecular reactions occur more rapidly than unimolecular homolytic splitting of hydroperoxide at the O–O bond. Various bimolecular reactions for free radicals generation can be divided into the following six classes:

1. Reactions of retrodisproportionation, in which one molecule (olefin, acetylene, ketone, or imine) acts as an acceptor and an other (RH) as a donor

of the hydrogen atom.

$$RH + CH_2{=}CHR^1 \rightarrow R^\bullet + CH_3C^\bullet HR^1$$
$$RH + HN{=}CHR^1 \rightarrow R^\bullet + NH_2C^\bullet HR^1$$
$$RH + HC{\equiv}CR^1 \rightarrow R^\bullet + H_2C{=}C^\bullet R^1$$
$$RH + O{=}CR^1R^2 \rightarrow R^\bullet + HOC^\bullet R^1R^2$$

These reactions are important in chain reactions for the decomposition of hydrocarbons and other organic compounds.

2. Reactions of olefins and acetylenes with molecules of haloids, for example,

$$F_2 + CH_2{=}CH_2 \rightarrow F^\bullet + FCH_2C^\bullet H_2$$

3. Reactions of hydrogen atom abstraction that are accompanied by a weak bond dissociation. Such reactions are typical for interaction of haloid molecules and hydroperoxides with hydrocarbons, for example,

$$CH_4 + F_2 \rightarrow C^\bullet H_3 + HF + F^\bullet$$
$$RH + H_2O_2 \rightarrow R^\bullet + H_2O + HO^\bullet$$

They are possible for hydrazines and disulfides.

$$RH + H_2NNH_2 \rightarrow R^\bullet + NH_3 + H_2N^\bullet$$
$$RH + R^1SSR^1 \rightarrow R^\bullet + RSR^1 + R^1S^\bullet$$

4. Thermal generation of radicals in monomers occurs through biradical formation succeeded by reactions of this biradical.[8]

$$PhCH{=}CH_2 + CH_2{=}CHPh \Leftrightarrow PhC^\bullet HCH_2CH_2C^\bullet HPh$$
$$PhC^\bullet HCH_2CH_2C^\bullet HPh + RH \rightarrow PhC^\bullet HCH_2CH_2CH_2Ph + R^\bullet$$
$$PhC^\bullet HCH_2CH_2C^\bullet HPh + CH_2{=}CHPh \rightarrow PhCH{=}CHCH_2C^\bullet HPh + CH_3C^\bullet HPh$$

5. Chain generation in the presence of dioxygen occurs in similar reactions:[3,6,7]

$$RCH{=}CH_2 + O_2 \rightarrow RC^\bullet HCH_2O_2^\bullet$$
$$RC^\bullet HCH_2O_2^\bullet + O_2 \rightarrow RCH(O_2^\bullet)CH_2O_2^\bullet \quad \text{and so on}$$
$$2RCH{=}CH_2 + O_2 \rightarrow RC^\bullet HCH_2OOCH_2C^\bullet HR$$

6. In oxidized hydrocarbons, free radicals are generated by two reactions: one bimolecular and the other trimolecular:[2]

   $$RH + O_2 \rightarrow R^\bullet + HO_2{}^\bullet$$

   $$RH + O_2 + HR \rightarrow R^\bullet + H_2O_2 + R^\bullet$$

   The bimolecular reactions for radical generation appeared to be rather difficult to study. The parabolic model for bimolecular homolytic reactions was found to be a very convenient method for calculation of rate constants for bimolecular reactions with the production of free radicals. The results with rate constants calculation are included in Part II of this handbook.

9.2 PRINCIPLES FOR THE PARABOLIC MODEL OF BIMOLECULAR HOMOLYTIC REACTION

9.2.1 Main Equations of IPM

The intersecting parabola model (IPM) as a semiempirical model of an elementary bimolecular reaction appeared to be very useful and efficient in the analysis and calculation of activation energies for a wide variety of radical abstraction and addition reactions.[9–13] As a result, it became possible to classify diverse radical abstraction reactions and to differentiate in each class the groups of isotypical reactions. Later, this conception was applied to calculations for activation energies and rate constants of bimolecular reactions for chain generation. In the IPM, the radical abstraction reaction, for example,

$$RH + O_2 \rightarrow R^\bullet + HOO^\bullet$$

in which the hydrogen atom is transferred from the initial molecule (RH) to the final radical ($HOO^\bullet$), is regarded as the result of an intersection of two potential curves, one that describes the potential energy $U_i(r)$ of the vibration of the H atom along the bond being dissociated in the initial molecule, and another that describes the potential energy $U_f(r)$ of the vibration of the same atom along the bond being formed in the reaction product (U is the potential energy and r is the amplitude of the atomic vibrations along the valence bond). The stretching vibrations of the H atom in RH and XH are regarded as harmonic and are described by the parabolic law

$$\sqrt{U(r)} = br \tag{9.1}$$

The following parameters are used to characterize the elementary step:[9,10]

1. The enthalpy of reaction ΔH_e includes the difference between the zero-point energies of the broken and generated bonds

   $$\Delta H_e = D_i - D_f + 0.5hL(\nu_i - \nu_f) \tag{9.2}$$

where D_i and D_f are the dissociation energies of the broken (i) and generated (f) bonds, ν_i and ν_f are the stretching vibration frequencies of these bonds.

2. The activation energy E_e is related to the experimentally determined Arrhenius energy E by the equation

$$E_e = E + 0.5(hL\nu_i - RT) \tag{9.3}$$

3. The coefficients b_i and b_f describe the dependence of the potential energy on the atomic vibration amplitude along the valence bonds. There is a parabolic relation between the potential energy and the vibration amplitude

$$U_i = b_i^2 r^2 \quad \text{and} \quad U_f = b_f^2 (r_e - r)^2 \tag{9.4}$$

The quantity $2b^2$ is the force constant for the corresponding bond with $b = \pi\nu(2\mu)^{1/2}$, where μ is the reduced mass of the atoms forming the bond.

4. The parameter r_e characterizes the distance between two minimum points of intersecting parabolas. This parameter is equal to the sum of the amplitudes for vibration of two bonds transformed in the reaction. In the IPM, these parameters are related by the equation

$$br_e = \alpha\sqrt{E_e - \Delta H_e} + \sqrt{E_e} \tag{9.5}$$

where $b = b_i$, that is, it refers to the attacked bond in the molecule, while $\alpha = b_i/b_f$. In the case of structurally isotypic reactions (br_e = const), a thermally neutral reaction ($\Delta H_e = 0$) occurs with the activation energy E_{e0}, which is determined by two parameters, namely, α and br_e (or r_e, b_i and b_r):

$$\sqrt{E_{e0}} = \frac{br_e}{1 + \alpha} \tag{9.6}$$

On substituting the parameter br_e in Eq (9.6) by its value from Eq (9.5), we obtain

$$(1 + \alpha)\sqrt{E_{e0}} = \alpha\sqrt{E_e - \Delta H_e} + \sqrt{E_e} \tag{9.7}$$

The transition state in the IPM is characterized by the distance $r^{\neq}$, which is related to other parameters by the equation

$$r^{\#}/r_e = E_e^{1/2}/br_e = [1 + \alpha(1 - \Delta H_e E_e^{-1})]^{-1} \tag{9.8}$$

In the case of a thermally neutral reaction, $r^{\neq}$ is equal to the ratio

$$(r^{\neq}/r_e)_0 = (1 + \alpha)^{-1} \tag{9.9}$$

The parabolic model is, in essence, empirical, because the parameter α is calculated from spectroscopic (ν_i and ν_f) and atomic (μ_i and μ_f) data, while parameter br_e (or E_{e0}) is found from the experimental activation energies E [$E = RT\ln(A/k)$], where A is the preexponential factor typical of the chosen group of reactions, and k is the rate constant. The enthalpy of reaction is calculated by Eq. (9.2). The calculations showed that $br_e = \text{const}$ for structurally similar reactions. The values of α and br_e for reactions of different types are given in Tables 9.1–9.3.

The activation energies for highly endothermic reactions are known to be virtually equal to the enthalpy of the reaction. According to IPM, each group of reactions is characterized by the critical value for the enthalpy of the reaction, $\Delta H_{e\,\max}$. When the reaction enthalpy $\Delta H_e > \Delta H_{e\,\max}$, activation energy $E = \Delta H + 0.5RT$, whereas $\Delta H_{e\,\max}$ depends on parameters α and br_e.[14]

$$\Delta H_{e,\max} = (br_e)^2 - 2\alpha br_e\sqrt{0.5hL\nu_f} + 0.5hL\nu_f(\alpha^2 - 1) \qquad (9.10)$$

Special attention should be paid to the preexponential factors for reactions.[14] For a separate group of reactions, the quantity A calculated for a single attacked bond is constant, $A = A_0$, when $\Delta H_e < \Delta H_{e\,\max}$. For reactions with $\Delta H_e > \Delta H_{e\,\max}$, the parameter r_e increases with an increase in ΔH_e and, hence, the preexponential factor A also increases. The dependence of A on ΔH is described by the formulas[14]

$$A = A_0\left\{1 + \beta\left[\sqrt{\Delta H_e} - \sqrt{\Delta H_{e\,\max}}\right]\right\}^2 \qquad (9.11)$$

The mean value of coefficient β is equal to 1.3. Tables 9.2 and 9.3 present the values of $\Delta H_{e\,\max}$ calculated by Eq (9.10). Evidently, the range of ΔH_e in which $A = A_0 = \text{const}$ depends on the parameter br_e and varies within wide limits.

9.2.2 Calculation of *E* and *k* for Bimolecular Reactions

Within the framework of the IPM, the values of E and k are calculated by means of the following formulas:

1. *Reactions with* $\Delta H_e < \Delta H_{e\,\max}$

(1) For $\alpha = 1$

$$\sqrt{E_e} = \frac{br_e}{2} + \frac{\Delta H_e}{2br_e} \qquad (9.12)$$

(2) For $\alpha \neq 1$

$$\sqrt{E_e} = \frac{br_e}{1-\alpha^2}\left[1 - \alpha\sqrt{1 - \frac{1-\alpha^2}{(br_e)^2}\Delta H_e}\right] \qquad (9.13)$$

(3) For $\Delta H_e(1-\alpha^2) \ll (br_e)^2$

$$\sqrt{E_e} = \frac{br_e}{1+\alpha} + \frac{\alpha\Delta H_e}{2br_e} \qquad (9.14)$$

The activation energy E and rate constant k are calculated by the formulas

$$E = E_e - 0.5hL\nu_i + 0.5RT \tag{9.15}$$

$$k = n_{C-H} \times A_0 \exp(-E/RT) = A \exp(-E/RT), \tag{9.16}$$

where n_{C-H} is the number of attacked C—H bonds with the same reactivity, and A_0 is the standard preexponential factor per one attacked C—H bond for the chosen group of reactions.

2. *Reactions with* $\Delta H_e > \Delta H_{e\,\max}$. The activation energy for these reactions is close to the enthalpy for reaction

$$E = \Delta H + 0.5RT \tag{9.17}$$

The preexponential factor depends on the reaction enthalpy, and the rate constant is equal the following:

$$k = n_{C-H} \times A_0 e^{-1/2} \left\{1 + \beta\left[\sqrt{\Delta H_e} - \sqrt{\Delta H_{e\max}}\right]\right\}^2 \exp(-\Delta H/RT) \tag{9.18}$$

3. *Reactions with concerted dissociation of a few bonds*. In bimolecular reactions of this type

$$\text{ROOH} + \text{HY} \rightarrow \text{RO}^{\bullet} + \text{H}_2\text{O} + \text{Y}^{\bullet}$$

more than one, namely, two bonds, O—O and Y—H, dissociate simultaneously. The concerted concentration of activation energy on two breaking bonds is necessary to perform this reaction. The probability of this event depends on the activation energy and the number of broken bonds. According to the oscillation theory for decay of the polyatomic molecule, this probability $P(E)$ for the reaction with the simultaneous dissociation of two bonds is described by the equation[15]

$$P(E) = \sqrt{\frac{2RT}{\pi E}} \tag{9.19}$$

and the rate constant of this reaction has the following form:

$$k = n_{Y-H} A_0 \sqrt{\frac{2RT}{\pi E}} \exp(-E/RT) = A\sqrt{\frac{2RT}{\pi E}} \exp(-E/RT) \tag{9.20}$$

where A_0 is the preexponential factor typical of similar reactions with dissociation of one Y—H bond. Activation energy is calculated as described above.

TABLE 9.1 Kinetic Parameters for Bimolecular Reactions of Free Radical Generation in IPM

Reaction	α	$b \times 10^{-11}$ $((\mathrm{kJ/mol})^{1/2}\,\mathrm{m}^{-1})$	$0.5hL\nu_i$ $(\mathrm{kJ\,mol^{-1}})$	$0.5hL(\nu_i - \nu_f)$, $(\mathrm{kJ\,mol^{-1}})$	$(r^{\neq}/r_e)_0$
$O_2(O_3) + HY \rightarrow HO_2^{\bullet}(HO_3^{\bullet}) + Y^{\bullet}$					
$O_2(O_3) + HR$	0.814	3.743	17.4	−3.8	0.551
$O_2(O_3) + HNR_2$	0.936	4.306	20.0	−1.2	0.516
$O_2(O_3) + HOR$	1.022	4.701	21.7	0.5	0.495
$O_2(O_3) + HOOR$	1.000	4.600	21.2	0.0	0.500
$O_2(O_3) + HSiR_3$	0.624	2.871	13.1	−8.1	0.616
$O_2(O_3) + HSR$	0.658	3.026	13.8	−7.4	0.603
$O_2(O_3) + HGeR_3$	0.608	2.796	12.6	−8.6	0.622
$O_2(O_3) + HSnR_3$	0.586	2.695	12.1	−9.1	0.630
$O_2 + CH_2{=}CHR \rightarrow {}^{\bullet}OOCH_2C^{\bullet}HR$					
$O_2 + CH_2{=}CHR$	1.737	5.389	9.9	4.6	0.366
$ROOH + HY \rightarrow RO^{\bullet} + H_2O + Y^{\bullet}$					
$ROOH + HR^1$	0.788	3.743	17.4	−4.8	0.559
$ROOH + HNR_2$	0.907	4.306	20.0	−2.2	0.524
$ROOH + HOR^1$	0.990	4.701	21.7	−0.5	0.502
$ROOH + HOOR^1$	0.969	4.600	21.2	−1.0	0.508
$ROOH + HSiR_3$	0.604	2.871	13.1	−9.1	0.623
$ROOH + HSR^1$	0.637	3.026	13.8	−8.4	0.611
$ROOH + HGeR_3$	0.589	2.796	12.6	−9.6	0.629
$ROOH + HSnR_3$	0.567	2.695	12.1	−10.1	0.638
$RC^{\bullet}HYH + R^1OOH \rightarrow RCH{=}Y + H_2O + R^1O^{\bullet}$					
$R^1OOH + RC^{\bullet}HCH_2{-}H$	0.788	3.743	17.4	−4.8	0.559
$R^1OOH + RC^{\bullet}HNH{-}H$	0.907	4.306	20.0	−2.2	0.524
$R^1OOH + RC^{\bullet}HO{-}H$	0.990	4.701	21.7	−0.5	0.502
$R^{\bullet} + HOOR^1 \rightarrow ROH + R^1O^{\bullet}$					
$R^{\bullet} + HOOR^1$	0.889	3.238	5.1	−1.1	0.529
$ROOR + HY \rightarrow RO^{\bullet} + ROH + Y^{\bullet}$					
$ROOR + HR^1$	0.796	3.743	17.4	−4.3	0.557
$ROOR + HNR_2$	0.916	4.306	20.0	−1.7	0.522
$ROOR + HOR^1$	1.000	4.701	21.7	0.0	0.500
$ROOR + HOOR^1$	0.978	4.600	21.2	−0.5	0.505
$ROOR + HSiR_3$	0.611	2.871	13.1	−8.6	0.621
$ROOR + HSR$	0.644	3.026	13.8	−7.9	0.608
$ROOR + HGeR_3$	0.595	2.796	12.6	−9.1	0.627
$ROOR + HSnR_3$	0.573	2.695	12.1	−9.6	0.636

(*continued overleaf*)

TABLE 9.1 (*continued*)

Reaction	α	$b \times 10^{-11}$ $((\mathrm{kJ/mol})^{1/2}\,\mathrm{m}^{-1})$	$0.5hL\nu_i$ $(\mathrm{kJ\,mol^{-1}})$	$0.5hL(\nu_i - \nu_f)$, $(\mathrm{kJ\,mol^{-1}})$	$(r^{\neq}/r_e)_0$
$RC^{\bullet}HYH + R^1OOR^1 \rightarrow RCH{=}Y + R^1OH + R^1O^{\bullet}$					
$RC^{\bullet}HCH_2{-}H + R^1OOR^1$	0.796	3.743	17.4	−4.3	0.557
$RC^{\bullet}HNH{-}H + R^1OOR^1$	0.916	4.306	20.0	−1.7	0.522
$RC^{\bullet}HO{-}H + R^1OOR^1$	1.000	4.701	21.7	0.0	0.500
$R^{\bullet} + R^1OOR^1 \rightarrow ROR^1 + R^1O^{\bullet}$					
$R^{\bullet} + R^1OOR^1$	0.849	3.238	5.1	−1.5	0.541
$ROOH + CH_2{=}CHR \rightarrow RO^{\bullet} + HOCH_2C^{\bullet}HR$					
$ROOH + CH_2{=}CHR^1$	0.889	3.238	5.1	−1.1	0.529
$ROOR + CH_2{=}CHR \rightarrow RO^{\bullet} + ROCH_2C^{\bullet}HR$					
$ROOR + CH_2{=}CHR^1$	0.849	3.238	5.1	−1.5	0.541
$RCH{=}CH_2 + HY \rightarrow RC^{\bullet}HCH_3 + Y^{\bullet}$					
$RCH{=}CH_2 + HR^1$	1.000	3.743	17.4	0.0	0.500
$RCH{=}CH_2 + HNR_2$	1.150	4.306	20.0	2.6	0.465
$RCH{=}CH_2 + HOR^1$	1.256	4.701	21.7	4.3	0.443
$RCH{=}CH_2 + HOOR^1$	1.229	4.600	21.2	3.8	0.449
$RCH{=}CH_2 + HSiR_3$	0.767	2.871	13.1	−4.3	0.566
$RCH{=}CH_2 + HSR$	0.808	3.026	13.8	−3.6	0.553
$RCH{=}CH_2 + HGeR_3$	0.747	2.796	12.6	−4.8	0.572
$RCH{=}CH_2 + HSnR_3$	0.720	2.695	12.1	−5.3	0.581
$RC{\equiv}CH + HY \rightarrow RC^{\bullet}{=}CH_2 + Y^{\bullet}$					
$RC{\equiv}CH + HR^1$	0.945	3.743	17.4	−1.0	0.514
$RC{\equiv}CH + HNR_2$	1.087	4.306	20.0	1.6	0.479
$RC{\equiv}CH + HOR^1$	1.187	4.701	21.7	3.3	0.457
$RC{\equiv}CH + HOOR^1$	1.161	4.600	21.2	2.8	0.463
$RC{\equiv}CH + HSiR_3$	0.725	2.871	13.1	−5.3	0.580
$RC{\equiv}CH + HSR^1$	0.764	3.026	13.8	−4.6	0.567
$RC{\equiv}CH + HGeR_3$	0.706	2.796	12.6	−5.8	0.586
$RC{\equiv}CH + HSnR_3$	0.680	2.695	12.1	−6.3	0.595
$R_1R_2C{=}O + HY \rightarrow R_1R_2C^{\bullet}OH + Y^{\bullet}$					
$R_1R_2C{=}O + HR^1$	0.796	3.743	17.4	−4.3	0.557
$R_1R_2C{=}O + HNR_2$	0.916	4.306	20.0	−1.7	0.522
$R_1R_2C{=}O + HOR^1$	1.00	4.701	21.7	0.0	0.500
$R_1R_2C{=}O + HOOR^1$	0.978	4.600	21.2	−0.5	0.505
$R_1R_2C{=}O + HSiR_3$	0.611	2.871	13.1	−8.6	0.621
$R_1R_2C{=}O + HSR^1$	0.644	3.026	13.8	−7.9	0.608

TABLE 9.1 (*continued*)

Reaction	α	$b \times 10^{-11}$ $((\mathrm{kJ/mol})^{1/2}\,\mathrm{m}^{-1})$	$0.5hL\nu_i$ $(\mathrm{kJ\,mol}^{-1})$	$0.5hL(\nu_i - \nu_f)$, $(\mathrm{kJ\,mol}^{-1})$	$(r^{\neq}/r_e)_0$
$R_1R_2C{=}O + HGeR_3$	0.595	2.796	12.6	−9.1	0.627
$R_1R_2C{=}O + HSnR_3$	0.573	2.695	12.1	−9.6	0.636
$RCH{=}NR^1(RN{=}NR,\ RC{\equiv}N) + HY \rightarrow RC^{\bullet}HNHR^1(RNHN^{\bullet}R,\ RC^{\bullet}{=}NH) + Y^{\bullet}$					
$RCH{=}NR^1 + HR^2$	0.869	3.743	17.4	−2.6	0.535
$RCH{=}NR^1 + HNR_2$	1.000	4.306	20.0	0.0	0.500
$RCH{=}NR^1 + HOR^2$	1.092	4.701	21.7	1.7	0.478
$RCH{=}NR^1 + HOOR^2$	1.068	4.600	21.2	1.2	0.484
$RCH{=}NR^1 + HSiR_3$	0.667	2.871	13.1	−6.9	0.600
$RCH{=}NR^1 + HSR^2$	0.703	3.026	13.8	−6.2	0.587
$RCH{=}NR^1 + HGeR_3$	0.649	0.279	12.6	−7.4	0.606
$RCH{=}NR^1 + HSnR_3$	0.626	2.700	12.1	−7.9	0.615
$RNO_2(RNO,\ NO_2) + HY \rightarrow RN(O^{\bullet})OH(RN^{\bullet}OH,\ ONOH) + Y^{\bullet}$					
$RNO_x + HR^1$	0.802	3.743	17.4	−4.1	0.555
$RNO_x + HNR_2$	0.923	4.306	20.0	−1.5	0.520
$RNO_x + HOR^1$	1.008	4.701	21.7	0.2	0.498
$RNO_x + HOOR^1$	0.986	4.600	21.2	−0.3	0.503
$RNO_x + HSiR_3$	0.615	2.871	13.1	−8.4	0.619
$RNO_x + HSR^1$	0.649	3.026	13.8	−7.7	0.606
$RNO_x + HGeR_3$	0.599	0.279	12.6	−8.9	0.625
$RNO_x + HSnR_3$	0.578	2.700	12.1	−9.4	0.634
$YX + CH_2{=}CHR \rightarrow Y^{\bullet} + XCH_2C^{\bullet}HR$					
$RCH{=}CH_2 + FY$	1.422	5.389	9.9	3.6	0.413
$RCH{=}CH_2 + ClY$	1.639	5.389	9.9	5.0	0.379
$RCH{=}CHCH{=}CH_2 + FY$	1.678	5.389	11.7	5.4	0.373
$RCH{=}CHCH{=}CH_2 + ClY$	1.934	5.389	11.7	6.8	0.341
$RCH{\equiv}CH_2 + FY$	1.824	6.912	12.7	6.4	0.354
$RCH{\equiv}CH_2 + ClY$	2.102	6.912	12.7	7.8	0.322
$XF + HY \rightarrow X^{\bullet} + FH + Y^{\bullet}$					
$XF + HR$	0.694	3.743	17.4	−7.4	0.590
$XF + HNR_2$	0.798	4.306	20.0	−4.8	0.556
$XF + HOR$	0.871	4.701	21.7	−3.1	0.534
$XF + HOOR$	0.853	4.600	21.2	−3.6	0.540
$XF + HSiR_3$	0.511	2.756	12.6	−12.2	0.662
$XF + HSR$	0.561	3.026	13.8	−11.0	0.641
$XCl + HY \rightarrow X^{\bullet} + ClH + Y^{\bullet}$					
$XCl + HR$	0.951	3.743	17.4	−0.5	0.513
$XCl + H_2NR$	1.094	4.306	20.1	2.1	0.478
$XCl + HOR$	1.194	4.701	21.7	3.8	0.456
$XCl + HOOR$	1.169	4.600	21.2	3.3	0.461
$XCl + HSiR_3$	0.700	2.756	12.6	−5.3	0.588
$XCl + HSR$	0.769	3.026	13.8	−4.1	0.565

TABLE 9.2 Kinetic Parameters of Bimolecular Reactions for Free Radical Generation in the IPM of the Transition State

Reaction	br_e ((kJ/mol)$^{1/2}$)	E_{e0} (kJ mol^{-1})	A_0 (L mol^{-1} s^{-1})	$\Delta H_{e\,max}$ (kJ mol^{-1})
$O_2 + HY \rightarrow HO_2^{\bullet} + Y^{\bullet a}$				
$O_2 + HR^1$	13.61	56.3	5.0×10^9	76.1
$O_2 + HR^2$	15.20	70.2	5.0×10^9	110.1
$O_2 + HR^3$	14.32	62.3	5.0×10^9	90.6
$O_2 + NH_3$	9.36	23.4	4.0×10^9	4.3
$O_2 + H_2NR$	10.80	31.1	4.0×10^9	20.9
$O_2 + HNR_2$	11.73	36.7	4.0×10^9	33.9
$O_2 + ROH$	14.45	51.1	5.0×10^9	73.7
$O_2 + ROOH$	13.13	43.1	5.0×10^9	51.5
$O_2 + HSiR_3$	12.41	58.4	5.0×10^9	69.7
$O_2 + RSH$	10.39	39.3	5.0×10^9	33.0
$O_2 + HGeR_3$	12.74	62.8	5.0×10^9	77.6
$O_2 + HSnR_3$	12.35	60.6	5.0×10^9	72.0
$O_2 + CH_2{=}CHR \rightarrow {}^{\bullet}OOCH_2C^{\bullet}HR^b$				
$CH_2{=}CHR$	26.04	90.5	2.0×10^9	408.5
$CH_2{=}CHPh$	27.23	99.0	2.0×10^8	540.3
$O_3 + HY \rightarrow HO_3^{\bullet} + Y^{\bullet c}$				
$O_3 + HR^1$	13.61	56.3	2.0×10^9	76.1
$O_3 + HR^2$	15.20	70.2	2.0×10^8	110.1
$O_3 + HR^3$	14.32	62.3	2.0×10^8	90.6
$O_3 + NH_3$	9.36	23.4	2.0×10^9	4.3
$O_3 + H_2NR$	10.80	31.1	2.0×10^9	20.9
$O_3 + HNR_2$	11.73	36.7	2.0×10^9	33.9
$O_3 + HOR$	14.45	51.1	2.0×10^9	73.7
$O_3 + HOOR$	13.13	43.1	2.0×10^9	51.5
$O_3 + HSiR_3$	12.41	58.4	2.0×10^9	69.7
$O_3 + RSH$	10.39	39.3	6.4×10^8	33.0
$O_3 + HGeR_3$	12.74	62.8	1.0×10^9	77.6
$O_3 + HSnR_3$	12.35	60.6	1.0×10^9	72.0
$ROOH + HY \rightarrow RO^{\bullet} + H_2O + Y^{\bullet d}$				
$ROOH + HR^1$	19.85	123.2	1.0×10^9	239.7
$ROOH + HR^2$	21.15	139.9	1.0×10^8	283.5
$ROOH + HR^3$	20.35	129.5	1.0×10^8	256.2
$ROOH + H_2NR^1$	17.33	82.6	1.0×10^9	149.7
$ROOH + HNR_2$	18.48	93.9	1.0×10^9	181.2
$ROOH + HOR_1$	19.94	101.4	1.0×10^9	213.0
$ROOH + HOOR$	20.45	107.9	1.0×10^9	228.6

TABLE 9.2 (*continued*)

Reaction	br_e ((kJ/mol)$^{1/2}$)	E_{e0} (kJ mol^{-1})	A_0 (L mol^{-1} s^{-1})	$\Delta H_{e\ max}$ (kJ mol^{-1})
$ROOH + HSiR_3$	15.80	97.0	1.0×10^9	145.6
$ROOH + HSR^1$	18.40	126.3	1.0×10^9	214.9
$ROOH + HGeR_3$	16.71	110.6	1.0×10^9	172.0
$ROOH + HSnR_3$	17.15	119.8	1.0×10^9	187.4
$R^1C^{\bullet}HYH + ROOH \rightarrow R^1CH{=}Y + H_2O + RO^{\bullet}$				
$R_1C^{\bullet}HCH_3 + ROOH$	19.85	123.2	1.0×10^9	239.7
$R_2C^{\bullet}HCH_3 + ROOH$	21.15	139.9	1.0×10^8	283.5
$R_3C^{\bullet}HCH_3 + ROOH$	20.35	129.5	1.0×10^8	256.2
$RC^{\bullet}HNH_2 + R^1OOH$	17.33	82.6	1.0×10^{10}	149.7
$RC^{\bullet}HNRH + R^1OOH$	18.48	93.9	1.0×10^{10}	181.2
$RC^{\bullet}HOH + R^1OOH$	20.45	107.9	1.0×10^{10}	228.6
$R^{\bullet} + R^1OOH \rightarrow ROH + R^1O^{\bullet}$				
$R^{1\bullet} + R^1OOH$	18.93	100.4	1.0×10^9	273.2
$R^{2\bullet} + R^1OOH$	19.92	111.2	1.0×10^9	307.3
$R^{3\bullet} + R^1OOH$	19.32	104.6	1.0×10^9	286.4
$ROOR + HY \rightarrow RO^{\bullet} + ROH + Y^{\bullet}$[d]				
$ROOR + HR^1$	21.34	141.2	2.0×10^9	289.2
$ROOR + HR^2$	22.64	158.9	2.0×10^8	336.7
$ROOR + HR^3$	21.84	147.9	2.0×10^8	307.1
$ROOR + H_2NR^1$	18.82	96.5	2.0×10^9	190.2
$ROOR + HNR_2$	19.97	108.6	2.0×10^9	225.0
$ROOR + HOR^1$	21.43	114.8	2.0×10^9	259.6
$ROOR + HOOR^1$	21.94	123.0	2.0×10^9	280.5
$ROOR + HSiR_3$	18.37	130.0	2.0×10^9	219.3
$ROOR + HSR^1$	18.63	128.4	2.0×10^9	222.6
$ROOR + HGeR_3$	18.80	138.9	2.0×10^9	235.2
$ROOR + HSnR_3$	19.24	149.6	2.0×10^9	252.9
$R^1C^{\bullet}HYH + ROOR \rightarrow RCH{=}Y + ROH + RO^{\bullet}$				
$R^1C^{\bullet}HCH_3 + ROOR$	21.34	141.2	2.0×10^9	289.2
$R^2C^{\bullet}HCH_3 + ROOR$	22.64	158.9	2.0×10^8	336.7
$R^3C^{\bullet}HCH_3 + ROOR$	21.84	147.9	2.0×10^8	307.1
$R^1C^{\bullet}HNH_2 + ROOR$	18.82	96.5	2.0×10^{10}	190.2
$R^1C^{\bullet}HNRH + ROOR$	19.97	108.6	2.0×10^{10}	225.0
$R^1C^{\bullet}HOH + ROOR$	21.94	123.0	2.0×10^{10}	280.5

(*continued overleaf*)

TABLE 9.2 (*continued*)

Reaction	br_e ((kJ/mol)$^{1/2}$)	E_{e0} (kJ mol^{-1})	A_0 (L mol^{-1} s^{-1})	$\Delta H_{e\,max}$ (kJ mol^{-1})
$R^{1\bullet} + ROOR \rightarrow ROR^1 + RO^{\bullet}$				
$R^{1\bullet}$ + ROOR	19.82	114.9	2.0×10^9	304.5
$R^{2\bullet}$ + ROOR	20.82	126.8	2.0×10^9	340.8
$R^{3\bullet}$ + ROOR	19.21	107.9	2.0×10^9	283.4
$RCH{=}CH_2 + HOOR^1 \rightarrow RC^{\bullet}HCH_2OH + R^1O^{\bullet d}$				
ROOH + $CH_2{=}CHR^1$	18.93	100.4	1.0×10^9	273.2
ROOH + $CH_2{=}CHCH{=}CHR^1$	19.92	111.2	1.0×10^9	307.3
ROOH + $CH_2{=}CHPh$	19.32	104.6	1.0×10^9	286.4
$RCH{=}CH_2 + R^1OOR^1 \rightarrow RC^{\bullet}HCH_2OR^1 + R^1O^{\bullet d}$				
ROOR + $CH_2{=}CHR$	19.82	114.9	2.0×10^9	304.5
ROOR + $CH_2{=}CHCH{=}CHR$	20.82	126.8	2.0×10^9	340.8
ROOR + $CH_2{=}CHPh$	19.21	107.9	2.0×10^9	283.4
$RCH{=}CH_2 + HY \rightarrow RC^{\bullet}HCH_3 + Y^{\bullet e}$				
$RCH{=}CH_2 + HR^1$	17.30	74.8	1.0×10^9	155.0
$RCH{=}CH_2 + HR^2$	18.60	86.5	1.0×10^8	190.8
$RCH{=}CH_2 + HR^3$	17.80	79.2	1.0×10^8	168.3
$RCH{=}CH_2 + H_2NR^1$	17.14	63.5	1.2×10^8	135.0
$RCH{=}CH_2 + HNR^1_2$	18.07	70.6	1.2×10^8	158.8
$RCH{=}CH_2 + HOR^1$	16.46	53.2	1.0×10^8	108.5
$RCH{=}CH_2 + HOOR^1$	16.73	56.3	1.0×10^8	117.2
$RCH{=}CH_2 + HSiR^1_3$	13.18	55.6	1.0×10^9	95.1
$RCH{=}CH_2 + HSR^1$	11.80	42.6	2.0×10^8	53.7
$RCH{=}CH_2 + HGeR^1_3$	13.82	62.6	1.0×10^9	112.1
$RCH{=}CH_2 + HSnR^1_3$	13.67	63.2	1.0×10^9	112.6
$RCH{=}CHCH{=}CH_2 + HY \rightarrow RCH{=}CHC^{\bullet}HCH_3 + Y^{\bullet e}$				
$RCH{=}CHCH{=}CH_2 + HR^1$	18.60	86.5	1.0×10^9	190.8
$RCH{=}CHCH{=}CH_2 + HR^2$	19.25	92.6	1.0×10^8	210.0
$RCH{=}CHCH{=}CH_2 + HR^3$	18.85	88.8	1.0×10^8	198.1
$RCH{=}CHCH{=}CH_2 + H_2NR^1$	18.64	75.2	1.2×10^8	174.2
$RCH{=}CHCH{=}CH_2 + HNR^1_2$	19.57	82.8	1.2×10^8	200.8
$RCH{=}CHCH{=}CH_2 + HOR^1$	17.76	62.0	1.0×10^8	139.4
$RCH{=}CHCH{=}CH_2 + HOOR^1$	18.68	70.2	1.0×10^8	166.4
$RCH{=}CHCH{=}CH_2 + HSiR^1_3$	14.12	64.6	1.0×10^9	115.6
$RCH{=}CHCH{=}CH_2 + HSR^1$	12.32	46.4	2.0×10^8	62.7
$RCH{=}CHCH{=}CH_2 + HGeR^1_3$	14.76	71.4	1.0×10^9	134.0
$RCH{=}CHCH{=}CH_2 + HSnR^1_3$	14.65	72.5	1.0×10^9	135.4

TABLE 9.2 (*continued*)

Reaction	br_e ((kJ/mol)$^{1/2}$)	E_{e0} (kJ mol^{-1})	A_0 (L mol^{-1} s^{-1})	$\Delta H_{e\,max}$ (kJ mol^{-1})
$PhCH{=}CH_2 + HY \rightarrow PhC^{\bullet}HCH_3 + Y^{\bullet e}$				
$PhCH{=}CH_2 + HR^1$	17.80	79.2	1.0×10^9	168.3
$PhCH{=}CH_2 + HR^2$	18.45	85.1	1.0×10^8	186.5
$PhCH{=}CH_2 + HR^3$	18.05	81.4	1.0×10^8	175.2
$PhCH{=}CH_2 + H_2NR$	17.71	67.8	1.2×10^8	149.3
$PhCH{=}CH_2 + HNR_2$	18.64	75.2	1.2×10^8	174.2
$PhCH{=}CH_2 + HOR$	16.96	56.5	1.0×10^8	120.0
$PhCH{=}CH_2 + HOOR$	17.60	62.3	1.0×10^8	138.1
$PhCH{=}CH_2 + HSiR_3$	13.54	58.7	1.0×10^9	102.8
$PhCH{=}CH_2 + HSR$	12.00	44.0	2.0×10^8	57.1
$PhCH{=}CH_2 + HGeR_3$	14.18	65.9	1.0×10^9	120.3
$PhCH{=}CH_2 + HSnR_3$	14.03	66.5	1.0×10^9	120.7
$RC{\equiv}CH + HY \rightarrow RC^{\bullet}{=}CH_2 + Y^{\bullet e}$				
$RC{\equiv}CH + HR^1$	16.88	75.3	1.0×10^9	146.1
$RC{\equiv}CH + HR^2$	18.18	87.4	1.0×10^8	181.1
$RC{\equiv}CH + HR^3$	17.18	78.0	1.0×10^8	153.9
$RC{\equiv}CH + H_2NR^1$	16.72	64.2	1.2×10^8	127.0
$RC{\equiv}CH + HNR^1_2$	17.65	71.5	1.2×10^8	150.2
$RC{\equiv}CH + HOR^1$	15.95	53.2	1.0×10^8	99.5
$RC{\equiv}CH + HOOR^1$	16.22	56.3	1.0×10^7	107.9
$RC{\equiv}CH + HSiR^1_3$	12.00	48.4	1.0×10^9	74.8
$RC{\equiv}CH + HSR^1$	11.38	41.6	2.0×10^7	47.2
$RC{\equiv}CH + HGeR^1_3$	12.56	54.2	1.0×10^9	88.5
$RC{\equiv}CH + HSnR^1_3$	12.62	56.4	1.0×10^9	93.1
$R_1R_2C{=}O + HY \rightarrow R^1R^2C^{\bullet}OH + Y^{\bullet e}$				
$R^1R^2C{=}O + HR^1$	13.10	53.2	1.0×10^9	66.6
$R^1R^2C{=}O + HR^2$	14.14	62.0	1.0×10^8	87.1
$R^1R^2C{=}O + HR^3$	13.50	56.5	1.0×10^8	74.2
$R^1R^2C{=}O + H_2NR$	11.95	38.9	1.0×10^8	37.3
$R^1R^2C{=}O + HNR_2$	12.88	45.2	1.0×10^9	52.4
$R^1R^2C{=}O + HOR$	13.62	46.4	1.0×10^9	61.3
$R^1R^2C{=}O + HOOR$	14.13	51.0	1.0×10^9	70.1
$R^1R^2C{=}O + HSiR_3$	10.13	39.5	1.0×10^9	49.6
$R^1R^2C{=}O + HSR$	10.39	39.9	1.0×10^9	32.9
$R^1R^2C{=}O + HGeR_3$	10.56	43.8	1.0×10^9	58.8
$R^1R^2C{=}O + HSnR_3$	11.00	48.9	1.0×10^9	69.0

(*continued overleaf*)

TABLE 9.2 (***continued***)

Reaction	br_e ((kJ/mol)$^{1/2}$)	E_{e0} (kJ mol^{-1})	A_0 (L mol^{-1} s^{-1})	$\Delta H_{e\,max}$ (kJ mol^{-1})
$RCH{=}NH + HY \rightarrow RC^{\bullet}HNH_2 + Y^{\bullet f}$				
$RCH{=}NH + HR^1$	14.90	63.6	1.5×10^8	101.3
$RCH{=}NH + HR^2$	16.21	75.2	1.5×10^7	131.9
$RCH{=}NH + HR^3$	15.40	67.9	1.5×10^7	112.5
$RCH{=}NH + H_2NR^1$	21.00	110.2	4.0×10^8	253.2
$RCH{=}NH + HNR^1_2$	21.90	119.9	2.0×10^8	283.7
$RCH{=}NH + HOR^1$	13.05	38.9	2.0×10^7	46.7
$RCH{=}NH + HOOR^1$	11.54	31.1	2.0×10^7	25.7
$RCH{=}NH + HSiR^1_3$	11.44	47.1	1.5×10^8	68.4
$RCH{=}NH + HSR^1$	9.75	32.8	2.0×10^7	23.6
$RCH{=}NH + HGeR^1_3$	12.26	55.3	1.5×10^8	67.7
$RCH{=}NH + HSnR^1_3$	11.05	46.2	1.5×10^8	57.8
$R^1CH{=}NR + HY \rightarrow R^1C^{\bullet}HNHR + Y^{\bullet f}$				
$R^1CH{=}NR^2 + HR^1$	15.80	71.5	1.5×10^8	121.9
$R^1CH{=}NR^2 + HR^2$	17.10	83.7	1.5×10^7	154.6
$R^1CH{=}NR^2 + HR^3$	16.30	76.1	1.5×10^7	134.1
$R^1CH{=}NR^2 + H_2NR$	21.90	119.9	4.0×10^8	283.7
$R^1CH{=}NR^2 + HNR_2$	22.80	130.0	2.0×10^8	315.9
$R^1CH{=}NR^2 + HOR$	13.94	44.4	2.0×10^7	122.8
$R^1CH{=}NR^2 + HOOR$	12.44	36.2	2.0×10^7	38.7
$R^1CH{=}NR^2 + HSiR_3$	12.34	54.8	1.5×10^8	67.6
$R^1CH{=}NR^2 + HSR$	10.65	39.1	2.0×10^7	36.3
$R^1CH{=}NR^2 + HGeR_3$	13.16	63.7	1.5×10^8	85.2
$R^1CH{=}NR^2 + HSnR_3$	11.95	54.0	1.5×10^8	63.7
$RCH{=}NPh + HY \rightarrow RC^{\bullet}HNHPh + Y^{\bullet f}$				
$RCH{=}NPh + HR^1$	13.00	48.4	1.5×10^8	63.1
$RCH{=}NPh + HR^2$	14.30	58.5	1.5×10^7	88.4
$RCH{=}NPh + HR^3$	13.50	52.2	1.5×10^7	72.4
$RCH{=}NPh + H_2NR^1$	19.10	91.2	4.0×10^8	194.0
$RCH{=}NPh + HNR_2$	20.00	100.0	2.0×10^8	221.1
$RCH{=}NPh + HOR^1$	13.45	41.3	2.0×10^7	87.5
$RCH{=}NPh + HOOR^1$	11.94	33.3	2.0×10^7	31.3
$RCH{=}NPh + HSiR_3$	9.54	32.8	1.5×10^8	23.0
$RCH{=}NPh + HSR^1$	7.85	21.2	2.0×10^7	2.1
$RCH{=}NPh + HGeR_3$	10.36	39.5	1.5×10^8	35.6
$RCH{=}NPh + HSnR_3$	9.15	31.7	1.5×10^8	20.3
$RC{\equiv}N + HY \rightarrow RC^{\bullet}{=}NH + Y^{\bullet f}$				
$RC{\equiv}N + HR^1$	15.33	67.3	3.0×10^8	111.0

TABLE 9.2 (***continued***)

Reaction	br_e ((kJ/mol)$^{1/2}$)	E_{e0} (kJ mol^{-1})	A_0 (L mol^{-1} s^{-1})	$\Delta H_{e\,max}$ (kJ mol^{-1})
$RC{\equiv}N + HR^2$	16.64	79.3	3.0×10^7	142.7
$RC{\equiv}N + HR^3$	15.83	71.7	3.0×10^7	122.6
$RC{\equiv}N + H_2NR^1$	21.43	114.8	8.0×10^8	267.6
$RC{\equiv}N + HNR^1_2$	22.33	124.7	4.0×10^8	298.9
$RC{\equiv}N + HOR^1$	14.00	44.8	4.0×10^7	127.7
$RC{\equiv}N + HOOR^1$	12.50	36.5	4.0×10^7	39.6
$RC{\equiv}N + HSiR^1_3$	11.90	51.0	3.0×10^8	59.6
$RC{\equiv}N + HSR^1$	10.18	35.7	4.0×10^7	29.5
$RC{\equiv}N + HGeR^1_3$	12.70	59.3	3.0×10^8	76.0
$RC{\equiv}N + HSnR^1_3$	11.50	50.0	3.0×10^8	55.7
$RN{=}NR + HY \rightarrow RN^{\bullet}NHR + Y^{\bullet f}$				
$RN{=}NR + HR^1$	13.80	54.5	3.0×10^8	78.3
$RN{=}NR + HR^2$	15.10	65.3	3.0×10^8	105.7
$RN{=}NR + HR^3$	14.30	58.5	3.0×10^8	88.4
$RN{=}NR + H_2NR^1$	19.90	99.0	4.0×10^8	218.0
$RN{=}NR + HNR^1_2$	20.80	108.2	4.0×10^8	246.6
$RN{=}NR + HOR^1$	12.44	35.4	4.0×10^8	32.9
$RN{=}NR + HOOR^1$	10.94	28.0	4.0×10^7	18.0
$RN{=}NR + HSiR^1_3$	10.37	38.7	3.0×10^8	241.5
$RN{=}NR + HSR^1$	8.65	25.7	4.0×10^8	10.3
$RN{=}NR + HGeR^1_3$	11.17	45.9	3.0×10^8	48.3
$RN{=}NR + HSnR^1_3$	10.03	38.0	3.0×10^8	32.3
$RNO_2(RNO) + HY \rightarrow RN(O^{\bullet})OH(RN^{\bullet}OH) + Y^{\bullet g}$				
$RNO_x + HR^1$	12.25	46.2	1.0×10^9	51.3
$RNO_x + HR^2$	13.68	57.6	1.0×10^8	77.7
$RNO_x + HR^3$	12.88	51.1	1.0×10^8	62.4
$RNO_x + H_2NR^1$	10.10	27.6	1.0×10^9	12.4
$RNO_x + HNR^1_2$	9.21	22.9	1.0×10^9	2.8
$RNO_x + HOR^1$	14.67	73.1	1.0×10^9	78.4
$RNO_x + HOOR^1$	13.40	45.5	1.0×10^9	56.4
$RNO_x + HSiR^1_3$	11.04	48.8	1.0×10^9	45.5
$RNO_x + HSR^1$	10.8	42.9	1.0×10^9	39.2
$RNO_x + HGeR^1_3$	11.37	50.6	1.0×10^9	52.3
$RNO_x + HSnR^1_3$	11.00	48.6	1.0×10^9	47.7
$R^1ONO_x + CH_2{=}CHR \rightarrow NO^{\bullet}_x + R^1OCH_2C^{\bullet}HR^d$				
$RONO_x + CH_2{=}CHR^1$	20.23	119.7	1.0×10^9	319.2
$RONO_x + CH_2{=}CHCH{=}CHR^1$	21.20	131.8	1.0×10^9	356.3

(*continued overleaf*)

TABLE 9.2 (*continued*)

Reaction	br_e ((kJ/mol)$^{1/2}$)	E_{e0} (kJ mol^{-1})	A_0 (L mol^{-1} s^{-1})	$\Delta H_{e\,\max}$ (kJ mol^{-1})
$\mathrm{RONO}_x + \mathrm{CH_2{=}CHPh}$	20.63	124.5	1.0×10^9	333.8
$\mathrm{RONO}_x + \mathrm{CH{\equiv}CR^1}$	29.05	106.7	2.0×10^9	594.0
$XF + HY \rightarrow X^\bullet + FH + Y^\bullet$ (gas phase)[h]				
$\mathrm{XF + HR^1 \rightarrow X^\bullet + FH + R^{1\bullet}}$	12.85	57.5	2.2×10^{10}	63.4
$\mathrm{XF + HR^2 \rightarrow X^\bullet + FH +} R^{2\bullet}$	13.73	65.7	2.5×10^9	80.7
$\mathrm{XF + HR^3 \rightarrow X^\bullet + FH + R^{3\bullet}}$	13.20	60.7	2.5×10^9	70.1
$\mathrm{XF + NH_3 \rightarrow X^\bullet + FH + N^\bullet H_2}$	14.40	64.1	7.5×10^{10}	83.9
$\mathrm{XF + H_2NR \rightarrow X^\bullet + FH + RN^\bullet H}$	14.67	66.6	7.5×10^{11}	89.6
$\mathrm{XF + HNR_2 \rightarrow X^\bullet + FH + N^\bullet R_2}$	14.86	68.3	7.5×10^{11}	93.7
$\mathrm{XF + HOR \rightarrow X^\bullet + FH + RO^\bullet}$	13.53	52.3	1.2×10^{10}	59.7
$\mathrm{XF + HOOR \rightarrow X^\bullet + FH + RO_2{}^\bullet}$	14.00	57.1	1.2×10^{10}	70.3
$\mathrm{XF + HSiR_3 \rightarrow X^\bullet + FH + Si^\bullet R_3}$	11.00	53.0	2.2×10^{10}	47.4
$\mathrm{XF + HSR \rightarrow X^\bullet + FH + RS^\bullet}$	12.18	60.9	7.5×10^{10}	63.3
$XCl + HY \rightarrow X^\bullet + ClH + Y^\bullet$ (gas phase)[h]				
$\mathrm{XCl + HR^1 \rightarrow X^\bullet + ClH + R^{1\bullet}}$	9.90	25.7	1.0×10^{10}	16.6
$\mathrm{XCl + HR^2 \rightarrow X^\bullet + ClH + R^{2\bullet}}$	11.10	32.4	1.0×10^{10}	32.2
$\mathrm{XCl + HR^3 \rightarrow X^\bullet + ClH + R^{3\bullet}}$	10.25	27.6	1.0×10^{10}	20.9
$\mathrm{XCl + NH_3 \rightarrow X^\bullet + ClH + N^\bullet H_2}$	10.52	25.2	1.6×10^{10}	16.8
$\mathrm{XCl + H_2NR \rightarrow X^\bullet + ClH + HN^\bullet R}$	11.05	27.8	1.6×10^9	23.3
$\mathrm{XCl + HNR_2 \rightarrow X^\bullet + ClH + N^\bullet R_2}$	10.38	24.6	1.6×10^9	15.2
$\mathrm{XCl + HOR \rightarrow X^\bullet + ClH + RO^\bullet}$	15.28	48.5	4.2×10^{10}	86.7
$\mathrm{XCl + HOOR \rightarrow X^\bullet + ClH + RO_2{}^\bullet}$	14.90	47.2	1.6×10^{10}	81.3
$\mathrm{XCl + HSiR_3 \rightarrow X^\bullet + ClH + R_3Si^\bullet}$	9.25	29.6	2.5×10^{10}	21.6
$\mathrm{XCl + HSR \rightarrow X^\bullet + ClH + RS^\bullet}$	9.85	31.0	1.0×10^{10}	25.6
$XF + CH_2{=}CHR \rightarrow X^\bullet + FCH_2C^\bullet HR$[i]				
$\mathrm{XF + CH_2{=}CHR}$	19.30	63.5	2.5×10^{10}	240.0
$\mathrm{XF + CH_2{=}CHCH{=}CHR}$	21.20	76.6	2.5×10^{10}	303.3
$\mathrm{XF + CH_2{=}CHPh}$	20.55	72.0	2.5×10^{10}	280.8
$XCl + CH_2{=}CHR \rightarrow X^\bullet + ClCH_2C^\bullet HR$[i]				
$\mathrm{XCl + CH_2{=}CHR}$	18.47	49.0	9.0×10^9	215.4
$\mathrm{XCl + CH_2{=}CHCH{=}CHR}$	20.35	59.5	9.0×10^9	274.7
$\mathrm{XCl + CH_2{=}CHPh}$	19.73	55.9	9.0×10^9	254.5

---

[a] See Refs. 16–18.

[b] See Ref. 19.

[c] See Refs. 20 and 21.

[d] See Refs. 22–25.

[e] See Refs. 26 and 27.

[f] See Ref. 28.

[g] See Refs. 29–31.

[h] See Ref. 32.

[i] See Ref. 33.

TABLE 9.3 Examples for the Calculation of Activation Energies and Rate Constants of Different Types of Reactions

Parameters	Eq.	Values of Parameters	Reference
Reaction:		$O_2 + HCMe_2Ph \rightarrow PhMe_2C^{\bullet} + HOO^{\bullet}$	
Parameters	Eqs.	$\alpha = 0.814$, $\Delta H_{e\,\max} = 90.6\ \text{kJ mol}^{-1}$	
ΔH		$\Delta H = 354.7 - 220.0 = 134.7\ \text{kJ mol}^{-1}$	
E	9.17	$E = \Delta H + 1.7 = 136.4\ \text{kJ mol}^{-1}$	
A	9.18	$A = n_{C\text{-}H} \times A_0[1 + 1.3(11.4 - 9.5)]^2 = 5.0 \times 10^9 \times 12.0 = 6.1 \times 10^{10}\ \text{L mol}^{-1}\ \text{s}^{-1}$	
$k(T = 400\ \text{K})$	9.16	$k = 6.1 \times 10^{10} \exp(-136.4/3.326) = 0.93 \times 10^{-7}\ \text{L mol}^{-1}\ \text{s}^{-1}$	
$k(T = 400\ \text{K})$	Experim.	$k = 2.58 \times 10^3 \exp(-77.5/RT) = 1.96 \times 10^{-7}\ \text{L mol}^{-1}\ \text{s}^{-1}$	34
Reaction:		$Me_2PhCOOH + Me_2PhCOOH \rightarrow Me_2PhCOO^{\bullet} + H_2O + Me_2PhCO^{\bullet}$	
Parameters	Eqs.	$\alpha = 1.0, br_e = 20.45, 0.5hL\nu_i = 21.2, 0.5hL(\nu_i - \nu_f) = -1.0$	
ΔH_e	9.2	$\Delta H_e = \Delta H - 1.0 = 358.6 + 180.0 - 498.0 - 1.0 = 39.6\ \text{kJ mol}^{-1}$	
$E_e^{1/2}$	9.12	$E_e^{1/2} = 10.225 + 39.6/40.9 = 11.19\ (\text{kJ/mol})^{1/2}$	
E	9.15	$E = 11.19^2 - 21.2 + 1.4 = 105.8\ \text{kJ mol}^{-1}$	
A	9.20	$A = n_{O\text{-}H} \times A_0 \times (2RT/\pi E)^{1/2} = 2 \times 1.0 \times 10^{10} \times (5.82/332.4)^{1/2} = 2.65 \times 10^9\ \text{L mol}^{-1}\ \text{s}^{-1}$	
$k(T = 350\ \text{K})$	9.16	$k = 2 \times 10^9 \exp(-105.8/2.91) = 4.3 \times 10^{-7}\ \text{L mol}^{-1}\text{s}^{-1}$	
$k(T = 350\ \text{K})$	Experim.	$k = 7.3 \times 10^4 \exp(-80.7/2.91) = 6.6 \times 10^{-8}\ \text{L mol}^{-1}\text{s}^{-1}$	35
Reaction:		$PhCH = CH_2 + HR \rightarrow PhC^{\bullet}HCH_3 + R^{\bullet}$ RH = 9,10-Dihydroanthracene	
Parameters	Eqs.	$\alpha = 1.0, br_e = 17.80, 0.5hL\nu_i = 17.4, 0.5hL(\nu_i - \nu_f) = 0$	
ΔH_e	9.2	$\Delta H_e = \Delta H = 322.0 - 190.3 = 131.7\ \text{kJ mol}^{-1}$	
$E_e^{1/2}$	9.12	$E_e^{1/2} = 8.9 + 131.7/35.6 = 12.60\ (\text{kJ/mol})^{1/2}$	
E	9.15	$E_e = 12.6^2 = 158.7$; $E = 158.7 - 17.4 + 2.3 = 143.6\ \text{kJ mol}^{-1}$	

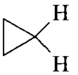
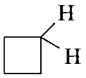
(continued overleaf)

TABLE 9.3 (*continued*)

Parameters	Eq.	Values of Parameters	Reference
A	Table 8.2	$A = n_{C\text{-}H} \times 1.0 \times 10^9 = 4.0 \times 10^9\ \text{L mol}^{-1}\,\text{s}^{-1}$	
$k(T = 550\ \text{K})$	9.16	$k = 4.0 \times 10^9 \exp(-143.6/4.573) = 9.2 \times 10^{-5}\ \text{L mol}^{-1}\,\text{s}^{-1}$	
$k(T = 550\ \text{K})$	Experim.	$k = 1.0 \times 10^{-4}\ \text{L mol}^{-1}\,\text{s}^{-1}$	36
Reaction:		$CH_4 + F_2 \rightarrow C^{\bullet}H_3 + HF + F^{\bullet}$	
Parameters	Eqs.	$\alpha = 0.694, br_e = 12.85, 0.5hL\nu_i = 17.4, 0.5hL(\nu_i - \nu_f) = -7.4\ \text{kJ mol}^{-1}$	
ΔH_e	9.2	$\Delta H_e = \Delta H - 7.4 = 440 + 158.7 - 570.3 - 7.4 = 21.0\ \text{kJ mol}^{-1}$	
$E_e^{1/2}$	9.13	$E_e^{1/2} = (12.85/0.518)[1 - 0.694(1 - 3.137 \times 10^{-3} \times 21)^{1/2}] = 8.17\ (\text{kJ/mol})^{1/2}$	
E	9.15	$E_e = 8.17^2 = 66.7;\ E = 66.7 - 17.4 + 1.7 = 51.0\ \text{kJ mol}^{-1}$	
A	9.20	$A = n_{C\text{-}H} \times A_0 \times (2RT/\pi E)^{1/2} = 4 \times 2.2 \times 10^{10}(6.65/160)^{1/2} = 1.8 \times 10^{10}\ \text{L mol}^{-1}\,\text{s}^{-1}$	
$k(T = 400\ \text{K})$	9.16	$k = 1.8 \times 10^{10} \exp(-51/3.326) = 3.9 \times 10^3\ \text{L mol}^{-1}\,\text{s}^{-1}$	
$k(T = 400\ \text{K})$	Experim.	$k = 2.0 \times 10^9 \exp(-47/3.326) = 1.5 \times 10^3\ \text{L mol}^{-1}\,\text{s}^{-1}$	37

9.3 PARAMETERS OF BIMOLECULAR HOMOLYTIC REACTION IN THE PARABOLIC MODEL

TABLE 9.4 The Values for the C–H Bond Dissociation Energies in Hydrocarbons, Amines, and Oxygen-Containing Compounds

Hydrocarbon	Bond	D (kJ mol^{-1})
	Aliphatic Hydrocarbons[a]	
Methane	$\mathrm{Me{-}H}$	440.0
Ethane	$\mathrm{Et{-}H}$	422.0
Propane	$\mathrm{EtCH_2{-}H}$	422.0
Propane	$\mathrm{Me_2CH{-}H}$	412.0
Butane	$\mathrm{EtMeCH{-}H}$	413.0
Pentane	$\mathrm{BuCH_2{-}H}$	422.0
Pentane	$\mathrm{PrMeCH{-}H}$	413.0
Pentane	$\mathrm{EtEtCH{-}H}$	414.5
Hexane	$\mathrm{BuCH_2CH_2{-}H}$	422.0
Hexane	$\mathrm{BuMeCH{-}H}$	413.0
Hexane	$\mathrm{PrEtCH{-}H}$	414.5
Heptane	$\mathrm{Bu(CH_2)_2CH_2{-}H}$	422.0
Heptane	$\mathrm{BuCH_2MeCH{-}H}$	413.0
Heptane	$\mathrm{BuEtCH{-}H}$	414.5
Heptane	$\mathrm{PrPrCH{-}H}$	415.7
Propane, 2-methyl-	$\mathrm{Me_2CHCH_2{-}H}$	422.0
Propane, 2-methyl-	$\mathrm{Me_3C{-}H}$	400.0
Propane, 2,2-dimethyl-	$\mathrm{Me_3CCH_2{-}H}$	422.0
Butane, 2-methyl-	$\mathrm{Me_2EtC{-}H}$	402.0
Butane, 2-methyl-	$\mathrm{Me_2CH(CH{-}H)Me}$	412.0
Butane, 2,2-dimethyl-	$\mathrm{Me_3CMeCH{-}H}$	410.2
Butane, 2,3-dimethyl-	$\mathrm{Me_2(C{-}H)CHMe_2}$	396.4
Butane, 2,2,3-trimethyl-	$\mathrm{Me_3C(C{-}H)Me_2}$	399.6
Pentane, 2-methyl-	$\mathrm{PrMe_2C{-}H}$	399.3
Pentane, 3-methyl-	$\mathrm{Et_2MeC{-}H}$	398.4
Pentane, 2,4-dimethyl-	$\mathrm{Me_2CHCH_2Me_2C{-}H}$	400.0
Pentane, 2,3,4-trimethyl-	$\mathrm{[Me_2CH]_2MeC{-}H}$	405.4
	Cycloparaffines[b]	
Cyclopropane		429.0
Cyclobutane		418.5

(*continued overleaf*)

TABLE 9.4 (*continued*)

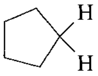
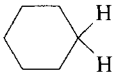
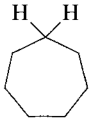
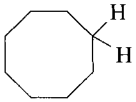
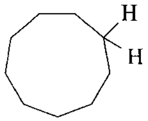
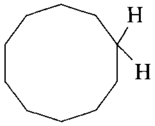
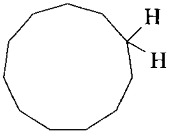
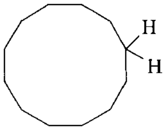
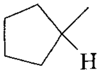
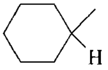
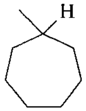
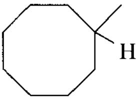
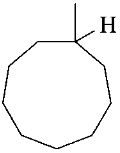
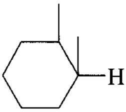
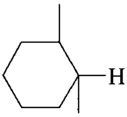
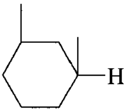
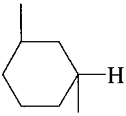
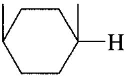
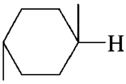
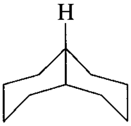
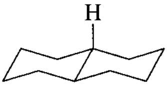
Hydrocarbon	Bond	D (kJ mol^{-1})
Cyclopentane		408.4
Cyclohexane		408.8
Cycloheptane		403.9
Cyclooctane		401.9
Cyclononane		402.9
Cyclodecane		404.5
Cycloundecane		404.7
Cyclododecane		410.0
Methylcyclopentane		392.2
Methylcyclohexane		395.5
Methylcycloheptane		390.0

TABLE 9.4 *(continued)*

Hydrocarbon	Bond	D (kJ mol^{-1})
Methylcyclooctane		395.0
Methylcyclononane		394.8
(Z)-1,2-Dimethylcyclohexane		392.8
(E)-1,2-Dimethylcyclohexane		407.7
(Z)-1,3-Dimethylcyclohexane		393.0
(E)-1,3-Dimethylcyclohexane		390.0
(Z)-1,4-Dimethylcyclohexane		392.0
(E)-1,4-Dimethylcyclohexane		396.8
(Z)-Decalin		387.6
(E)-Decalin		400.0

(continued overleaf)

TABLE 9.4 (*continued*)

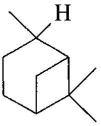
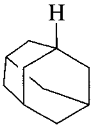
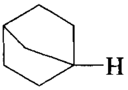
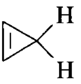
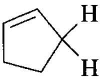
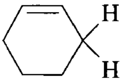
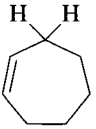
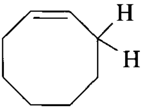
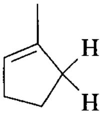
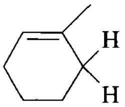
Hydrocarbon	Bond	D (kJ mol^{-1})
(Z)-Pinane		377.4
Adamantane		412.0
Norbornane		393.1
	Olefins^a	
Ethene	$CH_2=CH-H$	464.0
Propene	$CH_2=CHCH_2-H$	368.0
Propene	$CH_2=C-HMe$	459.0
Propene, 2-methyl-	$CH_2=C(Me)CH_2-H$	357.9
1-Butene	$CH_2=CH(CH-H)Me$	349.8
1-Butene	$CH_2=CHCH_2CH_2-H$	410.9
1-Butene, 2-methyl-	$CH_2=CMe(CH-H)Me$	347.2
1-Butene, 2-methyl-	$CH_2=CEt(CH_2-H)$	367.7
1-Butene, 3-methyl-	$CH_2=CH(C-H)Me_2$	339.6
(Z)-2-Butene	(Z)-$MeCH=CHCH_2-H$	355.8
(E)-2-Butene	(E)-$MeCH=CHCH_2-H$	356.8
2-Butene, 3-methyl-	$MeCH=CMeCH_2-H$	352.4
1-Butene, 2,3-dimethyl-	$CH_2=CMe(C-H)Me_2$	338.0
2-Butene, 2,3-dimethyl-	$Me_2C=CMeCH_2-H$	350.2
1-Pentene	$CH_2=CH(CH-H)Et$	349.8
(Z)-2-Pentene	(Z)-$MeCH=CH(CH-H)Me$	344.0
(E)-2-Pentene	(E)-$MeCH=CH(CH-H)Me$	346.2
2-Pentene, 2-methyl-	$Me_2C=CH(CH-H)Me$	332.0
2-Pentene, 3-methyl-	$MeCH=CMe(CH-H)Me$	333.2
(Z)-2-Pentene, 4-methyl-	(Z)-$MeCH=CH(C-H)Me_2$	331.7
(E)-2-Pentene, 4-methyl-	(E)-$MeCH=CH(C-H)Me_2$	333.9
2-Pentene, 2,3,4-trimethyl-	$Me_2C=CMe(C-H)Me_2$	322.8
2-Pentene, 3,4-dimethyl-	$MeCH=CMe(C-H)Me_2$	324.0
1-Hexene	$CH_2=CH(CH-H)Pr$	349.8
(E)-3-Hexene, 2,5-dimethyl-	(E)-$Me_2CHCH=CHC-HMe_2$	336.1
1,3-Pentadiene	$CH_2=CHCH=CHCH_2-H$	343.0
1,4-Pentadiene	$CH_2=CH(CH-H)CH=CH_2$	318.0

TABLE 9.4 (*continued*)

Hydrocarbon	Bond	D (kJ mol^{-1})
2,3-Pentadiene	$MeCH{=}C{=}CHCH_2{-}H$	365.0
1,4-Pentadiene, 3-methyl-	$CH_2{=}CH(CMe{-}H)CH{=}CH_2$	307.2
1,3-Hexadiene	$CH_2{=}CHCH{=}CH(CH{-}H)Me$	321.1
Propene, 2-phenyl-	$CH_2{=}CPh(CH_2{-}H)$	357.1
Propene, 1-phenyl-	$PhCH{=}CHCH_2{-}H$	349.7
Propene, 3-phenyl-	$CH_2{=}CH(CH{-}H)Ph$	342.8
	Cycloalkenes	
Cyclopropene		381.6
Cyclopentene		342.5
Cyclohexene		341.5
Cycloheptene		346.6
Cyclooctene		357.2
1-Methylcyclopentene		339.9
3-Methylcyclopentene		329.3
1-Methylcyclohexene		338.9

(*continued overleaf*)

TABLE 9.4 ***(continued)***

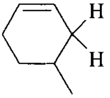
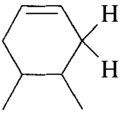
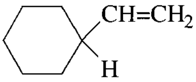
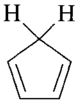
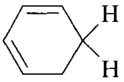
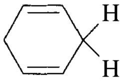
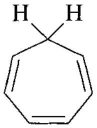
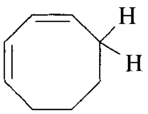
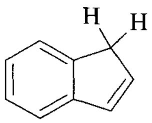
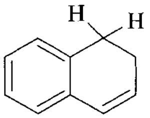
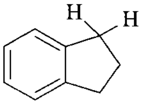
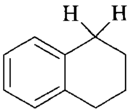
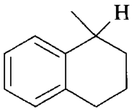
Hydrocarbon	Bond	D (kJ mol^{-1})
4-Methylcyclohexene		332.7
4,5-Dimethylcyclohexene		326.2
Vinylcyclohexane		341.8
1,3-Cyclopentadiene		288.8
1,3-Cyclohexadiene		330.9
1,4-Cyclohexadiene		312.6
Cycloheptatriene		301.0
1,3-Cyclooctadiene		347.1
Indene		339.9
1,2-Dihydronaphthalene		336.5

TABLE 9.4 (*continued*)

Hydrocarbon	Bond	*D* (kJ mol^{-1})
	Acetylenes[a]	
Acetylene (ethyne)	$HC\equiv C-H$	548.0
Propyne	$CH\equiv C(CH_2-H)$	359.8
1-Butyne	$CH\equiv C(CH-H)Me$	346.8
2-Butyne	$MeC\equiv CCH_2-H$	354.7
1-Butyne, 3-methyl-	$HC\equiv C(C-H)Me_2$	334.5
2-Pentyne	$MeC\equiv C(CH-H)Me$	341.7
2-Pentyne, 4-methyl-	$MeC\equiv C(C-H)Me_2$	329.4
	Alkylaromatic Hydrocarbons[b]	
Toluene	$PhCH_2-H$	375.0
Ethylbenzene	$PhMeCH-H$	364.1
Isopropylbenzene	$PhMe_2C-H$	354.7
Propylbenzene	$PhEtCH-H$	366.2
Propane, 2-methyl-1-phenyl-	$Ph(CH-H)CHMe_2$	365.1
Butylbenzene	$PhPrCH-H$	368.7
Ethane, 1,1-dimethyl-1-phenyl-	$PhCMe_2CH_2-H$	412.6
Butane, 2-phenyl-	$PhMeEtC-H$	359.4
Pentane, 3-phenyl-	$PhEtEtC-H$	366.8
Diphenylmethane	Ph_2CH-H	356.8
Triphenylmethane	Ph_3C-H	346.0
1,2-Diphenylethane	$(PhCH_2)PhCH-H$	364.2
1,1-Diphenylethane	Ph_2MeC-H	348.8
1,3-Diphenylpropane	$PhCH_2CH_2PhCH-H$	367.2
Indane		359.4
Tetralin		345.6
1-Methyltetralin		336.4

(*continued overleaf*)

TABLE 9.4 (*continued*)

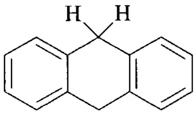
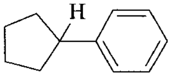
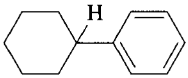
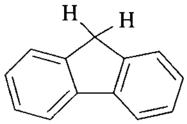
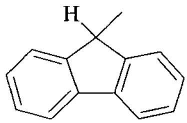
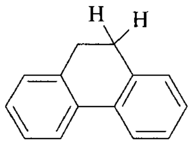
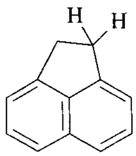
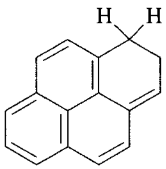
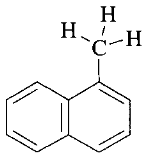
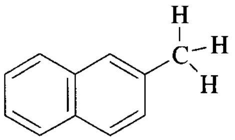
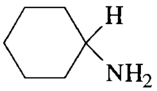
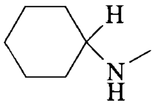
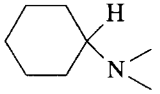
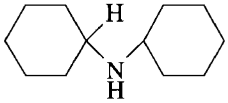
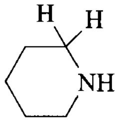
Hydrocarbon	Bond	D (kJ mol^{-1})
9,10-Dihydroanthracene		322.0
Phenylcyclopentane		349.1
Phenylcyclohexane		356.4
Fluorene		338.6
9-Methylfluorene		328.5
9,10-Dihydrophenanthrene		343.7
Acenaphthene		350.0
1,2-Dihydropyrene		341.4
1-Methylnaphthalene		365.1

TABLE 9.4 (*continued*)

Hydrocarbon	Bond	D (kJ mol^{-1})
2-Methylnaphthalene		358.3
	Amines^c	
Methanamine	H_2NCH_2-H	400.0
Methanamine, *N*-methyl-	$MeNHCH_2-H$	389.0
Methanamine, *N*,*N*-dimethyl-	Me_2NCH_2-H	376.6
Ethanamine	$Me(NH_2)CH-H$	389.6
Ethanamine, *N*-ethyl-	$(EtNH)MeCH-H$	384.6
Ethanamine, *N*,*N*-diethyl-	$(Et_2N)MeCH-H$	379.5
2-Propanamine	$Me_2(NH_2)C-H$	379.5
2-Propanamine, *N*-2-propyl-	$(Me_2CHNH)Me_2C-H$	375.0
2-Propanamine, *N*,*N*-di-2-propyl-	$(Me_2CH)_2NMe_2C-H$	370.0
Cyclohexanamine		395.9
Cyclohexanamine, *N*-methyl-		388.0
Cyclohexanamine, *N*,*N*-dimethyl-		381.0
Cyclohexanamine, *N*-cyclohexyl-		387.3
Piperidine		385.6
2-Propen-1-amin, *N*,*N*-di-2-propenyl-	$CH_2{=}CH(CH-H)N(CH_2CH{=}CH_2)_2$	345.6
Benzenamine, *N*,*N*-di-2-propenyl-	$CH_2{=}CH(CH-H)NPh(CH_2CH{=}CH_2)$	339.3

(*continued overleaf*)

TABLE 9.4 (*continued*)

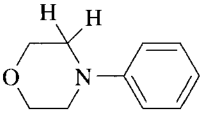
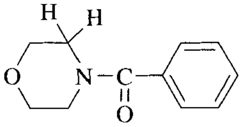
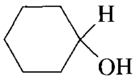
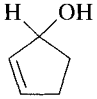
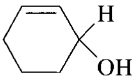
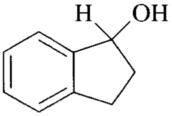
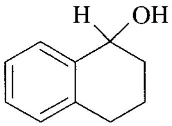
Hydrocarbon	Bond	D (kJ mol^{-1})
Benzenmethanamin	Ph(NH$_2$)CH−H	368.0
Benzenmethanamin, *N*,*N*-dimethyl-	Me$_2$NPhCH−H	370.8
Benzenmethanamin, *N*,*N*-dibenzyl-	(PhCH$_2$)$_2$NPhCH−H	372.8
Benzenamine, *N*,*N*-dimethyl-	PhNMeCH$_2$−H	383.7
Benzenamine, *N*,*N*-diethyl-	PhEtNCH−HMe	383.2
Benzenamine, *N*-methyl-*N*-phenyl-	Ph$_2$NCH$_2$−H	379.5
Morpholin, *N*-phenyl-		361.0
Acetamide, *N*-ethyl-	MeCONH(CH−H)Me	399.2
Acetamide, *N*-2-propyl-	(MeCONH)Me$_2$C−H	395.5
Acetamide, *N*,*N*-dimethyl-	(MeCO)MeNCH$_2$−H	386.9
Morpholin, *N*-benzoyl-		401.0
	Alcohols^{d}	
Methanol	HOCH$_2$−H	411.0
Ethanol	Me(HO)CH−H	399.8
Propanol	Et(HO)CH−H	399.5
Butanol	Pr(HO)CH−H	397.0
Pentanol	Bu(HO)CH−H	397.0
Ethanol, 1-methyl-	Me$_2$(HO)C−H	390.5
Propanol, 2,2-dimethyl-	Me$_3$C(HO)CH−H	395.2
Ethanol, 1,1-dimethyl-	Me$_2$(HO)CCH$_2$−H	417.4
Cyclohexanol		388.4
3-Cyclopentenol		330.7

TABLE 9.4 (*continued*)

Hydrocarbon	Bond	D (kJ mol^{-1})
3-Cyclohexenol		329.7
Ethyleneglycol	$\mathrm{HOCH_2(HO)CH{-}H}$	401.5
1,3-Butanediol	$\mathrm{HOCH_2CH_2(HO)MeCH{-}H}$	387.7
1,4-Butanediol	$\mathrm{HOCH_2(CH_2)_2(HO)CH{-}H}$	404.2
2,3-Butanediol	$\mathrm{MeCH(OH)C{-}H(OH)Me}$	383.1
Allyl alcohol	$\mathrm{CH_2{=}CH(HO)CH{-}H}$	360.0
2-Propen-1-ol, 2-methyl-	$\mathrm{CH_2{=}CMeCH{-}H(OH)}$	349.9
2-Buten-2-ol, 2-methyl-	$\mathrm{CH_2{=}CMeC{-}HMe(OH)}$	339.2
(*Z*)-2-Buten-1-ol	(Z)-$\mathrm{MeCH{=}CHCH{-}H(OH)}$	347.8
(*E*)-2-Buten-1-ol	(E)-$\mathrm{MeCH{=}CHCH{-}H(OH)}$	348.8
2-Buten-1-ol, 2-methyl-	$\mathrm{MeCH{=}CMeCH{-}H(OH)}$	344.4
2-Buten-1-ol, 2,3-dimethyl-	$\mathrm{Me_2C{=}CMeCH{-}H(OH)}$	342.2
(*Z*)-3-Penten-2-ol	(Z)-$\mathrm{MeCH{=}CHC{-}HMe(OH)}$	336.0
(*E*)-3-Penten-2-ol	(E)-$\mathrm{MeCH{=}CHC{-}HMe(OH)}$	338.2
3-Penten-2-ol, 4-methyl-	$\mathrm{Me_2C{=}CHC{-}HMe(OH)}$	324.0
3-Penten-2-ol, 3-methyl-	$\mathrm{MeCH{=}CMeC{-}HMe(OH)}$	325.2
2-Propin-1-ol	$\mathrm{CH{\equiv}CCH{-}H(OH)}$	351.8
3-Butin-2-ol	$\mathrm{CH{\equiv}CC{-}HMe(OH)}$	338.8
2-Butin-1-ol	$\mathrm{MeC{\equiv}CCH{-}H(OH)}$	346.7
3-Butin-2-ol	$\mathrm{MeC{\equiv}CC{-}HMe(OH)}$	333.8
Benzyl alcohol	$\mathrm{Ph(HO)CH{-}H}$	366.9
α-Phenylethanol	$\mathrm{PhMeC(OH){-}H}$	356.0
Butanol, 1-phenyl-	$\mathrm{PhPrC(OH){-}H}$	360.6
Diphenylmethanol	$\mathrm{Ph_2C{-}H(OH)}$	348.7
1-Indanol		351.3
1-Tetralol		337.5
	Carbonyl Compounds^e	
Formaldehyde	$\mathrm{H(O)C{-}H}$	377.8

(*continued overleaf*)

TABLE 9.4 (*continued*)

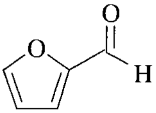
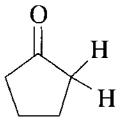
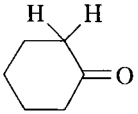
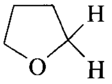
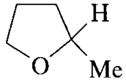
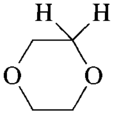
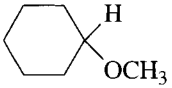
Hydrocarbon	Bond	D (kJ mol^{-1})
Acetaldehyde	Me(O)C−H	373.8
Acetaldehyde	CH_2−HCH(O)	394.3
Propanal	Et(O)C−H	372.0
Butanal	Pr(O)C−H	371.2
Pentanal	Bu(O)C−H	372.0
Propanal, 2-methyl-	$Me_2CH(C-H)(O)$	364.5
Butanal, 3-methyl-	$Me_2CHCH_2(C-H)(O)$	362.6
Butanal, 2-methyl-	$MeCH_2CH(CH_3)(C-H)(O)$	360.8
Propanal, 2,2-dimethyl-	$Me_3C(C-H)(O)$	375.1
Furfurol		387.5
Propenal	CH_2=CHC−H(O)	339.4
Benzaldehyde	PhC−H(O)	348.0
Propanal, 2-methyl-2-phenyl-	$PhMe_2CC-H(O)$	362.9
Arabinose	$CH_2OH(CHOH)_3C-H(O)$	369.8
Glucose	$CH_2OH(CHOH)_4C-H(O)$	371.4
d-Ribose	$CH_2OH(CHOH)_3C-H(O)$	370.0
Glyoxylic acid	(C−H)(O)C(O)OH	375.3
Acetone	$MeC(O)CH_2-H$	411.8
2-Butanone	MeC(O)(Me)CH−H	397.2
2-Butanone, 3-methyl-	$MeC(O)C-HMe_2$	387.6
2-Pentanone	MeC(O)CH−HEt	394.6
3-Pentanone	EtC(O)CH−HMe	396.5
4-Heptanone	PrC(O)CH−HEt	394.6
3-Pentanone, 2,4-dimethyl-	$Me_2CHC(O)Me_2C-H$	387.5
5-Nonanone	BuC(O)CH−HPr	395.8
Diacetyl	$MeCOCOCH_2-H$	411.8
2,4-Pentanedione	MeC(O)CH−HC(O)Me	399.1
Ethylacetoacetate	MeC(O)CH−HC(O)OEt	396.5
Cyclopentanone		401.2

TABLE 9.4 (*continued*)

Hydrocarbon	Bond	*D* (kJ mol^{-1})
Cyclohexanone		394.1
Acetophenone	PhC(O)CH$_2$−H	402.8
Ethylphenyl ketone	PhC(O)(Me)CH−H	394.4
1-Methylethylphenylketone	PhC(O)Me$_2$C−H	385.3
Dibenzyl ketone	PhCH$_2$C(O)(Ph)CH−H	353.6
1-Penten-4-on	CH$_2$=CHCH−HC(O)CH$_3$	346.6
	Ethers^f	
Methane, oxybis-	MeOCH$_2$−H	411.9
Ethane, oxybis-	EtOCH−HMe	399.5
Propane, 2,2′-oxybis-	Me$_2$CHOC−HMe$_2$	390.8
Butane, 1,1′-oxybis-	BuO(C−H)HPr	392.2
Tetrahydrofuran		391.6
Tetrahydrofuran, 2-methyl-		384.1
1,4-Dioxane		405.4
Cyclohexane, methoxy-		399.6
1-Propene, 3,3′-oxybis-	[CH$_2$=CH(CH−H)]$_2$O	360.0
1-Propene-2-methyl, 3,3′-oxybis-	[CH$_2$=CMeCH−H]$_2$O	349.9
1-Butene-2-methyl, 3,3′-oxybis-	[CH$_2$=CMe(C−H)Me]$_2$O	339.2
1-Propene-2-ethyl, 3,3′-oxybis-	[CH$_2$=CEtCH−H]$_2$O	359.7
(Z)-2-Butene, 1,1′-oxybis-	[(Z)-MeCH=CHCH−H]$_2$O	347.8

(*continued overleaf*)

TABLE 9.4 (*continued*)

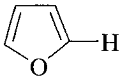
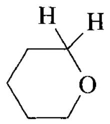
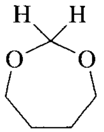
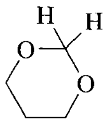
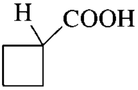
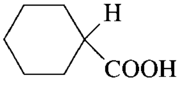
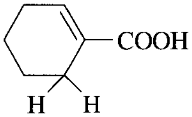
Hydrocarbon	Bond	D (kJ mol^{-1})
(E)-2-Butene, 1,1′-oxybis-	$[(E)\text{-MeCH=CHCH}-\text{H}]_2\text{O}$	348.8
2-Butene-2-methyl, 1,1′-oxybis-	$[\text{MeCH=CMeCH}-\text{H}]_2\text{O}$	344.4
1-Propin, 3,3′-oxybis-	$[\text{CH}\equiv\text{CCH}-\text{H}]_2\text{O}$	351.8
1-Butin, 3,3′-oxybis-	$[\text{CH}\equiv\text{CC}-\text{HMe}]_2\text{O}$	338.8
2-Butin, 4,4′-oxybis-	$[\text{MeC}\equiv\text{CCH}-\text{H}]_2\text{O}$	346.7
2-Pentin, 4,4′-oxybis-	$[\text{MeC}\equiv\text{CC}-\text{HMe}]_2\text{O}$	333.8
Anisole	PhOCH_2-H	385.0
Benzene, bis-1,1′-[oxybis(methylene)]	$[\text{Ph(C}-\text{H)H}]_2\text{O}$	359.0
Methane, diphenylmethoxy-	$\text{Ph}_2\text{(C}-\text{H)OMe}$	354.2
Dimethoxymethane	$\text{(MeO)}_2\text{CH}-\text{H}$	406.8
1,1-Dimethoxyethane	$\text{(MeO)}_2\text{MeC}-\text{H}$	385.0
1,1-Diethoxyethane	$\text{(EtO)}_2\text{MeC}-\text{H}$	390.8
Dimethoxyphenylmethane	$\text{PhC}-\text{H(OMe)}_2$	353.9
Furane		408.0
γ-Pyrane, tetrahydro-		401.7
1,3-Dioxepane		393.5
1,3-Dioxane		391.2
	Esters^f	
Acetic acid, methyl ester	$\text{MeC(O)OCH}_2-\text{H}$	404.0
Acetic acid, ethyl ester	$\text{MeC(O)O(Me)CH}-\text{H}$	399.5
Acetic acid, 1-methylethyl ester	$\text{MeC(O)O(Me}_2\text{)C}-\text{H}$	392.3
Acetic acid, 3-propenyl ester	$\text{MeC(O)O(CH}-\text{H)CH=CH}_2$	348.3

TABLE 9.4 (*continued*)

Hydrocarbon	Bond	D (kJ mol^{-1})
Oxalic acid, dimethyl ester	$MeOC(O)C(O)OCH_2{-}H$	403.9
Oxalic acid, diethyl ester	$EtOC(O)C(O)(Me)CH{-}H$	396.2
Oxalic acid, bis(1-methylethyl) ester	$Me_2CHOC(O)C(O)OMe_2C{-}H$	396.2
Malonic acid, dimethyl ester	$[MeOC(O)]_2CH{-}H$	390.4
Acetic acid, anhydride	$MeC(O)OC(O)CH_2{-}H$	406.0
Butanoic acid, methyl ester	$EtCH{-}HCOOMe$	394.9
Pentanoic acid, ethyl ester	$BuCOOCH{-}HMe$	392.3
Pentanoic acid, methylethyl ester	$BuCOOC{-}HMe_2$	387.9
1,1-Dimethylpropanoic acid, 1,1-dimethylester	$Me_3CCOOCCH_2{-}HMe_2$	415.0
1,3-Dipropanoic acid, dimethyl ester	$MeOCOCH{-}HCOOMe$	391.7
1,4-Dibutanoic acid, dimethyl ester	$MeOCOCH{-}HCH_2COOMe$	404.8
	Acids[f]	
Formic acid	$C{-}H(O)OH$	392.7
Acetic acid	$HOOCCH_2{-}H$	414.1
Propanoic acid	$HOOC(Me)CH{-}H$	398.9
Propanoic acid, 1-methyl-	$HOOC(Me)_2C{-}H$	388.3
Butanoic acid	$EtCH{-}HCOOH$	398.7
Propanoic acid, 2,2-dimethyl-	$Me_2CH_2{-}HCCOOH$	415.2
Pentanoic acid	$PrCH{-}HCOOH$	399.4
Hexanoic acid	$BuCH{-}HCOOH$	397.1
Cyclobutanecarboxylic acid		399.0
Cyclohexanecarboxylic acid		388.2
Benzenacetic acid	$Ph(COOH)CH{-}H$	367.0
Glycolic acid	$HOOC(HO)CH{-}H$	397.8
Propionic acid, 1-hydroxy-	$MeC{-}H(OH)COOH$	386.0
Acetic acid, chloro-	$HOOCClCH{-}H$	398.9
Propanoic acid, 2,2-dimethyl-	$Me_2(COOH)CCH_2{-}H$	415.1
1,4-Butanedioic acid	$HOOCCH{-}HCH_2COOH$	397.8

(*continued overleaf*)

TABLE 9.4 (*continued*)

Hydrocarbon	Bond	D (kJ mol^{-1})
1,4-Butanedioic acid, 2,3-dihydroxy-	HOOCC–H(OH)CH(OH)COOH	392.7
Cyclohexene, 1-carboxylic acid		370.0

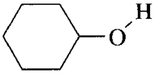
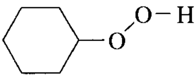
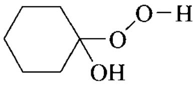
---

[a] See Refs. 38 and 39.
[b] See Ref. 40.
[c] See Refs. 41 and 42.
[d] See Refs. 38 and 43.
[e] See Refs. 37 and 43.
[f] See Ref. 43.

TABLE 9.5 Dissociation Energies for N–H, O–H, and Other Bonds

Compound	Bond	D (kJ mol^{-1})
	N–H Bonds[a]	
Ammonia	H_2N-H	449.4
Hydrazine	$(H_2N)NH-H$	366.1
Methylamine	MeNH–H	418.4
Ethylamine	EtNH–H	418.4
Dimethylamine	Me_2N-H	382.8
Diethylamine	Et_2N-H	382.8
	O–H Bonds for Water and Alcohols[b]	
Water	HO–H	498.0
Methanol	MeO–H	439.0
Ethanol	EtO–H	440.0
Propanol	$EtCH_2O-H$	440.0
Ethanol, 1-methyl-	Me_2CHO-H	443.0
Butanol	$PrCH_2O-H$	440.0
Propanol, 1-methyl-	MeEtCHO–H	443.0
Propanol, 2-methyl-	Me_2CHCH_2O-H	440.0
Ethanol, 1,1-dimethyl-	Me_3CO-H	446.0
Propanol, 1,1-dimethyl-	$EtMe_2CO-H$	446.0
Pentanol	$PrCH_2CH_2O-H$	440.0

TABLE 9.5 (*continued*)

Compound	Bond	D (kJ mol^{-1})
Butanol, 2-methyl-	$EtMeCHCH_2O{-}H$	440.0
Cyclohexanol		437.1
Phenylmethanol	$PhCH_2O{-}H$	436.2
Ethanol, 1-phenyl-	$PhMeCHO{-}H$	438.3
Ethanol, 1-methyl-1-phenyl-	$PhMe_2CO{-}H$	440.3
2-Propenol	$CH_2{=}CHCH_2O{-}H$	436.2
2-Propenol, 1-methyl-	$CH_2{=}CHMeCHO{-}H$	434.0
	O—H Bonds for Acids[c]	
Hypochlorous acid	$ClO{-}H$	406.7
Nitrous acid	$ONO{-}H$	327.6
Nitric acid	$O_2NO{-}H$	423.4
Formic acid	$HC(O)O{-}H$	438.1
Acetic acid	$MeC(O)O{-}H$	442.7
Propionic acid	$EtC(O)O{-}H$	440.7
Propionic acid, 1-methyl-	$Me_2CHCOO{-}H$	444.8
Benzoic acid	$PhC(O)O{-}H$	443.5
	O—H Bonds for Hydroperoxides[d]	
Hydrogen peroxide	$HOO{-}H$	369.0
Hydroperoxide, ethyl-	$EtOO{-}H$	365.5
Hydroperoxide, 1-methylethyl-	$Me_2CHOO{-}H$	365.5
Hydroperoxide, cyclohexyl-		365.5
Hydroperoxide, 1-phenylethyl-	$PhMeCHOO{-}H$	365.5
Hydroperoxide, 1,1-dimethylethyl-	$Me_3COO{-}H$	358.6
Hydroperoxide, 1-methyl-1-phenylethyl-	$PhMe_2COO{-}H$	358.6
Perbenzoic acid	$PhC(O)OO{-}H$	406.1
Hydroperoxide, 1-hydroxy-1-methylethyl-	$Me_2C(OH)OO{-}H$	371.6
Hydroperoxide, 1-hydroxycyclohexyl-		371.6
Hydroperoxide, trifluoromethyl-	$CF_3OO{-}H$	418.0
Hydroperoxide, trichloromethyl-	$CCl_3OO{-}H$	407.2

(*continued overleaf*)

TABLE 9.5 (*continued*)

Compound	Bond	D (kJ mol^{-1})
Hydroperoxide, tribromomethyl-	CBr_3OO-H	407.0
Hydroperoxide, chlorodifluoromethyl-	$CF_2ClOO-H$	415.4
Hydroperoxide, bromodifluoromethyl-	$CF_2BrOO-H$	415.8
Hydroperoxide, perchloroethyl-	CCl_3CCl_2OO-H	407.2
	O—O Bonds (see Chapters 4–6)	
Peroxide, dimethyl-	MeO—OMe	161.5
Peroxide, diethyl-	EtO—OEt	161.5
Peroxide, dipropyl-	PrO—OPr	161.5
Peroxide, bis-methylethyl-	$Me_2CHO-OCHMe_2$	163.6
Peroxide, bis(1,1-dimethylethyl)-	$Me_3CO-OCMe_3$	162.7
Peroxide, bis(1-methyl-1-phenylethyl)-	$Me_2PhCO-OCPhMe_2$	158.8
Peroxide, bis(trifluoromethyl)-	$F_3CO-OCF_3$	195.8
Peroxide, diacetyl-	MeC(O)O—OC(O)Me	131.6
Peroxide, dibenzoyl-	PhC(O)O—OC(O)Ph	124.4
Peroxide, bis(cyclohexyloxycarbonyl)-,	*cyclo*-$C_6H_{11}OC(O)OOC(O)O$-*cyclo*-C_6H_{11}	122.5
Peroxide, benzoyl 1,1-dimethylethyl-	$PhC(O)O-OCMe_3$	141.4
Peroxide, acetyl 1,1-dimethylethyl-	$MeC(O)O-OCMe_3$	149.5
Trioxide, dimethyl-	MeOO—OMe	86.2
Trioxide, diethyl-	EtOO—OEt	93.7
Trioxide, bis(1,1-dimethylethyl)-	$Me_3COO-OCMe_3$	78.2
Hydrogen peroxide	HO—OH	214.9
Methylhydroperoxide	MeO—OH	191.0
Ethylhydroperoxide	EtO—OH	193.0
Ethylhydroperoxide, dimethyl-	Me_3CO-OH	182.5
Ethylhydroperoxide, methylphenyl-	$PhMe_2CO-OH$	175.0
Hydrotrioxide, methyl-	MeOO—OH	108.8
Hydrotrioxide, ethyl-	EtOO—OH	105.4
Hydrotrioxide, 1,1-dimethylethyl-	$Me_3COO-OH$	98.7
	N—O Bonds^c	
Nitrous acid	ON—OH	209.7
Nitric acid	O_2N-OH	205.9
Nitrate, methyl-	$MeO-NO_2$	170.0
Nitrate, ethyl-	$EtO-NO_2$	167.3
Nitrate, propyl-	$PrO-NO_2$	170.6

TABLE 9.5 (*continued*)

Compound	Bond	D (kJ mol^{-1})
Nitrate, 1-methylethyl-	$Me_2CHO-NO_2$	171.9
Nitrate, butyl-	$BuO-NO_2$	171.5
Nitrate, 1,1-dimethylethyl-	Me_3CO-NO_2	173.5
Nitrate, 1-methylpropyl-	$EtMeCHO-NO_2$	173.5
Nitrate, benzyl-	$PhCH_2O-NO_2$	169.6
Nitrate, 1-phenylethyl-	$PhMeCHO-NO_2$	172.0
Nitrate, 1-methyl-1-phenylethyl-	$PhMe_2CO-NO_2$	173.7
Nitrite, methyl-	MeO−NO	170.5
Nitrite, ethyl-	EtO−NO	174.1
Nitrite, propyl-	PrO−NO	174.0
Nitrite, methylethyl-	$Me_2CHO-NO$	178.7
Nitrite, butyl-	BuO−NO	174.0
Nitrite, 1,1-dimethylethyl-	Me_3CO-NO	180.3
Nitrite, 1-methylpropyl-	EtMeCHO−NO	180.3
Nitrite, benzyl-	$PhCH_2O-NO$	170.0
Nitrite, 1-phenylethyl-	PhMeCHO−NO	175.2
Nitrite, 1-methyl-1-phenylethyl-	$PhMe_2CO-NO$	180.5
	Si−H Bonds[e]	
Silane	H_3Si-H	384.1
Silane, methyl-	MeH_2Si-H	386.0
Silane, dimethyl-	Me_2HSi-H	391.7
Silane, trimethyl-	Me_3Si-H	397.4
Silane, triethyl-	Et_3Si-H	398.0
Silane, bis(dimethylethyl)methyl-	$(Me_3C)_2MeSi-H$	372.8
Silane, tris(dimethylethyl)-	$(Me_3C)_3Si-H$	362.3
Silane, phenyl-	PhH_2Si-H	377.0
Silane, methylphenyl-	PhMeHSi−H	382.0
Silane, dimethylphenyl-	$PhMe_2Si-H$	364.0
Silane, diphenyl-	Ph_2HSi-H	359.0
Silane, diphenylmethyl-	$Ph_2MeSi-H$	359.2
Silane, triphenyl-	Ph_3Si-H	354.8
Silane, trifluoro-	F_3Si-H	419.0
Silane, trichloro-	Cl_3Si-H	382.0
Silane, fluorophenylmethyl-	PhMeFSi−H	378.4
Silane, chlorophenylmethyl-	PhMeClSi−H	369.6
Disilane	H_3SiH_2Si-H	361.0
Silane, dimethyltrimethylsilyl	Me_3SiMe_2Si-H	378.0
Silane, tris(trimethylsilyl)-	$(Me_3Si)_3Si-H$	351.0
Silane, trimethylthio-	$(MeS)_3Si-H$	366.0

(*continued overleaf*)

TABLE 9.5 (*continued*)

Compound	Bond	D (kJ mol^{-1})
	P−H Bonds[f]	
Phosphine	H_2P-H	351.0
Phosphine, ethyl-	EtHP−H	375.3
Phosphine, diethyl-	Et_2P-H	377.8
Phosphine, dibutyl-	Bu_2P-H	375.0
Phosphine, 4-cyanopropyl-	$NC(CH_2)_3HP-H$	373.4
Phosphine, bis(4-cyanopropyl)-	$[NC(CH_2)_3]P-H$	369.5
Phosphine, dicyclohexyl-	$(cyclo\text{-}C_6H_{11})_2P-H$	359.3
	Ge−H Bonds[g]	
Germane	H_3Ge-H	348.9
Germane, tributyl-	Bu_3Ge-H	347.3
Germane, triphenyl-	Ph_3Ge-H	322.5
Germane, tribenzyl-	$(PhCH_2)_3Ge-H$	324.3
Germane, benzylethyl-	$(PhCH_2)EtHGe-H$	341.6
Germane, tris(trimethylsilyl)-	$(Me_3Si)_3Ge-H$	305.2
	Sn−H Bonds[g]	
Stannane	H_3Sn-H	346.0
Stannane, trimethyl-	Me_3Sn-H	318.5
Stannane, tributyl-	Bu_3Sn-H	309.6
Stannane, triphenyl-	Ph_3Sn-H	296.9
	S−H Bonds[h]	
Hydrogen sulfide	HS−H	382.0
Methanethiol	MeS−H	366.0
Ethanethiol	EtS−H	366.0
Propanethiol	PrS−H	366.0
1-Methylethanthiol	Me_2CHS-H	366.0
Butanthiol	BuS−H	366.0
1,1-Dimethylethylthiol	Me_3CS-H	366.0
Phenylthiol	PhS−H	330.0
Hydrogen disulfide	HSS−H	325.0
Methylhydrodisulfide	MeSS−H	325.0
Ethylhydrodisulfide	EtSS−H	325.0
1,1-Dimethylethylhydrodisulfide	Me_3CSS-H	325.0
	F−Y Bonds[c]	
Hydrogen fluoride	F−H	570.3
Difluorine	F−F	158.7

TABLE 9.5 (*continued*)

Compound	Bond	D (kJ mol^{-1})
Chlorine fluoride, mono-	F—Cl	256.2
Bromine fluoride, mono-	F—Br	250.2
Iodine fluoride, mono-	F—I	271.6
Hypoflorous acid	F—OH	214.5
Perfluoromethanol	CF_3O—F	182.0
	Cl—Y Bonds[c]	
Hydrogen chloride	Cl—H	431.6
Dichlorine	Cl—Cl	242.6
Bromine chloride, mono-	Cl—Br	217.5
Iodine chloride, mono-	Cl—I	211.3
Nitrosyl chloride	Cl—NO	162.4
Nitrogen dioxide chloride	Cl—NO_2	141.8
Chlorine nitrite	Cl—ONO	72.1
Hypochlorous acid	Cl—OH	239.7
Hypochlorite, methyl-	Cl—OMe	195.4
Hypochlorite, ethyl-	Cl—OEt	196.6
Hypochlorite, 1-methylethyl-	Cl—$OCHMe_2$	197.5
Hypochlorite, 1,1-dimethylethyl-	Cl—$OCMe_3$	198.3

[a] See Refs. 41 and 42.
[b] See Refs. 44–46.
[c] See Ref. 45.
[d] See Refs. 47–49.
[e] See Refs. 50 and 51.
[f] See Refs. 51 and 52.
[g] See Refs. 18, 52, and 53.
[h] See Ref. 54.

TABLE 9.6 The Values for C—H, N—H, and O—H Bond Dissociation Energies in Free Radicals[a]

Radical	Bond	D (kJ mol^{-1})
	Alkyl Radicals, C—H Bonds	
Ethyl	$C^{\bullet}H_2CH_2$—H	150.4
Ethyl, 1-methyl-	$MeC^{\bullet}HCH_2$—H	148.7
Propyl	MeCH—$HC^{\bullet}H_2$	138.7

(*continued overleaf*)

TABLE 9.6 (*continued*)

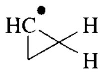
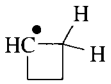
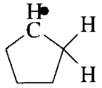
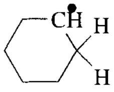
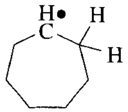
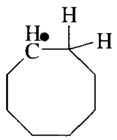
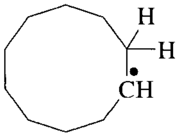
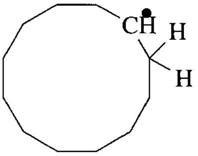
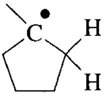
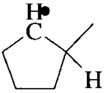
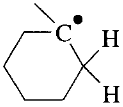
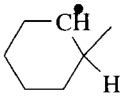
Radical	Bond	D (kJ mol^{-1})
Ethyl, 1,1-dimethyl-	$\mathrm{Me_2C^{\bullet}CH_2{-}H}$	153.6
Propyl, 2-methyl-	$\mathrm{Me_2C{-}HC^{\bullet}H_2}$	131.6
Propyl, 1-methyl-	$\mathrm{EtC^{\bullet}HCH_2{-}H}$	149.0
Propyl, 1-methyl-	$\mathrm{MeCH{-}HC^{\bullet}HMe}$	137.3
Propyl, 1,1-dimethyl-	$\mathrm{EtMeC^{\bullet}CH_2{-}H}$	153.5
Butyl	$\mathrm{C^{\bullet}H_2EtCH{-}H}$	140.0
Butyl, 1-methyl-	$\mathrm{PrC^{\bullet}HCH_2{-}H}$	149.0
Propyl, 1-ethyl-1-methyl-	$\mathrm{Et_2C^{\bullet}CH_2{-}H}$	152.6
Propyl, 1-ethyl-1-methyl-	$\mathrm{EtMeC^{\bullet}CH{-}HMe}$	144.8
Propyl, 1-ethyl-	$\mathrm{EtC^{\bullet}HMeCH{-}H}$	136.5
Propyl, 1-(1-methylethyl)-	$\mathrm{EtC^{\bullet}HMe_2C{-}H}$	128.7
Propyl, 1-(1-methylethyl)-	$\mathrm{MeCH{-}HC^{\bullet}HCHMe_2}$	137.3
	Cycloalkyl Radicals, C–H Bonds	
Cyclopropyl		230.0
Cyclobutyl		145.9
Cyclopentyl		141.8
Cyclohexyl		146.0
Cycloheptyl		141.3
Cyclooctyl		131.2
Cyclodecyl		169.5

TABLE 9.6 (*continued*)

Radical	Bond	D (kJ mol^{-1})
Cyclododecyl		144.2
Cyclopentyl, 1-methyl-		145.5
Cyclopentyl, 2-methyl-		129.3
Cyclohexyl, 1-methyl-		152.2
Cyclohexyl, 2-methyl-		138.9
Alkyl Radicals with Double Bond, C—H Bonds		
Ethenyl	$\mathrm{HC^{\bullet}{=}CH{-}H}$	145.7
Ethenyl, 1-methyl-	$\mathrm{MeC^{\bullet}{=}CH{-}H}$	142.0
Propenyl, 1-methyl-	$\mathrm{MeC^{\bullet}{=}CMe{-}H}$	130.0
Propenyl, 1-methyl-	$\mathrm{CH_2{=}CHC^{\bullet}HCH_2{-}H}$	197.6
3-Butenyl	$\mathrm{CH_2{=}CH(CH{-}H)C^{\bullet}H_2}$	124.4
Propenyl, 1,1-dimethyl-	$\mathrm{CH_2{=}CHC^{\bullet}MeCH_2{-}H}$	198.5
3-Butenyl, 2-methyl-	$\mathrm{CH_2{=}CH(MeC{-}H)C^{\bullet}H_2}$	116.1
Propenyl, 1-ethyl-	$\mathrm{CH_2{=}CHC^{\bullet}HMeCH{-}H}$	184.7
3-Butenyl, 1-methyl-	$\mathrm{CH_2{=}CH(CH{-}H)MeC^{\bullet}H}$	120.5
Propenyl, 1-methylethyl-	$\mathrm{CH_2{=}CHC^{\bullet}HMe_2C{-}H}$	179.2
3-Butenyl, 1,1-dimethyl-	$\mathrm{CH_2{=}CH(CH{-}H)Me_2C^{\bullet}}$	128.0
Propenyl, 1-methyl-1-ethyl-	$\mathrm{CH_2{=}CHC^{\bullet}MeMeCH{-}H}$	187.6
3-Butenyl, 1,2-dimethyl-	$\mathrm{CH_2{=}CH(MeC{-}H)MeC^{\bullet}H}$	114.2
Propenyl, 1-methyl-1-methylethyl-	$\mathrm{CH_2{=}CHC^{\bullet}MeMe_2C{-}H}$	180.6
3-Butenyl, 1,1,2-trimethyl-	$\mathrm{CH_2{=}CH(MeC{-}H)Me_2C^{\bullet}}$	120.2
2-Butenyl, 1-methyl-	$\mathrm{MeCH{=}CHC^{\bullet}HCH_2{-}H}$	197.4
3-Pentenyl	$\mathrm{MeCH{=}CH(CH{-}H)C^{\bullet}H_2}$	121.6
2-Butenyl, 1,1-dimethyl-	$\mathrm{MeCH{=}CHC^{\bullet}MeCH_2{-}H}$	206.0
3-Pentenyl, 2-methyl-	$\mathrm{MeCH{=}CH(MeC{-}H)C^{\bullet}H_2}$	117.9

(*continued overleaf*)

TABLE 9.6 (*continued*)

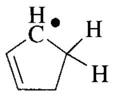
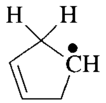
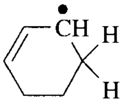
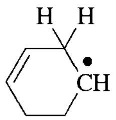
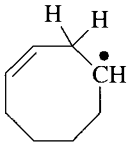
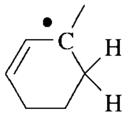
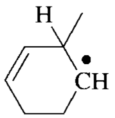
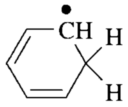
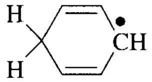
Radical	Bond	D (kJ.mol^{-1})
2-Butenyl, 1-ethyl-	$\mathrm{MeCH{=}CHC^{\bullet}HMeCH{-}H}$	193.7
3-Pentenyl, 1-methyl-	$\mathrm{MeCH{=}CH(CH{-}H)MeC^{\bullet}H}$	122.8
2-Butenyl, 1-methylethyl-	$\mathrm{MeCH{=}CHC^{\bullet}HMe_2C{-}H}$	188.2
3-Pentenyl, 1,1-dimethyl-	$\mathrm{MeCH{=}CH(CH{-}H)Me_2C^{\bullet}}$	135.7
2-Butenyl, 1-ethyl-1-methyl-	$\mathrm{MeCH{=}CHC^{\bullet}Me(CH{-}H)Me}$	201.8
3-Pentenyl, 1,2-dimethyl-	$\mathrm{MeCH{=}CH(MeC{-}H)C^{\bullet}H_2}$	122.7
2-Butenyl, 1-methyl-1-methylethyl-	$\mathrm{MeCH{=}CHMeC^{\bullet}Me_2C{-}H}$	196.3
3-Pentenyl, 1,1,2-trimethyl-	$\mathrm{MeCH{=}CH(MeC{-}H)Me_2C^{\bullet}}$	135.7
2-Butenyl, 1,3-dimethyl-	$\mathrm{Me_2C{=}CHC^{\bullet}HCH_2{-}H}$	202.7
3-Pentenyl, 4-methyl-	$\mathrm{Me_2C{=}CH(CH{-}H)C^{\bullet}H_2}$	122.7
2-Butenyl, 1,1,3-trimethyl-	$\mathrm{Me_2C{=}CHC^{\bullet}MeCH_2{-}H}$	216.3
3-Pentenyl, 2,4-dimethyl-	$\mathrm{Me_2C{=}CH(MeC{-}H)C^{\bullet}H_2}$	123.8
2-Butenyl, 1-ethyl-3-methyl-	$\mathrm{Me_2C{=}CHC^{\bullet}HMeCH{-}H}$	196.1
3-Pentenyl, 1,4-dimethyl-	$\mathrm{Me_2C{=}CH(CH{-}H)MeC^{\bullet}H}$	125.1
2-Butenyl, 1-methylethyl-3-methyl-	$\mathrm{Me_2C{=}CHC^{\bullet}HMe_2C{-}H}$	197.0
3-Pentenyl, 1,1,4-trimethyl-	$\mathrm{Me_2C{=}CH(CH{-}H)Me_2C^{\bullet}}$	139.0
2-Butenyl, 1-ethyl-1,3-dimethyl-	$\mathrm{Me_2C{=}CHMeC^{\bullet}MeCH{-}H}$	209.5
3-Pentenyl, 1,2,4-trimethyl-	$\mathrm{Me_2C{=}CH(MeC{-}H)MeC^{\bullet}H}$	126.0
2-Butenyl, 1-methylethyl-1,3-dimethyl-	$\mathrm{Me_2C{=}CHMeC^{\bullet}Me_2C{-}H}$	210.5
3-Pentenyl, 1,1,2,4-tetramethyl-	$\mathrm{Me_2C{=}CH(MeC{-}H)Me_2C^{\bullet}H}$	140.0
2-Propenyl, 1,2-dimethyl-	$\mathrm{CH_2{=}CMeC^{\bullet}HCH_2{-}H}$	199.3
3-Butenyl, 3-methyl-	$\mathrm{CH_2{=}CMe(CH{-}H)C^{\bullet}H_2}$	124.5
2-Propenyl, 1,1,2-trimethyl-	$\mathrm{CH_2{=}CMeC^{\bullet}MeCH_2{-}H}$	207.1
3-Butenyl, 2,3-dimethyl-	$\mathrm{CH_2{=}CMe(MeC{-}H)C^{\bullet}H_2}$	123.1
2-Propenyl, 1-ethyl-2-methyl-	$\mathrm{CH_2{=}CMeC^{\bullet}HMeCH{-}H}$	194.1
3-Butenyl, 1,3-dimethyl-	$\mathrm{CH_2{=}CMe(CH{-}H)MeC^{\bullet}H}$	129.3
2-Propenyl, 1-methylethyl-1,2-dimethyl-	$\mathrm{CH_2{=}CMeC^{\bullet}HMeMe_2C{-}H}$	189.4
3-Butenyl, 1,1,3-trimethyl-	$\mathrm{CH_2{=}CMe(CH{-}H)Me_2C^{\bullet}}$	136.6
2-Propenyl, 1-ethyl-1,2-dimethyl-	$\mathrm{CH_2{=}CMeC^{\bullet}MeMeCH{-}H}$	173.8
2-Propenyl, 1-methylethyl-1,2-dimethyl-	$\mathrm{CH_2{=}CMeC^{\bullet}MeMe_2C{-}H}$	168.3
3-Butenyl, 1,1,2,3-tetramethyl-	$\mathrm{CH_2{=}CMe(MeC{-}H)Me_2C^{\bullet}}$	111.8
2-Butenyl, 1,2-dimethyl-	$\mathrm{MeCH{=}CMeC^{\bullet}HCH_2{-}H}$	206.2
3-Pentenyl, 3-methyl-	$\mathrm{MeCH{=}CMe(CH{-}H)C^{\bullet}H_2}$	117.4
	Cycloalkenyl Radicals, C–H Bonds	
2-Cyclopentenyl		187.2
3-Cyclopentenyl		121.3

TABLE 9.6 (*continued*)

Radical	Bond	D (kJ mol^{-1})
2-Cyclohexenyl		205.4
3-Cyclohexenyl		138.1
3-Cyclooctenyl		220.6
2-Cyclohexenyl, 1-methyl-		219.3
3-Cyclohexenyl, 2-methyl-		139.8
2,4-Cyclohexadienyl		81.6
2,5-Cyclohexadienyl		98.3
	Alkylaromatic Radicals, C–H Bonds	
Ethyl, 1-phenyl-	$\mathrm{PhC^{\bullet}HCH_2{-}H}$	190.3
Ethyl, 2-phenyl-	$\mathrm{Ph(CH{-}H)C^{\bullet}H_2}$	132.4
Ethyl, 1-methyl-1-phenyl-	$\mathrm{PhC^{\bullet}MeCH_2{-}H}$	190.8
Ethyl, 2-methyl-2-phenyl-	$\mathrm{Ph(MeC{-}H)C^{\bullet}H_2}$	122.8
Propyl, 1-phenyl-	$\mathrm{PhC^{\bullet}HCH{-}HMe}$	178.5
Ethyl, 1-benzyl-	$\mathrm{Ph(CH{-}H)C^{\bullet}HMe}$	130.6
Propyl, 2-methyl-1-phenyl-	$\mathrm{PhC^{\bullet}HC{-}HMe_2}$	166.4
Ethyl, 1-benzyl-1-methyl-	$\mathrm{Ph(CH{-}H)C^{\bullet}Me_2}$	136.5
Ethyl, 1-(1-phenylethyl)-	$\mathrm{Ph(MeC{-}H)C^{\bullet}HMe}$	130.6

(*continued overleaf*)

TABLE 9.6 (*continued*)

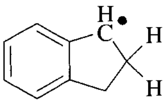
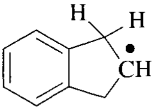
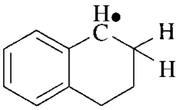
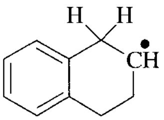
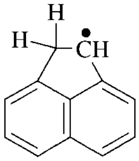
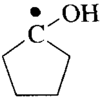
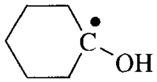
Radical	Bond	D (kJ mol^{-1})
Propyl, 1-methyl-1-phenyl-	$\mathrm{PhMeC^{\bullet}CH{-}HMe}$	187.9
Ethyl, 1-(1-phenylethyl)-1-methyl-	$\mathrm{Ph(MeC{-}H)C^{\bullet}Me_2}$	142.6
Propyl, 1,2-dimethyl-1-phenyl-	$\mathrm{PhMeC^{\bullet}HC{-}HMe_2}$	175.9
Ethyl, 1,2-diphenyl-	$\mathrm{PhC^{\bullet}HPhCH{-}H}$	163.0
Ethyl, 1,1-diphenyl-	$\mathrm{Ph_2C^{\bullet}CH_2{-}H}$	250.7
1-Indanyl		177.0
2-Indanyl		128.0
1-Tetralyl		178.5
2-Tetralyl		119.3
1-Acenaphthenyl		190.6
	Aminoalkyl Radicals, N–H Bonds	
Methyl, amino-	$\mathrm{C^{\bullet}H_2NH{-}H}$	145.1
Methyl, *N*-methylamino-	$\mathrm{MeN{-}HC^{\bullet}H_2}$	143.9
Methyl, *N*-ethylamino-	$\mathrm{EtN{-}HC^{\bullet}H_2}$	145.0
Ethyl, 1-amino-	$\mathrm{MeC^{\bullet}HNH{-}H}$	138.2
Ethyl, 1-methylamino-	$\mathrm{MeN{-}HC^{\bullet}HCH_3}$	132.6
Ethyl, 1-ethylamino-	$\mathrm{EtN{-}HC^{\bullet}HCH_3}$	132.2
Propyl, 1-amino-	$\mathrm{EtC^{\bullet}HNH{-}H}$	138.4
Propyl, 1-methylamino-	$\mathrm{EtC^{\bullet}H(N{-}H)Me}$	134.3
Ethyl, 1-amino-1-methyl-	$\mathrm{Me_2C^{\bullet}NH{-}H}$	139.5
Ethyl, 1-methyl-1-methylamino-	$\mathrm{MeN{-}HC^{\bullet}Me_2}$	133.0
Benzyl, amino-	$\mathrm{PhC^{\bullet}HNH{-}H}$	148.6
Methyl, phenylamino-	$\mathrm{PhN{-}HC^{\bullet}H_2}$	173.8

TABLE 9.6 (*continued*)

Radical	Bond	D (kJ mol^{-1})
Aminoalkyl Radicals, C—H Bonds		
Ethyl, 1-amino-	$H_2NC^{\bullet}HCH_2-H$	152.9
Ethyl, 2-amino-	$H_2N(CH-H)C^{\bullet}H_2$	119.9
Ethyl, 1-ethylamino-	$EtNC^{\bullet}HCH_2-H$	163.3
Ethyl, 2-ethylamino-	$EtNH(CH-H)C^{\bullet}H_2$	119.9
Propyl, 1-amino-	$Me(CH-H)C^{\bullet}HNH_2$	152.3
Ethyl, 1-aminomethyl-	$MeC^{\bullet}H(CH-H)NH_2$	129.9
Ethyl, 1-methyl-1-methylamino-	$MeNHC^{\bullet}MeCH_2-H$	141.9
Ethyl, 2-methyl-2-methylamino-	$MeNHC-HMeC^{\bullet}H_2$	119.9
Ketyl Radicals, O—H Bonds		
Hydroxymethyl	$H_2C^{\bullet}O-H$	110.2
Ethyl, 1-hydroxy-	$MeHC^{\bullet}O-H$	104.6
Propyl, 1-hydroxy-	$MeCH_2C^{\bullet}H(O-H)$	106.4
Butyl, 1-hydroxy-	$PrC^{\bullet}HO-H$	108.4
Ethyl, 1-hydroxy-1-methyl-	$Me_2C^{\bullet}O-H$	100.5
Propyl, 1-hydroxy-1-methyl-	$MeCH_2C^{\bullet}(O-H)Me$	99.4
Propyl, 1-hydroxy-2-methyl-	$Me_2CHC^{\bullet}HO-H$	93.5
Ethyl, 1,2-dihydroxy-	$HOCH_2C^{\bullet}H(O-H)$	105.1
Propyl, 2,2-dimethyl-1-hydroxy-	$Me_3CC^{\bullet}H(O-H)$	96.5
Propyl, 1-hydroxy-1-ethyl-	$Et_2C^{\bullet}O-H$	100.3
2-Propenyl, 1-hydroxy-	$CH_2{=}CHC^{\bullet}H(O-H)$	126.2
2-Propenyl, 1-hydroxy-1-methyl-	$CH_2{=}CHC^{\bullet}Me(O-H)$	127.9
Cyclopentyl, 1-hydroxy-		95.8
Cyclohexyl, 1-hydroxy-		112.0
Hydroxyphenylmethyl	$PhHC^{\bullet}(O-H)$	132.7
Ethyl, 1-hydroxy-1-phenyl-	$PhC^{\bullet}H(O-H)Me$	130.2
Propyl, 1-hydroxy-1-phenyl-	$PhC^{\bullet}H(O-H)Et$	127.0
Hydroxydiphenylmethyl	$Ph_2C^{\bullet}(O-H)$	150.0
Hydroxyalkyl Radicals, C—H Bonds		
Ethyl, 1-hydroxy-	$HC^{\bullet}(OH)CH_2-H$	145.5
Ethyl, 2-hydroxy-	$C^{\bullet}H_2CH-H(OH)$	123.2
Propyl, 1-hydroxy-	$MeCH-HC^{\bullet}H(OH)$	126.4

(*continued overleaf*)

TABLE 9.6 (*continued*)

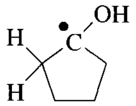
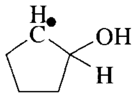
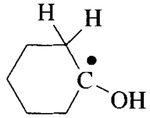
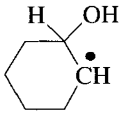
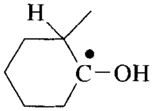
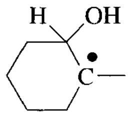
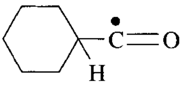
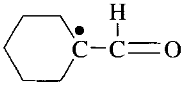
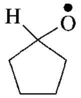
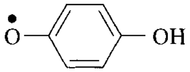
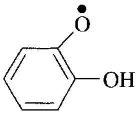
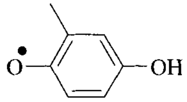
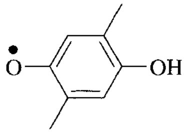
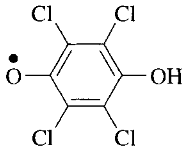
Radical	Bond	D (kJ mol^{-1})
Ethyl, 1-methylhydroxy-	$MeC^{\bullet}HCH{-}H(OH)$	111.4
Ethyl, 1-hydroxy-1-methyl-	$MeC^{\bullet}(OH)CH_2{-}H$	142.2
Propyl, 2-hydroxy-	$MeC{-}H(OH)C^{\bullet}H_2$	110.7
Propyl, 1-hydroxy-1-methyl-	$Me(CH{-}H)C^{\bullet}(OH)Me$	141.2
Ethyl, 1-(1-hydroxyethyl)-	$MeC^{\bullet}H(C{-}H)(OH)Me$	119.7
Ethyl, 1,2-dihydroxy-	$HO(CH{-}H)C^{\bullet}HOH$	103.9
	Hydroxycycloalkyl Radicals, C−H Bonds	
Cyclopentyl, 1-hydroxy-		169.0
Cyclopentyl, 2-hydroxy-		148.6
Cyclohexyl, 1-hydroxy-		168.6
Cyclohexyl, 2-hydroxy-		148.2
Cyclohexyl, 1-hydroxy-2-methyl-		161.5
Cyclohexyl, 2-hydroxy-1-methyl-		154.4
	Carbonyl Radicals, C−H Bonds	
Acetyl	$C^{\bullet}(O)CH_2{-}H$	166.4
Formylmethyl	$H{-}C(O)C^{\bullet}H_2$	144.0
Propionyl	$C^{\bullet}(O)(CH{-}H)Me$	133.2
Ethyl, 1-formyl-	$H{-}C(O)C^{\bullet}HMe$	121.0
Ethyl, 1-formyl-1-methyl-	$H{-}C(O)C^{\bullet}Me_2$	124.9
Propionyl, 2-methyl-	$C^{\bullet}(O)(C{-}H)Me_2$	132.0

TABLE 9.6 (*continued*)

Radical	Bond	D (kJ mol^{-1})
Cyclohexylformyl		132.0
Cyclohexyl, 1-formyl-		124.9
Acetyl, 2-phenyl-	$\mathrm{PhCH{-}HC^{\bullet}(O)}$	79.7
Formylbenzyl	$\mathrm{PhC^{\bullet}HC(O){-}H}$	108.2
Ethyl, 1-acyl	$\mathrm{AcC^{\bullet}HCH_2{-}H}$	140.7
Ethyl, 2-acyl	$\mathrm{AcCH{-}HC^{\bullet}H_2}$	116.5
Ethyl, 1-acyl-1-methyl-	$\mathrm{AcMeC^{\bullet}CH_2{-}H}$	129.9
Propyl, 2-acyl-	$\mathrm{AcMeC{-}HC^{\bullet}H_2}$	100.6
Propyl, 1-acyl-	$\mathrm{AcC^{\bullet}H(CH{-}H)Me}$	124.8
Propyl, 1-acyl-2-methyl-	$\mathrm{AcC^{\bullet}H(C{-}H)Me_2}$	142.8
Ethyl, 1-(1-acylethyl)-	$\mathrm{AcMeC{-}HC^{\bullet}HMe}$	149.5
Ethyl, 2-benzoyl-	$\mathrm{PhC(O)CH{-}HC^{\bullet}H_2}$	116.5
Ethyl, 1-benzoyl-	$\mathrm{PhC(O)C^{\bullet}HCH_2{-}H}$	151.3
	Aminyl Radicals, C—H Bonds	
Methylaminyl	$\mathrm{N^{\bullet}HCH_2{-}H}$	126.7
Dimethylaminyl	$\mathrm{MeN^{\bullet}CH_2{-}H}$	150.1
Ethylaminyl	$\mathrm{CH_3(CH{-}H)N^{\bullet}H}$	109.4
Ethylmethylaminyl	$\mathrm{MeN^{\bullet}(CH{-}H)Me}$	134.4
Ethylmethylaminyl	$\mathrm{EtN^{\bullet}(CH_2{-}H)}$	151.2
Diethylaminyl	$\mathrm{EtN^{\bullet}(CH{-}H)CH_3}$	134.0
Propylaminyl	$\mathrm{Et(CH{-}H)N^{\bullet}H}$	109.6
Methylpropylaminyl	$\mathrm{Et(CH{-}H)N^{\bullet}Me}$	130.4
1-Methylethylaminyl	$\mathrm{Me_2C{-}HN^{\bullet}H}$	100.6
Methyl-1-methylethylaminyl	$\mathrm{Me_2C{-}HN^{\bullet}Me}$	125.2
Benzylaminyl	$\mathrm{Ph(CH{-}H)N^{\bullet}H}$	133.8
Methylphenylaminyl	$\mathrm{PhN^{\bullet}(CH_2{-}H)}$	173.2
	Alkoxyl Radicals, C—H Bonds	
Methoxyl	$\mathrm{H{-}CH_2O^{\bullet}}$	82.2
Ethoxyl	$\mathrm{Me(CH{-}H)O^{\bullet}}$	64.4
Ethoxyl, 1-methyl-	$\mathrm{Me_2C{-}H(O^{\bullet})}$	48.0
Butoxyl	$\mathrm{Pr(CH{-}H)O^{\bullet}}$	65.4
Propoxyl, 1-methyl-	$\mathrm{EtMeC{-}HO^{\bullet}}$	46.9
Propoxyl, 2-methyl-	$\mathrm{Me_2CH(CH{-}H)O^{\bullet}}$	51.0
Cyclohexyl	*cyclo*-$\mathrm{[C{-}H(O^{\bullet})(CH_2)_5]}$	57.4

(*continued overleaf*)

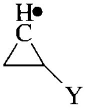
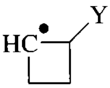
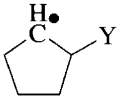
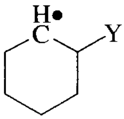
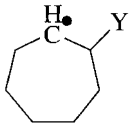
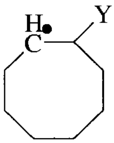
TABLE 9.6 (*continued*)

Radical	Bond	D (kJ mol^{-1})
Allyloxyl-	$CH_2{=}CH(CH{-}H)O^{\bullet}$	46.2
Ethoxyl, 1-vinyl-	$CH_2{=}CHMeC{-}HO^{\bullet}$	34.8
Benzyloxyl	$Ph(CH{-}H)O^{\bullet}$	59.6
Propoxyl, 1-phenyl-	$PhEt(C{-}H)O^{\bullet}$	42.1
Cyclopentyloxyl		40.8
Methoxyl, diphenyl-	$Ph_2C{-}HO^{\bullet}$	55.7
Ethoxyl, 1-phenyl-	$PhMeC{-}HO^{\bullet}$	43.2
	Semiquinone Radicals, O—H Bonds	
Phenoxyl, 4-hydroxy-		226.3
Phenoxyl, 2-hydroxy-		263.8
Phenoxyl, 4-hydroxy-2-methyl-		229.8
Phenoxyl, 2,5-dimethyl-4-hydroxy-		229.5
Tetrachlorophenoxyl, 4-hydroxy-		245.0
	Hydroperoxyl Radicals, O—H Bonds	
Hydrotrioxyl	$^{\bullet}OOO{-}H$	343.0
Hydroperoxyl	$^{\bullet}OO{-}H$	220.0

---

[a] Calculated from BDE values in Table 9.5.

TABLE 9.7 Dissociation Energies for C–F, C–Cl, C–OH, C–OR, and C–OC(O)R Bonds in Free Radicals[a]

	D (kJ mol^{-1})					
Radical	Y = F	Y = Cl	Y = OH	Y = OR	Y = OC(O)R	Y = OC(O)Ph
			Alkyl Radicals			
$C^{\bullet}H_2CH_2-Y$	191.4	79.4	125.4	85.8	90.8	100.1
$MeC^{\bullet}HCH_2-Y$	189.7	77.7	123.7	84.1	89.1	98.4
$MeCH-YC^{\bullet}H_2$	188.6	84.7	126.7	84.9	93.3	102.6
$Me_2C^{\bullet}CH_2-Y$	194.6	82.6	128.6	89.0	94.0	103.3
$Me_2C-YC^{\bullet}H_2$	196.6	83.6	119.6	69.3	84.2	93.5
$EtC^{\bullet}HCH_2-Y$	190.0	78.0	124.0	84.4	89.4	93.7
$C^{\bullet}H_2EtCH-Y$	190.0	86.0	128.0	86.2	94.6	103.9
$Et_2C^{\bullet}CH_2-Y$	193.6	81.6	127.6	88.0	93.0	102.3
$EtC^{\bullet}HMeCH-Y$	186.5	82.5	124.5	82.7	91.1	100.5
$EtC^{\bullet}HMe_2C-Y$	193.7	80.7	128.7	78.4	93.3	102.6
			Cycloalkyl Radicals			
	271.0	159.4	168.0	205.0	165.4	175.4
	195.9	91.9	129.8	92.1	100.5	109.8
	191.8	87.8	125.4	88.0	96.4	105.7
	196.0	92.0	123.7	92.2	100.6	109.9
	191.3	87.3	126.7	87.5	95.9	105.2
	181.2	77.2	128.6	77.4	85.8	95.1

(continued overleaf)

TABLE 9.7 (*continued*)

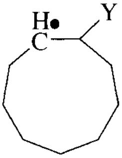
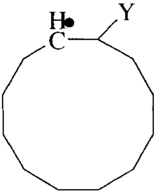
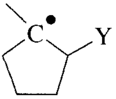
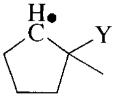
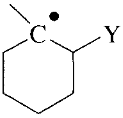
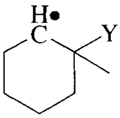
	D (kJ mol^{-1})					
Radical	Y = F	Y = Cl	Y = OH	Y = OR	Y = OC(O)R	Y = OC(O)Ph
	219.5	115.5	119.6	115.7	124.1	120.5
	194.2	90.2	124.0	90.4	98.8	108.1
	195.5	91.5	128.0	91.7	100.1	109.4
	194.3	81.3	127.6	79.0	93.9	103.2
	202.2	98.2	124.5	98.4	106.8	116.1
	203.9	90.9	128.7	88.6	103.5	112.8
Ethynyl Radicals						
$HC^{\bullet}{=}CH{-}Y$	201.7	66.7	145.7	105.1	110.7	120.0
$MeC^{\bullet}{=}CH{-}Y$	198.0	63.0	142.0	101.4	107.0	104.3
$MeC^{\bullet}{=}C{-}YMe$	186.0	51.0	130.0	89.4	95.0	116.3
Allyl Radicals						
$CH_2{=}CHC^{\bullet}HCH_2{-}Y$	238.6	126.6	172.6	133.0	138.0	147.3
$CH_2{=}CH(CH{-}Y)C^{\bullet}H_2$	164.0	48.0	98.4	56.6	65.0	74.3
$CH_2{=}CHC^{\bullet}MeCH_2{-}Y$	239.5	127.5	173.5	133.9	138.9	148.2
$CH_2{=}CH(MeC{-}Y)C^{\bullet}H_2$	156.1	40.1	90.1	39.8	54.7	64.0
$CH_2{=}CHC^{\bullet}HMeCH{-}Y$	234.7	130.7	172.7	130.9	139.3	148.6

TABLE 9.7 (*continued*)

	D (kJ mol^{-1})					
Radical	Y = F	Y = Cl	Y = OH	Y = OR	Y = OC(O)R	Y = OC(O)Ph
$CH_2=CH(CH-Y)MeC^{\bullet}H$	160.5	44.5	94.5	52.7	61.1	70.4
$CH_2=CHC^{\bullet}HMe_2C-Y$	244.2	131.2	179.2	128.9	143.8	153.1
$CH_2=CH(CH-Y)Me_2C^{\bullet}$	168.0	52.0	102.0	60.2	68.6	77.9
$CH_2=CHC^{\bullet}MeMeCH-Y$	237.6	133.6	175.6	133.8	142.2	151.5
$CH_2=CH(MeC-Y)MeC^{\bullet}H$	154.2	38.2	88.2	37.9	52.8	62.1
$CH_2=CHC^{\bullet}MeMe_2C-Y$	245.6	132.6	180.6	130.3	145.2	154.5
$CH_2=CH(MeC-Y)Me_2C^{\bullet}$	160.2	44.2	94.2	43.9	58.8	68.1
$MeCH=CHC^{\bullet}HCH_2-Y$	239.4	126.4	172.4	132.8	137.8	147.1
$MeCH=CH(CH-Y)C^{\bullet}H_2$	161.6	45.6	95.6	53.8	62.2	71.5
$MeCH=CHMeC^{\bullet}MeCH_2-Y$	247.0	135.0	181.0	141.4	146.4	155.7
$MeCH=CH(MeC-Y)C^{\bullet}H_2$	157.9	41.9	91.9	41.6	56.5	65.8
$MeCH=CHC^{\bullet}HMeCH-Y$	243.7	139.7	181.7	139.9	148.3	157.6
$MeCH=CH(CH-Y)MeC^{\bullet}H$	162.8	46.8	96.8	55.0	63.4	73.0
$MeCH=CHC^{\bullet}HMe_2C-Y$	253.2	140.2	188.2	137.9	152.8	162.1
$MeCH=CH(CH-Y)Me_2C^{\bullet}$	175.7	59.7	109.7	67.9	76.3	85.6
$MeCH=CHC^{\bullet}Me(CH-Y)Me$	251.8	147.8	189.8	148.0	156.4	165.1
$MeCH=CH(MeC-Y)C^{\bullet}H_2$	162.7	46.7	122.7	72.4	87.3	96.6
$MeCH=CHMeC^{\bullet}Me_2C-Y$	261.3	148.3	196.3	146.0	160.9	170.2
$MeCH=CH(MeC-Y)Me_2C^{\bullet}$	175.7	59.7	109.7	59.4	74.3	83.6
$Me_2C=CHC^{\bullet}HCH_2-Y$	244.7	131.7	177.7	138.1	143.1	152.4
$Me_2C=CH(CH-Y)C^{\bullet}H_2$	162.7	46.7	96.7	54.9	63.3	72.6
$Me_2C=CHMeC^{\bullet}CH_2-Y$	257.3	145.3	191.3	151.7	156.7	166.0
$Me_2C=CH(MeC-Y)C^{\bullet}H_2$	163.8	47.8	97.8	47.5	62.4	71.7
$Me_2C=CHC^{\bullet}HMeCH-Y$	246.1	142.1	184.1	142.3	150.7	160.0
$Me_2C=CH(CH-Y)MeC^{\bullet}H$	165.1	49.1	99.1	57.3	65.7	75.0
$Me_2C=CHC^{\bullet}HMe_2C-Y$	262.0	149.0	197.0	146.7	161.6	170.9
$Me_2C=CH(CH-Y)Me_2C^{\bullet}$	179.0	63.0	113.0	71.2	79.6	88.9
$Me_2C=CHMeC^{\bullet}MeCH-Y$	259.5	155.5	197.5	155.7	164.1	173.4
$Me_2C=CH(MeC-Y)MeC^{\bullet}H$	166.0	50.0	100.0	49.7	64.6	73.9
$Me_2C=CHMeC^{\bullet}Me_2C-Y$	275.5	162.5	210.5	160.2	175.1	184.4
$Me_2C=CH(MeC-Y)Me_2C^{\bullet}H$	180.0	64.0	114.0	63.7	78.6	87.9
$CH_2=CMeC^{\bullet}HCH_2-Y$	240.3	128.3	174.3	134.3	139.7	149.0
$CH_2=CMe(CH-Y)C^{\bullet}H_2$	164.5	48.5	98.5	56.7	65.1	74.4
$CH_2=CMeC^{\bullet}MeCH_2-Y$	248.1	136.1	182.1	142.5	147.5	156.8
$CH_2=CMe(MeC-Y)C^{\bullet}H_2$	163.1	47.1	97.1	46.8	61.7	71.0
$CH_2=CMeC^{\bullet}HMeCH-Y$	244.1	140.1	182.1	142.5	147.5	156.9
$CH_2=CMe(CH-Y)MeC^{\bullet}H$	169.3	53.3	103.3	61.5	69.9	79.2
$CH_2=CMeC^{\bullet}HMeMe_2C-Y$	254.4	141.4	189.4	139.1	154.0	163.3
$CH_2=CMe(CH-Y)Me_2C^{\bullet}$	176.6	60.6	136.6	94.8	103.2	112.5
$CH_2=CMeC^{\bullet}MeMeCH-Y$	223.8	119.8	161.8	120.0	128.4	137.7
$CH_2=CMeC^{\bullet}MeMe_2C-Y$	233.3	97.3	168.3	118.3	132.9	142.2
$CH_2=CMe(MeC-Y)Me_2C^{\bullet}$	151.8	35.8	85.8	35.5	50.4	59.7
$MeCH=CMeC^{\bullet}HCH_2-Y$	247.2	135.2	181.2	141.6	146.6	155.9
$MeCH=CMe(CH-Y)C^{\bullet}H_2$	157.4	41.4	105.4	63.6	72.0	81.3
$MeCH=CMeC^{\bullet}MeCH_2-Y$	256.4	144.4	190.4	150.8	155.8	165.1
$MeCH=CMe(MeC-Y)C^{\bullet}H_2$	157.4	41.4	91.4	41.1	56.0	65.3

(*continued overleaf*)

TABLE 9.7 (*continued*)

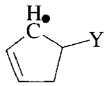
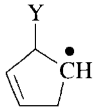
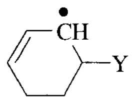
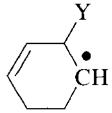
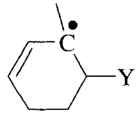
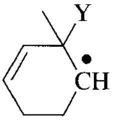
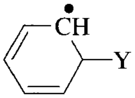
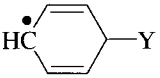
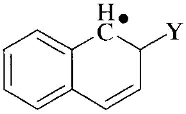
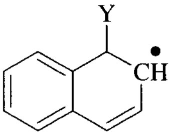
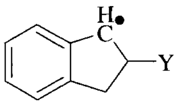
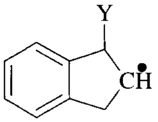
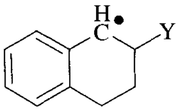
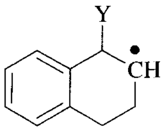
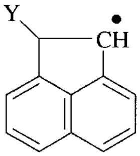
Radical	D (kJ mol^{-1}) Y = F	Y = Cl	Y = OH	Y = OR	Y = OC(O)R	Y = OC(O)Ph
MeCH=CMeC$^{\bullet}$HMeCH−Y	248.6	144.6	186.6	144.8	153.2	162.5
MeCH=CMe(CH−Y)MeC$^{\bullet}$H	159.8	43.8	93.8	52.0	60.4	69.7
MeCH=CMeC$^{\bullet}$HMe$_2$C−Y	251.1	138.1	161.1	110.8	125.7	135.0
MeCH=CMe(CH−Y)Me$_2$C$^{\bullet}$	171.8	55.8	105.8	64.0	72.4	81.7
MeCH=CMeC$^{\bullet}$MeMeCH−Y	257.8	153.8	195.8	154.0	162.4	171.7
MeCH=CMe(MeC−Y)MeC$^{\bullet}$H	159.8	43.8	93.8	43.5	58.4	67.7
MeCH=CMeC$^{\bullet}$MeMe$_2$C−Y	267.3	154.3	202.3	152.0	166.9	176.2
MeCH=CMe(MeC−Y)Me$_2$C$^{\bullet}$	171.8	55.8	105.8	55.5	70.4	79.7
Me$_2$C=CMeC$^{\bullet}$HCH$_2$−Y	260.5	148.5	194.5	154.9	159.9	169.2
Me$_2$C=CMe(CH−Y)C$^{\bullet}$H$_2$	169.5	53.5	103.5	61.7	70.1	79.4
Me$_2$C=CMeC$^{\bullet}$MeCH$_2$−Y	269.7	157.7	203.7	164.1	169.1	178.4
Me$_2$C=CMe(MeC−Y)C$^{\bullet}$H$_2$	169.5	53.5	103.5	53.2	68.1	77.4
Me$_2$C=CMeC$^{\bullet}$HMeCH−Y	261.9	157.9	200.0	158.2	166.6	175.9
Me$_2$C=CMe(CH−Y)MeC$^{\bullet}$H	179.5	63.5	113.5	71.7	80.1	89.4
Me$_2$C=CMeC$^{\bullet}$HMe$_2$C−Y	272.0	159.0	207.0	156.7	171.6	180.9
Me$_2$C=CMe(CH−Y)Me$_2$C$^{\bullet}$	191.5	75.5	125.5	83.7	92.1	101.4
Me$_2$C=CMeC$^{\bullet}$MeMeCH−Y	271.1	167.1	209.1	167.3	175.7	185.0
Me$_2$C=CMe(MeC−Y)MeC$^{\bullet}$H	179.5	63.5	113.5	63.2	78.1	87.4
Me$_2$C=CMeC$^{\bullet}$MeMe$_2$C−Y	273.6	160.6	208.6	158.3	173.2	182.5
Me$_2$C=CMe(MeC−Y)Me$_2$C$^{\bullet}$	191.5	75.5	125.5	75.2	90.1	99.4
			Cycloalkenyl Radicals			
	237.2	133.2	175.2	133.4	141.8	151.1
	161.3	45.3	95.3	53.5	61.9	71.2
	255.4	151.4	193.4	151.6	160.0	169.3
	178.1	62.1	112.1	70.3	78.7	88.0
	269.3	165.3	207.3	165.5	173.9	183.2

TABLE 9.7 (*continued*)

	D (kJ mol^{-1})					
Radical	Y = F	Y = Cl	Y = OH	Y = OR	Y = OC(O)R	Y = OC(O)Ph
	179.8	63.8	113.8	63.5	78.4	87.7
	21.6	27.6	55.6	13.8	22.2	31.5
	138.3	44.3	72.3	30.5	38.9	48.2
	159.9	43.4	93.4	51.6	60.0	69.3
	182.5	78.5	120.5	78.7	87.1	96.4
			Benzyl Radicals			
$PhC^{\bullet}HCH_2{-}Y$	232.3	119.3	165.3	125.7	130.7	140.0
$Ph(CH{-}Y)C^{\bullet}H_2$	172.4	56.4	104.4	62.6	71.0	80.3
$PhC^{\bullet}MeCH_2{-}Y$	232.8	119.8	165.8	126.2	131.2	140.5
$Ph(MeC{-}Y)C^{\bullet}H_2$	162.8	46.8	94.8	44.5	59.4	68.7
$PhC^{\bullet}HCH{-}YMe$	228.5	124.5	166.5	124.7	133.1	142.4
$Ph(CH{-}Y)C^{\bullet}HMe$	170.6	54.6	102.6	60.8	69.2	78.5
$PhC^{\bullet}HC{-}YMe_2$	231.4	118.4	166.4	116.1	131.0	140.3
$Ph(CH{-}Y)C^{\bullet}Me_2$	176.5	60.5	108.5	66.7	75.1	84.4
$Ph(MeC{-}Y)C^{\bullet}HMe$	170.6	54.6	102.6	52.3	67.2	76.5
$PhMeC^{\bullet}(CH{-}Y)Me$	237.9	133.9	175.9	134.1	142.5	151.8
$Ph(MeC{-}Y)C^{\bullet}Me_2$	182.6	66.6	114.6	64.3	79.2	88.5
$PhMeC^{\bullet}HC{-}YMe_2$	240.9	127.9	175.9	125.6	140.5	149.8
$PhC^{\bullet}HPhCH{-}Y$	203.0	109.8	138.0	96.2	104.6	113.9
$Ph_2C^{\bullet}CH_2{-}Y$	292.7	179.7	225.7	186.1	191.1	200.4
	227.0	123.0	165.0	123.2	131.6	140.9

(*continued overleaf*)

TABLE 9.7 (*continued*)

	D (kJ mol^{-1})					
Radical	Y = F	Y = Cl	Y = OH	Y = OR	Y = OC(O)R	Y = OC(O)Ph
	168.0	52.0	100.0	58.2	66.6	75.9
	228.5	124.5	166.0	124.2	132.6	141.9
	159.3	43.3	91.3	49.5	57.9	67.2
	230.6	114.6	162.6	120.8	129.2	138.5

[a]Calculated from BDE values in Table 9.5.

REFERENCES

1. N. N. Semenov, *Some Problems of Chemical Kinetics and Reactivity*, Pergamon Press, London, 1958, Vol. 1; 1959, Vol. 2.
2. E. T. Denisov, *Liquid-Phase Reaction Rate Constants*, IFI/Plenum, New York, 1974, p. 93.
3. N. M. Emanuel, E. T. Denisov, and Z. K. Maizus, *Liquid-Phase Oxidation of Hydrocarbons*, Plenum Press, New York, 1967, p. 71.
4. E. T. Denisov, N. I. Mitskevich, and V. E. Agabekov, *Liquid-Phase Oxidation of Oxygen-Containing Compounds*, Consultants Bureau, New York, 1977.
5. E. T. Denisov, in *Comprehensive Chemical Kinetics*, C. H. Bamford and C. F. H. Tipper (Eds.), Elsevier, Amsterdam, The Netherlands, 1980, Vol. 16, p. 125.
6. E. T. Denisov and T. G. Denisova, *Handbook of Antioxidants*, CRC Press, Boca Raton, FL, 2000.
7. E. T. Denisov and V. V. Azatyan, *Inhibition of Chain Reactions*, Gordon and Breach, London, 2000.
8. R. Houwink and A. J. Staverman, *Chemie und Technologie der Kunststoffe*, Akademische Verlagsgesellschaft, Leipzig, 1962, Vol. 1, p. 202.
9. E. T. Denisov, *Mendeleev Commun.* **2**, 1 (1992).

10. E. T. Denisov, *Kinet. Catal.* **35**, 617 (1994).
11. E. T. Denisov, *Russ. Chem. Rev.* **66**, 859 (1997).
12. E. T. Denisov, *Russ. Chem. Rev.* **69**, 153 (2000).
13. E. T. Denisov, in *General Aspects of the Chemistry of Radicals*, Z. B. Alfassi (Ed.), John Wiley & Sons, Inc., Chichester, U.K., 1999, p. 79.
14. E. T. Denisov, *Kinet. Catal.* **37**, 519 (1996).
15. I. V. Aleksandrov, *Teor. Experim. Khimiya*, **12**, 299 (1976).
16. E. T. Denisov, *Petroleum Chem.* **37**, 99 (1997).
17. E. T. Denisov, *Kinet. Catal.* **39**, 17 (1998).
18. T. I. Drozdova and E. T. Denisov, *Kinet. Catal.* **43**, 14 (2002).
19. T. G. Denisova and E. T. Denisov, *Petroleum Chem.* **38**, 12 (1998).
20. E. T. Denisov and T. G. Denisova, *Kinet. Catal.* **37**, 46 (1996).
21. T. G. Denisova and E. T. Denisov, *Polym. Degrad. Stab.* **60**, 345 (1998).
22. E. T. Denisov, *Neftekhimiya* **39**, 434 (1999).
23. T. G. Denisova and E. T. Denisov, *Kinet. Catal.* **40**, 223 (1999).
24. E. T. Denisov, *Kinet. Catal.* **40**, 217 (1999).
25. T. G. Denisova and E. T. Denisov, *Petroleum Chem.* **40**, 65 (2000).
26. E. T. Denisov, *Petroleum Chem.* **37**, 22 (1997).
27. E. T. Denisov, *Russ. Chem. Bull.* 2110 (1998).
28. T. G. Denisova and E. T. Denisov, *Kinet. Catal.* **43**, 5 (2002).
29. T. G. Denisova and E. T. Denisov, *Petroleum Chemistry* **37**, 187 (1997).
30. E. T. Denisov, *Kinet. Catal.* **36**, 351 (1995).
31. E. T. Denisov, T. G. Denisova, Yu. V. Geletii, and G. Balavoine, *Kinet. Catal.* **39**, 312 (1998).
32. E. T. Denisov, *Chem. Phys. Rep.* **17**, 705 (1998).
33. E. T. Denisov and T. G. Denisova, *Russian Chem. Rev.* **71**, 417 (2002).
34. V. L. Antonovskii, E. T. Denisov, I. A. Kuznetsov, Yu. Ya. Mekhryushev, and L. V. Solntseva, *Kinet. Katal.* **6**, 607 (1965).
35. T. G. Degtyareva, V. M. Solyanikov, and E. T. Denisov, *Neftekhimiya* **12**, 854 (1972).
36. C. Ruchardt, M. Gerst, and J. Ebenchoch, *Angew. Chem. Int. Ed. Engl.* **36**, 1406 (1997).
37. C. Seeger, G. Rotzoll, A. Lubbert, and Schugerl, *Int. J. Chem. Kinet.* **13**, 39 (1981).
38. W. Tsang, in *Energetics of Free Radicals*, A. Greenberg and J. Liebman (Eds.), Blackie Academic and Professional, New York, 1996, p. 22.
39. V. E. Tumanov and E. T. Denisov, *Neftekhimiya* **41**, 108 (2001).
40. E. A. Kromkin, V. E. Tumanov, and E. T. Denisov, *Neftekhimiya* **42**, 43 (2002).
41. S. G. Lias, J. F. Liebman, R. D. Levin, and S. A. Kafafi, *NIST Standard Reference Database*, 19A, NIST Positive Ion Energetics, Version 2.0, NIST, Gaithersburg, MD, 1993.
42. E. T. Denisov and S. L. Khursan, *Russian J. Phys. Chem.* **74**, Suppl. 3, 491 (2000).
43. V. E. Tumanov, E. A. Kromkin, and E. T. Denisov, *Izv. AN. Ser. Khim.* 1508 (2002).
44. V. F. Turi and K. M. Ervin, *J. Phys. Chem. A*, **103**, 6911 (1999).

45. D. R. Lide (Ed.), *Handbook of Chemistry and Physics*, 72 Ed., CRC Press, Boca Raton, FL, 1992.
46. D. F. McMillen and D. M. Golden, *Ann. Rev. Phys. Chem.* **33**, 493 (1982).
47. J. L. Holmes, F. P. Lossing, and P. M. Mayer, *J. Am. Chem. Soc.* **113**, 9723 (1991).
48. E. T. Denisov and T. G. Denisova, *Kinet. Catal.* **34**, 369 (1993).
49. Z. B. Alfassi, R. E. Huie, and P. Neta, in *Aqueous Solutions and Mixed Solvents in Peroxyl Radicals*, Z. B. Alfassi (Ed.), John Wiley & Sons, Inc., Chichester, U.K., 1997.
50. C. Chatgilialoglu, *Chem. Rev.* **95**, 1229 (1995).
51. E. T. Denisov, *Russ. Chem. Bull.* **47**, 1274 (1998).
52. J. Berkowitz, G. B. Ellson, and D. Gutman, *J. Phys. Chem.* **98**, 2744 (1994).
53. L. J. J. Laarhoven, P. Mulder, and D. D. M. Wayner, *Acc. Chem. Res.* **32**, 342 (1999).
54. D. A. Armstrong, in *The Chemistry of Sulfur-containing Functional Groups*, S. Patai and Z. Rappoport (Eds.), John Wiley & Sons, Inc., New York, 1993, p. 27.

Handbook of Free Radical Initiators. E.T. Denisov, T.G. Denisova, T.S. Pokidova
Copyright © 2003 John Wiley & Sons, Inc.
ISBN: 0-471-20753-5

10

BIMOLECULAR AND TRIMOLECULAR REACTIONS OF FREE RADICAL GENERATION BY DIOXYGEN

10.1 REACTION OF DIOXYGEN WITH C–H BONDS OF ORGANIC COMPOUNDS

Hydroperoxides, ROOH, are known to be the main autoinitiators of the chain oxidation of hydrocarbons and other organic compounds, RH, by dioxygen. The mechanism of chain initiation in oxidized RH in the absence of ROOH was intensively discussed in the 1950s and 1960s.[1–4] Bolland and Gee[5] were the first to propose the following reaction as the most probable:

$$RH + O_2 \rightarrow R^{\bullet} + HO_2^{\bullet}$$

The first experimental study of this reaction was performed by Cooper and Melville.[6] The main experimental evidence for this mechanism are the following:[7,8]

1. The rate of free radical generation in oxidized RH in the absence of ROOH or other initiator was found to be proportional to the product [RH] × [O_2].
2. The rate constant k_i for this reaction increases with a decrease in the BDE of the weakest C–H bond in the oxidized molecule.

RH	*cyclo*-C_6H_{12}	Me_2CHCH_2Me	$PhCH_3$	$PhMe_2CH$	*cyclo*-C_6H_{10}
D(kJ mol^{-1})	408.8	400.0	375.0	354.7	341.5
k_i (T = 403 K) (L mol^{-1} s^{-1})	1.5×10^{-10}	3.7×10^{-9}	1.6×10^{-8}	2.0×10^{-7}	1.3×10^{-7}
References	9	10	11	12	11

3. Compounds with C—D bonds react with dioxygen more slowly than those with C—H bonds. For example, the kinetic isotope effect $k_H/k_D = 5.2$ (diethyl sebacinate, 413 K).[13]
4. Reaction of RH with O_2 occurs more rapidly in polar solvent[14] due to the polar structure of the transition state $R(\delta^+)\cdots H\cdots O_2(\delta-)$.
5. The effect of interaction of a few dipoles is observed in reactions of peroxyl radicals and dioxygen with C—H bonds of polyatomic esters. The strong influence of a few polar group on the rate constant of both reactions was evidenced ($\Delta G_{n\mu}{}^{\neq} = -RT\ln(k_n/k_i)$).[15]

$Me_{4-n}C[CH_2OC(O)CH_2Me]_n + O_2 \rightarrow$ *Free radicals*

n	1	2	3	4
k(423 K) (L mol^{-1} s^{-1})	2.8×10^{-8}	1.1×10^{-7}	1.7×10^{-7}	8.5×10^{-7}
$\Delta G_{n\mu}{}^{\neq}$ (kJ mol^{-1})	0.0	−4.6	−6.1	−11.8

The values of rate constants and activation energies of radical generation by dioxygen that are measured experimentally are collected in Table 10.1 and those calculated by the IPM method (see Chapter 9) are in Table 10.2. For the values of rate constants of chain initiation in oxidized polymers, see Table 10.3.

10.2 REACTION OF DIOXYGEN WITH THE DOUBLE BOND OF OLEFINS

In addition to the reaction with the C—H bond, dioxygen attacks the double bond of olefins with free radical formation.[44]

$$RCH{=}CH_2 + O_2 \rightarrow RC^{\bullet}HCH_2OO^{\bullet}$$

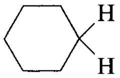
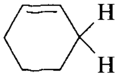
$$RC^{\bullet}HCH_2OO^{\bullet} + O_2 \rightarrow RCH(OO^{\bullet})CH_2OO^{\bullet}$$

This reaction was proposed by Farmer.[45] Mayo and co-worker[46] evidenced this reaction experimentally in oxidized styrene, and the rate constant value for this reaction was measured by the acceptors of free radical (AFR) method.[47] This reaction is endothermic. The activation energies for these reactions are sufficiently higher than the enthalpy values.

Monomer	$CH_2{=}CH_2$	$CH_2{=}CHEt$	$CH_2{=}CHPh$	$CH_2{=}CHCOOMe$	$CH_2{=}CMeCOOMe$
ΔH(kJ mol^{-1})	80.8	80.4	20.4	84.8	86.9
E(kJ mol^{-1})			118	117	115

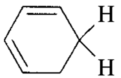
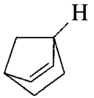
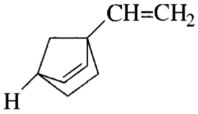
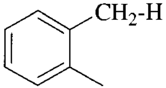
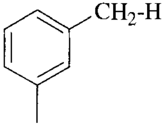
The transition state of this reaction has a polar structure and that is why this reaction occurs more rapidly in polar solvents (cf. rate constants in chlorobenzene

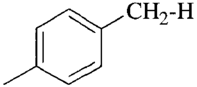
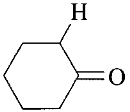
TABLE 10.1 Rate Constants and Activation Energies for the Reaction RH + O_2 → Free Radicals[a]

RH	Solvent	T (K)	E (kJ mol^{-1})	log A, A (L mol^{-1} s^{-1})	k (450 K) (L mol^{-1} s^{-1})	Reference
CH_3-H	Gas phase	300–2500	238.0	10.60	9.42×10^{-18}	16
CH_3-H	Gas phase	300–2500	238.1	10.60	9.20×10^{-18}	17
CH_3-H	Gas phase	300–2500	217.4	8.88	4.42×10^{-17}	18
CH_3-H	Gas phase	1000–2500	234.3	10.90	5.05×10^{-17}	19
CH_3-H	Gas phase	300–1000	246.1	10.63	1.16×10^{-18}	20
CH_3CH_2-H	Gas phase	500–2000	217.0	10.78	3.90×10^{-15}	16
CH_3CH_2-H	Gas phase	300–2000	212.8	10.60	7.93×10^{-15}	17
CH_3CH_2-H	Gas phase	865–905	213.4	10.00	1.70×10^{-15}	21
Me_2CH-H	Gas phase	300–2500	199.5	10.60	2.77×10^{-13}	22
$Me_2CH(C-H)Me_2$	Gas phase	773–813	173.0	10.31	1.69×10^{-10}	23
Me_3C-H	Gas phase	300–2500	184.1	10.60	1.70×10^{-11}	24
Me_2C-HCH_2Me	Benzene	410–439	159.0	12.18	5.30×10^{-7}	10
$Me(CH_2)_4(CH-H)Me$	Benzene	397–434	181.0	14.50	3.09×10^{-7}	11
$Me_3CCH_2C-HMe_2$	Benzene	400–466	159.0	12.00	3.50×10^{-7}	10
	Chlorobenzene	383–413	167.4	12.90	2.94×10^{-7}	9
$CH_2{=}CHCH_2-H$	Gas phase	600–1000	163.8	9.28	1.85×10^{-10}	25
$CH_2{=}CMeCH_2-H$	Gas phase	673–793	161.2	9.68	9.31×10^{-10}	26
	Benzene	373–413	104.6	7.20	1.14×10^{-5}	11

(*continued overleaf*)

TABLE 10.1 (*continued*)

RH	Solvent	T (K)	E (kJ mol^{-1})	log A, A (L mol^{-1} s^{-1})	k (450 K) (L mol^{-1} s^{-1})	Reference
	Gas phase	573–623	104.0	8.91	6.90×10^{-4}	27
	Benzene, 1,2-dichloro-	353			3.70×10^{-7}	28
	Benzene, 1,2-dichloro-	348–363	96.7	8.30	1.19×10^{-3}	28
$PhCH_2-H$	Benzene	378–418	134.0	9.85	1.98×10^{-6}	11
	Chlorobenzene	383–418	130.0	9.50	2.57×10^{-6}	29
	Chlorobenzene	383–418	135.0	10.50	6.76×10^{-6}	29

	Chlorobenzene	383–418	127.0	9.50	5.73×10^{-6}	29
$PhMe_2C-H$	Benzene	353–413	77.5	3.41	2.59×10^{-6}	12
$H-CH_2OH$	Gas phase	300–2500	187.9	10.31	3.16×10^{-12}	30
$HC(O)-H$	Gas phase	700–1000	170.1	10.78	1.08×10^{-9}	16
$HC(O)-H$	Gas phase	300–2500	163.0	10.31	2.45×10^{-9}	17
$HC(O)-H$	Gas phase	713–816	162.8	10.31	2.59×10^{-9}	31
$PrC(O)-H$	Chlorobenzene	283–303	117.0	4.60	1.04×10^{-9}	32
$Me_2CHC(O)-H$	Chlorobenzene	283–303	92.0	8.11	2.70×10^{-3}	32
$Me(CH_2)_8C(O)-H$	Decane	278–299	65.0	5.50	9.02×10^{-3}	6
	Chlorobenzene	376–413	109.5	9.00	1.70×10^{-4}	33
$CH_2{=}CHC(O)-H$	Benzene	413			6.3×10^{-2}	34
$MeCH{=}CHC(O)-H$	Chlorobenzene	288–308	124.0	15.11	5.21	35
$CH_2{=}CEtC(O)-H$	Chlorobenzene	288–308	96.0	13.40	1.81×10^{2}	36
$CH_2{=}CBuC(O)-H$	Chlorobenzene	288–308	94.0	10.00	0.12	37
$MeCH{=}CHC(O)-H$	Chlorobenzene	273–298	119.0	13.90	1.22	37

(continued overleaf)

TABLE 10.1 (*continued*)

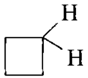
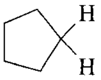
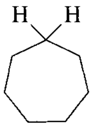
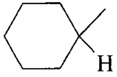
RH	Solvent	T (K)	E (kJ mol^{-1})	log A, A (L mol^{-1} s^{-1})	k (450 K) (L mol^{-1} s^{-1})	Reference
Pr(CH−H)C(O)OH	Benzene, 1,4-dichloro-	398–413	143.1	11.90	1.95×10^{-5}	38
EtC(O)O(CH−H)Me	Propionic acid, methyl ester	343–363	133.8	13.81	1.91×10^{-2}	39
Ph(CH−H)OC(O)Ph	Benzene, 1,2-dichloro-	373–403	96.5	5.90	5.00×10^{-6}	40
Ph(CH−H)OCH$_2$Ph	Chlorobenzene	398			7.80×10^{-9}	41
Ph(CH−H)OCH$_2$Ph	Dibenzyl ether	398			3.7×10^{-9}	41
Ph(CH−H)OCH$_2$Ph	Benzene, 1,2-dichloro-	398			9.50×10^{-9}	41
Ph(CH−H)OCH$_2$Ph	Nitrobenzene	398			4.1×10^{-8}	41
Ph(CH−H)OCH$_2$Ph	Benzene, 1,2-dichloro-	403			2.86×10^{-8}	14
Ph(CH−H)OCH$_2$Ph	Nitrobenzene	413			1.15×10^{-7}	14
MeOC(O)(CH$_2$)$_8$ (CH−H)C(O)OMe	Chlorobenzene	413–443	164.3	13.90	6.74×10^{-6}	42
EtOC(O)(CH$_2$)$_8$C(O)O (CH−H)Me	Chlorobenzene	413–443	141.7	11.72	1.87×10^{-5}	42
EtOC(O)(CH$_2$)$_8$C(O)O (CH−H)Me	Chlorobenzene	413			4.90×10^{-7}	13
C$_2$D$_5$OC(O)(CH$_2$)$_8$C(O)O (CD−D)CD$_3$	Chlorobenzene	413			9.00×10^{-8}	13

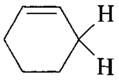
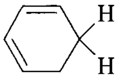
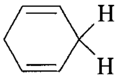
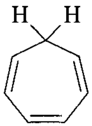
$EtOC(O)(CH_2)_8C(O)O(CH-H)Me$	Chlorobenzene	433			2.30×10^{-6}	13
$C_2D_5OC(O)(CH_2)_8C(O)O(CD-D)CD_3$	Chlorobenzene	433			3.00×10^{-7}	13
$Me_2CHOC(O)(CH_2)_8C(O)OC-HMe_2$	Chlorobenzene	413–443	145.1	12.00	1.44×10^{-5}	42
$EtC(O)O(CH-H)Me$	Chlorobenzene	343–363	134.0	13.80	1.76×10^{-2}	42
$(Me(CH-H)C(O)OCH_2)_4C$	Pentaerythritol tetrapropionate	423			3.4×10^{-6}	15
$(CH_3C(O)O(CH-H))_4C$	Pentaerythritol tetraacetate	423			9.4×10^{-7}	15
$(Me(CH-H)C(O)OCH_2)_3CEt$	1,2,3-Propane-triol-2-ethyl-tripropionate	423			5.2×10^{-7}	15
$(Me(CH-H)C(O)OCH_2)_2CMe_2$	1,3-Propanediol-2,2-dimethyl-tripropionate	423			2.2×10^{-7}	15

---

[a] Experimental data.

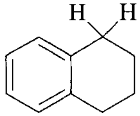
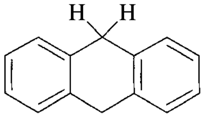
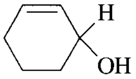
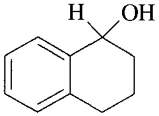
TABLE 10.2 Enthalpies and Rate Constants for the Reaction $RH + O_2 \rightarrow R^{\bullet} + HO_2^{\bullet}$ in Hydrocarbon Solution Calculated by the IPM Method[a]

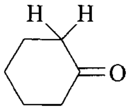
RH	D (kJ mol^{-1})	n_{C-H}	ΔH (kJ mol^{-1})	ΔH_{max} (kJ mol^{-1})	log A, A (L mol^{-1} s^{-1})	k (450 K) (L mol^{-1} s^{-1})
Me_3CCH_2-H	422.0	12	202.0	76.1	12.58	8.17×10^{-12}
$EtMeCH-H$	413.0	4	193.0	76.1	12.06	2.68×10^{-11}
Me_3C-H	400.0	1	180.0	76.1	11.38	1.86×10^{-10}
	418.5	8	198.5	76.1	12.39	1.32×10^{-11}
	408.4	10	188.4	76.1	12.43	2.16×10^{-10}
	403.9	14	183.9	76.1	12.55	9.49×10^{-10}
	395.5	1	175.5	76.1	11.35	5.68×10^{-10}
(Z)-Decalin	387.6	2	167.6	76.1	11.60	8.31×10^{-9}
$CH_2{=}CHCH_2-H$	368.0	3	148.0	110.1	11.12	5.25×10^{-7}
$CH_2{=}CH(CH-H)Me$	349.8	2	129.8	110.1	10.58	1.96×10^{-5}
$CH_2{=}CH(C-H)Me_2$	339.6	1	119.6	110.1	9.96	4.47×10^{-4}

Z-MeCH=CH(CH−H)Me	344.0	2	124.0	110.1	10.41	6.27×10^{-5}
Me_2C=CH(CH−H)Me	332.0	2	112.0	110.1	9.89	4.70×10^{-4}
Me_2C=CMe(C−H)Me_2	322.8	1	102.8	110.1	8.63	3.02×10^{-4}
CH_2=C(MeC−H)CH=CH_2	307.2	1	87.2	110.1	9.47	1.34×10^{-1}
	341.5	4	121.5	110.1	10.63	2.02×10^{-4}
	330.9	4	110.9	110.1	10.12	1.06×10^{-3}
	312.6	4	92.6	110.1	9.48	3.27×10^{-2}
	301.0	2	81.0	110.1	10.17	3.55
MeC≡CC−HMe_2	329.4	1	109.4	110.1	9.41	3.09×10^{-4}
$PhCH_2$−H	375.0	3	155.0	90.6	11.02	6.47×10^{-8}
PhMeCH−H	364.1	2	144.1	90.6	11.21	1.81×10^{-6}

(continued overleaf)

TABLE 10.2 (*continued*)

RH	D (kJ mol^{-1})	n_{C-H}	ΔH (kJ mol^{-1})	ΔH_{max} (kJ mol^{-1})	log A, A (L mol^{-1} s^{-1})	k (450 K) (L mol^{-1} s^{-1})
$PhMe_2C-H$	354.7	1	134.7	90.6	10.79	8.59×10^{-6}
	345.6	4	125.6	90.6	11.25	2.82×10^{-4}
	322.0	4	102.0	90.6	10.66	3.94×10^{-2}
Me_2NH_2C-H	379.5	1	159.5	76.1	11.24	3.16×10^{-8}
$(CH_2=CHCH-H)_3N$	345.6	6	125.6	110.1	10.94	1.38×10^{-4}
$Me_2(HO)C-H$	390.5	1	170.5	76.1	11.32	2.00×10^{-9}
	329.7	1	109.7	76.1	10.66	5.08×10^{-3}
$MeCH=CMe(C-H)MeOH$	325.2	1	105.2	110.1	9.00	3.72×10^{-4}
	337.5	1	117.5	90.6	10.49	4.25×10^{-4}

PhC(O)−H	348.0	1	128.0	90.6	9.69	4.02×10^{-6}
	394.1	4	174.1	76.1	11.94	3.24×10^{-9}
$(Me_2C-H)_2O$	390.8	2	170.8	76.1	11.62	3.72×10^{-9}
$(CH_2=CHCH-H)_2O$	360.0	4	140.0	110.1	10.11	4.30×10^{-7}
$Ph_2C-HOMe$	354.2	1	134.2	90.6	10.78	9.60×10^{-6}
Ph(C(O)OH)CH−H	367.0	2	147.0	90.6	11.24	9.04×10^{-7}
Me_3COO-H	358.6	1	138.6	51.5	11.39	1.21×10^{-5}
$(Me_3C)_3Si-H$	351.0	1	131.0	69.7	11.02	3.92×10^{-5}
Ph_3Ge-H	322.5	1	102.5	77.6	10.36	1.74×10^{-2}
Ph_3Sn-H	296.9	1	76.9	72.0	9.36	1.65

[a] See Chapter 9.

TABLE 10.3 Rate Constants for the Free Radical Generation by the Reaction of Dioxygen with Polymer[a]

Polymer	Crystallinity (%)	of ash (%)	T (K)	E (kJ mol^{-1})	k_i (L mol^{-1} s^{-1})
PE	65	0.7	391		7.0×10^{-7}
PE	65	0.04	391		2.10×10^{-7}
PE	65	0.14	391		1.40×10^{-7}
PE	55	0.45	378	117	5.41×10^{-7}
PE	55	0.45	386	117	2.67×10^{-6}
PE	55	0.45	388	117	3.60×10^{-6}
PE	55	0.45	398	117	8.01×10^{-6}
PE	55	0.45	404	117	1.26×10^{-5}
PE	40		362	146	3.70×10^{-7}
PE	40		367.5	146	8.60×10^{-7}
PE	40		372	146	1.19×10^{-6}
PE	40		377	146	2.84×10^{-6}
PE	40		377	146	2.48×10^{-6}
PP	65	0.4	380	92	1.76×10^{-5}
PP	65	0.4	389	92	3.36×10^{-5}
PP	65	0.4	398	92	4.57×10^{-5}
PP	65	0.4	405	92	8.46×10^{-5}
PP	PhCl	0.4	385	98	8.94×10^{-7}
PP	PhCl	0.4	389	98	1.52×10^{-6}
PP	PhCl	0.4	394	98	1.63×10^{-6}
PP	PhCl	0.4	399	98	2.02×10^{-6}
PP	PhCl	0.4	403	98	3.87×10^{-6}

[a] See Ref. 43.

and *N*,*N*-dimethylformamide for reactions of styrene and butyl methacrylate in Table 10.4). The multidipole interaction effect was observed for reactions of polyatomic esters.[48]

Monomer	$CH_2{=}CHCOOBu$	$CH_2{=}CHCOOCH_2C-(CH_2OCOEt)_3$	$(CH_2{=}CHC(O)-OCH_2)_4C$
k(363 K) (L mol^{-1} s^{-1})	1.72×10^{-7}	1.10×10^{-8}	1.4×10^{-8}
$\Delta G_{n\mu}^{\neq}$ (kJ mol^{-1})	0.0	8.2	7.8

The charge-transfer complex of dioxygen with monomer is very probable as a precursor for this reaction.[49]

$$RCH{=}CH_2 + O_2 \Leftrightarrow RCH{=}CH_2(\delta^+) \cdots O_2(\delta^-)$$

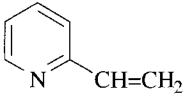
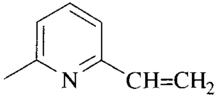
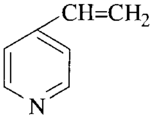
$$RCH{=}CH_2(\delta^+) \cdots O_2(\delta^-) \rightarrow RC^{\bullet}HCH_2OO^{\bullet}$$

TABLE 10.4 Rate Constants and Activation Energies for the Reaction $RCH{=}CH_2 + O_2 \rightarrow$ Free Radicals[a]

$RCH{=}CH_2$	Solvent	T (K)	E (kJ mol^{-1})	log A, A (L mol^{-1} s^{-1})	k (350 K) (L mol^{-1} s^{-1})	Reference
$PhCH{=}CH_2$	Chlorobenzene	378–398	125.5	11.56	6.77×10^{-8}	47
$PhCH{=}CH_2$	Chlorobenzene	343–363	118.1	10.25	4.21×10^{-8}	50
$PhMeC{=}CH_2$	Chlorobenzene	343			2.5×10^{-8}	51
$PhCH{=}CH_2$	*N*,*N*-Dimethylformamide	343			4.0×10^{-8}	51
$PhMeC{=}CH_2$	Benzonitrile	343			5.5×10^{-8}	51
$BuOC(O)CH{=}CH_2$	Chlorobenzene	343–363	88.6	6.04	6.57×10^{-8}	50
$BuOC(O)(Me)C{=}CH_2$	Chlorobenzene	342–363	91.5	6.72	1.16×10^{-7}	50
$BuOC(O)(Me)C{=}CH_2$	Chlorobenzene	363			3.4×10^{-7}	50
$BuOC(O)(Me)C{=}CH_2$	*N*,*N*-Dimethylformamide	363			8.1×10^{-7}	50
$Me_3COCOCH{=}CH_2$	Chlorobenzene	353			7.1×10^{-8}	50
$MeOCO(Me)C{=}CH_2$	Chlorobenzene	353			1.3×10^{-7}	50
$MeOCO(Et)C{=}CH_2$	Chlorobenzene	353			1.2×10^{-7}	50
$MeCH{=}CHC(O)OEt$	Chlorobenzene	363			5.1×10^{-8}	50
$NH_2COCH{=}CH_2$	Chlorobenzene	353			1.5×10^{-6}	50
$CH_2{=}CHC(O)OCH_2C(OCOEt)_3$	Chlorobenzene	363			1.40×10^{-8}	52
$(CH_2{=}CHC(O)OCH_2)_4C$	Chlorobenzene	363			1.10×10^{-8}	52

(*continued overleaf*)

TABLE 10.4 (*continued*)

$RCH{=}CH_2$	Solvent	T (K)	E (kJ mol^{-1})	log A, A (L mol^{-1} s^{-1})	k (350 K) (L mol^{-1} s^{-1})	Reference
$(CH_2{=}C(Me)C(O)OCH_2)_4C$	Chlorobenzene	343–393	180.6	18.20	1.77×10^{-9}	48
	*N*,*N*-Dimethyl-formamide	343			4.00×10^{-8}	50
	*N*,*N*-Dimethyl-formamide	343			8.00×10^{-8}	50
	*N*,*N*-Dimethyl-formamide	343			4.40×10^{-8}	50
Retinal acetate	Chlorobenzene	303–333	53.2	3.80	7.25×10^{-5}	53
(*E*)-β-Carotene	Benzene, 1,3-dimethyl-	323–343	107.5	12.60	3.60×10^{-4}	54

[a] Experimental data.

For the values of rate constants of the dioxygen reaction with monomers, see Table 10.4.

10.3 TRIMOLECULAR REACTION OF RADICAL INITIATION BY DIOXYGEN

In addition to bimolecular reactions of organic compounds with dioxygen, free radicals are generated in an oxidized substrate in the liquid phase by a trimolecular reaction.[43]

$$\mathrm{RH + O_2 + HR \rightarrow R^\bullet + H_2O_2 + R^\bullet}$$

This reaction was proposed in 1960 for compounds with weak C—H bond[55] and experimentally proved in oxidized cyclohexanol[56] and tetraline.[57] The rate of this reaction is proportional to the product $[\mathrm{RH}]^2 \times [\mathrm{O_2}]$. The enthalpy for this reaction $\Delta H = 2D_{\mathrm{R-H}} - 572\ \mathrm{kJ\,mol^{-1}}$. The enthalpy of the bimolecular reaction $\mathrm{RH + O_2}$, $\Delta H = D_{\mathrm{R-H}} - 220\ \mathrm{kJ\,mol^{-1}}$. So, $\Delta H(\mathrm{2RH + O_2}) < \Delta H(\mathrm{RH + O_2})$ at $D_{\mathrm{R-H}} < 352\ \mathrm{kJ\,mol^{-1}}$. The frequency factor of the trimolecular collisions (z_{03}) in liquids is close to bimolecular (z_{02}). The preexponential factor $A_{03} < A_{02}$ is the result of the concerted mechanism of simultaneous energy concentration on the two reacting C—H bonds.[43] The ratio $A_{03}/A_{02} = (z_{03}/z_{02}) \times (2RT/\pi E_3)^{1/2}$. As a result, the ratio $k_3[\mathrm{RH}]^2[\mathrm{O_2}]/k_2[\mathrm{RH}][\mathrm{O_2}] = (z_{03}[\mathrm{RH}]/z_{02}) \times (2RT/\pi E_3)^{1/2} \exp[-(E_3 - E_2)/RT] \approx (2RT/\pi E_3)^{1/2} \exp[-(D_{\mathrm{R-H}} - 352)/RT]$, and the trimolecular reaction should be faster than the bimolecular reaction for substrates with $D_{\mathrm{R-H}} < 340\ \mathrm{kJ\,mol^{-1}}$. Polar solvents accelerate the trimolecular reaction due to the polar structure of the transition state $\mathrm{C(\delta^+) \cdots H \cdots (\delta^-) O{-}O(\delta^-) \cdots H \cdots (\delta^+)C}$.

Unsaturated compounds, probably react with dioxygen by their double bonds, with the preliminary formation of a charge-transfer complex.[50]

$$\mathrm{RCH{=}CH_2 + O_2 \Leftrightarrow RCH{=}CH_2(\delta^+) \cdots O_2(\delta^-)}$$

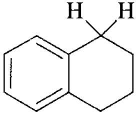
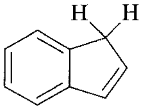
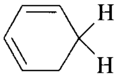
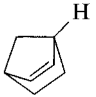
$$\mathrm{RCH{=}CH_2 \cdots O_2 + CH_2{=}CHR \rightarrow RC^\bullet HCH_2OOCH_2C^\bullet HR}$$

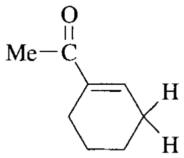
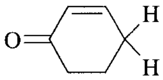
Another trimolecular reaction was found for ethylbenzene.[58]

$$\mathrm{O_2 + PhCH_2CH_3 + O_2 \rightarrow HO_2{}^\bullet + PhCH{=}CH_2 + HO_2{}^\bullet}$$

The rate constant for this reaction was found to be $k = 6.0 \times 10^8 \exp(-108.0/RT)\ \mathrm{L^2\,mol^{-2}\,s^{-1}}$. The values for the rate constants of the trimolecular reactions $\mathrm{2RH + O_2}$ and $\mathrm{2RCH{=}CH_2 + O_2}$ are in Table 10.5.

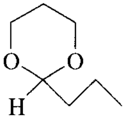
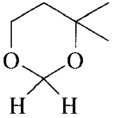
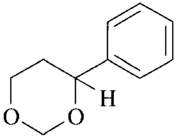
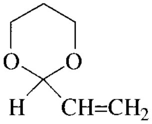
TABLE 10.5 Rate Constants and Activation Energies for the Trimolecular Reaction $2RH + O_2 \rightarrow$ Free Radicals[a]

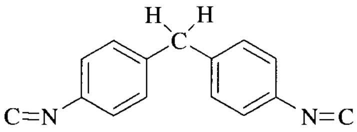
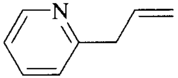
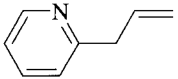
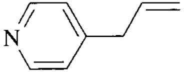
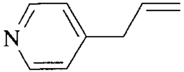
RH	Solvent	T (K)	E (kJ mol^{-1})	log A, A (L^2 mol^{-2} s^{-1})	k (400 K) (L^2 mol^{-2} s^{-1})	Reference
	$2RH + O_2 \rightarrow R^\bullet + H_2O_2 + R^\bullet$					
$CH_2{=}C(CH{-}H)(CH_2)_4Me$	1-Octene	373–393	130.0	8.73	5.67×10^{-9}	59
	Decane	403–423	86.5	3.54	1.75×10^{-8}	57
	Decane	345–365	78.5	3.59	2.18×10^{-7}	60
	Chlorobenzene	313–348	74.5	6.85	1.32×10^{-3}	61
	Benzene, 1,2-dichloro-	353			1.13×10^{-7}	28

	Chlorobenzene	353–393	114.0	9.23	2.20×10^{-6}	62
$C_6H_5C(O)-H$	Acetic acid	303			1.11×10^{-4}	63
$C_6H_5C(O)-H$	Carbon tetrachloride	300			5.42×10^{-5}	64
$MeCH=CHC(O)-H$	Decane	278–298	105.0	13.64	0.85	65
$CH_2=CMeC(O)-H$	Chlorobenzene	288–308	88.0	8.11	4.15×10^{-4}	35
	Chlorobenzene	386–393	153.2	14.60	3.93×10^{-6}	41
$[BuO]_2CH-H$	Chlorobenzene	383–413	73.0	1.54	1.02×10^{-6}	66
$[BuO]_2C-HMe$	Chlorobenzene	373–413	83.6	3.72	6.35×10^{-8}	66
$C_8H_{17}CH=CH(CH-H)(CH_2)_6\ C(O)OMe$	Chlorobenzene	313–333	142.0	12.30	5.71×10^{-7}	67
$Bu(CH_2CH=CH)_2(CH-H)\ (CH_2)_7C(O)OMe$	Chlorobenzene	313–333	93.0	6.30	1.43×10^{-6}	67
$Et(CH=CHCH-H)_3(CH_2)_6\ C(O)OMe$	Chlorobenzene	313–333	76.5	3.80	6.46×10^{-7}	67
Cholesteryl pelargonate	Chlorobenzene	364–388	73.0	5.43	7.89×10^{-5}	68

(*continued overleaf*)

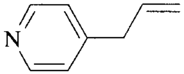
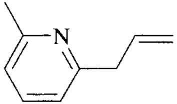
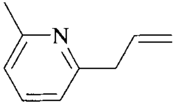
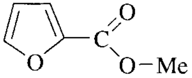
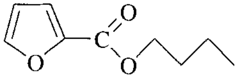
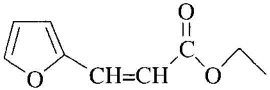
TABLE 10.5 (*continued*)

RH	Solvent	T (K)	E (kJ mol^{-1})	log A, A (L^2 mol^{-2} s^{-1})	k (400 K) (L^2 mol^{-2} s^{-1})	Reference
	Chlorobenzene	383–403	74.5	2.59	7.27×10^{-8}	69
	Chlorobenzene	343–403	60.0	0.48	4.41×10^{-8}	69
	Chlorobenzene	373–393	72.5	2.77	2.01×10^{-7}	69
	Chlorobenzene	373–393	84.0	5.08	1.29×10^{-6}	69

	Chlorobenzene	373–413	63.0	3.68	2.84×10^{-5}	70
$RCH{=}CH_2 + O_2 + CH_2{=}CHR \rightarrow R^{\bullet}CHCH_2OOCH_2CHR^{\bullet}$						
$\mathrm{PhCH{=}CH_2}$	*N*,*N*-Dimethyl-formamide	343			2.4×10^{-8}	50
$\mathrm{PhCH{=}CH_2}$	Chlorobenzene	333–353	113.2	8.53	5.59×10^{-7}	51
$\mathrm{PhMeC{=}CH_2}$	Benzonitrile	343			3.7×10^{-8}	50
$\mathrm{BuOC(O)MeC{=}CH_2}$	*N*,*N*-Dimethyl-formamide	363			6.0×10^{-8}	50
$\mathrm{MeCH{=}CHC(O)OEt}$	Chlorobenzene	363			4.2×10^{-7}	50
	Chlorobenzene	343–363	55.6	2.48	1.66×10^{-5}	50
	*N*,*N*-Dimethyl-formamide	343			1.5×10^{-6}	50
	Chlorobenzene	343–453	64.4	3.96	3.55×10^{-5}	50
	*N*,*N*-Dimethyl-formamide	343			1.3×10^{-6}	50

(*continued overleaf*)

TABLE 10.5 (*continued*)

RH	Solvent	T (K)	E (kJ mol^{-1})	log A, A (L^2 mol^{-2} s^{-1})	k (400 K) (L^2 mol^{-2} s^{-1})	Reference
	Benzene, 1,2-dichloro-	348–363	96.7	8.30	1.41×10^{-5}	50
	Chlorobenzene	343	61.5	3.86	6.75×10^{-5}	50
	*N*,*N*-Dimethyl-formamide	343			2.8×10^{-6}	50
	Chlorobenzene	303–363	54.0	1.70	4.45×10^{-6}	71
	Chlorobenzene	313–363	62.0	2.15	1.13×10^{-6}	71
	Chlorobenzene	313–363	52.0	0.26	2.95×10^{-7}	71

[a] Experimental Data.

REFERENCES

1. N. N. Semenov, *Some Problems of Chemical Kinetics and Reactivity*, Pergamon Press, London, 1958, Vol. 1; 1959, Vol. 2.
2. W. O. Landberg (Ed.), *Autooxidation and Antioxidants*, Wiley-Interscience, New York, 1962, Vols. 1 and 2.
3. N. M. Emanuel, E. T. Denisov, and Z. K. Maizus, *Liquid-Phase Oxidation of Hydrocarbons*, Plenum Press, New York, 1967.
4. C. Walling, *Free Radicals in Solution*, John Wiley & Sons, Inc., New York, 1962.
5. J. L. Bolland and G. Gee, *Trans. Faraday Soc.* **42**, 236, 244 (1946).
6. H. R. Cooper and H. W. Melville, *J. Chem. Soc.* 1984 (1951).
7. E. T. Denisov, *Zh. Fiz. Khim.* **42**, 1585 (1978).
8. E. T. Denisov, in *Comprehensive Chemical Kinetics*, C. H. Bamford and C. F. H. Tipper (Eds.), Elsevier, Amsterdam, The Netherlands, 1980, Vol. 16, p. 125.
9. L. N. Denisova and E. T. Denisov, *Kinet. Katal.* **10**, 1244 (1969).
10. T. G. Degtyareva, L. N. Denisova, and E. T. Denisov, *Kinet. Katal.*, **13**, 1400 (1972).
11. N. Ya. Shafikov, L. N. Denisova, and E. T. Denisov, *Kinet. Katal.* **16**, 872 (1975).
12. V. L. Antonovskii, E. T. Denisov, I. A. Kuznetsov, Yu. Ya. Mekhryushev, and L. V. Solntseva, *Kinet. Katal.* **6**, 607 (1965).
13. G. V. Butovskaya, V. E. Agabekov, and N. I. Mitskevich, *Dokl. AN BSSR* **25**, 722 (1981).
14. V. E. Agabekov, G. V. Butovskaya, and N. I. Mitskevich, *Neftekhimiya* **22**, 272 (1982).
15. N. N. Pozdeeva and E. T. Denisov, *Izv. AN SSSR, Ser. Khim.* 2681 (1987).
16. D. L. Baulch, C. J. Cobos, R. A. Cox, C. Esser, P. Frank, T. Just, J. A. Kerr, M. J. Pilling, J. Troe, R. W. Walker, and J. Warnatz, *J. Phys. Chem. Ref. Data* **21**, 411 (1992).
17. W. Tsang and R. F. Hampson, *J. Phys. Chem. Ref. Data* **15**, 1087 (1986).
18. R. Shaw, *J. Phys. Chem. Ref. Data* **7**, 1179 (1978).
19. G. B. Skinner, A. Lifshitz, K. Scheller, and A. Burcat, *J. Chem. Phys.* **56**, 3853 (1972).
20. S. W. Mayer and L. Schieler, *J. Phys. Chem.* **72**, 2628 (1968).
21. J. E. Taylor and D. M. Kulich, *Int. J. Chem. Kinet.* **5**, 455 (1973).
22. W. Tsang, *J. Phys. Chem. Ref. Data* **17**, 887 (1988).
23. R. R. Baldwin, G. R. Drewery, and R. W. Walker, *J. Chem. Soc., Faraday Trans. 1*, **80**, 3195 (1984).
24. W. Tsang, *J. Phys. Chem. Ref. Data* **19**, 1 (1990).
25. D. L. Baulch, C. J. Cobos, R. A. Cox, C. Esser, P. Frank, Th. Just, J. A. Kerr, M. J. Pilling, J. Troe, R. W. Walker, and J. Warnatz, *J. Phys. Chem. Ref. Data* **23**, 847 (1994).
26. T. Ingham, R. W. Walker, and R. E. Woolforel, *Symp. Int. Combust. Proc.* **25**, 767 (1994).
27. P. Mulder and R. Louw, *J. Chem. Soc., Perkin Trans 2*, 1135 (1985).

28. V. A. Machtin, M. I. Mishustina, E. M. Pliss, L. A. Kashina, and V. I. Mishustin, *Vestn. VVOATN RF, Ser. Khim. Khim. Techn.*, 1996, p. 63.
29. A. A. Kutuev and N. I. Terpilovskii, *Kinet. Katal.* **16**, 372 (1976).
30. W. Tsang, *J. Phys. Chem. Ref. Data* **16**, 471 (1987).
31. R. R. Baldwin, A. R. Fuller, D. Longthorn, and R. W. Walker, *J. Chem. Soc., Faraday Trans 1*, **70**, 1257 (1974).
32. B. I. Chernyak and L. A. Andrianova, *Neftekhimiya* **14**, 97 (1974).
33. G. V. Butovskaya, V. E. Agabekov, O. P. Dmitrieva, and N. I. Mitskevich, *Dokl. AN BSSR* **20**, 1103 (1976).
34. T. Hava, Y. Ohkatsu and T. Osa, *Chem. Lett.* 1973 (1953).
35. M. A. Maaraui, *Synthesis of alkylacroleins and study of its liquid phase oxidation*, Ph.D. Thesis (Russian), L'vov Polytech. Institute, L'vov, USSR, 1978.
36. M. A. Maaraui, D. K. Tolopko, and B. I. Chernyak, *Kinet. Katal.* **18**, 224 (1977).
37. M. A. Maaraui, B. I. Chernyak, and M. V. Nikipanchuk, *Zh. Org. Khim.* **16**, 1573 (1978).
38. G. V. Butovskaya, V. E. Agabekov, and N. I. Mitskevich, *Dokl. AN BSSR* **22**, 155 (1978).
39. G. V. Butovskaya, V. E. Agabekov, and N. I. Mitskevich, *Izv. AN BSSR, Ser. Khim.* 36 (1981).
40. S. G. Voronina, A. L. Perkel', and B. G. Freidin, *Kinet. Katal.* **33**, 266 (1992).
41. V. E. Agabekov, G. V. Butovskaya, and N. I. Mitskevich, *Neftekhimiya* **22**, 272 (1982).
42. G. V. Butovskaya, V. E. Agabekov, and N. I. Mitskevich, *React. Kinetic. Catal. Lett.* **4**, 105 (1976).
43. L. N. Denisova and E. T. Denisov, *Kinet. Katal.* **17**, 596 (1976).
44. E. T. Denisov, *Itogi Nauki i Tekhniki, Ser. Kinetika i Kataliz* (Russian), VINITI, Moscow, 1981, Vol. 9.
45. E. H. Farmer, *Trans. Faraday Soc.* **42**, 228 (1946).
46. A. A. Miller and F. R. Mayo, *J. Am. Chem. Soc.* **78**, 1017 (1956).
47. L. N. Denisova and E. T. Denisov, *Izv. AN SSSR, Ser. Khim.* 1702 (1965).
48. E. M. Pliss, V. M. Troshin, and E. T. Denisov, *Dokl. AN SSSR* **264**, 368 (1982).
49. E. M. Pliss and V. M. Troshin, *Neftekhimiya* **22**, 539 (1982).
50. M. M. Mogilevich and E. M. Pliss, *Oxidation and Oxidative Polymerisation of Nonsaturated Compounds* (Russian), Khimiya, Moscow, 1990.
51. V. A. Machtin, M. I. Mishustina, and E. M. Pliss, *Vestn. VVO ATN RF, Ser. Khim. and Khim. Techn.* 59 (1996).
52. A. V. Sokolov, E. M. Pliss, and E. T. Denisov, *Izv. AN SSSR, Ser. Khim.* 293 (1988).
53. E. I. Finkel'shteyn, N. A. Mednikova, I. S. Panasenko, and E. I. Kozlov, *Zh. Org. Khim.* **17**, 933 (1981).
54. A. B. Gagarina, O. T. Kasaikina, and N. M. Emanuel, *Dokl. AN SSSR* **212**, 399 (1973).
55. E. T. Denisov, *Dokl. AN SSSR* **130**, 1055 (1960).
56. E. T. Denisov, *Dokl. AN SSSR* **141**, 131 (1961).

57. E. T. Denisov, *Kinet. Katal.* **4**, 53 (1963).
58. L. N. Denisova, N. N. Shafikov, and E. T. Denisov, *Dokl. AN SSSR* **213**, 376 (1973).
59. B. I. Chernyak, M. V. Nikipanchuk, M. G. Kotur, and S. I. Kozak, *Kinet. Katal.* **37**, 818 (1996).
60. D. J. Carlsson, and J. C. Robb, *Trans. Faraday Soc.* **62**, 3403 (1966).
61. R. L. Vardanyan, I. G. Verner, and E. T. Denisov, *Kinet. Katal.* **14**, 575 (1973).
62. V. E. Agabekov, *The reactions and reactivity of oxygen-containing compounds in free radical reactions of oxidation*, Doctor Diss. Thesis (Russian), Institute of Chemical Physics, Chernogolovka, USSR, 1980.
63. E. Boga and F. Marta, *Acta Chim. Acad. Sci. Hung.* **78**, 105 (1973).
64. I. N. Komissarova, V. D. Komissarov, and E. T. Denisov, *Izv. AN SSSR, Ser. Khim.* 1991 (1978).
65. M. A. Maaraui, M. V. Nikipanchuk, and B. I. Chernyak, *Kinet. Katal.* **19**, 499 (1978).
66. S. A. Agisheva, S. S. Zlotskii, U. B. Imashev, and D. L. Rakhmankulov, *Izv. Vuzov, Ser. Khim. Khim. Technol.* **21**, 807 (1978).
67. N. Yanishilieva, I. P. Skibida, and Z. K. Maizus, *Izv. Otd. Khim. Nauk Bulg. AN*, **4**, 1 (1971).
68. G. E. Dingchan, N. S. Khanukova, and R. L. Vardanyan, *Arm. Khim. Zh.* **30**, 644 (1977).
69. D. L. Rakhmankulov, V. V. Zorin, E. M. Kuramshin, and S. S. Zlotskii, *Rate Constants of Homolytic Liquid-Phase Reactions of 1,3-Diheterocycloalkanes and Analogs*, Ufa, Reactiv, 1999.
70. Yu. A. Aleksandrov, G. B. Sadikov, I. L. Chelnokova, and V. G. Golov, *Zh. Org. Khim.* **12**, 855 (1976).
71. V. D. Sukhov and M. M. Mogilevich, *Zh. Fiz. Khim.* **53**, 1477 (1979).

Handbook of Free Radical Initiators. E.T. Denisov, T.G. Denisova, T.S. Pokidova
Copyright © 2003 John Wiley & Sons, Inc.
ISBN: 0-471-20753-5

11

BIMOLECULAR REACTIONS OF FREE RADICAL GENERATION BY OZONE

11.1 INITIATION OF RADICALS BY OZONE REACTIONS

Ozone is known to be a very active oxidizing agent. It reacts extremely fast with olefins and organometallic compounds without free radicals formation.[1–5] Reactions of ozone with C—H bonds of hydrocarbons, alcohols, ethers, and esters occur with free radical formation that was proved by different experimental methods.

1. Ozone initiates the chain oxidation of hydrocarbons in the gas and liquid phase.[6–10]
2. Peroxyl radicals were identified in the reaction of hydrocarbon and polymer oxidation by the O_3-O_2 mixture that was proved by EPR spectroscopy.[11,12]
3. Ozone induces chemiluminescence in oxidized hydrocarbons, RH, as a result of disproportionation of formed peroxyl radicals.[2,8,13] This reaction produces a carbonyl compound in the triplet state, the latter is the source of luminescence.
4. Oxidation of hydrocarbons in a tetrachloride solution produces alkyl chloride due to the following reaction:[14–17]

$$R^{\bullet} + CCl_4 \rightarrow RCl + C^{\bullet}Cl_3$$

Hydrogen chloride is formed in the oxidation of alcohols by ozone in carbon tetrachloride as a solvent due to the following reaction:[18]

$$R^1R^2C^{\bullet}OH + CCl_4 \rightarrow R^1R^2C{=}O + HCl + C^{\bullet}Cl_3$$

The initiation of free radical reactions by ozone in the gas phase at elevated temperatures occurs as the result of ozone monomolecular decomposition[19,20]

$$\mathrm{M + O_3 \rightarrow O_2 + O + M}$$

accompanied by the reaction

$$\mathrm{O + RH \rightarrow R^{\bullet} + HO^{\bullet}}$$

The enthalpy of ozone decomposition $\Delta H = D_{\mathrm{O_2-O}} = 107\ \mathrm{kJ\,mol^{-1}}$. The most probable reaction of initiation by ozone in solution is the abstraction reaction[21]

$$\mathrm{RH + O_3 \rightarrow [R^{\bullet} + HO_3{}^{\bullet}]}$$

$$\mathrm{[R^{\bullet} + HO_3{}^{\bullet}] \rightarrow R^{\bullet} + HO_3{}^{\bullet}}$$

$$\mathrm{[R^{\bullet} + HO_3{}^{\bullet}] \rightarrow ROOOH}$$

accompanied by the fast decomposition of unstable ROOOH and hydrotrioxide radical.

$$\mathrm{HO_3{}^{\bullet} \rightarrow HO^{\bullet} + O_2}$$

$$\mathrm{ROOOH \rightarrow RO_2{}^{\bullet} + HO^{\bullet}}$$

The rate constant of $\mathrm{HO_3{}^{\bullet}}$ decay is $k \approx 10^{10}\ \mathrm{s^{-1}}$ (300 K, quantum chemical calculation).[22]

The kinetic isotope effect proves the attack of ozone on the C—H and consequently on the C—D bond of the oxidized compound. The values of the kinetic isotope effect (k_H/k_D) are collected in Table 11.1.

Carbonyl compounds probably are oxidized by ozone with the formation of an unstable intermediate tetroxide[16]

$$\mathrm{RCHO + O_3 \Leftrightarrow RCHO_4}$$

$$\mathrm{RCHO_4 \rightarrow RC(O)OOOH}$$

$$\mathrm{RC(O)OOOH \rightarrow RC(O)OH + {}^1O_2}$$

in addition to direct hydrogen atom abstraction.

$$\mathrm{RC(O)H + O_3 \rightarrow RC^{\bullet}(O) + HO_3{}^{\bullet}}$$

The evidence for cyclic tetroxide formation is in the exchange between the labeled carbonyl group and ozone by ^{18}O (heptane, 195 K).[27]

$$\mathrm{R^1R^2C{=}O^{18} + O_3 \Leftrightarrow R^1R^2CO_4 \Leftrightarrow R^1R^2C{=}O + O_3{}^{18}}$$

The formation of free radicals in solution by the reaction of RH with ozone is accompanied by the cage effect.

TABLE 11.1 Kinetic Isotope Effect in Oxidation of Aliphatic Compounds by Ozone

Gas	RD	Solvent	T(K)	k_H/k_D	Reference
O_3-O_2	*cyclo*-C_6D_{12}	Carbon tetrachloride	295	4.5	13
O_3-O_2	*cyclo*-C_6D_{12}	Carbon tetrachloride	300	5.4	23
O_3-O_2	$PhCD_2OCMe_3$	Freon-11	273	4.1	24
O_3-O_2	$PhCD_2OCMe_3$	Freon-11	351	6.3	24
O_3-N_2	$PhCD_2OCMe_3$	Freon-11	273	3.8	24
O_3-N_2	$PhCD_2OCMe_3$	Freon-11	195	6.7	24
O_3-O_2	$PhCD_2OCMe_3$	Freon-11/Pyridine	195	4.2	24
O_3-N_2	$PhCD_2OCMe_3$	Freon-11/Pyridine	195	3.7	24
O_3-N_2	$PhCD_2OCMe_3$	Dichloromethane/Acetone	195	3.2	24
O_3-O_2	$PhCD_2OCMe_3$	Acetone	273	4.5	24
O_3-He	$PhCD_2OCMe_3$	Acetone	273	2.4	24
O_3-O_2	$PhCD_2OCMe_3$	Pyridine	273	2.6	24
O_3-N_2	Ph(cod)[a]	Butanone-2	273	1.4	25
O_3-N_2	Ph(cod)[a]	Carbon tetrachloride	273	2.2	25
O_3-N_2	Ph(cod)[a]	Pyridine	273	2.0	25
O_3-O_2	$MeCD_2OH$	Chloroform	293	5.9	26
O_3-O_2	CD_3CH_2OH	Carbon tetrachloride	293	1.2	26
O_3-O_2	$MeCH_2OD$	Carbon tetrachloride	293	0.9	26
O_3-O_2	CD_3CD_2OD	Carbon tetrachloride	293	7.1	26
O_3-O_2	$MeCH_2OD$	D_2O	293	1.2	26
O_3-O_2	CD_3CD_2OD	D_2O	293	6.3	26

[a] cod = 1,5-Cyclooctadiene (ligand).

$$RH + O_3 \Leftrightarrow [R^\bullet + HO_3{}^\bullet]$$

$$[R^\bullet + HO_3{}^\bullet] \rightarrow R^\bullet + HO_3{}^\bullet$$

$$[R^\bullet + HO_3{}^\bullet] \rightarrow ROOOH$$

$$HO_3{}^\bullet \rightarrow HO^\bullet + O_2$$

$$HO^\bullet + RH \rightarrow H_2O + R^\bullet$$

$$ROOOH \rightarrow RO_2{}^\bullet + HO^\bullet$$

A detailed study of the mechanism for free radical initiation (rate constant k_i) and ozone decay (rate constant k_d) by the reaction of cyclohexane, cumene, and aldehydes gave the following results (298 K):

RH	*cyclo*-C_6H_{12}	Me_2PhCH	$Me_2PhCOOH$	PhCH(O)	MeCH(O)
k_i(L mol^{-1} s^{-1})	1.1×10^{-3}	1.6×10^{-2}	0.15	2.0	1.6
k_d(L mol^{-1} s^{-1})	1.8×10^{-3}	0.32	0.11	2.0	2.7
e	0.30	2.5×10^{-2}	0.68	0.50	0.30
References	28	29	30	31	31

The very low yield of radicals from the reaction of ozone with cumene was found to be the result of an intensive ozone reaction with the benzene ring of cumene to yield molozonide formation. The values for parameter *e* in other reactions are typical of the cage effect of radical pairs in solutions. The rate constant values of ozone reactions with various compounds are presented in Table 11.2.

11.2 CHAIN REACTIONS OF OZONE DECOMPOSITION

Ozone as a very strong oxidizing agent reacts very rapidly with free radicals. Reactions of ozone with atoms and small radicals ($HO^•$, $N^•O_2$, $HO_2{}^•$) were the object of intensive study due to their important role in the chemistry of the stratosphere. For the values of rate constant for these reactions, see Ref. 43.

Due to high activity in reactions with free radicals, ozone undergoes chain decomposition in solutions. The chain reaction of ozone decomposition was found in 1973 in the kinetic study of cyclohexane and butanone-2 oxidation by a mixture of O_2/O_3.[44–50] It was observed that the rate of ozone consumption obeys Eq. (11.1).[28]

$$v_{O_3} = k_1[RH][O_3] + k_2[RH][O_3]^2[O_2]^{-1} \qquad (11.1)$$

The first term characterizes the rate of the ozone reaction with the substrate and the second term characterizes the reaction with chain propagation

$$R^• + O_3 \rightarrow RO^• + O_2$$

and with chain termination in the reactions

$$R^• + O_2 \rightarrow RO_2{}^•$$

$$RO_2{}^• + RO_2{}^• \rightarrow ROH + O_2 + R^1C(O)R^2$$

Chain decomposition of ozone was also observed in the oxidation of cumene by an O_3/O_2 mixture.[50] The rate of ozone consumption was found to be

$$v_{O_3} = k_1[RH][O_3] + k_2[RH]^{1/2}[O_3]^{3/2} \qquad (11.2)$$

with $k_1 = 1.0\ \mathrm{L\,mol^{-1}\,s^{-1}}, k_2 = 18.0\ \mathrm{L\,mol^{-1}\,s^{-1}}$(cumene, 395 K).[50]

The second term characterizes the chain decomposition of ozone. The mechanism of chain reaction was found to include the following reactions:

$$RH + O_3 \rightarrow R^• + HO_3{}^•$$

$$HO_3{}^• \rightarrow HO^• + O_2$$

$$HO^• + RH \rightarrow H_2O + R^•$$

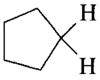
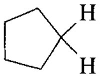
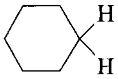
$$R^• + O_2 \rightarrow RO_2{}^•$$

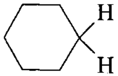
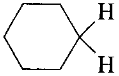
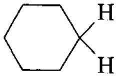
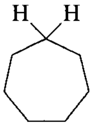
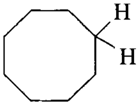
TABLE 11.2 Rate Constants of Ozone Reaction with Organic Compounds[a]

RH	Solvent	T(K)	E (kJ mol^{-1})	log A, A (L mol^{-1} s^{-1})	k (L mol^{-1} s^{-1})	Reference
Me_3CH	Carbon tetrachloride	298			8.7×10^{-2}	32
$Me(CH_2)_3Me$	Carbon tetrachloride	293			1.5×10^{-2}	33
$Me(CH_2)_3Me$	Carbon tetrachloride	298			6.5×10^{-3}	32
Me_3CCH_3	Carbon tetrachloride	298			3.8×10^{-5}	32
$Me(CH_2)_4Me$	Carbon tetrachloride	293	51.3	7.42	1.9×10^{-2}	33
$Me_2CHCHMe_2$	Carbon tetrachloride	298			0.20	32
Et_2CHMe	Carbon tetrachloride	298			0.10	32
Et_2CHMe	Carbon tetrachloride	293			0.15	33
$Me(CH_2)_5Me$	Carbon tetrachloride	293	52.0	7.67	2.1×10^{-2}	33
$Me_2CHCHMeEt$	Carbon tetrachloride	293			0.29	33
$Me_2CHCH_2CHMe_2$	Carbon tetrachloride	293			8.0×10^{-2}	33
$Me_2CH(CH_2)_3Me$	Carbon tetrachloride	293			0.13	33
$EtMeCH(CH_2)_2Me$	Carbon tetrachloride	293			0.20	33
$Me(CH_2)_6Me$	Carbon tetrachloride	298			1.4×10^{-2}	32
$Me(CH_2)_6Me$	Carbon tetrachloride	293	52.0	7.63	2.3×10^{-2}	33
$Me(CH_2)_6Me$	Carbon tetrachloride	298			1.4×10^{-2}	32
$Me_3CCHMeEt$	Carbon tetrachloride	293			0.59	33
$Me_3C(CH_2)_3Me$	Carbon tetrachloride	293			1.5×10^{-2}	33
Me_3CCMe_3	Octane	293			2.0×10^{-4}	33
$Me(CH_2)_7Me$	Carbon tetrachloride	293			2.6×10^{-2}	33
$Me_3CHCH_2CHMeEt$	Carbon tetrachloride	293			0.13	33

(*continued overleaf*)

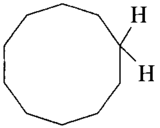
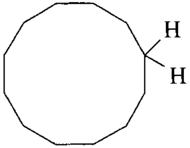
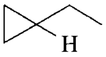
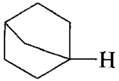
TABLE 11.2 (*continued*)

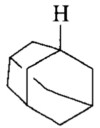
RH	Solvent	T(K)	E (kJ mol^{-1})	log A, A (L mol^{-1} s^{-1})	k (L mol^{-1} s^{-1})	Reference
$MeEtCH(CH_2)_5Me$	Carbon tetrachloride	293			0.20	33
$Me_3C(CH_2)_2CHMe_2$	Carbon tetrachloride	293			0.19	33
$Me(CH_2)_8Me$	Carbon tetrachloride	293	50.7	7.51	2.91×10^{-2}	33
$Me(CH_2)_8Me$	Carbon tetrachloride	293	56.5	8.60	3.33×10^{-2}	34
$Me(CH_2)_{12}Me$	Carbon tetrachloride	293			3.61×10^{-2}	33
$Me(CH_2)_{16}Me$	Carbon tetrachloride	293			4.62×10^{-2}	33
	Carbon tetrachloride	293			2.61×10^{-2}	32
	Carbon tetrachloride	293	51.2	7.52	2.50×10^{-2}	34
	Carbon tetrachloride	298			1.05×10^{-2}	32

	Carbon tetrachloride	298	56.9	7.83	4.81×10^{-3}	18
	Carbon tetrachloride	293	54.9	8.03	1.72×10^{-2}	34
	Carbon tetrachloride	293	57.7	8.30	1.04×10^{-2}	23
	Carbon tetrachloride	293	45.4	7.45	0.23	23
	Carbon tetrachloride	293	43.0	7.34	0.48	23

(continued overleaf)

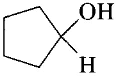
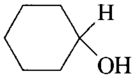
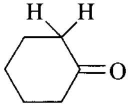
TABLE 11.2 (*continued*)

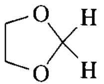
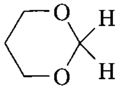
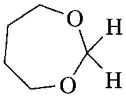
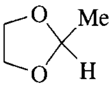
RH	Solvent	T(K)	E (kJ mol^{-1})	log A, A (L mol^{-1} s^{-1})	k (L mol^{-1} s^{-1})	Reference
	Carbon tetrachloride	293	54.7	9.36	0.41	23
	Carbon tetrachloride	293	59.0	9.32	6.22×10^{-2}	33
	Carbon tetrachloride	293			5.01×10^{-2}	33
	Carbon tetrachloride	293	56.6	8.25	1.42×10^{-2}	33
	Carbon tetrachloride	293			1.41×10^{-2}	33

	Carbon tetrachloride	293			0.22	33
PhMe	Acetic acid	294	40.0	7.01	0.80	35
1,2-$Me_2-C_6H_4$	Acetic acid	294			2.85	36
1,3-$Me_2-C_6H_4$	Acetic acid	294			4.15	36
1,4-$Me_2-C_6H_4$	Acetic acid	294			5.08	36
1,3,5-$Me_3-C_6H_3$	Acetic acid	294			45.0	36
1,2,4-$Me_3-C_6H_3$	Acetic acid	294			27.2	36
1,2,4,5-$Me_4-C_6H_2$	Acetic acid	294			87.2	36
4-$Br-C_6H_4Me$	Acetic acid	294			0.48	36
4-$Cl-C_6H_4Me$	Acetic acid	294			0.41	36
2-$NO_2-C_6H_4Me$	Acetic acid	294			2.3×10^{-2}	37
3-$NO_2-C_6H_4Me$	Acetic acid	294			3.5×10^{-2}	37
4-$NO_2-C_6H_4Me$	Acetic acid	294			3.2×10^{-2}	37
$PhCH_2Me$	Carbon tetrachloride	293	33.4	5.78	0.67	34
$PhCH_2Me$	Acetic acid	294			1.12	38
$PhCHMe_2$	Carbon tetrachloride	293	35.0	6.02	0.60	34
Ph_2CH_2	Carbon tetrachloride	293	39.2	6.60	0.41	34

(*continued overleaf*)

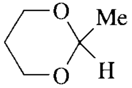
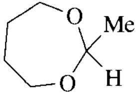
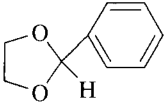
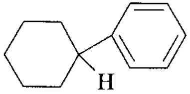
TABLE 11.2 (*continued*)

RH	Solvent	T(K)	E (kJ mol^{-1})	log A, A (L mol^{-1} s^{-1})	k (L mol^{-1} s^{-1})	Reference
$MeCH_2OH$	Carbon tetrachloride	298	40.2	6.72	0.35	39
Me_2CHOH	Carbon tetrachloride	298	41.2	7.30	0.89	39
$MeCH(OH)CH_2Me$	Carbon tetrachloride	298	38.8	7.12	1.61	39
$PrCH_2OH$	Carbon tetrachloride	298			0.39	32
$PrCH_2OH$	Carbon tetrachloride	298	42.4	7.30	0.54	39
$PhMe_2COH$	Carbon tetrachloride	298	27.6	4.82	0.78	29
Me_3COH	Carbon tetrachloride	298			5.0×10^{-2}	32
Me_3COH	Carbon tetrachloride	298	37.1	4.63	1.02×10^{-2}	39
	Carbon tetrachloride	298			1.35	32
	Carbon tetrachloride	298	34.5	6.62	2.92	18
$MeC(O)CH_2Me$	Carbon tetrachloride	293	69.8	9.56	1.30×10^{-3}	40
$MeC(O)CH_2Me$	Water	313			8.5×10^{-3}	41
	Carbon tetrachloride	295			5.9×10^{-3}	18
PhCHO	Carbon tetrachloride	282	38.2	7.42	2.21	31

PhCHO	Carbon tetrachloride	300			5.92	31
MeCHO	Carbon tetrachloride	300			4.30	31
	Carbon tetrachloride	298			10.1	42
	Carbon tetrachloride	298			0.90	42
	Carbon tetrachloride	298	32.1	6.30	4.70	42
	Carbon tetrachloride	298	31.7	6.92	23.0	42

(continued overleaf)

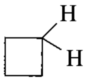
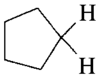
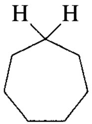
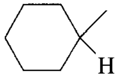
TABLE 11.2 (*continued*)

RH	Solvent	T(K)	E (kJ mol^{-1})	log A, A (L mol^{-1} s^{-1})	k (L mol^{-1} s^{-1})	Reference
	Carbon tetrachloride	298	30.1	6.03	5.7	42
	Carbon tetrachloride	298			11.5	42
	Carbon tetrachloride	298			56.3	42
	Carbon tetrachloride	298			19.5	42

---

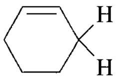
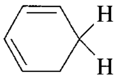
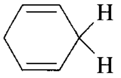
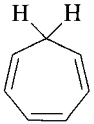
[a] Experimental data.

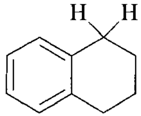
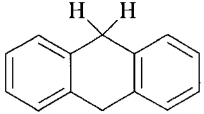
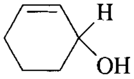
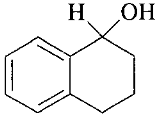
TABLE 11.3 Rate Constants and Activation Energies for the Reaction RH + O_3 → $R^\bullet + HO_3^\bullet$ in Hydrocarbon Solution Calculated by the IPM Method (Eqs. 9.13, 9.15, and 9.16, Tables 9.1 and 9.2)[a]

RH	D (kJ mol^{-1})	n	ΔH_e (kJ mol^{-1})	E (kJ mol^{-1})	log A, A (L mol^{-1} s^{-1})	k (300 K) (L mol^{-1} s^{-1})
EtMeCH−H	413.0	4	66.2	74.9	9.60	3.62×10^{-4}
Me_3C−H	400.0	1	53.2	67.2	9.00	1.99×10^{-3}
	418.5	8	71.7	78.3	9.90	1.85×10^{-4}
	408.4	10	61.6	72.1	10.00	2.80×10^{-3}
	403.9	14	57.1	69.5	10.15	1.12×10^{-2}
	395.5	1	48.7	64.7	9.00	5.43×10^{-3}
(Z)-Decalin	387.6	2	40.8	60.3	9.30	6.32×10^{-2}
CH_2=$CHCH_2$−H	368.0	3	21.2	63.9	8.48	2.26×10^{-3}
CH_2=CHMeCH−H	349.8	2	3.0	55.4	8.30	4.51×10^{-2}
CH_2=$CHMe_2C$−H	339.6	1	−7.2	50.8	8.00	0.14
(Z)-MeCH=CHMeCH−H	344.0	2	−2.8	52.8	9.30	1.28

(*continued overleaf*)

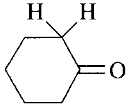
TABLE 11.3 (*continued*)

RH	D (kJ mol^{-1})	n	ΔH_e (kJ mol^{-1})	E (kJ mol^{-1})	log A, A (L mol^{-1} s^{-1})	k (300 K) (L mol^{-1} s^{-1})
$Me_2C{=}CHMeCH{-}H$	332.0	2	−14.8	47.6	8.30	1.03
$Me_2C{=}CMeMe_2C{-}H$	322.8	1	−24.0	43.7	8.00	2.46
$(CH_2{=}CH)_2CMe{-}H$	307.2	1	−39.6	37.6	8.00	28.4
	341.5	4	−5.3	51.7	9.60	3.97
	330.9	4	−15.9	47.1	9.60	25.1
	312.6	4	−34.2	39.6	9.60	5.07×10^2
	301.0	2	−45.8	35.2	9.30	1.47×10^3
$MeC{\equiv}CMe_2C{-}H$	329.4	1	−17.4	46.5	8.00	0.80
$PhMeCH{-}H$	364.1	2	17.3	54.2	8.30	7.31×10^{-2}
$PhMe_2C{-}H$	354.7	1	7.9	49.7	8.00	0.22

	345.6	4	−1.2	45.6	9.60	45.7
	322.0	4	−24.8	35.6	9.60	2.52×10^3
Me_2NH_2C-H	379.5	1	32.7	56.0	9.00	0.18
$(CH_2=CHCH-H)_3N$	345.6	6	−1.2	53.5	8.78	0.29
$Me_2(HO)C-H$	390.5	1	4.4	61.9	9.00	1.67×10^{-2}
	329.7	1	−17.1	32.7	9.00	2.02×10^3
MeCH=CMeC−HMeOH	325.2	1	−21.6	44.7	8.00	1.65
	337.5	1	−9.3	42.0	9.00	48.7
PhC(O)−H	348.0	1	1.2	54.5	9.00	0.32

(*continued overleaf*)

TABLE 11.3 (*continued*)

RH	D (kJ mol^{-1})	n	ΔH_e (kJ mol^{-1})	E (kJ mol^{-1})	log A, A (L mol^{-1} s^{-1})	k (300 K) (L mol^{-1} s^{-1})
	394.1	4	47.3	63.9	9.60	2.98×10^{-2}
$Me_2CHOC-HMe_2$	390.8	2	44.0	62.0	9.30	3.21×10^{-2}
$(CH_2=CHCH-H)_2O$	360.0	4	13.2	60.1	8.60	1.37×10^{-2}
$Ph_2C-HOMe$	354.2	1	7.4	49.5	8.00	0.24
$PhC(O)OCH_2-H$	367.0	2	20.2	55.6	8.30	4.17×10^{-2}
Me_3COO-H	358.6	1	15.6	31.2	9.00	3.69×10^{3}
$(Me_3C)_3Si-H$	351.0	1	−1.0	46.5	9.00	8.01
Ph_3Ge-H	322.5	1	−29.1	43.3	9.00	28.9
Ph_3Sn-H	296.9	1	−55.2	31.2	9.00	3.69×10^{3}

---

[a] See Chapter 9.

$$\mathrm{RO_2^{\bullet} + O_3 \rightarrow RO^{\bullet} + 2O_2}$$
$$\mathrm{RO^{\bullet} \rightarrow PhC(O)Me + C^{\bullet}H_3}$$
$$\mathrm{CH_3^{\bullet} + O_2 \rightarrow CH_3O_2^{\bullet}}$$
$$\mathrm{CH_3O_2^{\bullet} + O_3 \rightarrow CH_3O^{\bullet} + 2O_2}$$
$$\mathrm{CH_3O^{\bullet} + RH \rightarrow CH_3OH + R^{\bullet}}$$
$$\mathrm{CH_3O_2^{\bullet} + RO_2^{\bullet} \rightarrow CH_2O + O_2 + ROH}$$

A similar kinetic scheme was proposed for the ozone reaction with acetaldehyde.[49] The reaction rate obeys Eq. (11.3)

$$v_{O_3} = k_1[\mathrm{MeCHO}][\mathrm{O_3}] + k_2[\mathrm{MeCHO}]^{1/2}[\mathrm{O_3}]^{3/2} \tag{11.3}$$

with $k_1 = 4.3\ \mathrm{L\,mol^{-1}\,s^{-1}}$, $k_2 = 15.0\ \mathrm{L\,mol^{-1}\,s^{-1}}$ ($\mathrm{CCl_4}$, 300 K).[49]

A more complicated kinetic equation was found for ozone consumption in oxidized cyclohexane (295 K, $\mathrm{CCl_4}$).[44]

$$v_{O_3} = 3.2 \times 10^{-3}[\mathrm{RH}][\mathrm{O_3}] + 0.3[\mathrm{RH}]^{1/2}[\mathrm{O_3}]^{3/2} + 0.75[\mathrm{RH}][\mathrm{O_3}]^2[\mathrm{O_2}]^{-1} \tag{11.4}$$

The first term characterizes the initiation of free radicals by the reaction of ozone with cyclohexane, the second chain reaction with chain propagation

$$\mathrm{RO_2^{\bullet} + O_3 \rightarrow RO^{\bullet} + 2O_2}$$

and the third one with chain propagation by the reaction

$$\mathrm{R^{\bullet} + O_3 \rightarrow RO^{\bullet} + O_2}$$

Ozone chain decomposition occurs in the reaction of ozone with cumyl hydroperoxide.[44] The rate of this reaction is

$$v_{O_3} = k_1[\mathrm{ROOH}][\mathrm{O_3}] + k_2[\mathrm{ROOH}]^{1/2}[\mathrm{O_3}]^{3/2} \tag{11.5}$$

where $k_1 = 1.0\ \mathrm{L\,mol^{-1}\,s^{-1}}$ and $k_2 = 18.0\ \mathrm{L\,mol^{-1}\,s^{-1}}$ ($\mathrm{CCl_4}$, 298 K).[44] The chain reaction includes the following steps:

$$\mathrm{ROOH + O_3 \rightarrow RO_2^{\bullet} + HO_3^{\bullet}}$$
$$\mathrm{RO_2^{\bullet} + O_3 \rightarrow RO^{\bullet} + 2O_2}$$
$$\mathrm{HO^{\bullet} + ROOH \rightarrow H_2O + RO_2^{\bullet}}$$
$$\mathrm{RO^{\bullet} + ROOH \rightarrow ROH + RO_2^{\bullet}}$$
$$\mathrm{RO^{\bullet} + O_3 \rightarrow RO_2^{\bullet} + O_2}$$
$$\mathrm{RO_2^{\bullet} + RO_2^{\bullet} \rightarrow 2RO^{\bullet} + O_2}$$
$$\mathrm{RO_2^{\bullet} + RO_2^{\bullet} \rightarrow ROOR + O_2}$$

TABLE 11.4 Rate Constants for Free Radical Reactions with Ozone[a]

Radical	Phase, Solvent	T(K)	E (kJ mol^{-1})	log A, A (L mol^{-1} s^{-1})	k(298 K) (L mol^{-1} s^{-1})	Reference
$C^{\bullet}H_3$	Gas phase	298			1.57×10^9	51
$CH_3C^{\bullet}H_2$	Gas phase	298			2.0×10^7	52
$Me_3C^{\bullet}$	Carbon tetrachloride	298			3.28×10^{10}	53
cyclo-$C_6H_{11}^{\bullet}$	Carbon tetrachloride	295			5.0×10^8	44
$MeC(O)C^{\bullet}HMe$	Carbon tetrachloride	413			4.0×10^9	44
$C^{\bullet}H_2SH$	Gas phase	298			2.11×10^{10}	43
$MeO^{\bullet}$	Gas phase	298			$<1.21 \times 10^6$	54
$MeS^{\bullet}$	Gas phase	298–360	−2.4	9.08	3.19×10^9	43
$MeS^{\bullet}$	Gas phase	295–359	−2.4	9.07	3.10×10^9	55
$HO_2^{\bullet}$	Gas phase		8.4	7.30	6.74×10^5	56
$HO_2^{\bullet}$	Gas phase	300	.		1.8×10^6	57
$MeO_2^{\bullet}$	Gas phase	296			6.03×10^3	58
$MeO_2^{\bullet}$	Carbon tetrachloride	300			6.0×10^4	49
$MeO_2^{\bullet}$	Carbon tetrachloride	313–338	25	8.90	3.30×10^4	50
cyclo-$C_6H_{11}O_2^{\bullet}$	Carbon tetrachloride	295			5.0×10^3	47
$Me_2PhCO_2^{\bullet}$	Carbon tetrachloride	295			1.7×10^3	48

[a] Experimental data.

For the values of the rate constants for the free radical reactions with ozone in the gas and liquid phase, see Table 11.4.

So, three different chain reactions of ozone decomposition were observed in solutions:

1. Reaction with chain propagation.

$$R^{\bullet} + O_3 \rightarrow RO^{\bullet} + O_2$$

2. Reaction with chain propagation.

$$RO^{\bullet} + O_3 \rightarrow RO_2{}^{\bullet} + O_2$$

$$RO_2{}^{\bullet} + RO_2{}^{\bullet} \rightarrow 2RO^{\bullet} + O_2$$

3. Reaction with chain propagation.

$$RO_2{}^{\bullet} + O_3 \rightarrow RO^{\bullet} + 2O_2$$

REFERENCES

1. A. Rieche, *Peroxide und Ozonide*, Erlangen, Berlin, 1931.
2. S. D. Razumovskii and G. E. Zaikov, *Ozone Reactions with Organic Compounds (Russian)*, Nauka, Moscow, 1974.
3. R. S. Bailey, *Ozonation in Organic Chemistry*, Academic Press, New York, 1978, Vol. 1.
4. M. C. Whiting, A. J. Bolt, and J. H. Parish, *Adv. Chem. Ser.* **77**, 4 (1968).
5. G. A. Hamilton, B. S. Ribner, and T. M. Hellman, *Adv. Chem. Ser.* **77**, 15 (1968).
6. V. Ya. Shtern, *Mechanism of Hydrocarbons Oxidation in Gas Phase (Russian)*, Izd-vo AN SSSR, Moscow, 1960.
7. N. M. Emanuel, E. T. Denisov, and Z. K. Maizus, *Liquid-Phase Oxidation of Hydrocarbons*, Plenum Press, New York, 1967.
8. G. Wagner, *J. Pract. Chem.* **27**, 297 (1965).
9. E. T. Denisov and V. V. Kharitonov, *Dokl. AN SSSR* **132**, 595 (1960).
10. E. Briner, *Adv. Chem. Ser.* **21**, 184 (1959).
11. V. V. Shereshovets, E. E. Zaev, and V. D. Komissarov, *Izv. AN SSSR, Ser. Khim.* 983 (1975).
12. S. K. Rakovsky, S. D. Razumovskii, and G. E. Zaikov, *Izv. AN SSSR, Ser. Khim.* 701 (1976).
13. R. F. Vasiliev, S. M. Petukhov, and P. I. Zhuchkova, *Optiko-mekhanich. prom.* N **37**, 2 (1963).
14. A. V. Ruban, S. K. Rakovsky, and A. A. Popov, *Izv. AN SSSR, Ser. Khim.* 1950 (1976).
15. D. Barnard, G. P. McSweeney, and J. F. Smith, *Tetrahedron Lett.* N **1**, 1 (1960).

16. H. M. White and P. S. Bailey, *J. Org. Chem.* **30**, 3037 (1965).
17. T. M. Hellman and G. A. Hamilton, *J. Am. Chem. Soc.* **96**, 1530 (1974).
18. L. G. Galimova, *Mechanism of Cyclohexane Oxidation by Ozone*, Ph.D. Thesis (Russian), Bashkirian State University, Ufa, USSR, 1975.
19. N. A. Kleimenov, I. N. Antonova, A. M. Markevich, and A. B. Nalbandyan, *Zh. Fiz. Khim.* **30**, 794 (1956).
20. N. A. Kleimenov and A. B. Nalbandyan, *Dokl AN SSSR* **122**, 103 (1958).
21. E. T. Denisov and T. G. Denisova, *Kinet. Catal.* **37**, 46 (1996).
22. S. L. Khursan, *Organic Polyoxides*, Doctor Diss. Thesis (Russian), Institute of Organic Chemistry, Ufa, Russia, 1999.
23. A. A. Popov, S. K. Rakovsky, D. M. Shopov, and A. V. Ruban, *Izv. AN SSSR, Ser. Khim.* 982 (1976).
24. R. E. Erickson, R. T. Hansen, and J. Harkins, *J. Am. Chem. Soc.* **90**, 6777 (1968).
25. R. E. Erickson, D. Bakalik, C. Richards, M. Scanlon, and G. Huddleston, *J. Org. Chem.* **31**, 461 (1966).
26. V. V. Shereshovets, N. N. Shafikov, and V. D. Komissarov, *Kinet. Katal.* **21**, 1596 (1980).
27. G. Klopman and C. Joiner, *J. Am. Chem. Soc.* **97**, 5287 (1975).
28. V. V. Komissarov, *Mechanism of Oxidation of Saturated Compounds by Ozone*, Doctor Diss. Thesis (Russian), Institute of Khimii, Ufa, USSR, 1989.
29. V. V. Shereshovets, *Mechanism of Cumene Oxidation by Ozone*, Ph.D. Thesis (Russian), Institute of Chemical Physics, Chernogolovka, USSR, 1978.
30. V. V. Shereshovets, V. V. Komissarov, and E. T. Denisov, *Izv. AN SSSR, Ser. Khim.* 2482 (1978).
31. I. N. Komissarova, *Mechanism of Aldehydes Oxidation by Ozone*, Ph.D. Thesis (Russian), Institute of Chemical Physics, Chernogolovka, USSR, 1978.
32. D. G. Williamson and R. I. Cvetanovic, *J. Am. Chem. Soc.* **92**, 2949 (1970).
33. S. D. Razumovskii, S. K. Rakovsky, and G. E. Zaikov, *Izv. AN SSSR, Ser. Khim.* 1963 (1975).
34. A. A. Kefelli, *Reactions of ozone with saturated polymers and model compounds*, Ph.D. Thesis (Russian), Institute of Chemical Physics, Moscow, 1973.
35. I. M. Pluzhnik and G. A. Galstyan, *Neftekhimiya* **39**, 120 (1999).
36. G. A. Galstyan, T. M. Galstyan, and S. M. Sokolova, *Kinet. Katal.* **33**, 779 (1992).
37. A. G. Galstyan, G. A. Galstyan, and N. F. Tyupalo, *Neftekhimiya* **38**, 147 (1998).
38. G. A. Galstyan, *Zh. Fiz. Khim.* **66**, 875 (1992).
39. A. Ya. Gerchikov, E. P. Kuznetsova, and E. T. Denisov, *Kinet. Katal.* **15**, 509 (1974).
40. A. Ya. Gerchikov, V. D. Komissarov, E. T. Denisov, and G. B. Kochemasova, *Kinet. Katal.* **13**, 1123 (1972).
41. A. Ya. Gerchikov, E. M. Kuramshin, V. D. Komissarov, and E. T. Denisov, *Kinet. Katal.* **15**, 230 (1974).
42. B. M. Brudnik, S. S. Zlotskii, S. S. Imashev, and D. L. Rakhmankulov, *Dokl. AN SSSR* **241**, 129 (1978).
43. R. Atkinson, D. L. Baulch, R. A. Cox, R. F. Hampson, J. A. Kerr, M. J. Rossi, and J. Troe, *J. Phys. Chem. Ref. Data* **26**, 1329 (1997).

44. V. D. Komissarov, A. Ya. Gerchikov, L. G. Galimova, and E. T. Denisov, *Dokl. AN SSSR* **213**, 881 (1973).
45. A. Ya. Gerchikov, V. D. Komissarov, E. T. Denisov, and G. B. Kochemasova, *Kinet. Katal.* **13**, 1126 (1972).
46. L. G. Galimova, V. D. Komissarov, and E. T. Denisov, *Izv. AN SSSR, Ser. Khim.* 307 (1973).
47. V. D. Komissarov, L. G. Galimova, I. N. Komissarova, V. V. Shereshovets, and E. T. Denisov, *Dokl. AN SSSR* **235**, 1930 (1977).
48. V. V. Shereshovets, V. D. Komissarov, and E. T. Denisov, *Izv. AN SSSR, Ser. Khim.* 2482 (1978).
49. V. D. Komissarov, I. N. Komissarova, G. K. Farrakhova, and E. T. Denisov, *Izv. AN SSSR, Ser. Khim.* 1205 (1979).
50. V. V. Shereshovets, V. D. Komissarov, and E. T. Denisov, *Izv. AN SSSR, Ser. Khim.* 1212 (1979).
51. S. G. Cheskis, A. A. Iogansen, I. Yu. Razuvaev, O. M. Sarkisov, and A. A. Titov, *Chem. Phys. Lett.* **155**, 37 (1989)
52. R. Simonaitis and J. Heicklen, *J. Phys. Chem.* **79**, 298 (1975).
53. A. A. Turniseed, S. B. Barone, and R. A. Ravinshankara, *J. Phys. Chem.* **97**, 5926 (1993).
54. R. Atkinson, B. J. Finlayson, and J. N. Pitts, *J. Am. Chem. Soc.* **95**, 7592 (1973).
55. G. S. Tyndell, T. J. Wallington, and J. C. Ball, *J. Phys. Chem. A*, **102**, 2547 (1998).
56. R. Paltenghi, E. A. Ogryzlo, and K. D. Bayes, *J. Phys. Chem.* **88**, 2595 (1984).
57. R. Simonaitis and J. Heicklen, *J. Phys. Chem.* **77**, 1932 (1973).
58. W. B. De More, *Science* **180**, 735 (1973).

Handbook of Free Radical Initiators. E.T. Denisov, T.G. Denisova, T.S. Pokidova
Copyright © 2003 John Wiley & Sons, Inc.
ISBN: 0-471-20753-5

12

BIMOLECULAR REACTIONS OF HYDROPEROXIDES WITH FREE RADICAL GENERATION

12.1 BIMOLECULAR DECOMPOSITION OF HYDROPEROXIDES

The bimolecular reaction of hydroperoxide decomposition to free radicals

$$\mathrm{ROOH + HOOR \rightarrow RO^{\bullet} + H_2O + RO_2^{\bullet}}$$

was discovered by Bateman[1,2] in the kinetic study of the autoxidation of non-saturated acids and their esters. He found that the rate of chain initiation in an oxidized substrate was $v_i \sim [\mathrm{ROOH}]^2$. This result was proved later by the AFR method.[3] The rate of initiation by $\mathrm{Me_3COOH}$ was found to be

$$v_{03} = k_{i1}[\mathrm{ROOH}] + k_{i2}[\mathrm{ROOH}]^2 \times (1 + K[\mathrm{ROOH}])^{-1} \qquad (12.1)$$

where k_{i1} characterizes the unimolecular decay of hydroperoxide (or decay by the reaction of hydroperoxide with the solvent) and k_{i2} characterizes the decomposition of a complex between two molecules of ROOH, forming the hydrogen-bond $\mathrm{ROOH\cdots O(H)OR}$. The coefficient K is the equilibrium constant for formation of this complex. For values of K see Chapter 4. The "bimolecular" decomposition of hydroperoxide occurs in two steps.

$$\mathrm{ROOH + ROOH \Leftrightarrow ROOH\cdots O(H)OR} \qquad (K)$$

$$\mathrm{ROOH\cdots O(H)OR \rightarrow RO_2^{\bullet} + H_2O + RO^{\bullet}} \qquad (k_{i2})$$

This bimolecular decomposition of $\mathrm{Me_3COOH}$ proceeds with endothermicity $\Delta H = D_{\mathrm{O-H}} + D_{\mathrm{O-O}} - D_{\mathrm{HO-H}} = 358.6 + 175.0 - 498 = 35.6\ \mathrm{kJ\,mol^{-1}}$ in comparison with $\Delta H = 175$ kJ mol^{-1} for unimolecular decay (see Chapter 4). That is why the bimolecular decay occurs much more rapidly than unimolecular. The equilibrium constants K and k_{i2} were found to be $K = 1.9$ L mol^{-1} (363 K) and $k_{i2} = 5.8 \times 10^7 \exp(-96.1/RT) = 8.61 \times 10^{-7}$ L mol^{-1} s^{-1} (363 K) for 1,1-dimethylethyl hydroperoxide[3] and $K = 3.3 \times 10^{-4} \exp(25.0/RT) = 1.3$ L mol^{-1} (363 K), $k_{i2} = 2.2 \times 10^8 \exp(-106.0/RT) = 1.23 \times 10^{-7}$ L mol^{-1} s^{-1} (363 K) for 1-methyl-1-phenylethyl hydroperoxide.[4] Experimental data on the bimolecular homolytic decomposition of hydroperoxides are collected in Table 12.1 and activation energies and rate constants calculated by the IPM method (see Chapter 9) presented in Table 12.2.

12.2 BIMOLECULAR REACTIONS OF HYDROPEROXIDES WITH A π-BOND TO OLEFINS

Reaction of hydroperoxide (Me_3COOH) with the π-bond of styrene had free radical generation

$$ROOH + CH_2{=}CHPh \rightarrow RO^{\bullet} + HOCH_2C^{\bullet}HPh$$

evidenced by the AFR method in 1964.[11] The rate of free radical initiation was found to be

$$v_i = k_i[ROOH][PhCH{=}CH_2] \qquad (12.2)$$

with the rate constant $k_i = 1.2 \times 10^4 \exp(-72.0/RT)$ L mol^{-1} s^{-1}. Enthalpy for this reaction (see Chapter 9) $\Delta H{=}D_{O-O} - D_{R-OH} = 175 - 165 = 10$ kJ mol^{-1}. Rate constants for free radical generation by this reaction was measured by five different methods were found to be in good agreement.[12] It is very probable that the preliminary formation of the charge-transfer complex between hydroperoxide and olefin precedes the reaction.

$$ROOH + CH_2{=}CHR^1 \Leftrightarrow ROOH(\delta^-)\cdots CH_2{=}CHR^1(\delta^+)$$

$$ROOH(\delta^-)\cdots CH_2{=}CHR^1(\delta^+) \rightarrow [RO^{\bullet} + HOCH_2C^{\bullet}HR^1]$$

$$[RO^{\bullet} + HOCH_2C^{\bullet}HR^1] \rightarrow ROH + HOCH{=}CHR^1$$

$$[RO^{\bullet} + HOCH_2C^{\bullet}HR^1] \rightarrow HOCH_2C(OR)HR^1$$

$$[RO^{\bullet} + HOCH_2C^{\bullet}HR^1] \rightarrow RO^{\bullet} + HOCH_2C^{\bullet}HR^1$$

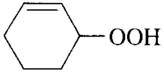
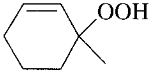
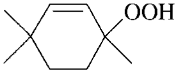
The formation of the hydrogen bond between hydroperoxide and polar monomer, for example, methyl acrylate or acrylonitrile, does not influence the rate constant of the hydroperoxide reaction with the double bond of monomer.[12] The effect of

TABLE 12.1 Rate Constants and Activation Energies for Bimolecular Reactions of Hydroperoxides $2ROOH \rightarrow RO_2^{\bullet} + H_2O + RO^{\bullet a}$

ROOH	Solvent	T (K)	E (kJ mol^{-1})	log A, A (L mol^{-1} s^{-1})	k(350 K) (L mol^{-1} s^{-1})	Reference
HOOH	Cyclohexanol	393–413	121.7	9.84	4.76×10^{-9}	5
Me_3COOH	Heptane	333–363	96.1	8.04	4.99×10^{-7}	3
$Me_2C(OOH)Et$	2-Methylbutane	333–363	100.0	7.80	7.52×10^{-8}	6
$CH_2{=}CHCHMeOOH$	1-Butene	338–353	108.8	11.70	2.90×10^{-5}	7
$MeCH{=}CHCH_2OOH$	2-Butene	338–353	117.1	12.70	1.67×10^{-5}	7
	Benzene	333–353	120.0	11.40	3.10×10^{-7}	8
$Me_2PhCOOH$	Cumene	333–368	80.7	4.86	6.55×10^{-8}	4
$Me_2PhCOOH$	Chlorobenzene	373–393	68.6	2.38	2.71×10^{-9}	9
$Me_2PhCOOH$	Cumene	393			1.90×10^{-6}	10
$Me_2PhCOOH$	Chlorobenzene	393			6.02×10^{-7}	10
$MePh_2COOH$	Nitrobenzene	393			4.47×10^{-5}	10
$PhCH(OOH)CH{=}CH_2$	Benzene, 2-propenyl-	388			2.82×10^{-7}	1
$CH_2{=}CHCH(OOH)CH_2Bu$	1-Octene	388			2.88×10^{-7}	1

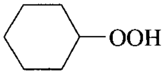
(continued overleaf)

TABLE 12.1 (*continued*)

ROOH	Solvent	T (K)	E (kJ mol^{-1})	log A, A (L mol^{-1} s^{-1})	k(350 K) (L mol^{-1} s^{-1})	Reference
	Cyclohexene	388			5.37×10^{-7}	1
	Cyclohexene, 3-methyl-	338			1.15×10^{-6}	1
	Cyclohexene, 3,3,6-trimethyl-	338			3.24×10^{-6}	1
EtCH=CMeCH(OOH)Et	4-Methylheptene-3	388			1.7×10^{-6}	1
Me_2C=CHCH(OOH)Bu	2-Methyloctene-2	388			5.0×10^{-7}	1

[a] Experimental data.

TABLE 12.2 Enthalpies, Activation Energies, and Rate Constants for Bimolecular Reactions of Hydroperoxides $2ROOH \rightarrow ROO^{\bullet} + H_2O + RO^{\bullet}$ Calculated by the IPM Method[a]

ROOH	n	ΔH_e (kJ mol^{-1})	E (kJ mol^{-1})	log A, A (L mol^{-1} s^{-1})	k(350 K) (L mol^{-1} s^{-1})
HOOH	2	50.0	114.1	8.93	7.97×10^{-9}
Me_2CHOOH	1	46.5	112.2	8.63	7.68×10^{-9}
	1	46.5	112.2	8.63	7.68×10^{-9}
Me_3COOH	1	39.6	108.4	8.64	2.90×10^{-8}
$PhMe_2COOH$	1	39.6	108.4	8.64	2.90×10^{-8}
$Me_2C(OH)OOH$	1	52.6	115.5	8.63	2.47×10^{-9}
CCl_3OOH	1	88.2	135.8	8.60	2.15×10^{-12}
CBr_3OOH	1	88.0	135.7	8.60	2.23×10^{-12}
CCl_3CCl_2OOH	1	88.2	135.8	8.60	2.15×10^{-12}

[a] See Chapter 9.

TABLE 12.3 The Reactivity of Polyfunctional Esters in Bimolecular Reaction with 1-Methyl-1-Phenylethyl Hydroperoxide

Monomer	$k_i \times 10^8$ (343 K) (L mol^{-1} s^{-1})	$\Delta G^{\neq}_{\mu}$ (kJ mol^{-1})	Reference
$CH_2{=}CHC(O)OMe$	17.5	0	13
$[CH_2{=}CHC(O)OCH_2]_3CEt$	6.1	3.0	14
$[CH_2{=}CHC(O)OCH_2]_4C$	2.4	5.6	14
$CH_2{=}CHC(O)OCH_2C[CH_2OC(O)Et]_3$	1.9	6.3	14

multidipole interaction was observed for reactions of hydroperoxide with polyfunctional monomers ($\Delta G^{\neq}_{\mu}$ is Gibbs energy of multidipole interaction in the transition state, see Table 12.3).

Carbonyl compounds (aldehydes and ketones) accelerate the decay of hydroperoxides due to the formation of unstable peroxides (see Chapter 4):

$$ROOH + O{=}CR^1R^2 \Leftrightarrow ROOC(OH)R^1R^2$$

$$ROOC(OH)R^1R^2 \rightarrow RO^{\bullet} + R^1R^2C(OH)O^{\bullet}$$

For the values of rate constants of initiation by the reaction of hydroperoxides with olefins, experimental and calculated by the IPM method, see Tables 12.4 and 12.5.

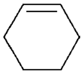
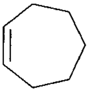
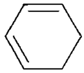
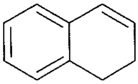
TABLE 12.4 Rate Constants and Activation Energies for Hydroperoxide Reaction with Monomers: ROOH + CH_2=CHR → $RO^•$ + $HOCH_2C^•HR$[a]

ROOH	CH_2=CHR	Solvent	T (K)	E (kJ mol^{-1})	log A, A (L mol^{-1} s^{-1})	k(350 K) (L mol^{-1} s^{-1})	Reference
Me_3COOH	CH_2=CHPh	Chlorobenzene	328–363	72.0	4.08	2.16×10^{-7}	11
Me_3COOH	CH_2=CHPh	Styrene	323–353	79.5	5.21	2.21×10^{-7}	12
$Me_2PhCOOH$	CH_2=CHPh	Styrene	323–353	84.2	6.35	6.08×10^{-7}	12
$Me_2PhCOOH$	CH_2=CHC(O)OMe	Methyl acrylate	323–353	82.6	5.88	3.12×10^{-7}	13
$Me_2PhCOOH$	CH_2=CHCN	Acrylonitrile	323			5.4×10^{-8}	13
$Me_2PhCOOH$	CH_2=CMeC(O)OMe	Methyl methacrylate	323–363	78.2	5.01	2.18×10^{-7}	13
$Me_2PhCOOH$	CH_2=CMeC(O)OBu	Butyl methacrylate	323			1.9×10^{-8}	13
$Me_2PhCOOH$	CH_2=CEtC(O)OMe	Methyl methacrylate	323			3.2×10^{-8}	13
$Me_2PhCOOH$	CH_2=CMePh	Benzene	363			7.1×10^{-7}	13
$Me_2PhCOOH$	$(CH_2$=$CHC(O)OCH_2)_4C$	Chlorobenzene	343			9.40×10^{-8}	14
$Me_2PhCOOH$	$(CH_2$=$CHC(O)OCH_2)_3CH$	Chlorobenzene	343			1.83×10^{-7}	14
$Me_2PhCOOH$	CH_2=$CHC(O)OCH_2C(CH_2OC(O)Et)_3$	Chlorobenzene	343			1.9×10^{-8}	15

---

[a] Experimental data.

TABLE 12.5 Enthalpies, Activation Energies, and Rate Constants for the Reaction of 1,1-Dimethylethyl Hydroperoxide with Monomers: $Me_3COOH + CH_2{=}CHR \rightarrow Me_3CO^\bullet + HOCH_2C^\bullet HR$ Calculated by the IPM Method[a]

$CH_2{=}CHR$	n_C	ΔH_e (kJ mol^{-1})	E (kJ mol^{-1})	log A, A (L mol^{-1} s^{-1})	k(350 K) (L mol^{-1} s^{-1})
$CH_2{=}CH_2$	2	53.5	124.0	9.00	6.23×10^{-10}
$CH_2{=}CHMe$	1	55.2	124.9	9.00	2.29×10^{-10}
$CH_2{=}CMe_2$	1	50.3	122.3	9.00	5.60×10^{-10}
$CH_2{=}CHEt$	1	54.9	124.8	9.00	2.37×10^{-10}
	2	55.2	124.9	9.00	2.29×10^{-10}
	2	52.2	123.3	9.00	3.97×10^{-10}
$HC{\equiv}CH$	2	33.2	113.3	9.30	4.91×10^{-8}
$HC{\equiv}CMe$	1	36.9	115.2	9.30	1.28×10^{-8}
$MeC{\equiv}CMe$	2	48.9	121.5	9.30	2.93×10^{-9}
$CH_2{=}CHCH{=}CH_2$	2	63.0	110.8	9.00	5.81×10^{-8}
$CH_2{=}CHCMe{=}CH_2$	1	54.0	110.4	9.00	3.34×10^{-8}
$CH_2{=}CHCH{=}CMe_2$	1	−0.3	107.7	9.00	8.45×10^{-8}
	2	−13.4	101.1	9.00	8.16×10^{-7}
$CH_2{=}CHPh$	1	13.6	107.7	9.00	8.45×10^{-8}
$CH_2{=}CMePh$	1	13.1	107.5	9.00	9.05×10^{-8}
$MeCH{=}CMePh$	1	3.0	102.6	9.00	4.87×10^{-7}
$Me_2C{=}CMePh$	1	3.0	102.6	9.00	4.87×10^{-7}
$CH_2{=}CPh_2$	1	−45.7	80.5	9.00	9.69×10^{-4}
	1	12.9	107.4	9.00	9.37×10^{-8}

[a] See Chapter 9, Eqs. (9.13), (9.15), and (9.16), Tables 9.1 and 9.2.

12.3 BIMOLECULAR REACTIONS OF HYDROPEROXIDES WITH C–H, N–H, AND O–H BONDS OF ORGANIC COMPOUNDS

Bimolecular reaction of the type

$$ROOH + HY \rightarrow RO^\bullet + H_2O + Y^\bullet$$

has a lower enthalpy than the unimolecular decomposition of hydroperoxide ($D_{O-O} = 180$ kJ mol^{-1}) because in most cases $D_{Y-H} < D_{HO-H} = 498$ kJ mol^{-1}. These reactions can occur with an activation energy lower than D_{O-O} of hydroperoxide.[16] A few reactions of this type with the initiation rate $v_i = k_i$ [ROOH] [YH] were seen where YH was a hydrocarbon,[4,9] alcohol,[6,17] and carbonic acid.[18,19] The experimental data are presented in Table 12.6. The IPM method opened the way for the calculation of activation energies and rate constants for such reactions (see Chapter 9). The results of calculation are presented in Tables 12.7 and 12.8.

12.3.1 Hydrocarbons

Enthalpy of the reaction

$$\mathrm{ROOH + HR^1 \rightarrow RO^\bullet + H_2O + R^{1\bullet}}$$

is $\Delta H = D_{C-H} + 175 - 498 = D_{C-H} - 323$ kJ mol^{-1} and decreases by decreasing the value for the BDE of the C−H bond. The activation energy for this reaction is sufficiently higher than its enthalpy (see Table 12.6) due to the influence of the triplet repulsion and nonlinear configuration of the reaction center of the transition state on the activation energy. The experimental values for activation energy of the hydroperoxide reaction with cumene (Table 12.6) are sufficiently lower than the calculated values (see Table 12.7). Probably this is the result of another parallel reaction of initiation, namely, the reaction of hydroperoxide with the aromatic ring.

$$\mathrm{ROOH + C_6H_5R^1 \rightarrow RO^\bullet + HOC_6{}^\bullet H_5R^1}$$

$$\mathrm{HOC_6{}^\bullet H_5R^1 + O_2 \rightarrow HO_2{}^\bullet + HOC_6H_4R^1}$$

As in the case of the hydroperoxide reaction with the π-bond of an olefin (see Section 12.2), the reaction of ROOH with the π-bond of an aromatic ring occurs more rapidly than the attack of ROOH on the C−H bond of alkylaromatic hydrocarbon.

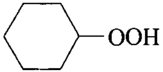
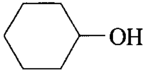
12.3.2 Alcohols and Acids

Reaction of alcohol with ROOH

$$\mathrm{ROOH + HOR^1 \rightarrow RO^\bullet + H_2O + R^1O^\bullet}$$

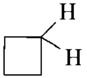
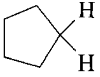
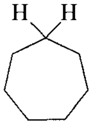
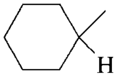
occurs with a rate constant (calculated by the IPM method) of a few orders of magnitude lower than the rate constant measured experimentally. Moreover, the experimental values for the activation energy are lower than ΔH of the hydrogen abstraction reaction. This implies that a different reaction from the reaction written above was observed experimentally. This reaction cannot be the reaction of hydroperoxide with the C−H bond of alcohol because rate constants for free radical generation in the reaction of ROOH with secondary and tertiary alcohols are close (see Table 12.6), whereas secondary and tertiary alcohols have C−H

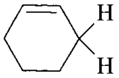
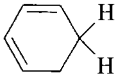
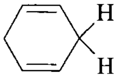
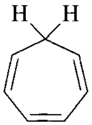
TABLE 12.6 Rate Constants and Activation Energies for Bimolecular Reactions of Hydroperoxides with Substrates ROOH + YH → Free Radicals[a]

ROOH	Y–H	Solvent	T (K)	E (kJ mol^{-1})	log A, A (L mol^{-1} s^{-1})	k(400 K) (L mol^{-1} s^{-1})	Reference
$EtMe_2COOH$	$MeCH_2O{-}H$	Isooctane	348			2.00×10^{-7}	6
$Me_2PhCOOH$	$Me_2PhC{-}H$	Chlorobenzene	373–393	109.0	7.70	2.92×10^{-7}	9
$Me_2PhCOOH$	$Me_2PhC{-}H$	Cumene	333–368	110.0	8.00	4.32×10^{-7}	4
$EtMe_2COOH$	$EtMe_2CO{-}H$	Isooctane	333–396	93.0	8.50	2.27×10^{-4}	6
		Chlorobenzene	353–393	92.0	8.64	4.23×10^{-4}	17
$Me_2PhCOOH$	$PhC(O)O{-}H$	Cumene	363–383	86.0	9.85	4.17×10^{-2}	18
$MeCH(OOH)(CH_2)_7Me$	$BuCH_2C(O)O{-}H$	Decane	293–433	67.4	6.30	3.15×10^{-3}	19
Me_3COOH	C_5H_5N	Chlorobenzene	333–368	53.0	3.54	4.16×10^{-4}	20

[a] Experimental data.

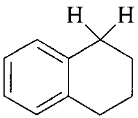
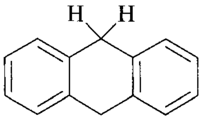
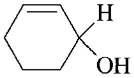
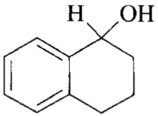
TABLE 12.7 Enthalpies, Activation Energies, and Rate Constants for Bimolecular Reactions of Hydroperoxides with Hydrocarbons $ROOH + HR \rightarrow RO^{\bullet} + H_2O + R^{\bullet}$ Calculated by the IPM Method[a]

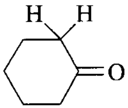
RH	D (kJ mol^{-1})	n_{RH}	ΔH_e (kJ mol^{-1})	E (kJ mol^{-1})	log A, A (L mol^{-1} s^{-1})	k(400 K) (L mol^{-1} s^{-1})
EtMeCH−H	413.0	4	90.2	153.2	9.60	3.93×10^{-11}
Me_3C-H	400.0	1	77.2	146.3	9.00	7.86×10^{-11}
	418.5	8	95.7	156.1	9.90	3.28×10^{-11}
	408.4	10	85.6	150.7	10.00	2.10×10^{-10}
	403.9	14	81.1	148.3	10.15	6.09×10^{-10}
	395.5	1	72.7	143.9	9.00	1.61×10^{-10}
(Z)-Decalin	387.6	2	64.8	139.9	9.30	1.09×10^{-9}
$CH_2{=}CHCH_2-H$	368.0	3	45.2	146.7	9.48	2.12×10^{-10}
$CH_2{=}CH(CH-H)Me$	349.8	2	27.0	138.0	9.30	1.88×10^{-9}
$CH_2{=}CH(C-H)Me_2$	339.6	1	16.8	133.4	9.00	3.87×10^{-9}
(Z)-MeCH=CH(CH−H)Me	344.0	2	21.2	135.4	9.30	4.22×10^{-9}

$Me_2C{=}CH(CH{-}H)Me$	332.0	2	9.2	129.9	9.30	2.17×10^{-8}
$Me_2C{=}CMe(C{-}H)Me_2$	322.8	1	0.0	125.8	9.00	3.72×10^{-8}
$(CH_2 = CH)_2CMe{-}H$	307.2	1	−15.6	119.1	9.00	2.85×10^{-7}
	341.5	4	18.7	134.2	9.60	1.19×10^{-8}
	330.9	4	8.1	129.4	9.60	7.57×10^{-8}
	312.6	4	−10.2	121.4	9.60	5.67×10^{-7}
	301.0	2	−21.8	116.4	9.30	1.26×10^{-6}
$MeC{\equiv}CC{-}HMe_2$	329.4	1	6.6	128.7	9.00	1.54×10^{-8}
$PhMeCH{-}H$	364.1	2	41.3	134.5	9.30	5.53×10^{-9}
$PhMe_2C{-}H$	354.7	1	31.9	130.0	9.00	1.06×10^{-8}

(*continued overleaf*)

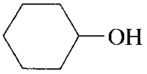
TABLE 12.7 (*continued*)

RH	D (kJ mol^{-1})	n_{RH}	ΔH_e (kJ mol^{-1})	E (kJ mol^{-1})	log A, A (L mol^{-1} s^{-1})	k(400 K) (L mol^{-1} s^{-1})
	345.6	4	22.8	125.7	9.60	1.53×10^{-7}
	322.0	4	−0.8	115.1	9.60	3.75×10^{-6}
Me_2NH_2C-H	379.5	1	56.7	135.8	9.00	1.86×10^{-9}
$(CH_2=CHCH-H)_3N$	345.6	6	22.8	136.1	9.78	1.01×10^{-8}
$Me_2(HO)C-H$	390.5	1	67.7	141.4	9.00	3.49×10^{-10}
	329.7	1	6.9	112.2	9.00	2.27×10^{-6}
$MeCH=CMe(C-H)MeOH$	325.2	1	2.4	126.9	9.00	2.71×10^{-6}
	337.5	1	14.7	122.0	9.00	1.17×10^{-7}

PhC(O)−H	348.0	1	25.2	126.8	9.00	2.73×10^{-8}
	394.1	4	71.3	143.2	9.60	8.00×10^{-10}
$(Me_2C-H)_2O$	390.8	2	68.0	141.5	9.30	6.66×10^{-10}
$(CH_2=CHCH-H)_2O$	360.0	4	37.2	142.8	9.60	8.94×10^{-10}
$Ph_2C-HOMe$	354.2	1	31.4	129.8	9.00	1.14×10^{-8}
Ph[C(O)OH]CH−H	367.0	2	44.2	135.9	9.30	3.63×10^{-9}
$(Me_3C)_3Si-H$	351.0	1	23.9	94.0	9.00	5.24×10^{-4}
Ph_3Ge-H	322.5	1	−5.1	96.4	9.00	2.60×10^{-4}
Ph_3Sn-H	296.9	1	−31.2	96.6	9.00	2.42×10^{-4}

[a] See Chapter 9, Eqs. (9.13) and (9.16), Tables 9.1 and 9.2.

TABLE 12.8 Enthalpies, Activation Energies, and Rate Constants for Bimolecular Reactions of Hydroperoxides with Substrates $ROOH + HY \rightarrow RO^{\bullet} + H_2O + Y^{\bullet}$ Calculated by the IPM Method[a]

Reaction	D ($kJ\,mol^{-1}$)	n	ΔH_e ($kJ\,mol^{-1}$)	E ($kJ\,mol^{-1}$)	$\log A$, A ($L\,mol^{-1}\,s^{-1}$)	k(400 K) ($L\,mol^{-1}\,s^{-1}$)
	$ROOH + HNR^1R^2 \rightarrow RO^{\bullet} + H_2O + R^1R^2N^{\bullet}$					
$H_2NNH{-}H$	366.1	4	45.9	139.3	8.59	2.51×10^{-10}
$EtNH{-}H$	418.4	2	98.2	173.8	8.24	3.50×10^{-15}
$Et_2N{-}H$	382.8	1	62.6	160.9	7.95	8.69×10^{-14}
	$ROOH + HOR^1 \rightarrow RO^{\bullet} + H_2O + R^1O^{\bullet}$					
$EtO{-}H$	440.0	1	121.5	205.7	7.90	1.09×10^{-19}
$Me_2CHO{-}H$	443.0	1	124.5	207.8	7.90	5.81×10^{-20}
$Me_3CO{-}H$	446.0	1	127.5	209.9	7.89	3.02×10^{-20}
	437.1	1	118.6	203.6	7.90	2.05×10^{-19}
$ONO{-}H$	327.6	1	9.1	134.2	7.99	2.92×10^{-10}
$MeC(O)O{-}H$	442.7	1	124.2	207.6	7.90	6.17×10^{-20}
$PhCH_2C(O)O{-}H$	443.5	1	125.0	208.1	7.90	5.31×10^{-20}

[a] See Chapter 9, Eqs. (9.13), (9.15), and (9.16), Tables 9.1 and 9.2.

bonds of different strengths (see Chapter 9), and rate constants for the reactions of ROOH with C—H bonds should be different. Experiment demonstrates the close rate constants (see Table 12.6). This implies that a different mechanism of free radical generation predominates in the system $ROOH + R^1OH$. The same situation is observed in the reaction of hydroperoxides with acids (see Table 12.6).

12.4 ACID CATALYSIS FOR HOMOLYTIC REACTIONS OF HYDROPEROXIDES

Acids are well known as catalysts for various heterolytic reactions. They catalyze the heterolytic decay of hydroperoxides. For example, they catalyze the decomposition of cumyl hydroperoxide to phenol and acetone (important technological reaction).[21]

$$Me_2PhCOOH \rightarrow Me_2C(O) + PhOH$$

In addition to the heterolysis of hydroperoxides, strong mineral acids catalyze the homolytic splitting of hydrogen peroxide and hydroperoxides into free radicals. This new catalytic ability of acids was found in the kinetic study of isopropanol

TABLE 12.9 Acid Catalysis for the Homolytic Decomposition of Hydroperoxides to Free Radicals[a]

ROOH	Acid	Solvent	T (K)	E (kJ mol^{-1})	log A, A (L^2 mol^{-2} s^{-1})	k(350 K) (L^2 mol^{-2} s^{-1})	Reference
			$v_i = k_i\ [ROOH]^2[Acid]$				
H_2O_2	H_2SO_4	Me_2CHOH	333–348	108.8	14.93	4.93×10^{-2}	23,25
H_2O_2	$HClO_4$	Me_2CHOH	333–348	102.1	14.01	5.92×10^{-2}	23
H_2O_2	$HClO_4$	Me_2CHOH	333–348	113.0	15.52	4.53×10^{-2}	25
Me_3COOH	$HClO_4$	Me_2CHOH	333–348	117.1	15.60	1.33×10^{-2}	26
Me_3COOH	$SbCl_5$	MeCN	313–343	73.2	11.27	2.21	27
			$v_i = k_i\ [ROOH][Acid]$				
Me_3COOH	BF_3	Me_2CHOH	343			0.10	24
Me_3COOH	$AlCl_3$	Me_2CHOH	343			3.6×10^{-2}	24
Me_3COOH	$SbCl_5$	Me_2CHOH	343			1.0×10^{-3}	24
Me_3COOH	LiCl	$MeCN/CH_2{=}CHPh$	343–353	77.4	11.75	1.58	28

[a] Experimental data.

oxidation.[22,23] Mineral acids, such as H_2SO_4, $HClO_4$, HCl, and HNO_3, were found to accelerate the chain oxidation of 2-propanol due to the catalysis of hydrogen peroxide decomposition with free radical generation. The initiation rate was found to be proportional to the product $[H_2O_2]^2$ [AH]. The homolytic decomposition of hydroperoxides was proved to be catalyzed by Brønsted, as well as by Lewis acids (e.g., BF_3, $AlCl_3$, and $SbCl_5$).[24] Experimental data on acid catalysis of the homolytic decomposition of hydroperoxides are in Table 12.9.

Earlier (see Section 11.3), a great discrepancy was noticed between the calculated rate constants for the reactions

$$\mathrm{ROOH + HOR^1 \rightarrow RO^\bullet + H_2O + R^1O^\bullet}$$

$$\mathrm{ROOH + HOC(O)R^1 \rightarrow RO^\bullet + H_2O + R^1CO_2^\bullet}$$

and the experimental values for chain generation by the interaction of hydroperoxides with alcohols and acids [k_i (calculated) $\ll$ k (experimental)]. The probable explanation of such a great difference lies in the participation of the more active protonated form of hydroperoxide in free radical generation.

$$\mathrm{ROOH + HOC(O)R^1 \Leftrightarrow ROOH_2{}^+ + R^1CO_2{}^-}$$

$$\mathrm{ROOH_2{}^+ + ROOH \rightarrow RO^\bullet + RO_2^\bullet + H_3O^+}$$

$$\mathrm{ROOH_2{}^+ + R^1C(O)OH \rightarrow RO^\bullet + H_3O^+ + RCO_2^\bullet}$$

$$\mathrm{ROOH + HOR^1 \Leftrightarrow ROOH_2{}^+ + R^1O^-}$$

$$\mathrm{ROOH_2{}^+ + R^1OH \rightarrow RO^\bullet + H_3O^+ + R^1O^\bullet}$$

12.5 REACTION OF PEROXIDES WITH AMINES

Amines react with peroxides very promptly.[29] The reactions of benzoyl peroxide with various amines were discovered and studied by Gambaryan and co-worker.[30,31] The products of the benzoyl peroxide reaction with dimethylamine in chloroform were found to be benzoic acid (yield close to 100%), methylaniline, formaldehyde, and *p*-benzoyloxydimethylaniline.[32,33] The reaction of benzoyl peroxide with tertiary amines initiate styrene polymerization with the rate[34]

$$v_i = k_i[\mathrm{PhC(O)OOC(O)Ph}][\mathrm{Amine}] \qquad (12.3)$$

The yield of free radicals in this reaction was found to be low (2–5%).[29] Apparently, the reaction can be either homolytic and heterolytic. The first step was supposed to be the electron transfer from the nitrogen atom of amine to peroxide with O—O bond splitting. The rate constants of reaction are listed in Table 12.10.

$$\mathrm{R_3N + PhC(O)OOC(O)Ph \rightarrow R_3N^{+\bullet} + PhCO_2^\bullet + PhCO_2{}^-}$$

The benzoyloxy radical escapes from the cage and initiates polymerization in the presence of the monomer.[32]

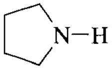
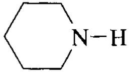
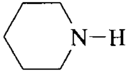
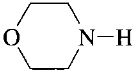
TABLE 12.10 Reactions of Amines with Peroxides (KDI Method)

Amine	Solvent	T (K)	E (kJ mol^{-1})	log A, A (L mol^{-1} s^{-1})	k(300 K) (L mol^{-1} s^{-1})	Reference
		PhC(O)OOC(O)Ph				
Et_2NH	Acetone	293			5.50×10^{-3}	35
Et_2NH	Benzene	273–293	39.3	4.62	5.99×10^{-3}	35
Et_2NH	Diethyl ether	273–293	43.5	4.80	1.68×10^{-3}	35
Et_2NH	*N*,*N*-Dimethyl formamide	293			9.55×10^{-3}	36
Et_2NH	Dioxane	293			5.69×10^{-3}	35
Et_2NH	Methyl acrylate	293			5.20×10^{-3}	36
Et_2NH	Pyridine	293			2.88×10^{-2}	36
Et_2NH	Styrene	293			5.70×10^{-3}	36
Pr_2NH	Diethyl ether	293			5.62×10^{-4}	35
Bu_2NH	Benzene	273–293	38.5	4.44	5.45×10^{-3}	35
$[Me_2CHCH_2]_2NH$	Diethyl ether	273			3.20×10^{-4}	35
Et_3N	Benzene	293–343	59.1	7.12	6.76×10^{-4}	37
$Me_2NCH_2CH_2OH$	Benzene	293–343	44.8	6.07	1.86×10^{-2}	38
$Me_2NCH_2CH_2OH$	1,1-Dimethyl ethylacrylate	293–343	51.3	7.11	1.51×10^{-2}	38
$Et_2NCH_2CH_2OH$	Benzene	293–343	59.4	6.72	2.39×10^{-4}	37
$Me_2NCH_2CHMeOH$	Benzene	293–343	51.0	6.08	1.59×10^{-3}	38
$Me_2NCH_2CMe_2CH_2OH$	Benzene	293–343	60.2	7.08	3.97×10^{-4}	38
$Et_2NCH_2CH_2CH_2OH$	Benzene	293–343	59.4	7.65	2.03×10^{-3}	38
$Et_2NCH_2CHMeOH$	Benzene	293–343	55.6	6.77	1.23×10^{-3}	38

(continued overleaf)

TABLE 12.10 (*continued*)

Amine	Solvent	T (K)	E (kJ mol^{-1})	log A, A (L mol^{-1} s^{-1})	k(300 K) (L mol^{-1} s^{-1})	Reference
$Et_2NCH_2CHMeOH$	Styrene	293–343	44.8	4.76	9.11×10^{-4}	38
$PhCH_2NH_2$	Benzene	273–298	51.0	6.79	8.13×10^{-3}	39
$PhCH_2NH_2$	Carbon tetrachloride	273–298	43.1	5.95	2.80×10^{-2}	40
$PhCH_2NH_2$	*N*,*N*-Dimethyl formamide	273–298	30.1	3.79	3.54×10^{-2}	40
$PhCH_2NH_2$	Pyridine	273–298	30.1	3.70	2.88×10^{-2}	40
$PhNH_2$	Benzene	293–343	44.8	4.27	2.95×10^{-4}	41
$PhNMe_2$	Benzene	293–343	53.5	7.50	1.53×10^{-2}	42
$PhNMe_2$	Benzene	279			2.04×10^{-2}	43
$PhNMe_2$	Benzene	298			2.30×10^{-3}	44
$4\text{-}MeC_6H_4NMe_2$	Benzene	278–308	56.5	7.92	1.21×10^{-2}	44
$4\text{-}MeC_6H_4NMe_2$	Carbon tetrachloride	278–308	56.5	7.49	4.49×10^{-3}	44
$4\text{-}MeC_6H_4N(CH_2CH{=}CH_2)_2$	Benzene	278–308	65.7	8.78	2.19×10^{-3}	44
$4\text{-}MeC_6H_4N(CH_2CH{=}CH_2)_2$	Carbon tetrachloride	298			8.04×10^{-4}	44
$4\text{-}MeC_6H_4NPr_2$	Benzene	298			1.26×10^{-2}	44
$4\text{-}MeC_6H_4NPr_2$	Carbon tetrachloride	298			3.40×10^{-3}	44
$4\text{-}MeC_6H_4NMePr$	Benzene	298			1.17×10^{-2}	44
$(4\text{-}MeC_6H_4)_2NMe$	Benzene	298			1.29×10^{-3}	44
Ph_2NH	Benzene	293–343	68.6	10.1	1.43×10^{-2}	41
Ph_2NH	Benzene	288–303	55.6	7.96	1.90×10^{-2}	45
Ph_2NH	Benzene	273–313	53.5	6.33	1.03×10^{-3}	46
$(4\text{-}MeC_6H_4)_2NMe$	Benzene	298			1.30×10^{-3}	44
$(4\text{-}MeC_6H_4)_3N$	Benzene	298			1.50×10^{-4}	44

	Benzene	288–303	29.3	4.12	1.04×10^{-1}	45
	Benzene	288–303	38.9	5.50	5.33×10^{-2}	45
		$Me_2PhCOOH$				
Et_2NH	Water	288–313	71.1	8.16	6.03×10^{-5}	47
Et_3N	Water	288–313	61.5	6.95	1.75×10^{-4}	48
$Et_2NCH_2CH_2OH$	Water	288–313	74.5	8.95	9.52×10^{-5}	48
$(HOCH_2CH_2)_3N$	Water	288–313	57.3	4.91	8.58×10^{-6}	49
	Water	288–313	77.4	10.17	4.94×10^{-4}	50
	Water	288–313	76.6	8.94	4.01×10^{-5}	50

REFERENCES

1. L. Bateman, *Quart. Rev.* **8**, 147 (1954).
2. L. Bateman, H. Hughes, and A. Moris, *Disc. Faraday Soc.* **14**, 190 (1953).
3. E. T. Denisov, *Zh. Fiz. Khim.* **38**, 2085 (1964).
4. N. I. Solomko, V. F. Tsepalov, and A. I. Yurzhenko, *Kinet. Katal.* **9**, 766 (1968).
5. E. T. Denisov and V. V. Kharitonov, *Kinet. Katal.* **5**, 781 (1964).
6. T. G. Degtyareva, V. M. Solyanikov, and E. T. Denisov, *Neftekhimiya* **12**, 854 (1972).
7. A. Chauvel, G. Clement, and J. C. Balaceanu, *Bull. Soc. Chim. Fr.* 2025 (1963).
8. A. V. Tobolsky and R. E. Mesrobian, *Organic Peroxides*, Wiley-Interscience, New York, 1954.
9. V. L. Antonovskii, E. T. Denisov, and L. V. Solntseva, *Kinet. Katal.* **6**, 815 (1965).
10. I. P. Shevchuk, *The Study of Solvent Influence on Liquid-Phase Oxidation of Cumene, 1,1-Diphenylethane and Nonene-1*, Ph.D. Thesis (Russian), L'vov State University, L'vov, USSR, 1968.
11. E. T. Denisov and L. N. Denisova, *Dokl. Akad. Nauk SSSR* **157**, 907 (1964).
12. M. M. Mogilevich and E. M. Pliss, *Oxidation and Oxidative Polymerization of Nonsaturated Compounds* (Russian), Khimiya, Moscow, 1990.
13. E. M. Pliss and V. M. Troshin, *Neftekhimiya* **22**, 539 (1982).
14. V. M. Troshin, E. M. Pliss, and E. T. Denisov, *Izv. Akad. Nauk SSSR, Ser. Khim.* 2191 (1984).
15. A. V. Sokolov, E. M. Pliss, and E. T. Denisov, *Izv. Akad. Nauk SSSR, Ser. Khim.* 293 (1988).
16. N. M. Emanuel, E. T. Denisov, and Z. K. Maizus, *Liquid-Phase Oxidation of Hydrocarbons*, Plenum Press, New York, 1967.
17. A. E. Semenchenko, V. M. Solyanikov, and E. T. Denisov, *Neftekhimiya* **10**, 864 (1970).
18. V. L. Antonovskii, E. T. Denisov, and L. V. Solntseva, *Kinet. Katal.* **7**, 409 (1966).
19. L. G. Privalova, Z. K. Maizus, and M. M. Emanuel, *Dokl. AN SSSR* **161**, 1135 (1965).
20. N. V. Zolotova and E. T. Denisov, *Izv. Akad. Nauk SSSR, Ser. Khim.* 767 (1966).
21. J. M. Tedder, A. Nechvatal, and A. H. Jubb, *Basic Organic Chemistry*, John Wiley & Sons, Inc., London, 1975.
22. V. M. Solyanikov and E. T. Denisov, *Dokl. AN SSSR* **173**, 1106 (1967).
23. E. T. Denisov, V. M. Solyanikov, and A. L. Aleksandrov, *Adv. Chem. Ser.* **75**, 112 (1967).
24. V. M. Solyanikov, L. V. Petrov, and Kh. E. Kharlampidi, *Dokl. AN SSSR* **223**, 1412 (1975).
25. V. M. Solyanikov and E. T. Denisov, *Neftekhimiya* **9**, 116 (1969).
26. V. M. Solyanikov and E. T. Denisov, *Izv. Akad. Nauk SSSR, Ser. Khim.* 1391 (1968).
27. L. V. Petrov and V. M. Solyanikov, *Izv. Akad. Nauk SSSR, Ser. Khim.* 1535 (1980).
28. L. V. Petrov, V. M. Solyanikov, and Z. Ya. Petrova, *Dokl. AN SSSR* **230**, 306 (1976).
29. C. Walling, *Free Radicals in Solution*, John Wiley & Sons, Inc., New York, 1957.
30. C. Gambaryan, *Ber.* **58B**, 1775 (1925).

31. C. Gambaryan and L. Kazaryan, *Zh. Obsch. Khim.* **3**, 222 (1933).
32. L. Horner and E. Schwenk, *Angew. Chem.* **61**, 411 (1949).
33. L. Horner and H. Junkermann, *Ann.* **591**, 53 (1955).
34. T. H. Melzer and A. V. Tobolsky, *J. Am. Chem. Soc.* **76**, 5178 (1954).
35. O. A. Chaltykyan, E. N. Atanasyan, A. A. Varkisyan, G. A. Marmaryan, and D. S. Gaybakyan, *Zh. Fiz. Khim.* **32**, 2601 (1958).
36. O. A. Chaltykyan, N. M. Beileryan, and E. R. Sarukhanyan, *Izv. AN Arm. SSR* **17**, 21 (1964).
37. E. R. Sarukhanyan, N. M. Beileryan, and O. A. Chaltykyan, *Dokl. AN Arm. SSR* **37**, 285 (1964).
38. O. A, Chaltykyan, E. R. Sarukhanyan, and N. M. Beileryan, *Dokl. AN Arm. SSR* **44**, 213 (1967).
39. N. M. Beileryan, F. O. Karapetyan, and O. A. Chaltykyan, *Arm. Khim. Zh.* **19**, 828 (1966).
40. N. M. Beileryan, F. O. Karapetyan, and O. A. Chaltykyan, *Dokl. AN Arm. SSR* **43**, 108 (1966).
41. R. I. Milyutinskaya and Kh. S. Bagdasaryan, *Zh. Fiz. Khim.* **34**, 405 (1960).
42. K. O. Driskol and A. Tobolsky, *J. Coll. Sci.* **11**, 244 (1956).
43. M. Imoto and S. Choc, *J. Polym. Sci.* **15**, 475 (1955).
44. F. Hrabak and N. Vacek, *Coll. Czech. Comm.* **30**, 573 (1965).
45. S. Kashino, Y. Mugino, and S. Hasegava, *Bull. Chem. Soc. Jpn.* **40**, 2004 (1967).
46. O. A. Chaltykyan, E. N. Atanasyan, N. M. Beileryan, and G. A. Marmaryan, *Zh. Fiz. Khim.* **33**, 36 (1959).
47. S. K. Grigoryan, Z. Z. Meliksetyan, and N. M. Beileryan, *Arm. Khim. Zh.* **20**, 333 (1967).
48. O. A. Chaltykyan, S. K. Grigoryan, and N. M. Beileryan, *Izv. AN Arm. SSR* **18**, 133 (1965).
49. N. M. Beileryan, S. K. Grigoryan, and O. A. Chaltykyan, *Izv. AN Arm. SSR* **17**, 245 (1964).
50. N. M. Beileryan, O. A. Chaltykyan, and G. A. Esayan, *Arm. Khim. Zh.* **21**, 7 (1968).

Handbook of Free Radical Initiators. E.T. Denisov, T.G. Denisova, T.S. Pokidova
Copyright © 2003 John Wiley & Sons, Inc.
ISBN: 0-471-20753-5

13

FREE RADICAL GENERATION BY OLEFINS

13.1 REACTIONS OF RETRODISPROPORTIONATION

Disproportionation of free radicals, for example,

$$CH_3C^{\bullet}H_2 + CH_3C^{\bullet}H_2 \rightarrow CH_3CH_3 + CH_2{=}CH_2$$

is a very exothermic reaction ($\Delta H = -270\ \mathrm{kJ\,mol^{-1}}$) and occurs very rapidly. Disproportionation of free radicals in solution occurs with diffusion rate constants ($k_D = 8 \times 10^8 – 4 \times 10^9\ \mathrm{L\,mol^{-1}\,s^{-1}}$).[1]

The backward reaction of retrodisproportionation

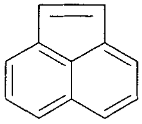
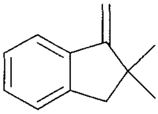
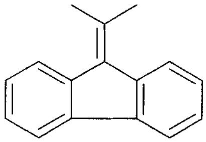
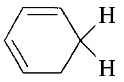
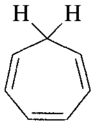
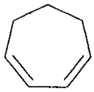
$$RH + CH_2{=}CHR^1 \rightarrow R^{\bullet} + CH_3C^{\bullet}HR^1$$

is endothermic and occurs slowly. This reaction was supposed to be important in the chain reaction of thermal hydrocarbon decomposition.[2] Many such reactions have been studied recently by Ruchardt and co-workers.[3–10] Activation energies for these reactions were found to be close to the values of reaction enthalpies. The substitution of hydrogen by deuterium in RH leads to the kinetic isotope effect (see Table 13.1). The influence of the solvent polarity on the disproportionation of hydrocarbons was found to be weak. For example, the ratio of rate constants of the α-methylstyrene reaction with 9,10-dihydroanthracene in *N*-acetamide and diphenyl ether is equal to 0.7 (593 K) and that of α-methylstyrene with 1,2-dihydronaphthalene is 0.9 (623 K).[3] However, the solvent effect is rather strong for the reaction of quinone as a hydrogen acceptor. For example, $\Delta G^{\#}$ for the reaction of 9,10-dihydroanthracene with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone has the following values in different solvents:[3]

Solvent	Dioxane	Acetonitrile	Acetic acid
$\Delta G^{\#}(298\ \mathrm{K})(\mathrm{kJ\ mol^{-1}})$	84.1	81.2	80.7
k/k(dioxane)	1	3.6	3.9

The experimental values for rate constants of the retrodisproportionation of 9,10-dihydroanthracene with various acceptors in a diphenyl ether solution are presented in Table 13.2. The enthalpies of retrodisproportionation reactions are collected in Table 13.3. Those calculated by the IPM method rate constants of retrodisproportionation reactions are collected in Tables 13.4–13.7.

TABLE 13.1 Kinetic Isotope Effect in Reactions of Olefins Retrodisproportionation with 9,10-Dihydroanthracene in Diphenyl Ether Solution[a]

Olefin	T (K)	k_H/k_D
$Ph(Me_2CH)C{=}CH_2$	573	2.25
$Ph(Me_3C)C{=}CH_2$	633	2.12
	553	2.27
	573	2.35
	593	1.64
$Ph_2C{=}CHPh$	593	2.22
	573	1.79
	583	1.98
	613	2.20

[a] See Ref. 3.

TABLE 13.2 Rate Constants and Activation Energies of 9,10-Dihydroanthracene Retrodisproportionation Reaction with Olefins[a]

Olefin	Solvent	T (K)	E (kJ mol^{-1})	log A, A (L mol^{-1} s^{-1})	k(550 K) (L mol^{-1} s^{-1})
Acenaphthylene	Diphenyl ether	553–583	114.8	7.36	2.87×10^{-4}
Azobenzene	Diphenyl ether	463–523	112.0	8.43	6.21×10^{-3}
Azobenzene, 4,4′-bis(1,1-dimethylethyl)-	Diphenyl ether	463–523	115.0	8.67	5.60×10^{-3}
Azobenzene, 4,4′-diamino-	Diphenyl ether	463–523	121.3	8.82	1.99×10^{-3}
Azobenzene, 4,4′-dibromo-	Diphenyl ether	463–523	119.6	9.73	2.35×10^{-2}
Azobenzene, 4,4′-dichloro-	Diphenyl ether	463–523	115.0	9.08	1.44×10^{-2}
Azobenzene, 4,4′-dimethoxy-	Diphenyl ether	463–523	116.6	8.51	3.11×10^{-3}
Azobenzene, 4,4′-dimethyl-	Diphenyl ether	463–523	111.2	8.16	3.97×10^{-3}
1,4-Benzoquinone, 2,3-dichloro-5,6-dicyano-	Acetic acid	298–338	43.6	6.28	1.37×10^{2}
1,4-Benzoquinone, 2,3-dichloro-5,6-dicyano-	Acetonitrile	298–338	37.4	5.11	3.64×10
1,4-Benzoquinone, 2,3-dichloro-5,6-dicyano-	Dioxane	298–338	51.6	7.11	1.62×10^{2}
1-Butene, 3-methyl-2-phenyl-	Diphenyl ether	553–583	131.1	7.67	1.66×10^{-5}
1-Butene, 2-phenyl-	Diphenyl ether	553–583	149.1	9.48	2.09×10^{-5}
1-Butene, 2-phenyl-3,3-dimethyl-	Diphenyl ether	553–583	148.3	8.32	1.72×10^{-6}

(*continued overleaf*)

TABLE 13.2 *(continued)*

Olefin	Solvent	T (K)	E (kJ mol^{-1})	log A, A (L mol^{-1} s^{-1})	k(550 K) (L mol^{-1} s^{-1})
1-Butene, 2,4,4-triacetoxy-	Diphenyl ether	553–583	137.8	8.13	1.10×10^{-5}
Cycloheptatriene	Diphenyl ether	553–583	137.8	8.71	4.20×10^{-5}
1,3-Cyclohexadiene	Diphenyl ether	553–583	129.0	8.30	1.12×10^{-4}
Dibenzofulvene	Diphenyl ether	553–583	96.8	7.10	8.07×10^{-3}
Ethene, 1,1-diphenyl-	Diphenyl ether	553–583	139.9	9.39	1.27×10^{-4}
Ethene, 1,2-diphenyl-	Diphenyl ether	553–583	162.1	9.72	2.11×10^{-6}
Ethene, triphenyl-	Diphenyl ether	553–583	155.0	9.02	1.99×10^{-6}
Fluorene, 9-ethylidene-	Diphenyl ether	553–583	130.3	9.22	7.00×10^{-4}
Fluorene, 9-isopropylidene-	Diphenyl ether	553–583	141.2	9.11	5.01×10^{-5}
Fluorene, 9-(1′,1′-dicyanoethylene)-	Diphenyl ether	553–583	139.9	9.17	7.65×10^{-5}
Indane, 2,2-diethyl-1-methylene-	Diphenyl ether	553–583	139.1	9.13	8.31×10^{-5}
Indane, 2,2-dimethyl-1-methylene-	Diphenyl ether	553–583	132.8	8.50	7.72×10^{-5}
Indene	Diphenyl ether	553–583	155.8	9.70	8.01×10^{-6}
Naphthalene, 1,2-dihydro-	Diphenyl ether	553–583	154.5	9.56	7.71×10^{-6}
Styrene	Diphenyl ether	553–583	111.5	6.60	1.02×10^{-4}
Styrene, 2,6-dimethyl-	Diphenyl ether	553–583	139.5	8.08	6.78×10^{-6}

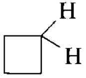
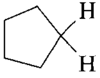
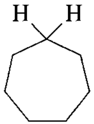
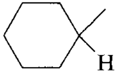
[a] See Refs. 3–10.

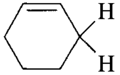
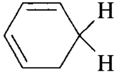
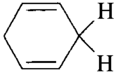
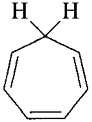
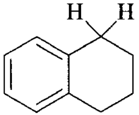
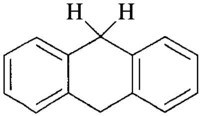
TABLE 13.3 Rate Constants and Activation Energies of α-Methylstyrene Retrodisproportionation Reaction with Different H-Donors[a]

Donor	Solvent	T (K)	E (kJ mol^{-1})	log A, A (L mol^{-1} s^{-1})	k(550 K) (L mol^{-1} s^{-1})
Anthrone	Tetraline	553–583	109.4	6.01	4.17×10^{-5}
Anthrone-d_2	Tetraline	573			4.29×10^{-5}
7-*H*-Benz[*de*]anthracene	Diphenyl ether	553–583	105.6	7.65	4.18×10^{-3}
7-*H*-Benz[*de*]anthracene-d_2	Diphenyl ether	523			4.70×10^{-4}
9,10-Dideuteroanthracene	Diphenyl ether	553–583	142.0	8.84	2.26×10^{-5}
9,9-Dideuterofluorene-d_2	2-Phenylbutane	573			4.05×10^{-6}
9,10-Dihydroanthracene, 1,4,5,8-tetramethyl-	Diphenyl ether	553–583	124.8	7.95	1.25×10^{-4}
(*Z*)-9,10-Dihydroanthracene 9,10-dimethyl-	Diphenyl ether	553–583	129.0	7.89	4.35×10^{-5}
(*E*)-9,10-Dihydroanthracene, 9,10-diphenyl-	Diphenyl ether	553–583	121.9	7.54	9.18×10^{-5}
(*Z*)-9,10-Dihydroanthracene, 9,10-diphenyl-	Diphenyl ether	553–583	122.7	6.75	1.25×10^{-5}
9,10-Dihydroanthracene, 9-phenyl-	Diphenyl ether	553–583	120.7	7.21	5.58×10^{-5}
9,10-Dihydroanthracene, 9,9-diphenyl-	Diphenyl ether	553–583	129.4	7.47	1.52×10^{-5}
1,4-Dihydronaphthalene-d_4	Diphenyl ether	573			2.74×10^{-4}
1,2-Dihydronaphthalene-d_4	Diphenyl ether	573			4.44×10^{-5}
9,10-Dihydroanthracene, 1,4,5,8-tetramethyl-9,9′,10,10′-d_4	Diphenyl ether	633			2.36×10^{-3}
9,10-Dihydroanthracene, 9,9,10-d_3-9-phenyl-	Diphenyl ether	633			9.36×10^{-4}
9,10-Dihydroanthracene, 9,9,10-d_3-9-phenyl-	Diphenyl ether	633			4.77×10^{-4}
Fluorene	2-Phenylbutane	553–583	120.2	5.90	3.05×10^{-6}
Naphthalene, 1,2-dihydro-	Diphenyl ether	553–583	138.6	8.52	2.27×10^{-5}
Naphthalene, 2,4-dihydro-	Diphenyl ether	553–583	126.5	8.34	2.12×10^{-4}
Phenalene	Diphenyl ether	553–583	86.8	6.29	1.11×10^{23}
Xanthene-d_2	2-Phenylbutane	573			4.63×10^{-5}

[a] See Ref. 3.

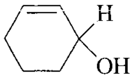
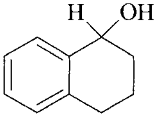
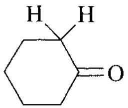
TABLE 13.4 Enthalpies of Retrodisproportionation Reactions (for BDE of C−H Bonds in Molecules and Radicals)[a]

	ΔH (kJ mol^{-1})								
RH	CH_2CH_2	CH_2CHEt	1,3-*cyclo*-C_6H_8	$PhNCH_2$	PhC(O)H	$OCCH_2$	$MeNCH_2$	PhNO	MeNNMe
EtMeCH−H	262.6	273.0	207.6	239.2	263.0	246.6	262.9	190.0	248.7
Me_3C-H	249.6	260.0	194.6	226.2	250.0	233.6	249.9	177.0	235.7
	268.1	278.5	213.1	244.7	268.5	252.1	268.4	195.5	254.2
	258.0	268.4	203.0	234.6	258.4	242.0	258.3	185.4	244.1
	253.5	263.9	198.5	230.1	253.9	237.5	253.8	180.9	239.6
	245.1	255.5	190.1	221.7	245.5	229.1	245.4	172.5	231.2
(*Z*)-Decalin	237.2	247.6	182.2	213.8	237.6	221.2	237.5	164.6	223.3
$CH_2{=}CHCH_2-H$	217.6	228.0	162.6	194.2	218.0	201.6	217.9	145.0	203.7
$CH_2{=}CHCH-HMe$	199.4	209.8	144.4	176.0	199.8	183.4	199.7	126.8	185.5
$CH_2{=}CHC-HMe_2$	189.2	199.6	134.2	165.8	189.6	173.2	189.5	116.6	175.3
(*Z*)-MeCH=CHCH−HMe	193.6	204.0	138.6	170.2	194.0	177.6	193.9	121.0	179.7
$Me_2C{=}CHCH-HMe$	181.6	192.0	126.6	158.2	182.0	165.6	181.9	109.0	167.7
$Me_2C{=}CMeC-HMe_2$	172.4	182.8	117.4	149.0	172.8	156.4	172.7	998.0	158.5
$(CH_2{=}CH)_2C-HMe$	156.8	167.2	101.8	133.4	157.2	140.8	157.1	842.0	142.9

	191.1	201.5	136.1	167.7	191.5	175.1	191.4	118.5	177.2
	180.5	190.9	125.5	157.1	180.9	164.5	180.8	107.9	166.6
	162.2	172.6	107.2	138.8	162.6	146.2	162.5	896.0	148.3
	150.6	161.0	956.0	127.2	151.0	134.6	150.9	780.0	136.7
$MeC{\equiv}CC{-}HMe_2$	179.0	189.4	124.0	155.6	179.4	163.0	179.3	106.4	165.1
$MePhCH{-}H$	213.7	224.1	158.7	190.3	214.1	197.7	214.0	141.1	199.8
$Me_2PhC{-}H$	204.3	214.7	149.3	180.9	204.7	188.3	204.6	131.7	190.4
	195.2	205.6	140.2	171.8	195.6	179.2	195.5	122.6	181.3
	171.6	182.0	116.6	148.2	172.0	155.6	171.9	990.0	157.7
$Me_2NH_2C{-}H$	229.1	239.5	174.1	205.7	229.5	213.1	229.4	156.5	215.2
$(CH_2{=}CHCH{-}H)_3N$	195.2	205.6	140.2	171.8	195.6	179.2	195.5	122.6	181.3
$Me_2C{-}H(OH)$	240.1	250.5	185.1	216.7	240.5	224.1	240.4	167.5	226.2

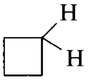
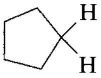
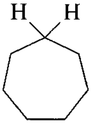
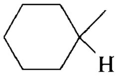
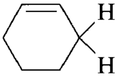
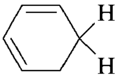
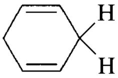
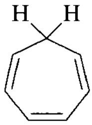
(continued overleaf)

TABLE 13.4 (*continued*)

RH	ΔH (kJ mol^{-1})								
	CH_2CH_2	CH_2CHEt	1,3-*cyclo*-C_6H_8	$PhNCH_2$	PhC(O)H	$OCCH_2$	$MeNCH_2$	PhNO	MeNNMe
	179.3	189.7	124.3	155.9	179.7	163.3	179.6	106.7	165.4
MeCH=CMeC−HMeOH	174.8	185.2	119.8	151.4	175.2	158.8	175.1	102.2	160.9
	187.1	197.5	132.1	163.7	187.5	171.1	187.4	114.5	173.2
PhC(O)−H	197.6	208.0	142.6	174.2	198.0	181.6	197.9	125.0	183.7
	243.7	254.1	188.7	220.3	244.1	227.7	244.0	171.1	229.8
$Me_2CHOC-HMe_2$	240.4	250.8	185.4	217.0	240.8	224.4	240.7	167.8	226.5
$(CH_2=CHCH-H)_2O$	209.6	220.0	154.6	186.2	210.0	193.6	209.9	137.0	195.7
$Ph_2C-HOMe$	203.8	214.2	148.8	180.4	204.2	187.8	204.1	131.2	189.9
Ph(C(O)OH)CH−H	216.6	227.0	161.6	193.2	217.0	200.6	216.9	144.0	202.7
Me_3COO-H	208.2	218.6	153.2	184.8	208.6	192.2	208.5	135.6	194.3
$(Me_3C)_3Si-H$	200.6	211.0	145.6	177.2	201.0	184.6	200.9	128.0	186.7
Ph_3Ge-H	172.1	182.5	117.1	148.7	172.5	156.1	172.4	99.5	158.2
Ph_3Sn-H	146.5	156.9	915.0	123.1	146.9	130.5	146.8	73.9	132.6

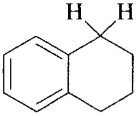
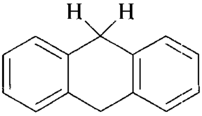
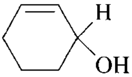
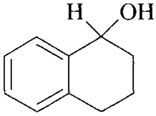
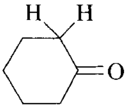
[a] See Chapter 9.

TABLE 13.5 Enthalpies and Rate Constants of Retrodisproportionation Reaction $CH_2{=}CHCH{=}CH_2 + HR \rightarrow CH_2{=}CHC^{\bullet}HCH_3 + R^{\bullet}$ (Calculated by the IPM Method)[a]

RH	*D* (kJ mol^{-1})	*n*	*E* (kJ mol^{-1})	log *A*, *A* (L mol^{-1} s^{-1})	*k*(550 K) (L mol^{-1} s^{-1})
EtMeCH−H	413.0	4	217.7	10.56	7.67×10^{-11}
$Me_3C{-}H$	400.0	1	204.7	9.68	1.74×10^{-10}
	418.5	8	223.2	10.95	5.66×10^{-11}
	408.4	1	213.1	10.87	4.28×10^{-10}
	403.9	1	208.6	10.92	1.28×10^{-9}
	395.5	1	200.2	9.55	3.44×10^{-10}
(*Z*)-Decalin	387.6	2	192.3	9.57	2.03×10^{-9}
$CH_2{=}CHCH_2{-}H$	368.0	3	182.3	8.48	1.47×10^{-9}
$CH_2{=}CHCH{-}HMe$	349.8	2	169.3	8.30	1.67×10^{-8}
$CH_2{=}CHC{-}HMe_2$	339.6	1	162.1	8.00	4.03×10^{-8}
(*Z*)-MeCH=CHCH−HMe	344.0	2	165.2	8.30	4.09×10^{-8}
$Me_2C{=}CHCH{-}HMe$	332.0	2	156.9	8.30	2.51×10^{-7}
$Me_2C{=}CMeC{-}HMe_2$	322.8	1	150.7	8.00	4.87×10^{-7}
$(CH_2{=}CH)_2C{-}HMe$	307.2	1	140.4	8.00	4.63×10^{-6}
	341.5	4	163.5	8.60	1.19×10^{-7}
	330.9	4	156.2	8.60	5.86×10^{-7}
	312.6	4	144.0	8.60	8.44×10^{-6}
	301.0	2	136.4	8.30	2.22×10^{-5}

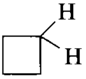
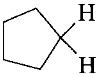
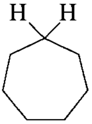
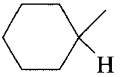
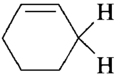
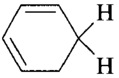
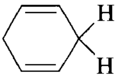
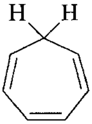
(continued overleaf)

TABLE 13.5 (***continued***)

RH	D (kJ mol^{-1})	n	E (kJ mol^{-1})	log A, A (L mol^{-1} s^{-1})	k(550 K) (L mol^{-1} s^{-1})
$MeC{\equiv}CC{-}HMe_2$	329.4	1	155.2	8.00	1.82×10^{-7}
$MePhCH{-}H$	364.1	2	176.5	8.30	3.46×10^{-9}
$Me_2PhC{-}H$	354.7	1	169.6	8.00	7.81×10^{-9}
	345.6	4	163.1	9.60	1.29×10^{-6}
	322.0	4	146.8	9.60	4.57×10^{-5}
$Me_2NH_2C{-}H$	379.5	1	186.2	8.00	2.07×10^{-10}
$(CH_2{=}CHCH{-}H)_3N$	345.6	6	166.3	8.78	9.69×10^{-8}
$Me_2C{-}H(OH)$	390.5	1	195.2	9.38	6.94×10^{-10}
	329.7	1	155.4	9.78	1.05×10^{-5}
$MeCH{=}CMeC{-}HMeOH$	325.2	1	152.3	8.00	6.87×10^{-7}
	337.5	1	160.7	9.00	5.47×10^{-7}
$PhC(O){-}H$	348.0	1	164.8	8.00	2.23×10^{-8}
	394.1	4	198.8	10.11	1.70×10^{-9}
$Me_2CHOC{-}HMe_2$	390.8	2	195.5	9.70	1.36×10^{-9}
$(CH_2{=}CHCH{-}H)_2O$	360.0	4	176.5	8.60	6.91×10^{-9}
$Ph_2C{-}HOMe$	354.2	1	169.3	8.00	8.34×10^{-9}
$Ph[C(O)OH]CH{-}H$	367.0	2	178.6	8.30	2.18×10^{-9}
$Me_3COO{-}H$	358.6	1	170.5	9.00	6.42×10^{-8}
$(Me_3C)_3Si{-}H$	351.0	1	155.7	10.22	2.77×10^{-5}
$Ph_3Ge{-}H$	322.5	1	126.6	9.00	9.48×10^{-4}
$Ph_3Sn{-}H$	296.9	1	110.9	9.00	2.94×10^{-2}

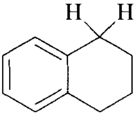
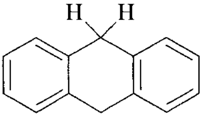
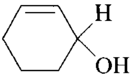
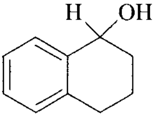
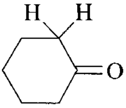
[a] See Ref. 11.

TABLE 13.6 Enthalpies and Rate Constants of Retrodisproportionation Reaction $PhCH{=}CH_2 + RH \rightarrow PhC^{\bullet}HCH_3 + R^{\bullet}$ (Calculated by the IPM Method)[a]

RH	D (kJ mol^{-1})	n	E (kJ mol^{-1})	log A, A (L mol^{-1} s^{-1})	k(550 K) (L mol^{-1} s^{-1})
EtMeCH−H	413.0	4	225.0	10.70	2.15×10^{-11}
Me_3C−H	400.0	1	212.0	9.94	6.40×10^{-11}
	418.5	8	230.5	11.06	1.48×10^{-11}
	408.4	1	220.4	11.05	1.31×10^{-10}
	403.9	1	215.9	11.14	4.32×10^{-10}
	395.5	1	207.5	9.88	1.49×10^{-10}
(Z)-Decalin	387.6	2	199.6	10.06	1.27×10^{-9}
$CH_2{=}CHCH_2$−H	368.0	3	182.0	8.48	1.57×10^{-9}
$CH_2{=}CHCH$−HMe	349.8	2	168.4	8.30	2.03×10^{-8}
$CH_2{=}CHC$−HMe_2	339.6	1	161.0	8.00	5.12×10^{-8}
(Z)-MeCH=CHCH−HMe	344.0	2	164.2	8.30	5.08×10^{-8}
$Me_2C{=}CHCH$−HMe	332.0	2	155.6	8.30	3.34×10^{-7}
$Me_2C{=}CMeC$−HMe_2	322.8	1	149.1	8.00	6.91×10^{-7}
$(CH_2{=}CH)_2C$−HMe	307.2	1	138.5	8.00	7.02×10^{-6}
	341.5	4	162.4	9.60	1.50×10^{-6}
	330.9	4	154.9	9.60	7.74×10^{-6}
	312.6	4	142.1	9.60	1.27×10^{-4}
	301.0	2	134.1	9.30	3.67×10^{-4}

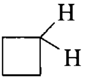
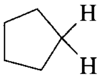
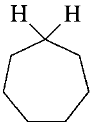
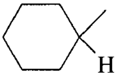
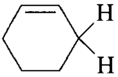
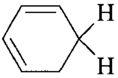
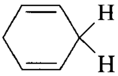
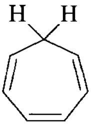
(*continued overleaf*)

TABLE 13.6 (*continued*)

RH	D (kJ mol^{-1})	n	E (kJ mol^{-1})	log A, A (L mol^{-1} s^{-1})	k(550 K) (L mol^{-1} s^{-1})
$MeC\equiv CC-HMe_2$	329.4	1	153.8	8.00	2.47×10^{-7}
$MePhCH-H$	364.1	2	176.1	8.30	3.76×10^{-9}
Me_2PhC-H	354.7	1	169.7	8.00	7.65×10^{-9}
	345.6	4	162.5	9.60	1.47×10^{-6}
	322.0	4	131.7	9.60	9.20×10^{-5}
Me_2NH_2C-H	379.5	1	191.5	9.61	2.65×10^{-9}
$(CH_2{=}CHCH-H)_3N$	345.6	6	169.5	8.78	4.81×10^{-8}
$Me_2C-H(OH)$	390.5	1	202.5	9.81	3.79×10^{-10}
	329.7	1	158.9	9.00	8.11×10^{-7}
$MeCH{=}CMeC-HMeOH$	325.2	1	155.8	8.00	1.60×10^{-7}
	337.5	1	156.6	9.00	1.34×10^{-6}
$PhC(O)-H$	348.0	1	164.3	8.00	2.49×10^{-8}
	394.1	4	206.1	10.46	7.70×10^{-10}
$Me_2CHOC-HMe_2$	390.8	2	202.8	10.11	7.08×10^{-10}
$(CH_2{=}CHCH-H)_2O$	360.0	4	176.0	8.60	7.68×10^{-9}
$Ph_2C-HOMe$	354.2	1	168.9	8.00	9.11×10^{-9}
$Ph(C(O)OH)CH-H$	367.0	2	179.0	8.30	2.00×10^{-9}
Me_3COO-H	358.6	1	170.0	9.83	4.84×10^{-7}
$(Me_3C)_3Si-H$	351.0	1	163.0	10.27	6.16×10^{-6}
Ph_3Ge-H	322.5	1	134.5	9.46	4.86×10^{-4}
Ph_3Sn-H	296.9	1	109.9	9.00	3.65×10^{-2}

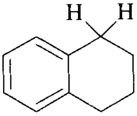
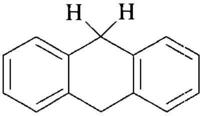
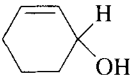
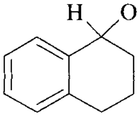
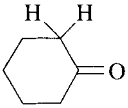
[a] See Chapter 9 and Ref. 11.

TABLE 13.7 Enthalpies and Rate Constants for the Retrodisproportionation Reaction $p\text{-}OC_6H_4O + RH \rightarrow p\text{-}HOC_6H_4O^\bullet + R^\bullet$ (Calculated by the IPM method)[a]

RH	D (kJ mol^{-1})	n	ΔH (kJ mol^{-1})	log A, A (L mol^{-1} s^{-1})	k(550 K) (L mol^{-1} s^{-1})
EtMeCH−H	413.0	4	186.7	11.70	5.64×10^{-7}
Me_3C−H	400.0	1	173.7	11.03	2.05×10^{-6}
	418.5	8	192.2	12.03	3.61×10^{-7}
	408.4	1	182.1	12.08	3.64×10^{-6}
	403.9	1	177.6	12.20	1.29×10^{-5}
	395.5	1	169.2	11.00	5.14×10^{-6}
(Z)-Decalin	387.6	2	161.3	11.25	5.14×10^{-5}
CH_2=$CHCH_2$−H	368.0	3	141.7	11.00	2.12×10^{-3}
CH_2=CHCH−HMe	349.8	2	123.5	10.57	4.20×10^{-2}
CH_2=CHC−HMe_2	339.6	1	113.3	10.08	0.12
(Z)-MeCH=CHCH−HMe	344.0	2	117.7	10.47	0.12
Me_2C=CHCH−HMe	332.0	2	105.7	10.19	0.84
Me_2C=CMeC−HMe_2	322.8	1	96.50	8.43	0.18
$(CH_2{=}CH)_2C$−HMe	307.2	1	80.90	8.00	0.53
	341.5	4	115.2	10.72	0.36
	330.9	4	104.6	10.45	1.99
	312.6	4	86.30	9.52	12.5
	301.0	2	74.70	8.30	2.42

(*continued overleaf*)

TABLE 13.7 (*continued*)

RH	D (kJ mol^{-1})	n	ΔH (kJ mol^{-1})	log A, A (L mol^{-1} s^{-1})	k(550 K) (L mol^{-1} s^{-1})
$\mathrm{MeC{\equiv}CC{-}HMe_2}$	329.4	1	103.1	9.81	0.62
$\mathrm{MePhCH{-}H}$	364.1	2	137.8	10.97	4.57×10^{-3}
$\mathrm{Me_2PhC{-}H}$	354.7	1	128.4	10.56	1.41×10^{-2}
	345.6	4	119.3	11.05	0.31
	322.0	4	95.70	10.60	19.5
$\mathrm{Me_2NH_2C{-}H}$	379.5	1	153.2	10.89	1.33×10^{-4}
$\mathrm{(CH_2{=}CHCH{-}H)_3N}$	345.6	6	119.3	10.98	0.27
$\mathrm{Me_2C{-}H(OH)}$	390.5	1	164.2	10.97	1.43×10^{-5}
	329.7	1	103.4	9.82	0.59
$\mathrm{MeCH{=}CMeC{-}HMeOH}$	325.2	1	98.90	9.66	1.11
	337.5	1	111.2	10.32	0.35
$\mathrm{PhC(O){-}H}$	348.0	1	121.7	10.48	5.02×10^{-2}
	394.1	4	167.8	11.59	2.74×10^{-5}
$\mathrm{Me_2CHOC{-}HMe_2}$	390.8	2	164.5	11.27	2.68×10^{-5}
$\mathrm{(CH_2{=}CHCH{-}H)_2O}$	360.0	4	133.7	11.03	1.29×10^{-2}
$\mathrm{Ph_2C{-}HOMe}$	354.2	1	127.9	10.56	1.55×10^{-2}
$\mathrm{Ph(C(O)OH)CH{-}H}$	367.0	2	140.7	11.00	2.59×10^{-3}
$\mathrm{Me_3COO{-}H}$	358.6	1	132.3	10.71	8.31×10^{-3}
$\mathrm{(Me_3C)_3Si{-}H}$	351.0	1	124.7	10.84	5.90×10^{-2}
$\mathrm{Ph_3Ge{-}H}$	322.5	1	96.20	10.30	8.78
$\mathrm{Ph_3Sn{-}H}$	296.9	1	70.60	8.40	29.8

[a] See Chapter 9 and Ref. 11.

13.2 CHAIN INITIATION IN THERMAL RADICAL POLYMERIZATION

Usually radical polymerization is initiated by an initiator or the photochemical generation of radicals. However, radical polymerization occurs slowly in the absence of an initiator. Free radicals are generated by thermal reactions of self-initiation.[12,13] Mayo was the first to study the thermal polymerization of styrene.[14] He found that the rate of thermal initiation was proportional to $[\text{styrene}]^3$ and proposed the trimolecular reaction.

$$3\text{PhCH}{=}\text{CH}_2 \rightarrow \text{PhC}^{\bullet}\text{HCH}_3 + \text{PhC}^{\bullet}\text{HCH}_2\text{CH}{=}\text{CHPh}$$

The following two mechanisms are discussed as the most probable reactions of thermal radical generation in monomers:

1. Formation of biradical succeeded by retrodisproportionation, for example,

$$\text{PhMeC}{=}\text{CH}_2 + \text{PhMeC}{=}\text{CH}_2 \Leftrightarrow \text{PhMeC}^{\bullet}\text{CH}_2\text{CH}_2\text{C}^{\bullet}\text{MePh}$$

$$\text{PhMeC}^{\bullet}\text{CH}_2\text{CH}_2\text{C}^{\bullet}\text{MePh} + \text{CH}_2{=}\text{CPhCH}_3 \rightarrow \text{PhMeCHCH}_2\text{CH}_2\text{C}^{\bullet}\text{MePh} + \text{CH}_2{=}\text{CPhC}^{\bullet}\text{H}_2$$

   This mechanism is valid for monomers with a sufficient weak C—H bond (α-methylstyrene, methyl methacrylate, etc.).

2. Biradical formation from the monomer succeeded by the hydrogen-transfer reaction from the biradical to the monomer, for example

$$\text{PhCH}{=}\text{CH}_2 + \text{CH}_2{=}\text{CHPh} \Leftrightarrow \text{PhC}^{\bullet}\text{HCH}_2\text{CH}_2\text{C}^{\bullet}\text{HPh}$$

$$\text{PhC}^{\bullet}\text{HCH}_2\text{CH}_2\text{C}^{\bullet}\text{HPh} + \text{CH}_2{=}\text{CHPh} \rightarrow \text{PhC}^{\bullet}\text{HCH}_2\text{CH}{=}\text{CHPh} + \text{CH}_3\text{C}^{\bullet}\text{HPh}$$

   Calculated values for the enthalpy, entropy, and equilibrium constant for biradical formation from the monomer are presented in Table 13.8. For the values of rate constants and activation energies of retrodisproportionation reactions calculated by the IPM method, see Table 13.9. Rate constants and activation energies of hydrogen-exchange reactions are collected in Table 13.10.

TABLE 13.8 Values of $\Delta H, \Delta S, \Delta G$, and Equilibrium Constant K of Reaction: $2RCH{=}CH_2 \Leftrightarrow RC^{\bullet}HCH_2CH_2C^{\bullet}HR$

Monomer	ΔH (kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})	ΔG (298 K) (kJ mol^{-1})	K (450 K) (L mol^{-1})
$CH_2{=}CH_2$	177.0	−111.0	210.1	4.54×10^{-24}
$CH_2{=}CHMe$	182.9	−128.1	221.1	1.20×10^{-28}
$CH_2{=}CHEt$	185.4	−126.6	223.1	7.36×10^{-29}
$CH_2{=}CHCH{=}CH_2$	86.5	−103.4	117.3	4.60×10^{-16}
$CH_2{=}CHPh$	98.7	−127.8	136.8	7.38×10^{-19}
$CH_2{=}CMePh$	99.0	−148.8	143.3	5.45×10^{-20}
$CH_2{=}CHCOOMe$	170.4	−125.2	207.7	4.80×10^{-27}
$CH_2{=}CMeCOOMe$	166.2	−140.8	208.2	2.26×10^{-27}
$CH_2{=}CHCOOEt$	169.4	−125.2	206.7	6.27×10^{-27}
$CH_2{=}CHCl$	167.0	−117.0	201.9	3.19×10^{-26}

TABLE 13.9 Activation Energies and Rate Constants of Hydrogen-Transfer Reactions $RCH{=}CH_2 + RC^{\bullet}HCH_2CH_2C^{\bullet}HR \rightarrow RC^{\bullet}HCH_3 + RCH{=}CHCH_2C^{\bullet}HR$ (Calculated by the IPM Method)[a]

$RC^{\bullet}H(CH_2)_2C^{\bullet}HR$	$RCH{=}CH_2$	E (kJ mol^{-1})	log A, A (L mol^{-1} s^{-1})	k(450 K) (L mol^{-1} s^{-1})	kK(450 K) (L^2 mol^{-2} s^{-1})
$C^{\bullet}H_2CH_2CH_2C^{\bullet}H_2$	$CH_2{=}CH_2$	53.6	9.60	2.41×10^3	1.09×10^{-20}
$C^{\bullet}H_2CH_2CH_2C^{\bullet}H_2$	$CH_2{=}CHCH{=}CH_2$	44.0	9.60	3.12×10^4	1.42×10^{-19}
$C^{\bullet}H_2CH_2CH_2C^{\bullet}H_2$	$CH_2{=}CHPh$	40.0	9.30	4.55×10^4	2.07×10^{-19}
$(CH_2{=}CHC^{\bullet}HCH_2)_2$	$CH_2{=}CH_2$	77.4	9.60	4.15	1.91×10^{-15}
$(CH_2{=}CHC^{\bullet}HCH_2)_2$	$CH_2{=}CHCH{=}CH_2$	70.3	9.60	2.77×10	1.27×10^{-14}
$(CH_2{=}CHC^{\bullet}HCH_2)_2$	$CH_2{=}CHPh$	66.8	9.30	3.52×10	1.62×10^{-14}
$PhC^{\bullet}HCH_2CH_2C^{\bullet}HPh$	$CH_2{=}CH_2$	78.4	9.60	3.17	2.34×10^{-18}
$PhC^{\bullet}HCH_2CH_2C^{\bullet}HPh$	$CH_2{=}CHCH{=}CH_2$	60.2	9.60	4.11×10^2	3.03×10^{-16}
$PhC^{\bullet}HCH_2CH_2C^{\bullet}HPh$	$CH_2{=}CHPh$	60.1	9.30	2.11×10^2	1.56×10^{-16}
$(CH_2C^{\bullet}MeCOOMe)_2$	$CH_2{=}CH_2$	56.5	9.60	1.11×10^3	2.51×10^{-24}
$(CH_2C^{\bullet}MeCOOMe)_2$	$CH_2{=}CHCH{=}CH_2$	46.6	9.60	1.56×10^4	3.52×10^{-23}
$(CH_2C^{\bullet}MeCOOMe)_2$	$CH_2{=}CHPh$	42.6	9.30	2.27×10^4	5.13×10^{-23}
$(CH_2C^{\bullet}MeCOOMe)_2$	$CH_2{=}CMeCOOMe$	55.0	9.30	8.26×10^2	1.87×10^{-24}
$ClC^{\bullet}HCH_2CH_2C^{\bullet}HCl$	$CH_2{=}CH_2$	60.4	9.60	3.90×10^2	1.24×10^{-23}
$ClC^{\bullet}HCH_2CH_2C^{\bullet}HCl$	$CH_2{=}CHCH{=}CH_2$	49.9	9.60	6.45×10^3	2.06×10^{-22}
$ClC^{\bullet}HCH_2CH_2C^{\bullet}HCl$	$CH_2{=}CHPh$	46.0	9.30	9.15×10^3	2.92×10^{-22}
$ClC^{\bullet}HCH_2CH_2C^{\bullet}HCl$	$CH_2{=}CHCl$	57.8	9.30	3.91×10^2	1.25×10^{-23}

[a] See Refs. 15 and 16.

TABLE 13.10 Activation Energies and Rate Constants of Hydrogen-Atom Abstraction by Biradical $RC^{\bullet}HCH_2CH_2C^{\bullet}HR + CH_2{=}CRCH_3 \rightarrow RC^{\bullet}HCH_2CH_2CH_2R + CH_2{=}CRC^{\bullet}H_2$ (Calculated by the IPM Method)[a]

Biradical	$CH_2{=}C(CH_3)R$	E (kJ mol^{-1})	log A, A (L mol^{-1} s^{-1})	k(450 K) (L mol^{-1} s^{-1})	kK(450 K) (L^2 mol^{-2} s^{-1})
$(MeC^{\bullet}HCH_2)_2$	$CH_2{=}CHMe$	50.4	9.78	8.51×10^3	1.02×10^{-24}
$(MeC^{\bullet}HCH_2)_2$	$CH_2{=}CHEt$	42.7	9.60	4.42×10^4	5.30×10^{-24}
$(MeC^{\bullet}HCH_2)_2$	$CH_2{=}CMePh$	45.7	8.78	2.97×10^3	3.56×10^{-25}
$(MeC^{\bullet}HCH_2)_2$	$CH_2{=}CMeCO_2Me$	46.9	8.78	2.16×10^3	2.59×10^{-26}
$(EtC^{\bullet}HCH_2)_2$	$CH_2{=}CHMe$	49.3	9.78	1.14×10^3	8.39×10^{-25}
$(EtC^{\bullet}HCH_2)_2$	$CH_2{=}CHEt$	41.7	9.60	5.78×10^4	4.25×10^{-24}
$(EtC^{\bullet}HCH_2)_2$	$CH_2{=}CMePh$	44.7	8.78	3.89×10^3	2.86×10^{-25}
$(EtC^{\bullet}HCH_2)_2$	$CH_2{=}CMeCO_2Me$	45.9	8.78	2.82×10^3	2.07×10^{-25}
$(PhMeC^{\bullet}CH_2)_2$	$CH_2{=}CHMe$	80.0	9.78	3.10	1.69×10^{-15}
$(PhMeC^{\bullet}CH_2)_2$	$CH_2{=}CHEt$	70.8	9.60	24.2	1.32×10^{-18}
$(PhMeC^{\bullet}CH_2)_2$	$CH_2{=}CMePh$	74.4	8.78	1.39	7.57×10^{-20}
$(PhMeC^{\bullet}CH_2)_2$	$CH_2{=}CMeCO_2Me$	75.9	8.78	0.93	5.07×10^{-20}
$(MeOC(O)C^{\bullet}HCH_2)_2$	$CH_2{=}CHMe$	56.3	9.78	1.75×10^3	8.40×10^{-24}
$(MeOC(O)C^{\bullet}HCH_2)_2$	$CH_2{=}CHEt$	48.2	9.60	1.02×10^4	4.90×10^{-27}
$(MeOC(O)C^{\bullet}HCH_2)_2$	$CH_2{=}CMePh$	51.4	8.78	6.48×10^2	3.11×10^{-26}
$(MeOC(O)C^{\bullet}HCH_2)_2$	$CH_2{=}CMeCO_2Me$	52.7	8.78	4.58×10^2	2.20×10^{-24}

[a] See Refs. 15 and 16.

REFERENCES

1. N. N. Semenov, *Some Problems of Chemical Kinetics and Reactivity*, Pergamon Press, London, 1958, Vol. 1; 1959, Vol. 2.
2. Z. B. Alfassi, in *General Aspects of the Chemistry of Radicals*, Z. B. Alfassy (Ed.), John Wiley & Sons, Inc., Chichester, U.K., 1999.
3. C. Ruchardt, G. Matthias, and J. Ebenhoch, *Angew. Chem. Int. Ed. Engl.* **36**, 1406 (1997).
4. K. Rakus, S. P. Verevkin, J. Schatzer, H.-D. Beckhaus, and C. Ruchardt, *Ber. Bunsenges. Phys. Chem.* **127**, 1095 (1994).
5. C. Ruchardt, M. Gerst, and M. Nolke, *Angew. Chem. Int. Ed. Engl.* **31**, 1523 (1992).
6. C. Herberg, H.-D. Beckhaus, and C. Ruchardt, *Ber. Bunsenges. Phys. Chem.* **127**, 2065 (1994).
7. M. Gerst, J. Morgenthaler, and C. Ruchardt, *Ber. Bunsenges. Phys. Chem.* **127**, 691 (1994).
8. H. Friebolin and C. Ruchardt, *Liebigs Ann. Chem.* 1339 (1995).
9. H. Friebolin, R. Roers, J. Ebenhoch, and C. Ruchardt, *Liebigs Ann. Chem.* 385 (1996).
10. M. Gerst and C. Ruchardt, *Ber. Bunsenges. Phys. Chem.* **126**, 1039 (1993).
11. E. T. Denisov, *Petroleum Chemistry* **37**, 22 (1997).

12. C. Walling, *Free Radicals in Solution*, John Wiley & Sons, Inc., New York, 1962.
13. R. Houwink and A. J. Staverman, *Chemie und Technologie der Kunststoffe*, Akademische Verlagsgeselschaft, Leipzig, Germany, 1962, B. 1.
14. F. R. Mayo, *J. Am. Chem. Soc.* **75**, 6133 (1953).
15. E. T. Denisov, *Russ. Chem. Bull.* **47**, 2110 (1998).
16. E. T. Denisov and T. G. Denisova, *Russ. Chem. Rev.* **71**, 417 (2002).

Handbook of Free Radical Initiators. E.T. Denisov, T.G. Denisova, T.S. Pokidova
Copyright © 2003 John Wiley & Sons, Inc.
ISBN: 0-471-20753-5

14

INITIATION BY HALOID MOLECULES AND NITROGEN DIOXIDE

14.1 REACTIONS OF FLUORINE COMPOUNDS

Difluorine is an extremely active reagent and reacts with organic molecules at low temperatures (200 K and lower).[1-3] Such a high activity for F_2 is the result of the very high BDE in the formed hydrogen fluoride molecule (D_{F-H} = 570.3 kJ mol^{-1}) and the relatively low BDE in the difluorine molecule (D_{F-F} = 158.7 kJ mol^{-1}, see Chapter 9). Due to this great difference in the BDE of reactants and products, bimolecular reactions of hydrogen-atom abstraction[4]

$$RH + F_2 \rightarrow R^{\bullet} + HF + F^{\bullet}$$

are exothermic for most organic molecules (see ΔH values in Table 14.1).

Initiation of reactions of pentachloroethane oxidation and chlorination by traces of difluorine was noticed by Miller and co-workers.[5,6] The rate constant for the difluorine reaction with methane that has C—H bonds of high strength (D_{C-H} = 440 kJ mol^{-1}, see Chapter 9) is $k = 2.0 \times 10^9 \exp(-47/RT)$ L mol^{-1} s^{-1} (298 K, experimental values).[7] The values for the activation energies and rate constants of the F_2 bimolecular reaction with several organic molecules calculated by the IPM model are presented in Table 14.2.[8] The enthalpy of these reactions varies from −6 to −118 kJ mol^{-1} and the activation energy ranges from 12 to 36 kJ mol^{-1} for chosen molecules.

Another fast reaction of radical initiation is difluorine addition to the double bond of the unsaturated compounds.[1,2,4]

$$F_2 + CH_2{=}CHR \rightarrow F^{\bullet} + FCH_2C^{\bullet}HR$$

TABLE 14.1 Enthalpies of Reactions of Hydrogen-Atom Abstraction RH + FY → R$^\bullet$ + HF + Y$^\bullet$

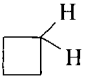
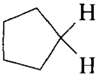
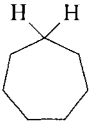
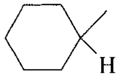
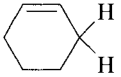
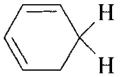
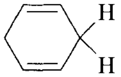
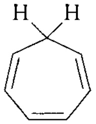
FY		F_2	FCl	FBr	FI	FOH	CFOF
RH	D (kJ mol^{-1})	ΔH (kJ mol^{-1})					
EtMeCH–H	413.0	1.4	98.9	92.9	114.3	57.2	24.7
Me_3C–H	400.0	−11.6	85.9	79.9	101.3	44.2	11.7
	418.5	6.9	104.4	98.4	119.8	62.7	30.2
	408.4	−3.2	94.3	88.3	109.7	52.6	20.1
	403.9	−7.7	89.8	83.8	105.2	48.1	15.6
	395.5	−16.1	81.4	75.4	96.8	39.7	7.2
(*Z*)-Decalin	387.6	−24.0	73.5	67.5	88.9	31.8	−70.0
$CH_2=CHCH_2$–H	368.0	−43.6	53.9	47.9	69.3	12.2	−20.3
$CH_2=CHCH$–HMe	349.8	−61.8	35.7	29.7	51.1	−6.0	−38.5
$CH_2=CHC$–HMe_2	339.6	−72.0	25.5	19.5	40.9	−16.2	−48.7
(*Z*)-MeCH=CHCH–HMe	344.0	−67.6	29.9	23.9	45.3	−11.8	−44.3
$Me_2C=CHCH$–HMe	332	−79.6	17.9	11.9	33.3	−23.8	−56.3
$Me_2C=CMeC$–HMe_2	322.8	−88.8	8.7	2.7	24.1	−33.0	−65.5
$(CH_2=CH)_2CMe$–H	307.2	−104.4	−6.9	−12.9	8.5	−48.6	−81.1
	341.5	−70.1	27.4	21.4	42.8	−14.3	−46.8
	330.9	−80.7	16.8	10.8	32.2	−24.9	−57.4
	312.6	−99.0	−1.50	−7.5	13.9	−43.2	−75.7
	301.0	−110.6	−13.1	−19.1	2.3	−54.8	−87.3

TABLE 14.1 (*continued*)

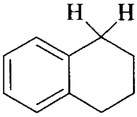
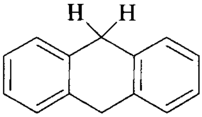
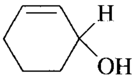
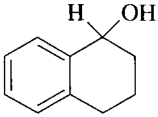
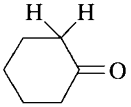
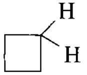
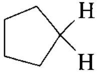
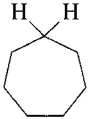
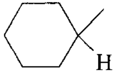
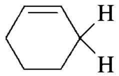
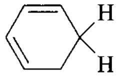
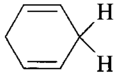
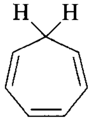
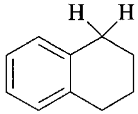
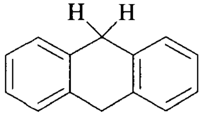
FY		F_2	FCl	FBr	FI	FOH	CFOF
RH	D (kJ mol^{-1})	ΔH (kJ mol^{-1})					
$MeC\equiv CC-HMe_2$	329.4	−82.2	15.3	9.3	30.7	−26.4	−58.9
$PhMeCH-H$	364.1	−47.5	50.0	44.0	65.4	8.3	−24.2
$PhMe_2C-H$	354.7	−56.9	40.6	34.6	56.0	−1.1	−33.6
	345.6	−66.0	31.5	25.5	46.9	−10.2	−42.7
	322.0	−89.6	7.9	1.9	23.3	−33.8	−66.3
Me_2NH_2C-H	379.5	−32.1	65.4	59.4	80.8	23.7	−88.0
$(CH_2=CHCH_2)_3N$	345.6	−66.0	31.5	25.5	46.9	−10.2	−42.7
$Me_2(HO)C-H$	390.5	−21.1	76.4	70.4	91.8	34.7	2.2
	329.7	−81.9	15.6	9.6	31.0	−26.1	−58.6
$MeCH=CMeC-HMeOH$	325.2	−86.4	11.1	5.1	26.5	−30.6	−63.1
	337.5	−74.1	23.4	17.4	38.8	−18.3	−50.8
$PhC(O)-H$	348.0	−63.6	33.9	27.9	49.3	−7.8	−40.3
	394.1	−17.5	80.0	74.0	95.4	38.3	5.8
$Me_2CHOC-HMe_2$	390.8	−20.8	76.7	70.7	92.1	35.0	2.5
$(CH_2=CHCH-H)_2O$	360.0	−51.6	45.9	39.9	61.3	42.0	−28.3
$Ph_2C-HOMe$	354.2	−57.4	40.1	34.1	55.5	−1.6	−34.1
$Ph(C(O)OH)CH-H$	367.0	−44.6	52.9	46.9	68.3	11.2	−21.3
Me_3COO-H	358.6	−53.0	44.5	38.5	59.9	2.8	−29.7
$(Me_3C)_3Si-H$	351.0	−60.6	36.9	30.9	52.3	−4.8	−37.3
Ph_3Ge-H	322.5	−89.1	8.4	2.4	23.8	−33.3	−65.8
Ph_3Sn-H	296.9	−114.7	17.2	−23.2	−1.8	−58.9	−91.4

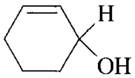
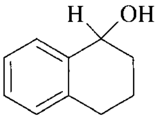
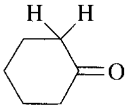
TABLE 14.2 Enthalpies, Activation Energies, and Rate Constants for the Reaction $F_2 + HR \rightarrow F^\bullet + HF + R^\bullet$ (Calculated by the IPM Method)[a]

RH	D (kJ mol^{-1})	n	ΔH_e (kJ mol^{-1})	E (kJ mol^{-1})	log A (A (L mol^{-1} s^{-1}))	k(300 K) (L mol^{-1} s^{-1})
EtMeCH–H	413.0	4	−6	36.5	10.94	3.84×10^4
Me_3C–H	400.0	1	−19	31.5	10.34	7.17×10^4
	418.5	8	−0.5	38.7	11.25	3.25×10^4
	408.4	10	−10.6	33.0	11.34	3.93×10^5
	403.9	14	−15.1	31.3	11.49	1.10×10^6
	395.5	1	−23.5	28.2	10.34	2.69×10^5
(Z)-Decalin	387.6	2	−31.4	25.4	10.64	1.65×10^6
CH_2=$CHCH_2$–H	368.0	3	−51	26.7	10.82	1.48×10^6
CH_2=CHCH–HMe	349.8	2	−69.2	21.1	10.64	9.25×10^6
CH_2=CHC–HMe_2	339.6	1	−79.4	18.1	10.34	1.54×10^7
(Z)-MeCH=CHCH–HMe	344.0	2	−75	23.5	10.64	3.53×10^6
Me_2C=CHCH–HMe	332.0	2	−87	20.1	10.64	1.38×10^7
Me_2C=CMeC–HMe_2	322.8	1	−96.2	17.6	10.34	1.89×10^7
$(CH_2$=$CH)_2C$–HMe	307.2	1	−111.8	13.7	10.34	9.01×10^7

	341.5	4	−77.5	22.8	10.94	9.34×10^6
	330.9	4	−88.1	19.8	10.94	3.11×10^7
	312.6	4	−106.4	15.0	10.94	2.13×10^8
	301.0	2	−118	12.2	10.64	3.28×10^8
$MeC{\equiv}CC{-}HMe_2$	329.4	1	−89.6	19.4	10.34	9.17×10^6
$MePhCH{-}H$	364.1	2	−54.9	24.8	10.64	2.10×10^6
$Me_2PhC{-}H$	354.7	1	−64.3	21.9	10.34	3.36×10^6
	345.6	4	−73.4	19.3	10.94	3.80×10^7
	322.0	4	−97	13.0	10.94	4.75×10^8
$Me_2NH_2C{-}H$	379.5	1	−39.5	26.7	10.34	4.91×10^5
$(CH_2{=}CHCH{-}H)_3N$	345.6	6	−73.4	23.9	11.12	9.09×10^6
$Me_2C{-}H(OH)$	390.5	1	−28.5	30.5	10.34	1.07×10^5

(continued overleaf)

TABLE 14.2 (*continued*)

RH	D (kJ mol^{-1})	n	ΔH_e (kJ mol^{-1})	E (kJ mol^{-1})	log A (A (L mol^{-1} s^{-1}))	k(300 K) (L mol^{-1} s^{-1})
	329.7	1	−89.3	19.5	10.34	8.81×10^6
MeCH=CMeC−HMeOH	325.2	1	−93.8	18.3	10.34	1.42×10^7
	337.5	1	−81.5	17.1	10.34	2.30×10^7
PhC(O)−H	348.0	1	−71	20.0	10.34	7.21×10^6
	394.1	4	−24.9	31.8	10.94	2.53×10^5
$Me_2CHOC-HMe_2$	390.8	2	−28.2	30.6	10.64	2.05×10^5
$(CH_2{=}CHCH-H)_2O$	360.0	4	−59	28.3	10.94	1.03×10^6
$Ph_2C-HOMe$	354.2	1	−64.8	21.8	10.34	3.50×10^6
Ph(C(O)OH)CH−H	367.0	2	−52	25.7	10.64	1.46×10^6
Me_3COO-H	358.6	1	−56	18.4	10.34	1.37×10^7
$(Me_3C)_3Si-H$	351.0	1	−72.8	16.8	10.34	2.60×10^7

[a] See Ref. 8.

The C−F bond is strong [($D_{\mathrm{C-F}} = 464$ kJ mol^{-1} in MeF) and its formation compensates for the energy of difluorine dissociation and π-C−C bond splitting. The values for the reaction enthalpies of difluorine and other FY molecules with selected olefins are in Table 14.3.

Rate constants value for the difluorine reaction with ethene in the gas phase were found to be the following:

$$k = 7.76 \times 10^7 \exp(-19.2/RT) = 2.04 \times 10^4 (298\ \mathrm{K})^9$$

$$k = 1.81 \times 10^4\ \mathrm{L\,mol^{-1}\,s^{-1}} (298\ \mathrm{K})^{10}$$

$$k = 4.16 \times 10^4\ \mathrm{L\,mol^{-1}\,s^{-1}} (315\ \mathrm{K})^{11}$$

For the values of rate constants and activation energies of difluorine and perfluorinated methanol with olefins, calculated by the IPM method,[12] see Tables 14.4 and 14.5.

TABLE 14.3 Enthalpies (kJ mol^{-1}) for Addition Reactions $RCH{=}CH_2 + FY \rightarrow RC^{\bullet}HCH_2F + Y^{\bullet}$ (Y = F, Cl, Br, I, OH)

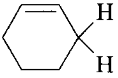
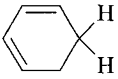
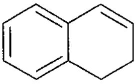
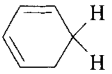
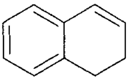
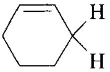
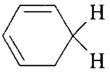
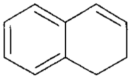
FY	F_2	CF_3OF	FOH	FBr	FCl	FI
Olefin			ΔH (kJ mol^{-1})			
$CH_2{=}CH_2$	−32.7	−9.4	23.1	58.8	64.8	80.2
$Me_2C{=}CH_2$	−35.9	−12.6	19.9	55.6	61.6	77.0
$EtCH{=}CH_2$	−31.3	−8.0	24.5	60.2	66.2	81.6
	−37.3	−14.0	18.5	54.2	60.2	75.6
$CH{\equiv}CH$	−43.0	−19.7	12.8	48.5	54.5	69.9
$MeC{\equiv}CMe$	−27.3	−4.0	28.5	64.2	70.2	85.6
$CH_2{=}CHCH{=}CH_2$	−79.9	−56.6	−24.1	11.6	17.6	33.0
$CH_2{=}CHCH{=}CMe_2$	−85.5	−62.2	−29.7	6.0	12.0	27.4
$Me_2C{=}CMeCMe{=}CMe_2$	−114.9	−91.6	−59.1	−23.4	−17.4	−2.0
	−96.7	−73.4	−40.9	−5.2	0.8	16.2
$PhCH{=}CH_2$	−73.6	−50.3	−17.8	17.9	23.9	39.3
$PhCH{=}CHMe$	−69.8	−46.5	−14.0	21.7	27.7	43.1
$Ph_2C{=}CH_2$	−141.0	−117.7	−85.2	−49.5	−43.5	−28.1
	−69.8	−46.5	14.0	21.7	27.7	43.1

TABLE 14.4 Enthalpies (ΔH_e), Activation Energies, and Rate Constants of Addition Reactions $YF + CH_2{=}CHR \rightarrow Y^{\bullet} + FCH_2C^{\bullet}HR$ (Calculated by the IPM Method)[a]

Olefin	ΔH_e (kJ mol^{-1})	E (kJ mol^{-1})	log A, A (L mol^{-1} s^{-1})	k(300 K) (L mol^{-1} s^{-1})
$F_2 + CH_2{=}CHR \rightarrow F^{\bullet} + FCH_2C^{\bullet}HR$				
$CH_2{=}CH_2$	−29.1	38.6	11.00	1.90×10^4
$Me_2C{=}CH_2$	−32.3	36.9	10.70	1.88×10^4
$EtCH{=}CH_2$	−27.7	39.3	10.70	7.20×10^3
	−33.7	36.2	11.00	4.98×10^4
$CH_2{=}CHCH{=}CH_2$	−74.5	13.4	11.00	4.64×10^7
$CH_2{=}CHCH{=}CMe_2$	−80.1	11.0	10.70	6.09×10^8
$Me_2C{=}CMeCMe{=}CMe_2$	−109.5	0.03	11.00	9.88×10^{10}
	−91.3	6.4	11.00	7.68×10^9
$PhCH{=}CH_2$	−70.0	26.7	10.70	1.12×10^6
$PhCH{=}CHMe$	−66.2	28.4	10.70	5.69×10^5
$Ph_2C{=}CH_2$	−137.2	1.9	10.70	2.34×10^{10}
	−66.2	28.4	10.70	5.69×10^5
$CF_3OF + CH_2{=}CHR \rightarrow CF_3O^{\bullet} + FCH_2C^{\bullet}HR$				
$CH_2{=}CH_2$	−5.8	51.4	10.70	56.3
$Me_2C{=}CH_2$	−9.0	49.6	10.40	58.1
$EtCH{=}CH_2$	−4.4	52.2	10.40	20.5
	−10.4	48.8	10.70	1.60×10^2
$CH_2{=}CHCH{=}CH_2$	−51.6	24.6	10.70	2.61×10^6
$CH_2{=}CHCH{=}CMe_2$	−56.8	21.8	10.40	4.02×10^6
$Me_2C{=}CMeCMe{=}CMe_2$	−86.2	8.4	10.70	1.73×10^9
	−68.0	16.4	10.70	6.99×10^7
$PhCH{=}CH_2$	−46.7	37.8	10.40	6.58×10^3
$PhCH{=}CHMe$	−42.9	39.7	10.40	3.07×10^3
$Ph_2C{=}CH_2$	−114.1	9.1	10.40	6.54×10^8
	−42.9	39.7	10.40	3.07×10^3

---

[a] See Chapter 9, Eqs. (9.13), (9.15), and (9.16), Tables 9.1 and 9.2.

TABLE 14.5 Enthalpies, Activation Energies, and Rate Constants for FY Addition to Ethylene and Styrene

FY	ΔH_e (kJ mol^{-1})	E (kJ mol^{-1})	log A, A (L mol^{-1} s^{-1})	k(300 K) (L mol^{-1} s^{-1})
		$CH_2{=}CH_2 + FY \rightarrow C^{\bullet}H_2CH_2F + Y^{\bullet}$		
F_2	−29.1	38.6	11.00	1.90×10^4
CF_2OF	−5.8	51.4	10.70	56.3
FOH	26.7	71.1	10.70	2.09×10^{-2}
FBr	62.4	94.9	10.70	1.50×10^{-6}
FCl	68.4	99.0	10.70	2.90×10^{-7}
FI	83.4	110.0	10.70	3.53×10^{-9}
		$PhCH{=}CH_2 + FY \rightarrow PhC^{\bullet}HCH_2F + Y^{\bullet}$		
F_2	−70.0	26.7	10.70	1.12×10^6
CF_3OF	−46.7	37.8	10.40	6.58×10^3
FOH	−14.2	55.1	10.40	6.40
FBr	21.5	76.3	10.40	1.30×10^{-3}
FCl	27.5	80.1	10.40	2.84×10^{-4}
FI	42.9	90.0	10.40	5.37×10^{-6}

14.2 REACTIONS OF DICHLORINE AND OTHER CHLORINE COMPOUNDS

Chlorination of hydrocarbons occurs by the chain mechanism.[1–3] Chlorine atoms are generated photochemically or by the introduction of an initiator. However, liquid-phase chlorination occurs slowly in the dark in the absence of an initiator. The most probable reaction of thermal initiation in RH chlorination is the bimolecular reaction[1]

$$Cl_2 + HR \rightarrow Cl^{\bullet} + HCl + R^{\bullet}$$

For the entropy values of reactions YCl + RH, see Table 14.6.

TABLE 14.6 Enthalpies of Reactions $RH + ClY \rightarrow R^{\bullet} + HCl + Y^{\bullet}$

ClY	Cl_2	ClBr	ClNO	$ClNO_2$	ClONO	ClOMe
RH	ΔH (kJ mol^{-1})					
EtMeCH−H	224.0	198.9	143.8	123.2	53.5	176.8
$Me_3C{-}H$	211.0	185.9	130.8	110.2	40.5	163.8

(*continued overleaf*)

TABLE 14.6 (*continued*)

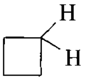
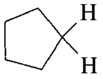
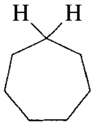
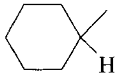
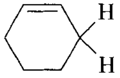
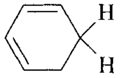
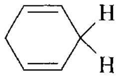
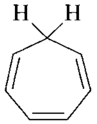
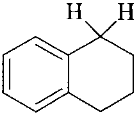
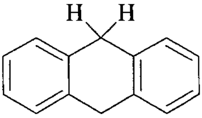
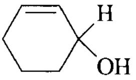
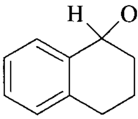
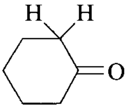
ClY	Cl_2	ClBr	ClNO	$ClNO_2$	ClONO	ClOMe
RH	ΔH (kJ mol^{-1})					
	229.5	204.4	149.3	128.7	59.0	182.3
	219.4	194.3	139.2	118.6	48.9	172.2
	214.9	189.8	134.7	114.1	44.4	167.7
	206.5	181.4	126.3	105.7	36.0	159.3
(*Z*)-Decalin	198.6	173.5	118.4	97.8	28.1	151.4
$CH_2{=}CHCH_2{-}H$	179.0	153.9	98.8	78.2	8.5	131.8
$CH_2{=}CHCH{-}HMe$	160.8	135.7	80.6	60.0	−9.7	113.6
$CH_2{=}CHC{-}HMe_2$	150.6	125.5	70.4	49.8	−19.9	103.4
(*Z*)-MeCH=CHCH−HMe	155.0	129.9	74.8	54.2	−15.5	107.8
$Me_2C{=}CHCH{-}HMe$	143.0	117.9	62.8	42.2	−27.5	95.8
$Me_2C{=}CMeC{-}HMe_2$	133.8	108.7	53.6	33.0	−36.7	86.6
$(CH_2{=}CH)_2C{-}HMe$	118.2	93.0	38.0	17.4	−52.3	71
	152.5	127.4	72.3	51.7	−18.0	105.3
	141.9	116.8	61.7	41.1	−28.6	94.7
	123.6	98.5	43.4	22.8	−46.9	76.4
	112.0	86.9	31.8	11.2	−58.5	64.8
$MeC{\equiv}CC{-}HMe_2$	140.4	115.3	60.2	39.6	−30.1	93.2
MePhCH−H	175.1	150.0	94.9	74.3	4.6	127.9
$Me_2PhC{-}H$	165.7	140.6	85.5	64.9	−4.8	118.5

TABLE 14.6 (*continued*)

ClY	Cl_2	ClBr	ClNO	$ClNO_2$	ClONO	ClOMe
RH	ΔH (kJ mol^{-1})					
	156.6	131.5	76.4	55.8	−13.9	109.4
	133.0	107.9	52.8	32.2	−37.5	85.8
$Me_2NH_2C{-}H$	190.5	165.4	110.3	89.7	20.0	143.3
$(CH_2{=}CHCH{-}H)_3N$	156.6	131.5	76.4	55.8	−13.9	109.4
$Me_2C{-}H(OH)$	201.5	176.4	121.3	100.7	31.0	154.3
	140.7	115.6	60.5	39.9	−29.8	93.5
MeCH=CMeC−HMeOH	136.2	111.1	56.0	35.4	−34.3	89.0
	148.5	123.4	68,3	47.7	−22	101.3
PhC(O)−H	159.0	133.9	78.8	58.2	−11.5	111.8
	205.1	180.0	124.9	104.3	34.6	157.9
$Me_2CHOC{-}HMe_2$	201.8	176.7	121.6	101	31.3	154.6
$(CH_2{=}CHCH{-}H)_2O$	171.0	145.9	90.8	70.2	50.0	123.8
$Ph_2C{-}HOMe$	165.2	140.1	85.0	64.4	−5.3	118.0
Ph(C(O)OH)CH−H	178.0	152.9	97.8	77.2	7.5	130.8
$Me_3COO{-}H$	169.6	144.5	89.4	68.8	−90.0	122.4
$(Me_3C)_3Si{-}H$	162.0	136.9	81.8	61.2	−8.5	114.2
$Ph_3Ge{-}H$	133.5	108.4	53.3	32.7	−37.0	86.3
$Ph_3Sn{-}H$	107.9	82.8	27.7	7.1	−62.6	60.7

The rate constant of the reaction

$$Cl_2 + HCF_3 \rightarrow Cl^{\bullet} + HCl + C^{\bullet}F_3$$

in the gas phase is $k = 5.0 \times 10^9 \exp(-142.2/RT) = 2.1 \times 10^{-3}$ (600 K) L mol^{-1} s^{-1}.[13]

TABLE 14.7 Enthalpies, Activation Energies, and Rate Constants for the Reaction $RH + Cl_2 \rightarrow R^{\bullet} + HCl + Cl^{\bullet}$ (Calculated by the IPM Method)[a]

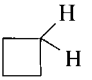
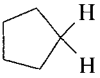
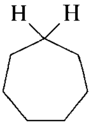
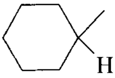
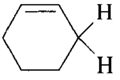
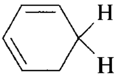
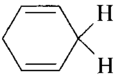
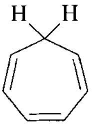
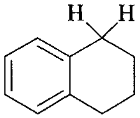
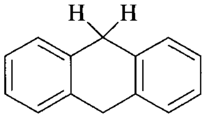
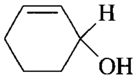
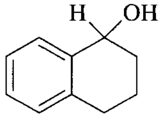
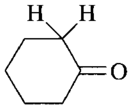
RH	D (kJ mol^{-1})	n	ΔH (kJ mol^{-1})	log A, A (L mol^{-1} s^{-1})	k(400 K) (L mol^{-1} s^{-1})
EtMeCH−H	413.0	4	224.0	10.60	3.10×10^{-17}
Me_3C−H	400.0	1	211.0	10.00	3.62×10^{-16}
	418.5	8	229.5	10.90	1.22×10^{-17}
	408.4	10	219.4	11.00	9.03×10^{-16}
	403.9	14	214.9	11.15	1.61×10^{-15}
	395.5	1	206.5	10.00	1.35×10^{-15}
(Z)-Decalin	387.6	2	198.6	10.30	4.76×10^{-14}
CH_2=$CHCH_2$−H	368.0	3	179.0	10.48	1.32×10^{-11}
CH_2=CHCH−HMe	349.8	2	160.8	10.30	1.80×10^{-9}
CH_2=CHC−HMe_2	339.6	1	150.6	10.00	1.77×10^{-8}
(Z)-MeCH=CHCH−HMe	344.0	2	155.0	10.30	9.77×10^{-9}
Me_2C=CHCH−HMe	332.0	2	143.0	10.30	3.22×10^{-7}
Me_2C=CMeC−HMe_2	322.8	1	133.8	10.00	2.36×10^{-6}
$(CH_2$=$CH)_2C$−HMe	307.2	1	118.2	10.00	2.15×10^{-4}
	341.5	4	152.5	10.60	4.04×10^{-8}
	330.9	4	141.9	10.60	8.88×10^{-7}
	312.6	4	123.6	10.60	1.80×10^{-4}
	301.0	2	112.0	10.30	2.56×10^{-3}
MeC≡CC−HMe_2	329.4	1	140.4	10.00	3.45×10^{-7}
MePhCH−H	364.1	2	175.1	10.30	2.73×10^{-11}

TABLE 14.7 (*continued*)

RH	D (kJ mol^{-1})	n	ΔH (kJ mol^{-1})	log A, A (L mol^{-1} s^{-1})	k(400 K) (L mol^{-1} s^{-1})
Me_2PhC-H	354.7	1	165.7	10.30	4.28×10^{-10}
	345.6	4	156.6	10.60	1.22×10^{-8}
	322.0	4	133.0	10.60	1.05×10^{-5}
Me_2NH_2C-H	379.5	1	190.5	10.00	1.49×10^{-13}
$(CH_2=CHCH-H)_3N$	345.6	6	156.6	10.78	1.85×10^{-8}
$Me_2C-H(OH)$	390.5	1	201.5	10.00	5.89×10^{-15}
	329.7	1	140.7	10.00	3.15×10^{-7}
$MeCH=CMeC-HMeOH$	325.2	1	136.2	10.00	1.16×10^{-6}
	337.5	1	148.5	10.00	3.26×10^{-8}
$PhC(O)-H$	348.0	1	159.0	10.00	1.53×10^{-9}
	394.1	4	205.1	10.60	8.14×10^{-15}
$Me_2CHOC-HMe_2$	390.8	2	201.8	10.30	1.08×10^{-14}
$(CH_2=CHCH-H)_2O$	360.0	4	171.0	10.60	1.81×10^{-10}
$Ph_2C-HOMe$	354.2	1	165.2	10.00	2.49×10^{-10}
$Ph(C(O)OH)CH-H$	367.0	2	178.0	10.30	1.17×10^{-11}
Me_3COO-H	358.6	1	169.6	10.20	1.05×10^{-12}
$(Me_3C)_3Si-H$	351.0	1	162.0	10.40	1.34×10^{-9}

[a] See Chapter 9, Eq. (9.20), Tables 9.1 and 9.2.

The values for the activation energies of reactions $Cl_2 + RH$ are close to the reaction enthalpy. Among the molecules Cl_2, ClBr, ClNO, $ClNO_2$, and ClONO, the latter is the most active free radical generator due to its weak Cl−ONO bond (72 kJ mol^{-1}) (see Table 14.6). Rate constants of reactions $Cl_2 + RH$ calculated by the IPM method are collected in Table 14.7.

Thermal initiation in the reaction of dichlorine with olefins proceeds via the bimolecular reaction of addition[1]

$$Cl_2 + CH_2{=}CHR \rightarrow Cl^\bullet + ClCH_2C^\bullet HR$$

These reactions of dichlorine with olefins are endothermic (see Table 14.8), ΔH varies from 63 ($Ph_2C{=}CH_2$) to 191 kJ mol^{-1} ($MeC{\equiv}CMe$). Rate constants for the Cl_2 and $ClNO_2$ reactions with olefins are calculated by the IPM method presented in Table 14.9.

Free radicals can be generated by the bimolecular reaction of alkyl haloid with alkyl metal, for example,

$$CH_3CH_2Cl + NaCH_2CH_3 \rightarrow CH_3C^\bullet H_2 + NaCl + CH_3C^\bullet H_2$$

D'yachkovskii and Shilov studied a series of reactions of this type in a hydrocarbon solution (see Table 14.10).[4,14,15] These reactions are exothermic due to the formation of haloid metal molecules with the strong ionic bond Me^+X^-.

TABLE 14.8 Enthalpies of Addition Reactions $RCH{=}CH_2 + ClY \rightarrow RC^\bullet HCH_2Cl + Y^\bullet$ (Y = Cl, Br, I, NO, NO_2, OMe)

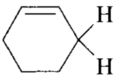
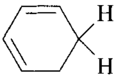
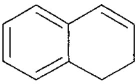
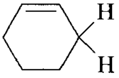
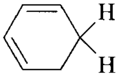
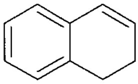
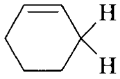
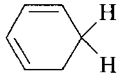
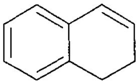
ClY	Cl_2	ClONO	$ClNO_2$	ClNO	ClOMe	ClI	ClBr
Olefin	ΔH (kJ mol^{-1})						
$CH_2{=}CH_2$	163.2	−7.3	62.4	83.0	116.0	131.9	138.1
$Me_2C{=}CH_2$	160.0	−10.5	59.2	79.8	112.8	128.7	134.9
$EtCH{=}CH_2$	164.6	−5.9	63.8	84.4	117.4	133.3	139.5
	150.6	−19.9	49.8	70.4	103.4	119.3	125.5
$CH{\equiv}CH$	175.9	5.4	75.1	95.7	128.7	144.6	150.8
$MeC{\equiv}CMe$	191.6	21.1	90.8	111.4	144.4	160.3	166.5
$CH_2{=}CHCH{=}CH_2$	116.0	−54.5	15.2	35.8	68.8	84.7	90.5
$CH_2{=}CHCH{=}CMe_2$	111.4	−59.1	10.6	31.2	64.2	80.1	86.3
$Me_2C{=}CMeCMe{=}CMe_2$	82.0	−88.5	−18.8	1.8	34.8	50.7	56.9
	91.2	−79.3	−9.6	11.0	44.0	59.9	66.1
$PhCH{=}CH_2$	123.3	−47.2	22.5	43.1	76.1	92.0	98.2
$PhCH{=}CHMe$	118.1	−52.4	17.3	37.9	70.9	86.8	93.0
$Ph_2C{=}CH_2$	62.9	−107.6	−37.9	−17.3	15.7	31.6	37.8
	119.6	−50.9	18.8	39.4	72.4	88.3	94.5

TABLE 14.9 Enthalpies, Activation Energies, and Rate Constants of Reactions YCl + $CH_2{=}CHR \rightarrow Y^\bullet + ClCH_2C^\bullet HR$ (Calculated by the IPM Method)[a]

$RCH{=}CH_2$	ΔH_e (kJ mol^{-1})	E (kJ mol^{-1})	$\log A$, A (L mol^{-1} s^{-1})	k(400 K) (L mol^{-1} s^{-1})
	$RCH{=}CH_2 + Cl_2 \rightarrow RC^\bullet HCH_2Cl + Cl^\bullet$			
$CH_2{=}CH_2$	168.2	169.3	10.56	2.83×10^{-12}
$Me_2C{=}CH_2$	165.0	166.5	10.26	3.29×10^{-12}
$EtCH{=}CH_2$	169.6	170.5	10.26	9.89×10^{-13}
	155.6	158.3	10.56	7.73×10^{-11}
$HC{\equiv}CH$	183.7	205.5	10.86	1.06×10^{-16}
$MeC{\equiv}CMe$	199.4	218.8	10.86	1.94×10^{-18}
$CH_2{=}CHCH{=}CH_2$	122.8	131.3	10.56	2.59×10^{-7}
$CH_2{=}CHCH{=}CMe_2$	118.2	127.5	10.26	4.08×10^{-7}
$Me_2C{=}CMeCMe{=}CMe_2$	88.8	103.4	10.56	1.14×10^{-3}
	98.0	110.8	10.56	1.23×10^{-4}
$PhCH{=}CH_2$	128.3	140.8	10.26	7.48×10^{-9}
$PhCH{=}CHMe$	123.1	136.6	10.26	2.64×10^{-8}
$Ph_2C{=}CH_2$	67.9	93.8	10.26	1.03×10^{-2}
	124.6	137.8	10.26	1.84×10^{-8}
	$RCH{=}CH_2 + ClNO_2 \rightarrow RC^\bullet HCH_2Cl + N^\bullet O_2$			
$CH_2{=}CH_2$	67.4	86.8	10.26	8.42×10^{-2}
$Me_2C{=}CH_2$	64.2	84.4	9.95	8.48×10^{-2}
$EtCH{=}CH_2$	68.8	87.9	9.95	2.96×10^{-2}
	54.8	77.5	10.26	1.38
$HC{\equiv}CH$	82.9	123.8	10.56	2.47×10^{-6}
$MeC{\equiv}CMe$	98.6	136.0	10.56	6.32×10^{-8}
$CH_2{=}CHCH{=}CH_2$	22.0	52.6	10.26	2.46×10^{3}
$CH_2{=}CHCH{=}CMe_2$	17.4	49.4	9.95	3.16×10^{3}
$Me_2C{=}CMeCMe{=}CMe_2$	−12.4	29.6	10.26	2.48×10^{6}
	−2.8	35.8	10.26	3.85×10^{5}
$PhCH{=}CH_2$	26.1	61.3	9.95	88.1
$PhCH{=}CHMe$	20.9	57.8	9.95	2.52×10^{2}

(*continued overleaf*)

TABLE 14.9 (*continued*)

$RCH{=}CH_2$	ΔH_e (kJ mol^{-1})	E (kJ mol^{-1})	log A, A (L mol^{-1} s^{-1})	k(400 K) (L mol^{-1} s^{-1})
$Ph_2C{=}CH_2$	−34.3	24.4	9.95	5.80×10^6
	22.4	58.8	9.95	1.87×10^2

[a] See Chapter 9, Eq. (9.18), Tables 9.1 and 9.2.

TABLE 14.10 Enthalpies, Activation Energies, and Rate Constants for the Reactions $YCl + CH_2{=}CHR \rightarrow Y^{\bullet} + ClCH_2C^{\bullet}HR$ (Calculated by the IPM Method)[a]

$RCH{=}CH_2$	ΔH_e (kJ mol^{-1})	E (kJ mol^{-1})	k(400 K) (L mol^{-1} s^{-1})
	$YCl + CH_2{=}CH_2 \rightarrow Y^{\bullet} + ClCH_2C^{\bullet}H_2$		
Cl_2	168.2	169.3	2.83×10^{-12}
ClONO	−2.3	38.9	1.50×10^{5}
$ClNO_2$	67.4	86.8	8.33×10^{-2}
ClNO	88.0	102.6	7.20×10^{-4}
ClOMe	121.0	129.1	2.49×10^{-7}
ClI	136.9	142.4	4.57×10^{-9}
ClBr	143.1	147.6	9.57×10^{-10}
	$YCl + CH_2{=}CHPh \rightarrow Y^{\bullet} + ClCH_2C^{\bullet}HPh$		
Cl_2	128.3	140.8	7.48×10^{-9}
ClONO	−42.2	23.1	8.66×10^{6}
$ClNO_2$	27.5	65.0	29.3
ClNO	48.1	79.3	0.40
ClOMe	81.1	103.5	2.75×10^{-4}
ClI	97.0	115.7	7.01×10^{-6}
ClBr	103.2	120.5	1.65×10^{-6}

[a] See Chapter 9, Eq. (9.18), Tables 9.1 and 9.2.

TABLE 14.11 Rate Constants for the Bimolecular Reactions $C_2H_5Li + XR \rightarrow C_2H_5^{\bullet} + LiX + R^{\bullet}$

RX	T (K)	E (kJ mol^{-1})	log A, A (L mol^{-1} s^{-1})	k(298 K) (L mol^{-1} s^{-1})	Reference
EtCl	363			3.98×10^{-5}	14
Me_2CHCl	353			2.51×10^{-4}	14

TABLE 14.11 (*continued*)

RX	*T* (K)	*E* (kJ mol^{-1})	log *A*, *A* (L mol^{-1} s^{-1})	*k*(298 K) (L mol^{-1} s^{-1})	Reference
$PrCH_2Cl$	353–393	78.7	6.97	1.50×10^{-7}	14
Me_3CCl	303			5.62×10^{-2}	14
$CH_2{=}CHCH_2Cl$	273–308	59.0	7.59	1.77×10^{-3}	14
$PhCH_2Cl$	293–333	43.9	4.54	7.00×10^{-4}	14
Ph_3CCl	193–229	24.3	4.32	1.15	15
EtBr	295–333	68.2	7.08	1.33×10^{-5}	15
EtI	276–296	56.9	6.74	5.83×10^{-4}	15

14.3 INITIATION BY NITROGEN DIOXIDE

Nitrogen dioxide plays an important role in the atmospheric chemistry of the ozone layer, participating in the chain reaction of ozone decomposition by the reaction[16]

$$NO^{\bullet} + O_3 \rightarrow NO_2^{\bullet} + O_2$$

$$NO_2^{\bullet} + O_3 \rightarrow NO_3^{\bullet} + O_2$$

$$NO^{\bullet} + NO_3^{\bullet} \rightarrow 2NO_2^{\bullet}$$

Nitrogen dioxide influences the oxidation of engine lubricants oxidizing antioxidants and stimulating lubricant degradation and deposit formation.[17–22] Nitrogen dioxide initiates the chain liquid-phase oxidation of hydrocarbons as a result of the following reactions:[23]

$$RH + NO_2^{\bullet} \rightarrow R^{\bullet} + HONO$$

$$ONOH \rightarrow NO^{\bullet} + HO^{\bullet}$$

$$HO^{\bullet} + RH \rightarrow H_2O + R^{\bullet}$$

$$R^{\bullet} + O_2 \rightarrow RO_2^{\bullet}$$

$$RO_2^{\bullet} + NO_2^{\bullet} \rightarrow ROONO_2$$

$$ROONO_2 \rightarrow RO^{\bullet} + NO_3^{\bullet}$$

$$RO^{\bullet} + RH \rightarrow ROH + R^{\bullet}$$

$$NO_3^{\bullet} + RH \rightarrow HNO_3 + R^{\bullet}$$

$$ROOH + ONOH \rightarrow RO^{\bullet} + H_2O + NO_2^{\bullet}$$

Nitrogen dioxide plays a dualistic role in the thermal cracking of hydrocarbons.[24] It retards the chain reaction of hydrocarbon decay accepting active alkyl radicals by the reaction

$$R^{\bullet} + NO_2^{\bullet} \rightarrow RNO_2$$

and accelerates the chain initiation by the reaction

$$RH + NO_2^{\bullet} \rightarrow R^{\bullet} + ONOH$$

Nitrogen dioxide is a stable radical with an unpaired electron and forms the dimmer N_2O_4 in the equilibrium reaction

$$2NO_2^{\bullet} \Leftrightarrow N_2O_4$$

This equilibrium reaction proceeds with enthalpy $\Delta H = -58.2\ \text{kJ mol}^{-1}$ and entropy $\Delta S = -177\ \text{J mol}^{-1}\ \text{K}^{-1}$.[25] Nitrogen dioxide decays at elevated temperatures in the gas phase by the reaction

$$2NO_2^{\bullet} \rightarrow 2NO^{\bullet} + O_2$$

with a rate constant $k = 2.0 \times 10^9 \exp(-111.0/RT)\ \text{L mol}^{-1}\ \text{s}^{-1}$.[26]

Three mechanisms of radical initiation by nitrogen dioxide are known.[27]

1. Hydrogen abstraction by NO_2 from RH.

$$NO_2^{\bullet} + HR \rightarrow ONOH + R^{\bullet}$$

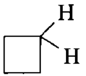
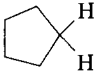
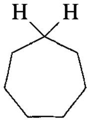
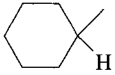
This reaction is endothermic, its enthalpy is $\Delta H = D_{R-H} - 327.6\ \text{kJ mol}^{-1}$. Experimental rate constants for these reactions are in Table 14.12 and those calculated by the IPM method are in Table 14.13.

TABLE 14.12 Rate Constants for the Reactions $N^{\bullet}O_2 + HR \rightarrow ONOH + R^{\bullet}$ in the Gas Phase[a]

RX	T (K)	E (kJ mol^{-1})	log A, A (L mol^{-1} s^{-1})	k(298 K) (L mol^{-1} s^{-1})	Reference
CH_4	1300–1900	125.5	8.84	6.93×10^{-14}	28
$MeCH_2Me$	423–498	94.6	8.38	6.27×10^{-9}	29
$(CH_2{=}CH)_2CH_2$	296			1.22	30
CH_3OH	640–713	89.5	8.56	7.45×10^{-8}	31
CH_3OH	900–1100	94.5	8.30	3.64×10^{-9}	32
EtCHO	295–390	51.9	7.40	2.02×10^{-2}	33
PrCHO	295–390	51.9	7.40	2.02×10^{-2}	33
CF_3CHO	533–584	98.7	8.94	4.35×10^{-9}	34
MeCOMe	298–373	29.8	2.58	2.24×10^{-3}	35
EtNOH	298			3.31×10^{3}	36
Me_2NNH_2	298			1.39×10^{4}	37

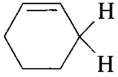
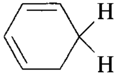
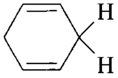
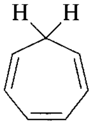
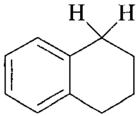
[a] Experimental data.

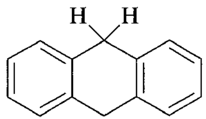
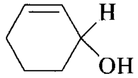
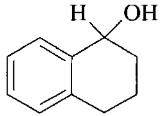
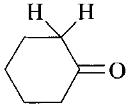
TABLE 14.13 Enthalpies, Activation Energies, and Rate Constants for the Reaction $RH + N^{\bullet}O_2 \rightarrow R^{\bullet} + HONO$ (Calculated by the IPM Method)[a]

RH	D (kJ mol^{-1})	n	ΔH_e (kJ mol^{-1})	E (kJ mol^{-1})	log A, A (L mol^{-1} s^{-1})	k(300 K) (L mol^{-1} s^{-1})
EtMeCH–H	413.0	4	81.3	86.6	10.67	3.91×10^{-5}
Me_3C–H	400.0	1	68.3	73.6	9.77	9.02×10^{-4}
	418.5	8	86.8	82.0	11.06	6.06×10^{-4}
	408.4	10	76.7	82.0	10.98	5.04×10^{-4}
	403.9	14	72.2	77.5	11.02	3.36×10^{-3}
	395.5	1	63.8	69.1	9.63	3.67×10^{-3}
(*Z*)-Decalin	387.6	2	55.9	61.2	9.60	8.80×10^{-2}
$CH_2{=}CHCH_2{-}H$	368.0	3	36.3	59.0	8.48	1.61×10^{-2}
$CH_2{=}CHCH{-}HMe$	349.8	2	18.1	49.8	8.30	0.43
$CH_2{=}CHC{-}HMe_2$	339.6	1	7.9	45.0	8.00	1.46
(*Z*)-MeCH=CHCH–HMe	344.0	2	12.3	47.1	8.30	1.26
$Me_2C{=}CHCH{-}HMe$	332	2	0.3	41.6	8.30	11.40

(continued overleaf)

TABLE 14.13 (*continued*)

RH	D (kJ mol^{-1})	n	ΔH_e (kJ mol^{-1})	E (kJ mol^{-1})	log A, A (L mol^{-1} s^{-1})	k(300 K) (L mol^{-1} s^{-1})
$Me_2C{=}CMeC{-}HMe_2$	322.8	1	−8.9	37.5	8.00	29.60
$(CH_2{=}CH)_2C{-}HMe$	307.2	1	−24.5	31.1	8.00	3.85×10^2
	341.5	4	9.8	45.9	9.60	40.6
	330.9	4	−0.8	41.1	9.60	2.78×10^2
	312.6	4	−19.1	33.3	9.60	6.34×10^3
	301.0	2	−30.7	28.7	9.30	2.01×10^4
$MeC{\equiv}CC{-}HMe_2$	329.4	1	−2.3	40.4	8.00	9.24
$MePhCH{-}H$	364.1	2	32.4	50.6	8.30	0.15
$Me_2PhC{-}H$	354.7	1	23.0	45.8	8.00	1.06
	345.6	4	13.9	41.3	9.60	2.56×10^2

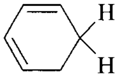
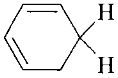
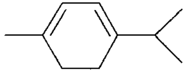
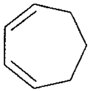
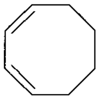
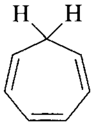
	322.0	4	−9.7	30.7	9.60	1.80×10^4
Me_2NH_2C-H	379.5	1	47.8	53.1	8.66	0.25
$(CH_2=CHCH-H)_3N$	345.6	6	13.9	47.8	8.78	2.87
$Me_2C-H(OH)$	390.5	1	58.8	64.1	9.44	1.90×10^{-2}
	329.7	1	−2.0	40.5	9.00	88.8
$MeCH=CMeC-HMeOH$	325.2	1	−6.5	38.6	8.00	19.0
	337.5	1	5.8	37.5	9.00	2.96×10^2
$PhC(O)-H$	348.0	1	16.3	42.5	8.00	3.98
	394.1	4	62.4	67.7	10.19	2.53×10^{-2}
$Me_2CHOC-HMe_2$	390.8	2	59.1	64.4	9.75	3.44×10^{-2}
$(CH_2=CHCH-H)_2O$	360.0	4	28.3	54.9	8.60	0.11
$Ph_2C-HOMe$	354.2	1	22.5	45.5	8.00	1.20
$Ph(C(O)OH)CH-H$	367.0	2	35.3	52.2	8.30	0.16
Me_3COO-H	358.6	1	30.7	45.9	9.00	10.19
$(Me_3C)_3Si-H$	351.0	1	15.0	40.8	9.00	78.7
Ph_3Ge-H	322.5	1	−14.0	29.8	9.00	6.41×10^3
Ph_3Sn-H	296.9	1	−40.1	20.4	9.00	2.81×10^5

---

[a] See Chapter 9 and Ref. 38.

TABLE 14.14 Rate Constants for the Addition Reactions $N^{\bullet}O_2 + CH_2{=}CHR \rightarrow RC^{\bullet}HCH_2NO_2$ in the Gas Phase[a]

$CH_2{=}CHR$	T (K)	E ($kJ\,mol^{-1}$)	$\log A$, A ($L\,mol^{-1}\,s^{-1}$)	k(298 K) ($L\,mol^{-1}\,s^{-1}$)	Reference
$CH_2{=}CH_2$	298–382	58.6	9.97	0.50	39
$CH_2{=}CHMe$	323			4.73×10^{-2}	40
$CH_2{=}CHMe$	293–373	23.4	2.38	1.90×10^{-2}	41
$CH_2{=}CHMe$	298–373	33.0	3.50	5.19×10^{-3}	35
$CH_2{=}CHEt$	298–382	30.5	3.40	1.13×10^{-2}	35
$CH_2{=}CHPr$	298–373	30.1	0.20	8.39×10^{-6}	35
$CH_2{=}CHBu$	293–333	29.3	4.89	0.57	41
$CH_2{=}CMe_2$	298–373	16.7	1.60	4.71×10^{-2}	35
(Z)-$MeCH{=}CHMe$	298–382	47.7	8.64	1.90	39
(E)-$MeCH{=}CHMe$	298–382	48.5	8.87	2.34	39
(Z)-$CH_2{=}CHCH{=}CHMe$	298			1.0×10^{2}	42
(E)-$CH_2{=}CHCH{=}CHMe$	298			1.26×10^{2}	42
$CH_2{=}CMeCH{=}CH_2$	298			1.09×10^{2}	43
$CH_2{=}CMeCH{=}CH_2$	298			1.08×10^{2}	42
$CH_2{=}CMeCH{=}CH_2$	295			6.21×10^{1}	16
$Me_2C{=}CMe_2$	298			6.44	44
$Me_2C{=}CMe_2$	295			9.27	16
(E)-$CH_2{=}CHCH{=}CH_2$	298			18.7	16
(E)-$CH_2{=}CHCH{=}CH_2$	298			17.1	30
$CH_2{=}CMeCMe{=}CH_2$	298			1.81×10^{2}	42
$CH_2{=}CMeCMe{=}CH_2$	298			1.50×10^{2}	30
$CH_2{=}CHCMe{=}CHMe$	298			3.31×10^{2}	42
$Me_2C{=}CHCH{=}CH_2$	298			2.59×10^{2}	42
$Me_2C{=}CHCH{=}CMe_2$	298			1.32×10^{3}	42
(E)-$CH_2{=}CHCH{=}CHEt$	298			1.21×10^{2}	42

(E,Z)-CH_2=CMeCH=CHCH=CHMe	298			3.25×10^2	42
(E,E)-CH_2=CMeCH=CHCH=CHMe	298			3.56×10^2	42
(Z)-CH_2=CHCH=CHCH=CH_2	298			4.04×10^2	42
(E)-CH_2=CHCH=CHCH=CH_2	298			5.78×10^2	42
CH_2=CMe$(CH_2)_3$C(CH=CH_2)=CH_2	294			1.57×10^2	16
	298			1.10×10^3	42
	295			1.07×10^3	16
	295			3.92×10^3	16
	295			1.46×10^{-2}	16
	298			30.1	42
	298			54.2	42
ClCH=CCl_2	303–343	36.8	2.61	1.44×10^{-4}	45
HC≡CH	298–382	60.2	9.77	0.16	39

---

[a] Experimental data.

2. Reactions of nitrogen dioxide addition to the double bond of olefins occurs much more rapidly. However, this reaction is reversible and, hence, the formed radical is stabilized due to the addition of the second nitrogen dioxide.

$$NO_2^{\bullet} + CH_2{=}CHR \Leftrightarrow NO_2CH_2C^{\bullet}HR$$

$$NO_2^{\bullet} + NO_2CH_2C^{\bullet}HR \rightarrow NO_2CH_2CH(NO_2)R$$

The enthalpy of $NO_2^{\bullet}$ addition to ethylene is $\Delta H = 14.6\ \mathrm{kJ\,mol^{-1}}$. Due to reverse reaction, the measured experimentally preexponential factor A is very often very low (see Table 14.14).

3. Reactions of electron transfer from anion B^- to $NO_2^{\bullet}$ are very fast. For the data on these reactions, see Chapter 15.

REFERENCES

1. N. N. Semenov, *Some Problems of Chemical Kinetics and Reactivity*, Pergamon Press, London, 1958, Vol. 1; 1959, Vol. 2.
2. C. Walling, *Free Radicals in Solution*, John Wiley & Sons, Inc., New York, 1962.
3. M. L. Poutsma, *Halogenation in Free Radicals*, J. K. Kochi (Ed.), John Wiley & Sons, Inc., New York, 1973, Vol. 2, p. 159.
4. F. S. D'yachkovskii and A. E. Shilov, *Usp. Khim.* **35**, 699 (1966).
5. W. T. Miller and A. L. Dittman, *J. Am. Chem. Soc.* **78**, 2793 (1956).
6. W. T. Miller, S. D. Koch, and F. W. McLafferty, *J. Am. Chem. Soc.* **78**, 4992 (1956).
7. C. Seeger, G. Rotzoll, A. Lubbert, and K. Schugerl, *Int. J. Chem. Kinet.* **13**, 39 (1981).
8. E. T. Denisov, *Chem. Phys. Rep.* **17**, 705 (1998).
9. G. A. Kapralova, A. M. Chaikin, and A. E. Shilov, *Kinet. Katal.* **8**, 421 (1967).
10. Zh. Kh. Gyulbekyan, O. M. Sarkisov, and V. I. Vedeneev, *Kinet. Katal.* **15**, 993 (1974).
11. V. L. Orkin and A. M. Chaikin, *Kinet. Katal.* **23**, 438 (1982).
12. E. T. Denisov, *Russ. Chem. Rev.* **66**, 859 (1997).
13. G. F. Zhdanow, *Kinet. Katal.* **34**, 871 (1993).
14. F. S. D'yachkovskii, A. E. Shilov, and L. I. Elterman, *Kinet. Katal.* **4**, 644 (1963).
15. F. S. D'yachkovskii and A. E. Shilov, *Kinet. Katal.* **4**, 919 (1963).
16. R. Atkinson, S. M. Aschmonn, A. M. Winer, and J. N. Pitts, *Int. J. Chem. Kinet.* **16**, 697 (1984).
17. E. Dimitroff, J. V. Moffitt, and R. D. Quillian, *Transactions of the ASME* **91**, 406 (1969).
18. J. B. Hanson, S. W. Harris, and C. T. West, *SAE Technical Paper* 881581 (1988).
19. K. L. Kreuz, *Lubrication* **55**, N 6 (1969).
20. R. R. Kuhn, *ACS Preprints, Div. Petrov. Chem.* **18**, 697 (1973).
21. M. D. Johnson and S. Korcek, *Lubrication Sci.* N **3**, 95 (1991).

22. M. D. Johnson, S. Korcek, and M. J. Rokosz, *Lubrication Sci.* N **6**, 247 (1994).
23. I. V. Berezin, E. T. Denisov, and N. M. Emanuel, *The Oxidation of Cyclohexane*, Pergamon Press, Oxford, 1966.
24. K. J. Laidler and L. F. Loucks, in *Comprehensive Chemical Kinetics*, C. H. Bamford and C. F. H. Tipper (Eds.), Elsevier, Amsterdam, The Netherlands 1972, Vol. 5, p. 1.
25. S. W. Benson and H. E. O'Neal, *Kinetic Data on Gas Phase Unimolecular Reactions*, NSRDS, Washington, D.C., 1970.
26. K. J. Laidler, *Chemical Kinetics*, Harper and Row, New York, 1987.
27. R. E. Huie, *Toxicology*, **89**, 193 (1994).
28. M. W. Slack and A. R. Grillo, *Proc. Int. Symp. Shock Tubes Waver* **11**, 408 (1078).
29. T. A. Titarchuk, A. P. Ballod, and V. Ya. Shtern, *Kinet. Katal.* **17**, 1070 (1976).
30. W. A. Glasson and C. S. Tuesday, *Environ. Sci. Technol.* **4**, 752 (1970).
31. C. Anastasi and D. U. Hancock, *J. Chem. Soc., Faraday Trans. 2*, **84**, 1697 (1988).
32. S. Koda and M. Tanaka, *Combust. Sci. Technol.* **47**, 165 (1986).
33. S. Jaffe and E. Wan, *Environ. Sci. Technol.* **8**, 1024 (1974).
34. P. C. Jackson, R. Silverwood, and J. H. Thomas, *Trans. Faraday Soc.* **67**, 3250 (1971).
35. S. Jaffe, *Chem. React. Urban Atmos. Proc. Symp.* 1969 (1971).
36. J. G. Gleim and J. Heicklen, *Int. J. Chem. Kinet.* **14**, 699 (1982).
37. E. C. Tuazon, W. P. L. Carter, R. V. Brown, A. W. Winer, and J. N. Pitts, *J. Phys. Chem.* **87**, 1600 (1983).
38. T. G. Denisova and E. T. Denisov, *Petroleum Chemistry*, **37**, 187 (1997).
39. J. L. Sprung, H. Akimoto, and J. N. Pitts, *J. Am. Chem. Soc.* **96**, 6549 (1974).
40. V. Sotiropoulou, N. Katsanos, H. Metuxa, and F. Roubani-Kalantzopoulou, *Chromatographia* **42**, 441 (1996).
41. V. A. Gryaznov and A. I. Rozowskii, *Dokl. Phys. Chem.* **230**, 1129 (1976).
42. T. Ohta, H. Nagura, and S. Suzuki, *Int. J. Chem. Kinet.* **18**, 1 (1986).
43. S. E. Paulson, R. C. Flagan, and J. H. Seinfeld, *Int. J. Chem. Kinet.* **24**, 79 (1992).
44. H. Niki, P. D. Maker, C. M. Savage, L. P. Breitenbach, and M. D. Hurley, *Int. J. Chem. Kinet.* **18**, 1235 (1986).
45. J. Cazarnowski, *Int. J. Chem. Kinet.* **24**, 679 (1992).

Handbook of Free Radical Initiators. E.T. Denisov, T.G. Denisova, T.S. Pokidova
Copyright © 2003 John Wiley & Sons, Inc.
ISBN: 0-471-20753-5

15

FREE RADICAL GENERATION BY REACTIONS OF IONS WITH MOLECULES

15.1 DECOMPOSITION OF HYDROGEN PEROXIDE CATALYZED BY TRANSITION METAL IONS

Electron transfer reactions from an ion to a molecule with homolytic splitting of the molecule into free radicals is an important way to generate free radicals, for example,

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^\bullet + HO^-$$

$$Br^- + ROOH \rightarrow RO^\bullet + Br^\bullet + OH^-$$

The ion (Fe^{2+}, Br^-) reacts as an electron donor, peroxide reacts as an electron acceptor. Accepting the electron, peroxide splits into an ion (OH^-) and a free radical ($HO^\bullet$ or $RO^\bullet$). The strong oxidative effect of the mixture $H_2O_2 + FeSO_4$ dissolved in water was known for about the century as Fenton's reagent. The formation of very active hydroxyl radicals in this system was postulated by Haber and Willstatter in 1931.[1] It was the following year when Haber and Weiss put forward the chain mechanism for hydrogen peroxide decomposition under the action of transition metal ions.[2,3]

$$M^{n+} + H_2O_2 \rightarrow M^{n+1} + HO^\bullet + HO^-$$

$$HO^\bullet + H_2O_2 \rightarrow H_2O + HO_2^\bullet$$

$$M^{n+1} + HO_2^\bullet \rightarrow M^{n+} + O_2 + H^+$$

The generation of hydroxyl radicals by the system $Fe^{2+} + H_2O_2$ was proved later by Baxendale *et al.*[4] in experiments with radical polymerization of vinyl monomers. During the years 1955–1975, the decomposition of hydrogen peroxide catalyzed by heavy metal ions was the object of intensive study.[5–10] Generation of free radicals by oxidation–reduction reactions of transition metal ions played an important role in the technology of polymer production, especially in emulsion polymerization.[11–14] Hydrogen peroxide and superoxide ion ($O_2^{\bullet -}$) play a very important role in the oxidative processes in a living body. That is why enzyme catalysis for the formation and decay of hydrogen peroxide and the superoxide ion is still the object of study.[15–20]

The values of ΔH, ΔS, and ΔG (298 K) for the hydrogen peroxide reactions with heavy metal ions in water solutions are presented in Table 15.1.

The reaction of hydrogen peroxide with Fe^{2+} in water solution occurs in two steps.[7–10] First is a substitution of one H_2O molecule in the inner sphere of Fe^{2+}. This is an equilibrium process. The second step is the intrasphere electron transfer from the ferrous ion to H_2O_2 with splitting of the H_2O_2 along the O—O bond.

$$Fe^{2+}_{\bullet}H_2O + H_2O_2 \Leftrightarrow Fe^{2+}_{\bullet}H_2O_2 + H_2O \tag{15.1}$$

$$Fe^{2+}_{\bullet}H_2O_2 \rightarrow FeOH^{2+} + HO^{\bullet} \tag{15.2}$$

The first step proceeds very rapidly with a rate constant $k_1 = 3 \times 10^5$ L mol^{-1} s^{-1} (H_2O, 218 K) and the second step limits the reaction, producing $k_2K_1 = 60$ L mol^{-1} s^{-1} (H_2O, 298 K).[7] This mechanism predominates in acid water solutions at pH < 3.

An increase in pH (pH > 3) stimulates the acid dissociation of a water molecule as a ligand in the inner sphere of the ferrous ion

$$(H_2O{\cdot}Fe{\cdot}H_2O_2)^{2+} \Leftrightarrow (HOFe{\cdot}H_2O_2)^{+} + H^{+} \tag{15.3}$$

TABLE 15.1 Enthalpies, Entropies, and Gibbs Energies of Metal Ion Oxidation–Reduction Reactions with Hydrogen Peroxide in Aqueous Solution (T = 298 K)

Reaction	ΔG (kJ mol^{-1})	ΔH (kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})
$Ce^{3+} + H_2O_2 + H^+ = Ce^{4+} + HO^{\bullet} + H_2O$	88.8	32.4	−189
$Co^{2+} + H_2O_2 + H^+ = Co^{3+} + HO^{\bullet} + H_2O$	108.0	48.0	−201
$Cr^{2+} + H_2O_2 + H^+ = Cr^{3+} + HO^{\bullet} + H_2O$	−37.0	−88.5	−173
$Cu^{+} + H_2O_2 + H^+ = Cu^{2+} + HO^{\bullet} + H_2O$	−62.4	−171.4	−366
$Fe^{2+} + H_2O_2 + H^+ = Fe^{3+} + HO^{\bullet} + H_2O$	−2.8	−41.2	−129
$Mn^{2+} + H_2O_2 + H^+ = Mn^{3+} + HO^{\bullet} + H_2O$	71.5	49.1	−75
$Ce^{4+} + H_2O_2 = Ce^{3+} + HO_2^{\bullet} + H^+$	−23.2	59.7	278
$Co^{3+} + H_2O_2 = Co^{2+} + HO_2^{\bullet} + H^+$	−42.4	44.1	290
$Cu^{2+} + H_2O_2 = Cu^{+} + HO_2^{\bullet} + H^+$	128.0	180.6	176.5
$Fe^{3+} + H_2O_2 = Fe^{2+} + HO_2^{\bullet} + H^+$	68.4	133.3	218
$Mn^{3+} + H_2O_2 = Mn^{2+} + HO_2^{\bullet} + H^+$	−5.9	43.0	164

and this ion is supposed to be oxidized by hydrogen peroxide to the ferryl ion.[21–27]

$$(HOFe{\cdot}H_2O_2)^+ \rightarrow (HOFeO)^+ + H_2O \qquad (15.4)$$

The ferryl ion is a very active oxidant and reacts with water with hydroxyl radical generation

$$HOFeO^+ + H_2O \rightarrow Fe(OH)_2{}^+ + HO^\bullet \qquad (15.5)$$

or oxidizes the second ferrous ion

$$HOFeO^+ + Fe^{2+} + H^+ \rightarrow 2FeOH^{2+} \qquad (15.6)$$

The following values for rate constants were estimated for steps 2–3 at $T = 298$ K: $k_2 = 2.8 \times 10^3$ s^{-1}, $k_3 = 3.7 \times 10^4$ s^{-1}.[7] The reaction rate constants for transition metal ions and complexes with hydrogen peroxide are in Table 15.2.

Due to the precipitation of iron ions at pH > 5, the reaction between hydrogen peroxide and iron ions cannot be studied at a higher pH. The pH range of the reaction is extended by addition of a strong complex forming agent such as EDTA (ethylenediaminetetraacetic acid). Tachiev *et al.*[50] studied hydrogen peroxide decomposition catalyzed by Fe(III) complexes with EDTA and other ligands at different pH values. They came to the conclusion that four active forms of the complex exist in this system and the proportion between them depends on the pH. Hydrogen peroxide enters into the ligand sphere of the iron ion in the form of an anion. Its decomposition occurs in the inner sphere of the complex. The following kinetic scheme was proposed:[50]

$$Fe^{(III)}{\cdot}EDTA{-}H^+ + HO_2{}^- \Leftrightarrow EDTA{\cdot}Fe^{(III)}{\cdot}H_2O_2 \rightarrow \text{Decay}$$

$$Fe^{(III)}{\cdot}EDTA{\cdot}H_2O + HO_2{}^- \Leftrightarrow EDTA{\cdot}Fe^{(III)}{\cdot}H_2O{\cdot}HO_2{}^- \rightarrow \text{Decay}$$

$$Fe^{(III)}{\cdot}EDTA{\cdot}OH^- + HO_2{}^- \Leftrightarrow EDTA{\cdot}Fe^{(III)}{\cdot}OH^-{\cdot}HO_2{}^- \rightarrow \text{Decay}$$

$$Fe^{(III)}{\cdot}EDTA(OH^-)_2 + HO_2{}^- \Leftrightarrow EDTA{\cdot}Fe^{(III)}{\cdot}(OH^-)_2{\cdot}HO_2{}^- \rightarrow \text{Decay}$$

Each of these stages was characterized by a rate constant k_1, k_2, and k_3., the ratio $(k_1 + k_2)/k_3 = K_m$ (mol L^{-1}). The values for this rate constants are in Table 15.3.

Hydroperoxyl radical, $HO_2{}^\bullet$, has a dual, namely, oxidative and reducing, activity. As an oxidative reactant, it abstracts a hydrogen atom and an electron, for example,

$$HO_2{}^\bullet + RH \rightarrow H_2O_2 + R^\bullet$$

$$HO_2{}^\bullet + Fe^{2+} \rightarrow HO_2{}^- + Fe^{3+}$$

On the other side, it dissociate as an acid ($pK_a = 4.4$)

$$HO_2{}^\bullet \Leftrightarrow H^+ + O_2{}^{\bullet -}$$

TABLE 15.2 Rate Constants for Transition Metal Ion Reactions with Hydrogen Peroxide in Aqueous Solutions

Ion[a]	Conditions	T (K)	E ($\mathrm{kJ\,mol^{-1}}$)	log A, A ($\mathrm{L\,mol^{-1}\,s^{-1}}$)	k(298 K) ($\mathrm{L\,mol^{-1}\,s^{-1}}$)	Reference
Ce^{4+}		298			8.61×10^5	28
Ce^{4+}	0.8 N H_2SO_4	298			1.00×10^6	29
Cu^+	pH 2.3	298	39.2	10.0	1.35×10^3	30
$Cu^{(I)}$	$\kappa = 1$; Cl^-	298			49.0	31
$Cu(dipy)_2$	pH 5.0	298			8.51×10^2	32
Fe^{2+}		285–308	42.3	9.25	68.5	4
Fe^{2+}	1.35 M $HClO_4$	273–298	39.3	8.65	57.7	33
Fe^{2+}		298			50.0	34
Fe^{2+}	0.8 N H_2SO_4	291			41.7	35
Fe^{2+}	0.8 N H_2SO_4	298			64.6	35
Fe^{2+}	1.0 N H_2SO_4	293			61.7	36
Fe^{2+}	0.5 N H_2SO_4	298			60.3	37
Fe^{2+}	0.5–0.8 N H_2SO_4	288–314	35.4	8.02	65.3	38
Fe^{2+}	0.01–1.0 N $HClO_4$	273–313	39.5	8.72	62.6	39
Fe^{2+}	0.8 N H_2SO_4	273–313	40.8	8.98	67.4	39
Fe^{2+}	0.001–1.0 N $HClO_4$	273–318	30.5	7.14	62.2	40
Fe^{2+}		298			53.0	41
Fe^{2+}		298			58.0	42
Fe^{2+}		298			66.0	43
Fe^{2+}		298			49.5	44
Fe^{2+}		298			73.0	45
Fe^{2+}		298			76.0	46
FeF_2		273–318	58.6	12.4	1.34×10^2	40
$FeCl^+$		283–318	35.1	8.08	84.6	40
$FeBr^+$		273–298	40.2	8.95	80.1	40
$FePF_6{}^+$		273–298	42.7	11.0	3.28×10^3	40
$Fe(dipy)^{2+}$		290			2.29×10^2	47
$Fe^{(II)}$(DTPA)		298			1.37×10^3	26
$MnO_4{}^-$	0.1 N H_2SO_4	291			3.02×10^3	28
Mn^{3+}		298			7.24×10^4	48
$MnOH^{2+}$		298			3.16×10^4	48
Ti^{3+}		298			5.00×10^2	28
$U^{(IV)}$	2 M $HClO_4$	275–307	52.3	11.0	67.6	49

[a] DTPA = Diethylenetriamine–N, N, N', N'', N''–pentaacetate; *ortho*, *ortho*–Dipiridyl.

The formed superoxide ion is an active reductive species and reduces ions in the higher valence state, for example,

$$O_2{}^{\bullet -} + Fe^{3+} \rightarrow O_2 + Fe^{2+}$$

TABLE 15.3 Rate Constants of Decay for $Fe^{(III)}$ Complexes with Hydrogen Peroxide in Aqueous Solutions (T = 298 K)[a]

Complex	k_3 (s^{-1})	K_m ($mol\,L^{-1}$)
Nitrilotriacetic acid–$Fe^{(III)}$–H_2O_2	0.37	3.0×10^{-5}
Nitrilotriacetic acid–$Fe^{(III)}$–H_2O–HO_2^-	0.50	8.0×10^{-7}
Nitrilotriacetic acid–$Fe^{(III)}$–$HO^-{\cdot}HO_2^-$	0.80	7.0×10^{-9}
Nitrilotriacetic acid–$Fe^{(III)}$–$(HO^-)_2{\cdot}HO_2^-$	0.0	1.0×10^{-5}
Ethylenedinitrilotetraacetic acid–$Fe^{(III)}$–H_2O_2	0.13	1.0×10^{-3}
Ethylenedinitrilotetraacetic acid–$Fe^{(III)}$–H_2O–HO_2^-	0.20	2.0×10^{-6}
Ethylenedinitrilotetraacetic acid–$Fe^{(III)}$–$HO^-{\cdot}HO_2^-$	0.30	3.0×10^{-9}
Ethylenedinitrilotetraacetic acid–$Fe^{(III)}$–$(HO^-)_2{\cdot}HO_2^-$	0.0	2.6×10^{-5}
Ethylenebis(oxyethylenenitrilo)tetraacetic acid–$Fe^{(III)}$–H_2O_2	0.15	7.0×10^{-4}
Ethylenebis(oxyethylenenitrilo)tetraacetic acid–$Fe^{(III)}$–H_2O–HO_2^-	0.26	1.0×10^{-6}
Ethylenebis(oxyethylenenitrilo)tetraacetic acid–$Fe^{(III)}$–$HO^-{\cdot}HO_2^-$	0.513	1.0×10^{-6}
Ethylenebis(oxyethylenenitrilo)tetraacetic acid–$Fe^{(III)}$–$(HO^-)_2{\cdot}HO_2^-$	0.0	1.6×10^{-5}
Diethylenetriaminepentaacetic acid–$Fe^{(III)}$–H_2O_2	0.12	7.0×10^{-3}
Diethylenetriaminepentaacetic acid–$Fe^{(III)}$–H_2O–HO_2^-	0.09	8.0×10^{-7}
Diethylenetriaminepentaacetic acid–$Fe^{(III)}$–$HO^-{\cdot}HO_2^-$	0.15	3.0×10^{-7}
Diethylenetriaminepentaacetic acid–$Fe^{(III)}$–$(HO^-)_2{\cdot}HO_2^-$	0.0	3.3×10^{-5}

[a] See Ref. 50.

15.2 CATALYSIS BY IONS AND COMPLEXES OF TRANSITION METALS IN LIQUID-PHASE OXIDATION OF ORGANIC COMPOUNDS

Salts and complexes of heavy metals accelerate the liquid-phase oxidation of organic compounds. This accelerating action was found to be the result of the catalytic decomposition of formed hydroperoxides to free radicals in cyclic reactions[51–54]

$$M^{n+} + ROOH \rightarrow M^{n+1} + RO^{\bullet} + OH^-$$

$$M^{n+1} + ROOH \rightarrow M^{n+} + RO_2^{\bullet} + H^+$$

$$H^+ + HO^- \Leftrightarrow H_2O$$

Slow reactions of unimolecular and bimolecular homolytic decomposition of hydroperoxides are replaced by two rather fast ion reactions F_2^{2+}/Fe^{3+}, Co^{2+}/Co^{3+}, Mn^{2+}/Mn^{3+}, Ce^{3+}/Ce^{4+}, and Cu^+/Cu^{2+} with electron transfer between the ion and hydroperoxide.

Oxidation–reduction catalysis of transition metal ions is widely used in chemical technology.[55–59] Cobalt salts (stearate, naphthenate, etc.) catalyze the oxidation of cyclohexane to cyclohexanone and cyclohexanol,[55,56] and cumene oxidation to cumyl hydroperoxide.[55,58,59] Manganese salts are used as catalysts for the paraffin oxidation to fatty acids.[54] Cobalt-bromide catalysis of dimethyl benzene oxidation is the technological process for phthalic acid production.[58,59]

The acceleration effect of iron and copper salts on some oxidation–reduction reactions was discovered in the nineteenth century.[60] In 1931, Haber and Willstatter[1] proposed a mechanism for the action of ions of transition metals on the chain oxidation and decomposition reactions. They introduced the concept of an elementary reaction between an ion and a reactant in which a change in the valence of the ion and the formation of a free radical initiating a chain reaction took place. Twenty years later this mechanism was experimentally demonstrated by Bawn with co-workers in the study of aldehyde oxidation.[61–64] The metal ion changes valence during the oxidation process, which was proved spectrophotometrically. The catalytic decomposition of cumyl, tetralyl, and 1,1-dimethylethyl hydroperoxides (ROOH) in butadiene is accompanied by the formation of the following compounds:[65]

$$ROCH_2CH{=}CHCH_2CH_2CH{=}CHCH_2OR$$

and

$$ROCH_2CH{=}CHCH_2CH(CH{=}CH_2)CH_2OR$$

These compounds are the result of the addition of an alkoxyl radical formed from ROOH to the butadiene molecule.

The mechanism of hydrocarbon oxidation catalyzed by Co^{2+}/Co^{3+} salts includes the following stages:[51–54]

$$R^{\bullet} + O_2 \rightarrow RO_2{}^{\bullet}$$

$$RO_2{}^{\bullet} + RH \rightarrow ROOH + R^{\bullet}$$

$$Co^{2+} + ROOH \rightarrow Co^{3+} + RO^{\bullet} + OH^-$$

$$Co^{3+} + ROOH \rightarrow Co^{2+} + RO_2{}^{\bullet} + H^+$$

$$RO^{\bullet} + RH \rightarrow ROH + R^{\bullet}$$

$$RO_2{}^{\bullet} + RO_2{}^{\bullet} \rightarrow ROOR + O_2$$

The following two reactions initiate the chain oxidation of benzaldehyde catalyzed by cobalt(II) and cobalt(III) ions:[61–64]

$$Co^{2+} + PhC(O)OOH \rightarrow Co^{3+} + PhCO_2{}^{\bullet} + HO^-$$

$$Co^{3+} + PhC(O)H \rightarrow Co^{2+} + PhC^{\bullet}(O) + H^+$$

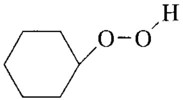
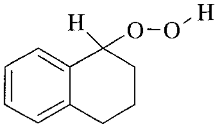
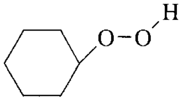
The values for the rate constants of hydroperoxide decomposition by heavy metal salts and complexes are in Table 15.4.

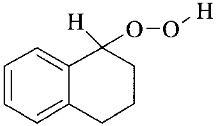
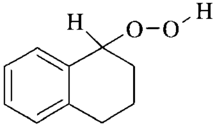
TABLE 15.4 Rate Constants of Transition Metal Ions and Complex Reactions with Peroxides

ROOH	Solvent	T (K)	E (kJ mol^{-1})	log A, A (L mol^{-1} s^{-1})	k(298 K) (L mol^{-1} s^{-1})	Reference
			Co^{2+}			
Me_3COOH	$MeC(O)OH/H_2O$	308	82.8	9.91	2.49×10^{-5}	66
			$Co[O(O)CCHEtBu]_2$			
Me_3COOH	$MeC(O)OH$	313			6.10×10^{-3}	67
Me_3COOH	PhCl	293	50.2	8.38	0.38	68
			$Co(edta)^{2-}$ [a]			
Me_3COOH	$MeC(O)OH$	333			2.19×10^{-2}	69
Me_3COOH	PhCl	293			10.5	69
			$Co[O(O)C(CH_2)_6Me]_2$			
$Me_2PhCOOH$	PhCl	318	50.2	7.58	6.04×10^{-2}	58
			$Co[O(O)C(CH_2)_{14}Me]_2$			
$Me_2PhCOOH$	n-C_9H_{20}	364–389	39.3	3.86	9.36×10^{-4}	70

(continued overleaf)

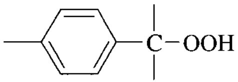
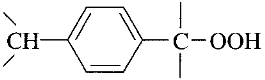
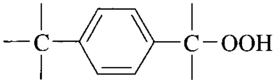
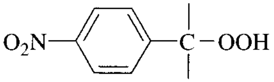
TABLE 15.4 (*continued*)

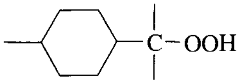
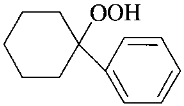
ROOH	Solvent	T (K)	E (kJ mol^{-1})	log A, A (L mol^{-1} s^{-1})	k(298 K) (L mol^{-1} s^{-1})	Reference
			Co$^{(II)}$ Phthalocyanine			
$Me_2PhCOOH$	n-C_9H_{20}	323–393	39.7	7.21	1.78	71
			Co[O(O)C(CH$_2$)$_{16}$Me]$_2$			
	*cyclo*-C_6H_{12}	303–342	42.0	7.93	3.70	72
	PhCl	323			6.17	73
			Co[O(O)C(CH$_2$)$_{16}$Me]$_3$			
	*cyclo*-C_6H_{12}	298			0.01	72

		$Co[O(O)CMe]_2$				
MeC(O)OOH	*cyclo*-C_6H_{12}	303–342	79.5	12.38	2.79×10^{-2}	72
	Tetralin	323			2.88	73
		$Cu[O(O)C(CH_2)_{16}CH_3]_2$				
MePhCHOOH	$MePhCH_2$	343–363	66.1	9.92	2.16×10^{-2}	74
		$Cu[O(O)C(CH_2)_7CH{=}CH(CH_2)_7Me]_2$				
	Tetralin	330			1.0×10^{-2}	75

(*continued overleaf*)

TABLE 15.4 (*continued*)

ROOH	Solvent	T (K)	E (kJ mol^{-1})	log A, A (L mol^{-1} s^{-1})	k(298 K) (L mol^{-1} s^{-1})	Reference
			Fe^{2+}			
Me_3COOH	H_2O	273–298	41.0	8.31	13.3	76
Me_3COOH	H_2O, pH 1.0	273–298	38.6	7.97	16.0	77
Me_3COOH	H_2O, pH 2.0	298			14.0	77
$Me_2PhCOOH$	H_2O	273–298	37.9	8.55	80.7	78
$Me_2PhCOOH$	D_2O	273–298	45.3	8.97	10.7	78
$Me_2PhCOOH$	H_2O	273–298	50.2	10.03	17.0	79
$Me_2PhCOOH$	H_2O	273–298	46.4	9.59	28.6	80
$Me_2PhCOOH$	H_2O	273–298	41.6	8.49	15.8	77
	H_2O; pH 1.2	273–298	32.2	7.00	22.5	77
	H_2O; pH 4.2	284–299	45.2	9.60	47.6	81
	H_2O; pH 4.2	273–288	41.4	9.255	99.6	81
	H_2O; pH 4.2	273–298	54.8	10.90	19.7	82

	H_2O; pH 4.2	273–289	46.0	9.80	54.6	82
	H_2O; pH 4.2	273–298	45.2	9.38	28.7	82
PhC(O)OO(O)CPh	EtOH	288–305	59.4	11.34	8.48	83
PhC(O)OO(O)CPh	EtOH	283–303	50.2	9.36	3.64	84
PhC(O)OO(O)CPh	EtOH	290–300	48.4	9.00	3.28	85
PhC(O)OO(O)CPh	MeOH	298–313	82.8	13.52	0.10	84
PhC(O)OO(O)CPh	*n*-PhOH	278–288	62.8	11.94	8.56	84
PhC(O)OO(O)CPh	*n*-BuOH	278–288	51.9	9.875	6.00	84
(p-$MeOC_6H_4C(O)O)_2$	EtOH	290–300	40.4	7.75	4.66	84
(p-$MeC_6H_4C(O)O)_2$	EtOH	290–300	40.6	7.75	4.30	84
(p-$ClC_6H_4C(O)O)_2$	EtOH	290–300	61.8	11.35	3.29	84
(p-$NO_2C_6H_4C(O)O)_2$	EtOH	290–300	58.9	10.77	2.79	84
		$Mn[O(O)C(CH_2)_{16}Me]_2$				
n-$C_8H_{17}CH(OOH)Me$	n-$C_{10}H_{22}$	353–377	75.3	11.45	1.78×10^{-2}	86

[a] edta = ethylenediaminetetraacetate.

The main reaction for initiation by a metal catalyst is the reaction of a metal cation with a hydroperoxide resulting in free radicals formation. The efficiency of initiation *e* depends on the metal ion.[87] Salts of cobalt, iron, and manganese decompose hydroperoxides in hydrocarbon solutions with high values of *e*, close to unity. This implies that homolytic splitting of hydroperoxides predominate in reactions with a metal catalyst. By contrast, complexes of vanadium, molybdenum, nickel, and copper decompose hydroperoxides with a low yield of radicals (see Table 15.5). In these catalytic reactions, heterolytic decomposition of hydroperoxides predominates.

Free radicals react with heavy metal ions very rapidly too. This fast reaction of the peroxyl radical with metal ions leads to another composition of products and ways for their formation. A direct influence of the catalyst on the composition of the oxidation products was observed in the study of the catalyzed oxidation of cyclohexane.[56] Hydroperoxide is the primary intermediate product of hydrocarbon chain oxidation. The oxidation of cyclohexane catalyzed by heavy metal salts occurs with the parallel formation of hydroperoxide, cyclohexanol, and cyclohexanone.[56,93] The relative initial rates of cyclohexyl hydroperoxide, cyclohexanol, and cyclohexanone formation in the catalytic oxidation of cyclohexane are given in Table 15.6.

In addition to hydroperoxide splitting into free radicals, metal catalysts can initiate oxidation by the activation of dioxygen. For example, cobalt(II)

TABLE 15.5 The Yield of Free Radical Generation *e* in Reactions of Hydroperoxides Decomposition Catalyzed by Transition Metal Complexes

Catalyst	ROOH	Solvent	T (K)	e	Reference
Vanadyl, bis(acetylacetonate)	*cyclo*-$C_6H_{11}OOH$	*cyclo*-C_6H_{12}	403	0.08	88
Vanadyl, bis(acetylacetonate)	*cyclo*-$C_6H_{11}OOH$	*cyclo*-C_6H_{12}	333	0.20	88
Vanadyl, bis(acetylacetonate)	$Me_2PhCOOH$	*cyclo*-C_6H_{12}	333	0.50	89
Chromium(III), tris(acetylacetonate)	*cyclo*-$C_6H_{11}OOH$	*cyclo*-C_6H_{12}	393	0.08	88
Manganese, acetate	Me_3COOH	*n*-$C_{10}H_{22}$	393	0.017	90
Manganese, stearate	*sec*-$C_{10}H_{11}OOH$	*n*-$C_{10}H_{22}$	413	0.04	90
Cobalt(II), stearate	$Me_2PhCOOH$	PhCl	323	0.36	91
Cobalt(II), stearate	$Me_2PhCOOH$	*n*-$C_{10}H_{22}$	323	0.38	91
Cobalt(II), stearate	Me_3COOH	C_6H_6	323	1.00	91
Cobalt(II), stearate	*sec*-$C_{10}H_{11}OOH$	*n*-$C_{10}H_{22}$	323	1.00	91
Cobalt(II), bis(acetylacetonate)	$Me_2PhCOOH$	PhCl	318	0.82	91
Cobalt(II), bis(acetylacetonate)	*sec*-$C_{10}H_{11}OOH$	*n*-$C_{10}H_{22}$	318	1.00	91
Nickel(II), bis(acetylacetonate)	*sec*-$C_{10}H_{11}OOH$	PhCl	363	0.02	91
Nickel(II), bis(acetylacetonate)	MePhCHOOH	PhCl	363	0.04	91
Nickel(II), stearate	MePhCHOOH	$PhCH_2CH_3$	393	0.012	91
Copper(II), stearate	*sec*-$C_{10}H_{11}OOH$	*n*-$C_{10}H_{22}$	353	0.016	92
Molybdenum dioxide, bis(acetylacetonate)	*cyclo*-$C_6H_{11}OOH$	*cyclo*-C_6H_{12}	403	0.017	92

TABLE 15.6 The Relative Rates of Cyclohexyl Hydroperoxide, Cyclohexanol, and Cyclohexanone Formation in Catalytic Oxidation of Cyclohexane[a,b]

Catalyst	T (K)	v_{ROOH} %	v_{ROH} %	v_{ketone} %
Cerium(III), stearate	383	>90	<5	<5
Cobalt(II), stearate	408	47	35	18
Cobalt(II), stearate	383	40	40	20
Cobalt(II), stearate	373	31	42	27
Copper(II), stearate	408	71	15	14
Copper(II), stearate	383	71	15	14
Manganese(II), stearate	408	62	30	8
Manganese(II), stearate	383	61	30	9
Nickel(II), stearate	383	>90	<5	<5
Zincum(II)	383	>90	<5	<5

[a] Concentration of catalyst = 5.0×10^{-5} mol L^{-1}.
[b] See Refs. 56 and 93.

acetylacetonate initiates chain generation in styrene oxidation with the rate $v_i = k_i[\mathrm{Co(acac)_2}][\mathrm{PhCH{=}CH_2}][\mathrm{O_2}]$, and a rate constant $k = 6.3 \times 10^{-2}$ L^2 mol^{-2} s^{-1} ($T = 388$ K).[94] The following mechanism of initiation was proposed:

$$\mathrm{Co(acac)_2 + O_2 \Leftrightarrow O_2{\cdot}Co(acac)_2}$$

$$\mathrm{PhCH{=}CH_2 + O_2{\cdot}Co(acac)_2 \rightarrow Free\ radicals}$$

$$\mathrm{acac = acetylacetonate}$$

For data concerning reactions of metal ions with dioxygen, see Section 15.4.

A mixture of cobaltous ions and bromides in carbonic acid media is a very effective catalyst for alkyl aromatic oxidation.[95-100] Cobalt–bromide catalysis is used in chemical technology for the production of phthalic acids from dimethylbenzene.[101] A detailed study of the mechanism of this catalysis proved the following kinetic scheme of dimethylbenzene oxidation:[95,96]

$$\mathrm{R^\bullet + O_2 \rightarrow RO_2^\bullet}$$

$$\mathrm{RO_2^\bullet + RH \rightarrow ROOH + R^\bullet}$$

$$\mathrm{ROOH + Co^{2+} \rightarrow RO^\bullet + Co^{3+} + HO^-}$$

$$\mathrm{RO^\bullet + RH \rightarrow ROH + R^\bullet}$$

$$\mathrm{HO^- + H^+ \Leftrightarrow H_2O}$$

$$\mathrm{Co^{3+} + Br^- \rightarrow Co^{2+} + Br^\bullet}$$

$$\mathrm{Br^\bullet + RH \rightarrow BrH + R^\bullet}$$

$$\mathrm{RO_2^\bullet + RO_2^\bullet \rightarrow ROH + ArCH(O)}$$

Chain propagation in this system provides the following three parallel reactions: $RO_2^{\bullet} + RH$, $Co^{2+} + ROOH$, and $RH + Br^{\bullet}$. The fast chain propagation step helps to perform the effective oxidation of the hydrocarbon at a moderate temperature and produce phthalic acid in high yield.

Oscillation kinetics is observed in some oxidation–reduction systems with heavy metal ions as catalysts (Belousov–Zhabotinsky reaction).[102] The change in the metal valence and formation of free radicals were detected in these systems.

15.3 REACTIONS OF FREE RADICALS WITH TRANSITION METAL IONS

Free radicals formed in reactions of metal ions with peroxides and other molecules react with metal ions in turn.[101–104] Oxygen-centered radicals ($HO^{\bullet}$, $RO^{\bullet}$, $RO_2^{\bullet}$), as a rule, oxidize reducing ions to their higher valence state, for example,

$$RO^{\bullet} + Co^{2+} \rightarrow RO^{-} + Co^{3+}$$

Hydrogen atoms and alkyl radicals reduce oxidizing ions reacting as electron donors.

$$R^{\bullet} + Cu^{2+} \rightarrow R^{+} + Cu^{+}$$

Reactions of free radicals play an important role in the chain reactions of polymerization[13] and oxidation by dioxygen (see Section 15.2) as well as in various free radical synthetic reactions.[101]

The hydroxyl radical is a very active electron acceptor (see Table 15.7). For example, it reacts with ferrous ions in an aqueous solution 100–1000 times more rapidly than exchange by water molecules in the inner sphere of Fe^{2+}. This implies that the electron transfer between Fe^{2+} and hydroxyl proceeds as an outer-sphere action. The reaction of hydroxyl with the chloride ion depends on the hydrogen ion concentration: An increase in $[H_3O^+]$ accelerates the reaction.[105]

pH	0	1	2	3
$\log k$ $[k(\mathrm{L\,mol^{-1}\,s^{-1}})]$	9.60	8.60	7.60	7.20
$k/[H_3O^+](s^{-1})$	4.0×10^9	4.0×10^9	4.0×10^9	1.6×10^{10}

This implies that the oxidation of Cl^- proceeds as a hydrogen atom abstraction from hydrogen chloride.

$$HO^{\bullet} + HCl \rightarrow H_2O + Cl^{\bullet}$$

A similar situation is observed in the reaction of hydroxyl with a bromide anion. For rate constants of hydroxyl radicals reactions with metal ions, see Table 15.7.

Alkyl radicals react with metal ions in the upper valence state to form carbocations as the active intermediates. Cupric ions oxidize alkyl radicals to olefins and alcohols as a result of the following reactions:[104]

$$\mathrm{R}^{\bullet} + \mathrm{Cu}^{2+} \rightarrow \mathrm{R}^{+} + \mathrm{Cu}^{+}$$

$$\mathrm{R}^{+} \rightarrow \text{Olefin} + \mathrm{H}^{+}$$

$$\mathrm{R}^{+} + \mathrm{H_2O} \rightarrow \mathrm{ROH} + \mathrm{H}^{+}$$

Ions of high reducing activity (Ti^{3+}, V^{2+}, Cr^{2+}) reduce the alkyl radical to a carbanion.[104] The formation of deuterated methane from a methyl radical in a solution of $\mathrm{D_2O}$ was proved as a result of the reactions

$$\mathrm{C^{\bullet}H_3} + \mathrm{Cr}^{2+} \rightarrow \mathrm{CH_3}^{-} + \mathrm{Cr}^{3+}$$

$$\mathrm{CH_3}^{-} + \mathrm{D_2O} \rightarrow \mathrm{CH_3D} + \mathrm{DO}^{-}$$

Alkyl radicals form complexes with metal ions.[103] Formation of complexes decreases the reactivity of the radical in its reaction with molecules. That is why the formation of complexes increases the yield of product from radical recombination. For example, the decomposition of 1,1-dimethylethyl hydroperoxide leads to the ratio $[\mathrm{C_2H_6}]/[\mathrm{CH_4}] = 0.33$ in the absence of ions; 0.95 in the presence of Mn^{2+}; 0.95 in the presence of Co^{2+}; and 4.9 in the presence of Ni^{2+}. Similar phenomena are observed for the case of ethyl radical generation. The following kinetic scheme explains these results:

$$\mathrm{R}^{\bullet} + \mathrm{Me}^{n+} \rightarrow (\mathrm{R}^{\bullet}\cdot\mathrm{Me}^{n+})$$

$$\mathrm{R}^{\bullet} + (\mathrm{R}^{\bullet}\cdot\mathrm{Me}^{n+}) \rightarrow \mathrm{RR} + \mathrm{Me}^{n+}$$

$$(\mathrm{R}^{\bullet}\cdot\mathrm{Me}^{n+}) + (\mathrm{R}^{\bullet}\cdot\mathrm{Me}^{n+}) \rightarrow \mathrm{RR} + \mathrm{Me}^{n+} + \mathrm{Me}^{n+}$$

Transition metal ions retard free radical polymerization due to a reaction with growing macroradicals.[104-106] Chain termination induces oxidizing ions (Fe^{3+}, Cu^{2+}, CeOH^{3+}) as well as reducing ions (Cr^{2+}, V^{2+}, Ti^{3+}). The rate v of monomer M polymerization in the presence of the metal ion Me^{n+} was found to be[106]

$$v = k_{\mathrm{p}}[\mathrm{M}]v_{\mathrm{i}}/k_{\mathrm{t}}[\mathrm{Me}^{n+}] \tag{15.7}$$

The values for the rate constants of free radical reactions with transition metal ions are in Table 15.7.

The hydroperoxyl radical possesses dual reactivity: oxidative as other peroxyl radicals and reducing due to the weak O–H bond. If the hydroperoxyl radical propagates the chain in the reaction of substrate oxidation, transition metal ions

TABLE 15.7 Rate Constants for Free Radical Reactions with Transition Metal Ions and Complexes

Ion	Solvent	T(K)	k(L mol^{-1} s^{-1})	Reference
	HO$^{\bullet}$			
Cerium(III) ion	Water	298	3.0×10^8	107
Cerium(III) ion	Water	296	2.2×10^8	108
Cerium(III) ion	Water	296	3.5×10^8	109
Cerium(IV) ion	Water, pH 0.4	298	2.7×10^6	29
Cobalt(III) ion	Water	298	8.0×10^5	110
Cobalt(III), pentacyanonitrate	Water	298	1.2×10^8	111
Cobalt(III), pentaaminenitride	Water	298	1.8×10^9	112
Cobalt(III), tris-acetylacetonate	Water	298	4.9×10^9	113
Copper(I) ion	Water	298	2.0×10^{10}	114
Copper(II) ion	Water	298	3.5×10^8	115
Copper(II) ion	Water, pH 7	296	3.5×10^8	116
Chromium(II) ion	Water, pH 1.0	298	4.8×10^9	117
Chromium(III) ion	Water, pH < 7	298	3.1×10^8	118
Chromium(III), pentacyanonitrosyl	Water	298	7.9×10^9	119
Europium(II) ion	Water	298	1.1×10^9	115
Iron(II) ion	Water, pH 1.0	298	3.0×10^8	120
Iron(II) ion	Water, pH 1.0	298	3.2×10^8	121
Iron(II) ion	Water, pH 1.6	298	3.2×10^8	105
Iron(II) ion	Water, pH 2.1	296	2.5×10^8	109
Iron(II) ion	Water, pH 2.0	296	2.6×10^8	122
Iron(II) ion	Water, pH 0.4	296	2.7×10^8	123
Iron(II) ion	Water, pH 0	288	3.3×10^8	124
Iron(II) ion	Water, pH 3.0	298	4.3×10^8	125
Iron(II) ion	Water, pH 7.0	298	3.2×10^8	126
Iron(II) ion	Water, pH 1.0	298	2.3×10^8	127
Iron(II) ion	Water, pH 4.5–6.2	298	3.5×10^8	128
Iron(II) ion	Water	298	1.0×10^9	129
Iron(III) ion	Water	298	7.9×10^7	109
Ferrocyanide ion	Water, pH 2.5–10.5	296	2.1×10^9	130
Ferrocyanide ion	Water, pH 7.0	296	1.7×10^{10}	131
Ferrocyanide ion	Water, pH 10.7	296	8.1×10^9	132
Ferrocyanide ion	Water, pH 9.0	296	7.5×10^9	133
Ferrocyanide ion	Water, pH 3–10	296	1.1×10^{10}	134
Ferrocyanide ion	Water	298	1.1×10^{10}	115
Manganese(II) ion	Water, pH 7.0	298	$>1.4 \times 10^8$	135
Manganese(II) ion	Water, pH 3.9–6.7	298	3.0×10^7	115
Silver(I) ion	Water	298	1.2×10^{10}	136
Stannum(II) ion	Water, pH 1.0	296	2.0×10^9	137
Thallium(I) ion	Water, pH 7.0	296	7.6×10^9	138
Thallium(I) ion	Water, pH 1.0	296	8.9×10^9	139

TABLE 15.7 *(continued)*

Ion	Solvent	T(K)	k(L mol^{-1} s^{-1})	Reference
	$HO_2^\bullet$			
Cerium(III) ion	Water, pH 0.4	298	2.1×10^5	140
Cerium(IV) ion	Water, pH 0.4	298	2.7×10^6	29
Copper(I) ion	Water, pH 2.3	298	2.3×10^9	141
Copper(I) ion	Water	296	4.3×10^9	30
Copper(II) ion	Water, pH 2.3	296	1.5×10^7	142
Copper(II) ion	Water, pH 2.3	298	1.1×10^8	30
Copper(II) ion	Water, pH 0.8–2	298	1.0×10^8	143
Ferrocyanide ion	Water, pH 0.5–4.4	298	3.0×10^4	144
Ferrocyanide ion $HFe(CN)_6^{3-}$	Water, pH 0.5–4.4	298	1.4×10^5	144
Ferrocyanide ion $H_2Fe(CN)_6^{2-}$	Water, pH 0.5–4.4	298	1.0×10^4	144
Iron(II) ion	Water, 0.5 M H_2SO_4	296	7.2×10^5	36
Iron(II) ion	Water, pH 1.0	298	1.2×10^6	145
Iron(II) ion	Water	298	1.5×10^6	146
Iron(II) ion	Water	298	1.2×10^6	147
Iron(II) ion	Water, pH 0.0–2.1	298	2.1×10^6	148
Iron(III) ion	Water, pH 1.5	298	2.0×10^4	149
Iron(III) ion	Water, pH 2.05	298	3.3×10^5	39
Iron(III) ion	Water, pH 2.7	298	3.1×10^5	149
Iron(III) ion	Water, pH 1.0	298	4.0×10^5	150
Iron(III) ion	Water, pH 2.1	298	1.2×10^5	105
Iron(III) ion	Water, pH 2.0	298	1.3×10^5	151
Iron(III) ion	Water, pH 2.7	298	3.6×10^5	151
Iron(III) ion	Water	298	7.3×10^5	152
Manganese(II) ion	Water, pH 3–9	298	1.1×10^8	153
Manganese(II) ion	Water, pH 2.7–3.4	298	6.0×10^6	154
Manganese(II) formiate	Water, pH 2.2–3.0	298	6.0×10^6	154
Thallium(II) ion	Water, pH 1.0	298	2.5×10^9	155
	cyclo-$C_6H_{11}OO^\bullet$			
Cobalt(II),	Cyclohexane	303	2.7×10^4	72
Cobalt(II),	Cyclohexane	342	9.3×10^4	72
Cobalt(III),	Cyclohexane	303	2.0×10^4	72
Cobalt(III),	Cyclohexane	342	1.0×10^5	72
Copper(II),	Cyclohexane	303	8.6×10^2	72
Copper(II),	Cyclohexane	342	1.0×10^4	72
Manganese(II)	Cyclohexane	303	9.9×10^2	72
Manganese(II)	Cyclohexane	342	6.5×10^3	72
Manganese(III)	Cyclohexane	303	1.8×10^3	72
Manganese(III)	Cyclohexane	342	2.2×10^4	72

(continued overleaf)

TABLE 15.7 ***(continued)***

Ion	Solvent	T(K)	k(L mol^{-1} s^{-1})	Reference
	$MePhCHOO^{\bullet}$			
Cobalt(II), ethylenediaminetetraacetate	Acetic acid/ethylbenzene	333	3.8×10^5	156
Cobalt(II), bis-8-quinolinolate	Acetic acid/ethylbenzene	333	9.0×10^7	156
Copper(II), bis-8-quinolinolate	Acetic acid/ethylbenzene	333	7.9×10^5	156
Ferrocene	Acetic acid/ethylbenzene	333	2.4×10^5	157
Ferrocene, ethyl-	Acetic acid/ethylbenzene	333	1.8×10^5	157
Ferrocene, phenyl-	Acetic acid/ethylbenzene	333	8.3×10^4	157
Ferrocene, acetyl-	Acetic acid/ethylbenzene	333	3.3×10^4	157
Ferrocene, cyano-	Acetic acid/ethylbenzene	333	4.0×10^3	157
Ferrocene, carbonic acid	Acetic acid/ethylbenzene	333	1.2×10^4	157
Manganese, bis-8-quinolinolate	Acetic acid/ethylbenzene	333	4.2×10^5	156
Manganese(II), ethylenediaminetetraacetate	Acetic acid/ethylbenzene	333	1.0×10^6	156
Nickel(II), bis-8-quinolinolate	Acetic acid/ethylbenzene	333	2.2×10^5	156
	$Me_2(CN)COO^{\bullet}$			
Manganese(II), stearate	Chlorobenzene	333	2.0×10^5	158
Manganese(II), stearate	Chlorobenzene	353	3.0×10^5	158
Cobalt(II), bis(acetylacetonate)	Chlorobenzene	347	2.3×10^4	159
	$\sim CH_2C(OO^{\bullet})HPh$			
Cobalt(II), bis(acetylacetonate)	Chlorobenzene	328	1.8×10^4	159
Cobalt(II), bis(acetylacetonate)	Chlorobenzene	353	4.9×10^4	159
Iron(II) ion	Water	298	1.7×10^6	160
	$C^{\bullet}H_3$			
Copper(II), acetate	Acetonitrile/acetic acid (2/3)	298	1.5×10^6	161
	$Me_2C^{\bullet}H$			
Copper(II) ion	Acetonitrile/acetic acid (2/3)	298	5.0×10^6	162
	$PrC^{\bullet}H_2$			
Copper(II) ion	Acetonitrile/acetic acid (2/3)	298	3.1×10^6	162
Copper(II), dipyridyl-	Acetonitrile/acetic acid (2/3)	298	1.7×10^7	162

TABLE 15.7 (*continued*)

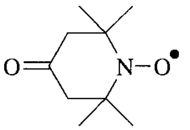
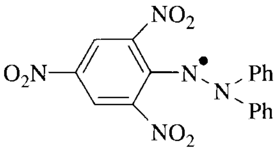
Ion	Solvent	T(K)	k(L mol^{-1} s^{-1})	Reference
	$Me_3CC^{\bullet}H_2$			
Copper(II) ion	Acetonitrile/acetic acid (2/3)	298	4.5×10^5	162
Copper(II), dipyridyl-	Acetonitrile/acetic acid (2/3)	298	2.5×10^4	162
	$CH_2{=}CH(CH_2)_3C^{\bullet}H_2$			
Copper(II), acetate	Acetonitrile/acetic acid (2/3)	298	1.5×10^6	161
	$PhCH_2C^{\bullet}H_2$			
Copper(II) ion	Acetonitrile/acetic acid (2/3)	298	1.6×10^6	162
Copper(II), dipyridyl-	Acetonitrile/acetic acid (2/3)	298	1.4×10^7	162
	$C^{\bullet}H_2OH$			
Iron(III) ion	Water	298	1.0×10^8	163
Iron(III) ion	Water	298	8.0×10^7	164
Copper(II) ion	Water, pH 2–5	298	1.6×10^8	164
	$C^{\bullet}H_2CH_2OH$			
Copper(II) ion	Water, pH 4.5	298	1.9×10^7	164
Copper(II) ion	Water, pH 2	298	2.2×10^7	164
Iron(II) ion	Water	298	1.0×10^6	129
	$MeC^{\bullet}HOH$			
Copper(II) ion	Water, pH 2–5	298	9.4×10^7	164
Copper(II) ion	Water	298	2.7×10^8	164
Copper(II) ion	Water	298	3.8×10^8	164
Iron(III) ion	Water	298	6.0×10^8	129
	$Me_2C^{\bullet}OH$			
Copper(II) ion	Water, pH 2–5	298	5.2×10^7	164
Iron(II) ion	Water	298	2.9×10^6	165
Iron(III) ion	Water, pH 1	298	4.5×10^8	160
Iron(III) ion	Water, pH 1	298	1.8×10^8	163
Iron(III) ion	Water	298	5.8×10^8	164

(*continued overleaf*)

TABLE 15.7 (*continued*)

Ion	Solvent	T(K)	k(L mol^{-1} s^{-1})	Reference
	$C^{\bullet}H_2Me_2COH$			
Copper(II) ion	Water, pH 4.5	298	2.7×10^6	164
Copper(II) ion	Water, pH 3.0	298	3.2×10^6	164
	$\sim CH_2C^{\bullet}HCONH_2$			
Titan(III) ion	Water, 0.8 N H_2SO_4	298	6.0×10^2	166
Titan(III) ion	D_2O, 0.8 N H_2SO_4	298	8.1×10^2	166
Vanadyl(IV) ion	Water, 0.8 N H_2SO_4	298	1.1×10^3	166
Vanadium(II) ion	Water, 0.8 N H_2SO_4	298	1.1×10^5	166
Chromium(III) ion	Water, 0.8 N H_2SO_4	298	2.8×10^5	166
Iron(III) ion	Water; pH 1	298	2.0×10^3	167
Iron(III) ion	Water; pH 1	298	2.0×10^3	168
Iron(III) ion	D_2O; pH 0	298	1.9×10^3	168
Hydroxoiron(III) ion	Water	298	1.1×10^4	167
Hydroxoiron(III) ion	Water	298	2.1×10^4	166
Chloroiron(III) ion	Water	298	8.1×10^4	166
Dichloroiron(III) ion	Water	298	1.7×10^4	166
Trichloroiron(III) ion	Water	298	1.0×10^6	166
Bromoiron(III) ion	Water	298	1.7×10^6	166
Azidoiron(III) ion	Water	298	1.5×10^6	166
Rodanidoiron(III) ion	Water	298	1.3×10^7	166
Iron(III), tris(dipyridyl)-	Water	298	8.1×10^4	166
Iron(III), tris-*o*-phenantrolin-	Water	298	3.1×10^5	166
Iron(III), tris(5-methyl-*o*-phenantrolin)-	Water	298	2.6×10^5	166
Iron(III), tris(5-phenyl-*o*-phenantrolin)-	Water	298	5.1×10^5	166
Iron(III), tris(5-chloro-*o*-phenantrolin)-	Water	298	2.3×10^5	166
Ferricyanide ion	Water	298	8.5×10^5	166
Copper(II) ion	Water, 1 N $HClO_4$	298	1.2×10^5	168
Copper(II) ion	D_2O; 1 N $HClO_4$	298	1.4×10^3	168
Hydroxocerium(IV) ion	Water, pH 0–1	298	3.3×10^3	168
Europium(II) ion	Water, 0.8 N	298	8.4×10^4	166
Thallium(III) ion	Water, 0.1 N $HClO_4$	298	21.0	168
	p-$MeOC_6H_4CH_2C^{\bullet}H_2$			
Copper(II) ion	Acetonitrile/acetic acid (2/3)	298	2.1×10^4	162
Copper(II), dipyridyl-	Acetonitrile/acetic acid (2/3)	298	3.0×10^6	162

TABLE 15.7 (*continued*)

Ion	Solvent	T(K)	k(L mol^{-1} s^{-1})	Reference
	$\sim CH_2C^{\bullet}MeCONH_2$			
Iron(III) ion	Water	298	53.1	169
Hydroxoiron(III) ion	Water	298	1.7×10^3	169
Iron(III) methacrylamidyl-	Water	298	6.1×10^3	169
	$\sim CH_2C^{\bullet}HCN$			
Ferricyanide ion	Water	298	6.8×10^6	170
Trichloroiron(III) ion	Formamid, N,N-dimethyl-	298	6.4×10^3	171
Trichloroiron(III) ion	Formamid, N,N-dimethyl-	298	8.1×10^3	172
	$\sim CH_2C^{\bullet}MeCN$			
Trichloroiron(III) ion	Formamid, N,N-dimethyl-	298	6.2×10^2	171
	$\sim CH_2C^{\bullet}HPh$			
Trichloroiron(III) ion	Formamid, N,N-dimethyl-	298	5.4×10^4	171
	$\sim CH_2C^{\bullet}MeCOOMe$			
Dichlorocopper(II) ion	Formamid, N,N-dimethyl-	333	7.8×10^5	173
				
Iron(II) ion	Water, 0.1 N HCl; 0.4 M NaCl	298	5.9×10^5	174
Iron(II) ion	Water, 0.05 N HCl; 0.45 M NaCl	298	1.7×10^5	174
				
Iron(II) ion	Water/EtOH (1/1)	293	23.0	175
Iron(II) ion	Water/EtOH (1/4)	293	1.2×10^2	176

(*continued overleaf*)

TABLE 15.7 (*continued*)

Ion	Solvent	T(K)	k(L mol^{-1} s^{-1})	Reference
Iron(II) ion	Methanol	295	6.7×10^2	177
Iron(II), dichloride	Methanol	295	3.7×10^5	177
Iron(II) ion	Ethanol	295	28.8	177
Iron(II), dichloride	Ethanol	295	7.5×10^2	177
Iron(II) ion	Propanol	295	32.0	177
Iron(II), dichloride	Propanol	295	7.1×10^3	177
Iron(II) ion	2-Propanol	295	1.0×10^2	177
Iron(II), dichloride	2-Propanol	295	5.0×10^3	177
Iron(II) ion	Butanol	295	32.0	177
Iron(II), dichloride	Butanol	295	3.9×10^3	177
Iron(II) ion	Pentanol	295	15.8	177
Iron(II), dichloride	Pentanol	295	3.5×10^3	177
Iron(II) ion	Heptanol	295	69.1	177
Iron(II), dichloride	Heptanol	295	3.0×10^3	177
Iron(II), 1,3-propanedicarboxylate	Butanol + 0.5 *M* $NaClO_4$	293	2.1×10^3	177
Iron(II), 1,3-butanedicarboxylate	Butanol + 0.5 *M* $NaClO_4$	293	1.6×10^2	177
Iron(II), 1,3-pentanedicarboxylate	Butanol + 0.5 *M* $NaClO_4$	293	1.1×10^2	177
Iron(II), 1,3-hexanedicarboxylate	Butanol + 0.5 *M* $NaClO_4$	293	78.5	177
Iron(II), 1,3-heptanedicarboxylate	Butanol + 0.5 *M* $NaClO_4$	293	75.0	177
Iron(II), 1,3-nonanedicarboxylate	Butanol + 0.5 *M* $NaClO_4$	293	71.6	177
Iron(II), 1,3-decanedicarboxylate	Butanol + 0.5 *M* $NaClO_4$	293	1.0×10^2	177
Iron(II), 1,3-propane dicarboxylate, 2,2-dimethyl-	Butanol + 0.5 *M* $NaClO_4$	293	1.2×10^2	177

retard chain oxidation during an infinitely long period of time as the result of cyclic chain termination.[178–183]

$$HO_2^{\bullet} + Me^{n+} \rightarrow Me^{n+1} + HO_2^{-} \qquad (k_1)$$

$$HO_2^{\bullet} + Me^{n+1} \rightarrow Me^{n+} + O_2 + H^{+} \qquad (k_2)$$

The phenomena of cyclic chain termination was first observed in experiments on the oxidation of cyclohexanol in the presence of a copper salt and was explained by a cycle of reactions.[178] The effective retardation of the chain reaction by transition metal ions and complexes was found in the oxidation of other primary and secondary alcohols, cyclohexadienes, 1,2-substituted ethylenes, and aliphatic amines.[180–183] This inhibiting effect was found to be the result of chain termination according the cyclic chain termination. The dual reactivity inherent in peroxyl radicals formed from alcohols $\left[>C(OH)OO^{\bullet}\right]$ and aliphatic amines $\left[>C(NHR)OO^{\bullet}\right]$. For the enthalpies, entropies, and Gibbs free energies of transition metals reactions with hydroperoxyl radicals, see Table 15.8.

The values for the rate constants of cyclic chain termination are collected in Table 15.9. Every rate constant consists of the sum that in stationary state conditions is $k = k_1([Me^{n+}]/([Me^{n+}] + [Me^{n+1}]) + k_2[Me^{n+1}]/([Me^{n+}] + [Me^{n+1}]) = 2k_1k_2/(k_1 + k_2)$. Depending on the values of k_1 and k_2, the effective rate constant k can be close to one of them (k_1 or k_2).

As one can see from Table 15.9, the values for the rate constants change dramatically depending on the metal, as well as on the ligands around it. Unlike organic inhibitors, the ions of metals are not consumed during the oxidation process. The cessation of their inhibitory action takes place for other reasons. The point is that the metal ions (salts) for transition metals not only react with peroxyl radicals, but also generate them by decomposing the formed hydroperoxide. In the course of substrate oxidation, the hydroperoxide (hydrogen peroxide) gradually

TABLE 15.8 Enthalpies, Entropies, and Gibbs Energies for Metal Ion Oxidation–Reduction Reactions with Hydroperoxyl Radical in Aqueous Solution (T = 298 K)

Reaction	ΔG (kJ mol^{-1})	ΔH (kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})
$Ce^{3+} + HO_2^{\bullet} + H^+ = Ce^{4+} + H_2O_2$	23.2	−59.7	−278
$Co^{2+} + HO_2^{\bullet} + H^+ = Co^{3+} + H_2O_2$	42.4	−44.1	−290
$Cu^{+} + HO_2^{\bullet} + H^+ = Cu^{2+} + H_2O_2$	−128.0	−180.6	−176.5
$Fe^{2+} + HO_2^{\bullet} + H^+ = Fe^{3+} + H_2O_2$	−68.4	−133.3	−218
$Mn^{2+} + HO_2^{\bullet} + H^+ = Mn^{3+} + H_2O_2$	5.9	−43.0	−164
$Ce^{4+} + HO_2^{\bullet} = Ce^{3+} + O_2 + H^+$	−170.8	−101.9	231
$Co^{3+} + HO_2^{\bullet} = Co^{2+} + O_2 + H^+$	−190.0	−117.5	243
$Cu^{2+} + HO_2^{\bullet} = Cu^{+} + O_2 + H^+$	−19.6	19.0	130
$Fe^{3+} + HO_2^{\bullet} = Fe^{2+} + O_2 + H^+$	−79.2	−28.3	171
$Mn^{3+} + HO_2^{\bullet} = Mn^{2+} + O_2 + H^+$	−153.5	−118.6	117

TABLE 15.9 Rate Constants for Cyclic Chain Termination by Transition Metal Ions in Oxidizing Alcohols, Amines, and Olefins

Metal Complex	Substrate	T (K)	k (L mol^{-1} s^{-1})	Reference
Cerium (III), stearate	*cyclo*-$C_6H_{11}OH$	348	1.1×10^5	184
Cerium (III), stearate	*cyclo*-$C_6H_{11}NH_2$	348	8.6×10^5	185
Cobalt(II), chloride	*cyclo*-$C_6H_{11}OH$	348	6.1×10^4	185
Cobalt(II), acetate	*cyclo*-$C_6H_{11}NH_2$	348	1.2×10^5	186
Cobalt(II), stearate	*cyclo*-$C_6H_{11}OH$	348	2.8×10^5	184
Cobalt(II), stearate	*cyclo*-$C_6H_{11}NH_2$	348	3.2×10^4	186
Cobalt(II), bis(acetylacetonate)	*cyclo*-$C_6H_{11}OH$	348	6.4×10^6	186
Cobalt(II), bis(acetylacetonate)	*cyclo*-$C_6H_{11}NH_2$	348	6.4×10^4	186
Cobalt(II), cyclohexylcarboxylate	*cyclo*-$C_6H_{11}OH$	348	8.7×10^4	185
Cobalt(II), bis(dimethylglyoximato)-amine chloride	*cyclo*-$[(CH{=}CH)_2CH_2CH_2]$	348	8.4×10^2	187
Cobalt(II), bis(dimethylglyoximato)-amine chloride	Me_2CHOH	344	5.0×10^3	188
Cobalt(II), bis(dimethylglyoximato)-amine iodide	*cyclo*-$[(CH{=}CH)_2CH_2CH_2]$	348	2.3×10^4	187
Cobalt(II), bis(dimethylglyoximato)-amine iodide	Me_2CHOH	344	3.1×10^2	188
Cobalt(II), bis(dimethylglyoximato) pyridyl iodide	Me_2CHOH	344	7.0×10^4	188
Cobalt(II), bis(dimethylglyoximato)-bis-(pyridyl)	Me_2CHOH	344	1.2×10^4	188
Cobalt(II), bis(*o*-salicylatethenediimine)	*cyclo*-$C_6H_{11}OH$	348	3.3×10^5	189
Porphyrine	*cyclo*-$C_6H_{11}OH$	348	3.6×10^4	189

Cobalt(II), 2,4-dioxo-1,5,8,12-tetraazatetradecano stearate	*cyclo*-$C_6H_{11}OH$	343	1.5×10^5	190
Cobalt(II), 2,4-dioxo-1,5,8,12-tetraazatetradecano stearate	*cyclo*-$C_6H_{11}OH$	363	1.1×10^5	190
Cobalt(III), tris-(acetylacetonate)	Me_2CHOH	344	2.9×10^2	188
Copper(II), sulfate	*cyclo*-$C_6H_{11}OH$	353	8.8×10^6	178
Copper(II), chloride	(*E*)-$C_6H_5CH{=}CHCOOEt$	348	5.9×10^5	191
Copper(II), chloride	(*E*)-$C_6H_5CH{=}CHCHCOOMe$	323	5.6×10^5	191
Copper(II), chloride	(*E*)-$C_6H_5CH{=}CHPh$	323	2.6×10^5	191
Copper(II), acetate	$PhCH_2NH_2$	323	1.5×10^8	185
Copper(II), acetate	$PhCOOC_2H_4NMe_2$	338	1.3×10^7	192
Copper(II), acetate	$BuMe_2$	323	1.0×10^7	192
Copper(II), acetate	$PhCH{=}CHCOOEt$	323	2.2×10^5	191
Copper(II), acetate	$PhCH{=}CHCOOMe$	323	4.5×10^5	191
Copper(II), acetate	$PhCH{=}CHPh$	323	5.3×10^5	191
Copper(II), stearate	*cyclo*-$[(CH{=}CH)_2CH_2CH_2]$	348	4.5×10^6	193
Copper(II), stearate	*cyclo*-$C_6H_{11}OH$	348	2.9×10^6	184
Copper(II), stearate	Bu_2NH	348	4.1×10^6	185
Copper(II), stearate	*cyclo*-$C_6H_{11}NH_2$	348	9.5×10^7	186
Copper(II), stearate	*cyclo*-$C_6H_{11}NH_2$	348	1.0×10^7	185
Copper(II), stearate	$Me_2NCH_2CH_2NMe_2$	313	2.7×10^5	194
Copper(II), bis(acetylacetonate)	$PhCH_2NH_2$	338	1.3×10^6	185
Copper(II), bis(acetylacetonate)	*cyclo*-$C_6H_{11}NH_2$	348	7.2×10^5	185

(continued overleaf)

TABLE 15.9 (*continued*)

Metal Complex	Substrate	T (K)	k ($\mathrm{L\,mol^{-1}\,s^{-1}}$)	Reference
Copper(II), bis(dimethylglyoximato)	*cyclo*-[$(CH{=}CH)_2CH_2CH_2$]	348	1.5×10^5	187
Copper(II), bis(dimethylglyoximato)	Me_2CHOH	344	5.0×10^5	188
Copper(II), bis(salicylate)	*cyclo*-[$(CH{=}CH)_2CH_2CH_2$]	348	1.7×10^5	187
Copper(II), bis(salicylate)	Me_2CHOH	344	1.2×10^6	189
Copper(II), bis(diphenylglyoximato)	Me_2CHOH	344	5.9×10^4	189
Copper(II), bis(4-nitrosalicylanilidato)	*cyclo*-$C_6H_{11}NH_2$	363	2.8×10^8	189
Copper(II), bis(salicylate)	*cyclo*-$C_6H_{11}NH_2$	363	1.4×10^8	189
Copper(II), bis(4-hydroxysalicylanilidato)	*cyclo*-$C_6H_{11}NH_2$	363	9.2×10^7	189
Copper(II), bis(4-methoxysalicylanilidato)	*cyclo*-$C_6H_{11}NH_2$	363	1.1×10^8	189
Copper(II), bis(*o*-salicylatethenediimine)	*cyclo*-$C_6H_{11}NH_2$	363	3.6×10^7	189
Copper(II), bis[*o*-salicylate-bis(ethenediimine)]	*cyclo*-$C_6H_{11}NH_2$	348	4.7×10^6	189
Copper(II), bis[*o*-salicylate-tris(ethenediimine)]	*cyclo*-$C_6H_{11}NH_2$	348	7.9×10^5	189
Copper(II), 1,2-phenylen-bis(*o*-salicylate)	*cyclo*-$C_6H_{11}NH_2$	348	7.9×10^6	189
Copper(II), 4,4′-diphenyl-bis(*o*-salicylate)	*cyclo*-$C_6H_{11}NH_2$	348	2.6×10^6	189
Copper(II), porphyrine	*cyclo*-$C_6H_{11}NH_2$	348	7.3×10^5	185
Copper(II), porphyrine	$PhCH_2NH_2$	338	1.5×10^6	185
Copper(II), 2,4-dioxo-1,5,8,12-tetraazatetradecano stearate	*cyclo*-$C_6H_{11}OH$	343	1.4×10^6	190
Copper(II), 2,4-dioxo-1,5,8,12-tetraazatetradecano stearate	*cyclo*-$C_6H_{11}OH$	363	1.2×10^6	190
Iron(III), stearate	*cyclo*-$C_6H_{11}OH$	348	1.3×10^4	189

Iron(III), stearate	*cyclo*-$C_6H_{11}NH_2$	348	1.2×10^6	189
Iron(III), tris(acetylacetonate)	*cyclo*-$C_6H_{11}NH_2$	348	1.0×10^5	185
Iron(III), bis(dimethylglyoximato)-bis(pyridyl)	*cyclo*-$[(CH{=}CH)_2CH_2CH_2]$	348	2.3×10^3	187
Iron(III), bis(dimethylglyoximato)-bis(pyridyl)	Me_2CHOH	344	1.0×10^3	188
Manganese(II), acetate	Bu_2NH	348	2.5×10^6	185
Manganese(II), acetate	$Me_2NCH_2CH_2NMe_2$	313	1.1×10^6	194
Manganese(II), acetate	*cyclo*-$C_6H_{11}NH_2$	348	7.3×10^7	195
Manganese(II), acetate	$PhCH_2NH_2$	338	2.8×10^8	186
Manganese(II), acetate	$CH{=}CMeC(O)OC_2H_4NMe_2$	323	1.2×10^7	196
Manganese(II), acetate	$PhOCOC_2H_4NMe_2$	323	1.5×10^7	196
Manganese(II), stearate	*cyclo*-$[(CH{=}CH)_2CH_2CH_2]$	348	1.9×10^6	193
Manganese(II), stearate	*cyclo*-$C_6H_{11}OH$	348	6.8×10^6	184
Manganese(II), stearate	Bu_2NH	348	3.5×10^6	195
Manganese(II), stearate	*cyclo*-$C_6H_{11}NH_2$	348	1.6×10^8	195
Manganese(II), stearate	$MeCONEt_2$	348	7.8×10^5	185
Manganese(II), bis(acetylacetonate)	*cyclo*-$C_6H_{11}NH_2$	363	9.8×10^7	189
Manganese(II), bis(*o*-salicylatethenediimine)	*cyclo*-$C_6H_{11}NH_2$	348	3.1×10^8	189
Manganese(II), 2,4-dioxo-1,5,8,12-tetraazatetradecano stearate	*cyclo*-$C_6H_{11}OH$	343	5.4×10^7	190
Manganese(II), 2,4-dioxo-1,5,8,12-tetraazatetradecano stearate	*cyclo*-$C_6H_{11}OH$	363	4.3×10^7	190

accumulates, thereby increasing the rate of radical generation. Once the rate of catalyzed termination and generation of chains has been equalized, oxidation goes on as a noninhibited process.

15.4 OXIDATION OF TRANSITION METAL IONS BY DIOXYGEN

Dioxygen oxidizes transition metal ions in the lower valence state generating the hydroxyperoxyl radicals or superoxide ions.[197,198] The thermodynamic characteristics of these reactions are presented in Table 15.10.

The vast majority of the studies in this field relate to the oxidation of iron ions by molecular oxygen. The oxidation of Fe^{2+} is first order with respect to oxygen and, depending on conditions, first or second order with respect to Fe^{2+}. The limiting step includes the transfer of an electron from Fe^{2+} to oxygen. The following is the postulated reaction mechanism:

$$Fe_{aq}{}^{2+} + O_2 \Leftrightarrow FeO_2{}^{2+}$$

$$FeO_2{}^{2+} \rightarrow Fe^{3+} + O_2{}^{\bullet-} \qquad \text{(limiting stage)}$$

$$O_2{}^{\bullet-} + Fe^{2+} \rightarrow O_2{}^{2-} + Fe^{3+}$$

$$O_2{}^{2-} + 2H^+ \Leftrightarrow H_2O_2$$

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + HO^- + HO^\bullet$$

$$HO^\bullet + Fe^{2+} \rightarrow HO^- + Fe^{3+}$$

Second order with respect to Fe^{2+} is explained by the formation of a binuclear complex and its faster oxidation:

$$FeO_2{}^{2+} + Fe^{2+} \Leftrightarrow Fe^{2+}O_2Fe^{2+}$$

$$Fe^{2+}O_2Fe^{2+} \rightarrow Fe^{3+} + FeO_2{}^{+} \qquad \text{(limiting step)}$$

$$FeO_2{}^{+} \rightarrow Fe^{3+} + O_2{}^{2-}$$

TABLE 15.10 Enthalpies, Entropies, and Gibbs Energies for Transition Metal Ion Oxidation–Reduction Reactions with Dioxygen in Aqueous Solution (T = 298 K)

Reaction	ΔG (kJ mol^{-1})	ΔH (kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})
$Ce^{3+} + O_2 + H^+ = Ce^{4+} + HO_2{}^\bullet$	170.8	101.9	−231
$Co^{2+} + O_2 + H^+ = Co^{3+} + HO_2{}^\bullet$	190.0	117.5	−243
$Cu^{+} + O_2 + H^+ = Cu^{2+} + HO_2{}^\bullet$	19.6	−19.0	−130
$Fe^{2+} + O_2 + H^+ = Fe^{3+} + HO_2{}^\bullet$	79.2	28.3	−171
$Mn^{2+} + O_2 + H^+ = Mn^{3+} + HO_2{}^\bullet$	153.5	118.6	−117

By increasing the hydrogen-ion concentration, the rate of Fe^{2+} oxidation decreases; this is related to the hydrolysis of Fe^{2+}:

$$Fe_{aq}{}^{2+} \Leftrightarrow FeOH^+ + H^+$$

and a faster oxidation for $FeOH^+$. However, in concentrated hydrochloric acid, an increase in the oxidation rate is observed as the acid concentration increases. This is explained by the formation and rapid oxidation of Fe^{2+} HCl complexes:[197]

$$Fe_{aq}{}^{2+} + HCl \Leftrightarrow Fe^{2+}ClH$$
$$Fe^{2+}ClH + O_2 \rightarrow FeCl^{2+} + HO_2{}^{\bullet}$$

Tin(II) was found to be oxidized by dioxygen via a chain branching mechanism.[198–203] The oxidation rate is $v = k[O_2]^2$ in organic solvents and $v = k[Sn^{(II)}]^{1/2}[O_2]^{1/2}$ in aqueous solutions. The reaction, under certain conditions, has an induction period. Free radical acceptors retard this reaction. The following kinetic scheme was proposed for tin(II) oxidation by dioxygen:

$$Sn^{(II)} + O_2 \rightarrow Sn^{(III)} + HO_2{}^{\bullet}$$
$$Sn^{(III)} + O_2 \rightarrow Sn^{(IV)} + HO_2{}^{\bullet}$$
$$Sn^{(II)} + HO_2{}^{\bullet} \rightarrow Sn^{(III)} + H_2O_2$$
$$Sn^{(II)} + HO_2{}^{\bullet} \rightarrow Sn^{(IV)} + HO^{\bullet}$$
$$Sn^{(II)} + H_2O_2 \rightarrow Sn^{(III)} + HO^{\bullet}$$
$$Sn^{(II)} + H_2O_2 \rightarrow Sn^{(IV)} + H_2O$$
$$Sn^{(II)} + HO^{\bullet} \rightarrow Sn^{(III)}$$
$$Sn^{(III)} + Sn^{(III)} \rightarrow Sn^{(II)} + Sn^{(IV)}$$

The very active unstable tin(III) ion is supposed to play an important role in this chain mechanism for tin(II) oxidation. Cyclohexane, introduced in the system $Sn^{(II)} + O_2$, is oxidized to cyclohexanol as the result of the coupled oxidation of tin and RH. Very strong hydrogen-atom acceptors, namely, hydroxyl radicals, attack the cyclohexane, RH, with the formation of cyclohexyl radicals that participate in the following transformations:

$$R^{\bullet} + O_2 \rightarrow RO_2{}^{\bullet}$$
$$RO_2{}^{\bullet} + Sn^{(II)} \rightarrow Sn^{(III)} + ROOH$$
$$RO_2{}^{\bullet} + Sn^{(II)} \rightarrow Sn^{(IV)} + RO^{\bullet}$$
$$ROOH + Sn^{(II)} \rightarrow Sn^{(III)} + RO^{\bullet}$$
$$ROOH + Sn^{(II)} \rightarrow Sn^{(IV)} + ROH$$

$$\mathrm{RO^{\bullet} + RH \rightarrow ROH + R^{\bullet}}$$

$$\mathrm{RO^{\bullet} + Sn^{(II)} \rightarrow ROH + Sn^{(III)}}$$

$$\mathrm{Sn^{(III)} + Sn^{(III)} \rightarrow Sn^{(II)} + Sn^{(IV)}}$$

Very fast reactions of $RO_2^{\bullet}$ and ROOH with tin(II) and a fast reaction of $RO^{\bullet}$ with cyclohexane provide the formation of cyclohexanol as the main oxidation product.

The kinetic parameters characterizing the oxidation of transition metal ion oxidation by dioxygen are presented in Table 15.11.

15.5 OXIDATION OF ORGANIC COMPOUNDS BY TRANSITION METAL IONS

Oxidation of organic compounds by transition metal ions are widely used in synthetic organic chemistry. Polar organic compounds (alcohols, ketones, aldehydes, acids, etc.) are oxidized by transition metal ions (Co^{3+}, Ce^{4+}, Mn^{3+}, VO^{3+}, etc.) through a one-electron-transfer mechanism with the formation of free radicals.[220–222] In water, water–alcohol, and acetic acid solutions, oxidation normally includes two or several steps. First, the organic compound enters to the internal coordination sphere of the ion-oxidant by an equilibrium reaction. Then, in this complex, the oxidation–reduction reaction takes place. The scheme of such a reaction is represented in simplified form as follows:[220]

$$\mathrm{RH + Me^{n+1}} \overset{K}{\Leftrightarrow} \mathrm{HR{\cdot}Me^{n+1}} \xrightarrow{k_1} \mathrm{R^{\bullet} + Me^{n+1} + H^+}$$

If the equilibrium is shifted to the left, then

$$v = Kk_1[\mathrm{RH}][\mathrm{Me}^{n+1}] \tag{15.8}$$

If a considerable number of the metal ions are bound in a complex, then

$$\frac{[\mathrm{Me}^{n+1}]}{v} = \frac{1}{k_1} + \frac{1}{k_1 K[\mathrm{RH}]} \tag{15.9}$$

As a rule, the rate of the oxidation reaction depends on the hydrogen ion concentration. In the case of alcohol oxidation, it is governed by the presence of two or several forms of oxidant ions: Co^{3+} and $CoOH^{2+}$, Ce^{4+} and $CeOH^{3+}$, and so on, related to each other by the equilibrium

$$\mathrm{Co_{aq}}^{3+} \Leftrightarrow \mathrm{CoOH^{2+} + H^+}$$

The oxidation rate is given by the pH dependent equation

$$v = k_1[\mathrm{RH}][\mathrm{Co^{3+}}] + k_2[\mathrm{RH}][\mathrm{CoOH^{2+}}] \tag{15.10}$$

$$\begin{aligned} v &= k_1[\mathrm{RH}][\mathrm{Co^{3+}}] + K_{\mathrm{H}}k_2[\mathrm{RH}][\mathrm{Co^{3+}}][\mathrm{H_3O^+}]^{-1} \\ &\approx K_{\mathrm{H}}k_2[\mathrm{RH}][\mathrm{Co^{3+}}][\mathrm{H_3O^+}]^{-1} \end{aligned} \tag{15.11}$$

TABLE 15.11 Rate Constants for the Oxidation of Transition Metal Ions by Dioxygen

Equation of the Reaction Rate	Conditions	T (K)	E (kJ mol^{-1})	log A, A (L mol^{-1} s^{-1})	k(298 K) (L mol^{-1} s^{-1})	Reference
		Co(l-Histidine)$_2$				
$k[\mathrm{Co^{(II)}}][\mathrm{O_2}]$ (L mol^{-1} s^{-1})	pH 8–11, κ 0–1 M	298	20.9	7.22	3.60×10^3	204
		Co(d-Histidine)$_2$				
$k[\mathrm{Co^{(II)}}][\mathrm{O_2}]$ (L mol^{-1} s^{-1})	pH 8–11, $\kappa = 0–1$ M	298	20.9	7.08	2.61×10^3	204
		[Co(Glycylglycine)$_2$(OH)$_2$]$^{2-}$				
$k[\mathrm{Co^{(II)}}][\mathrm{O_2}]$, (L mol^{-1} s^{-1})	H_2O	298			1.0×10^3	205
		Cu$^+$				
$k[\mathrm{Cu^+}][\mathrm{O_2}]$, (L mol^{-1} s^{-1})	HCl	298			1.0×10^3	206
		CuCl$_2$$^-$				
$k[\mathrm{CuCl_2^-}][\mathrm{O_2}]$, (L mol^{-1} s^{-1})	1 M HCl + KCl	298			2.51×10^2	206
		Cu(NH$_3$)$_2$$^+$				
$k[\mathrm{Cu^{(I)}}][\mathrm{NH_3}][\mathrm{O_2}]$, (L^2 mol^{-2} s^{-1})	κ 1	298			1.62×10^4	207

(*continued overleaf*)

TABLE 15.11 (*continued*)

Equation of the Reaction Rate	Conditions	T (K)	E (kJ mol^{-1})	log A, A (L mol^{-1} s^{-1})	k(298 K) (L mol^{-1} s^{-1})	Reference
		Cu(Imidazole)$_2$				
$k[\mathrm{Cu^{(I)}}][\mathrm{imidazole}][\mathrm{O_2}]$ (L^2 mol^{-2} s^{-1})	κ 1	298			6.61×10^3	207
		Cu(dipy)$_2$$^+$				
$k[\mathrm{Cu(dipy)_2}^+][\mathrm{O_2}]$, (L mol^{-1} s^{-1})	pH 5.0	298			6.46×10^3	208
		Fe^{2+} ion				
$k[\mathrm{Fe^{2+}}][\mathrm{H_2PO_4}^-]^2 p_{\mathrm{O_2}}$ (L^2 mol^{-2} atm^{-1} s^{-1})	pH 2–3	293–303	83.7	11.55	7.57×10^{-4}	209
$k[\mathrm{Fe^{2+}}]^2 p_{\mathrm{O_2}}$ (L mol^{-1} atm^{-1} s^{-1})	$[\mathrm{FeSO_4}] = 0.5$ *M*	333			6.17×10^{-5}	210
$k[\mathrm{Fe^{2+}}]^2 p_{\mathrm{O_2}}$ (L mol^{-1} atm^{-1} s^{-1})	$[\mathrm{FeSO_4}] = 1$ *M*	293–333	68.2	6.38	2.66×10^{-6}	210
$k[\mathrm{Fe^{2+}}]^2 p_{\mathrm{O_2}}$ (L mol^{-1} atm^{-1} s^{-1})	$[\mathrm{FeSO_4}] = 1$ *M* $[\mathrm{H_2SO_4}] = 1$ *M*	293–333	61.9	5.14	1.95×10^{-6}	210
$k[\mathrm{Fe^{2+}}]^2 p_{\mathrm{O_2}}$ (L mol^{-1} atm^{-1} s^{-1})	$[\mathrm{FeCl_2}] = 0.5$ *M*	333			8.71×10^{-6}	210
$k[\mathrm{Fe^{2+}}]^2 p_{\mathrm{O_2}}$ (L mol^{-1} atm^{-1} s^{-1})	$[\mathrm{FeCl_2}] = 1$ *M*	293–333	56.5	4.01	1.28×10^{-6}	210
$k[\mathrm{Fe^{2+}}]^2 p_{\mathrm{O_2}}$ (L mol^{-1} atm^{-1} s^{-1})	$[\mathrm{FeCl_2}] = 1$ *M* $[\mathrm{HCl}] = 2$ *M*	293–333	61.5	5.39	4.07×10^{-6}	210

$k[Fe^{2+}][O_2]$ (L mol^{-1} s^{-1})	$Fe(NH_4)_2(SO_4)_2$ pH 0.76–1.34	293			4.79 × 10^{-3}	211
$k[Fe^{2+}][O_2]$ (L mol^{-1} s^{-1})	[HCl] = 8 *M*	272–308	61.1	10.41	0.50	212
$k[Fe^{2+}]^2 p_{O_2}$ (L mol^{-1} atm^{-1} s^{-1})	$[HClO_4]$ = 0.51 *M*	298–313	72.8	6.36	3.98 × 10^{-7}	213
$k[Fe^{2+}]^2[H_2P_2O_7{}^{2-}][O_2]$ (L^2 mol^{-2} s^{-1})	$HClO_4$, pH 2–3	303			5.13	214
$k[Fe^{2+}]\ p_{O_2}$ (atm^{-1} s^{-1})	$[H_2SO_4]$ = 1 *N*	413–453		2.08	1.76 × 10^{-8}	215
$k[Fe^{2+}]\ p_{O_2}$ (atm^{-1} s^{-1})	$[H_2SO_4]$ = 0.5 *M*	303			3.80 × 10^{-6}	216
$k[Fe^{2+}]\ p_{O_2}$ (L mol^{-1} atm^{-1} s^{-1})	CH_3OH	303			1.20 × 10^{-3}	217
		Ti^{3+}				
$k[Ti^{3+}]\ p_{O_2}$ (atm^{-1} s^{-1})	[HCl] = 1 *M*	293–323	71.1	8.08	4.14 × 10^{-5}	218
		V^{3+}				
$k([V^{3+}]\ p_{O_2}/[H^+])$ (mol L^{-1} atm^{-1} s^{-1})	$[HClO_4]$ = 1.6–8.3	298	84.1	7.91	1.47 × 10^{-7}	219

under the condition that $k_1 \ll (K_H k_2)/[H^+]$. Organic acids themselves dissociate into ions. In solution both molecules and anions of these acids are oxidized, so that the reaction rate depends on the pH. When mineral acids with anions that form stable complexes with metal ions are introduced into the solution, this complicates the kinetic relationships still more, since, in this case, the solution contains a collection of different complexes of the metal, all having different reactivities. The reaction rate, in this case, depends on both the pH and anion concentration.

The oxidation of ketones and aldehydes very often is independent of an oxidant concentration and is limited by the rate of enolization. Aromatic and unsaturated hydrocarbons are oxidized by metal ions in polar solvents by an electron transfer reaction

$$RH + Me^{n+1} \rightarrow R^{\bullet} + Me^{n+} + H^+$$

For oxygen-containing compounds, the replacement of the hydrogen atoms in the vicinity of the oxygen group by deuterium slow down the oxidation rate (isotope effect). This indicates that the α-C−H bond participates in the elementary oxidizing act in the oxidation of alcohols, formic acid, and other compounds. For carbonyl compounds, the isotope effect is explained by the enolization as the limiting stage in the oxidation process.

15.5.1 Oxidation by Tetravalent Cerium

The Ce^{4+} ion is a strong oxidizer too. The rate of oxidation by cerium ions depends on pH as a consequence of the equilibrium.[220]

$$Ce_{aq}{}^{4+} \Leftrightarrow CeOH^{3+} + H^+$$

along with the difference in activity between Ce^{4+} and $CeOH^{3+}$. The oxidation of oxygen-containing compounds proceeds through the preliminary formation of a complex. For the values of rate constants, see Table 15.12.

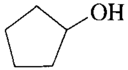
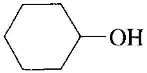
15.5.2 Oxidation by Trivalent Cobalt

The trivalent cobalt ion is a strong oxidizer, oxidizing even water. Oxidation reactions by Co(III) ions are studied in strongly acidic solutions.[220] The oxidation rate depends on pH as a result of the equilibrium

$$Co_{aq}{}^{3+} \Leftrightarrow CoOH^{2+} + H^+$$

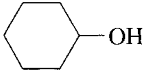
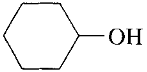
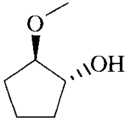
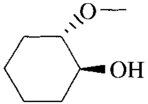
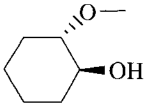
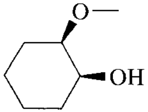
The scheme for oxidation by Co^{3+} ions is the same as that for trivalent manganese. As the hydrogen-ion concentration increases, the reaction is slower, since the value of k_1K for $CoOH^{2+}$ is larger than that for Co^{3+}. In the presence of sulfuric acid, the reaction rate depends on both the hydrogen-ion concentration and on $[HSO_4^-]$. For the values of rate constants, see Table 15.13.

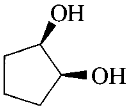
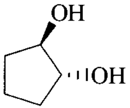
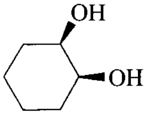
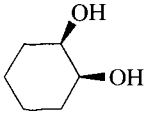
TABLE 15.12 Rate Constants for the Oxidation of Organic Compounds by Ce(IV) Ions in Aqueous Solutions

Substance	Conditions	T (K)	E (kJ mol^{-1})	log A, A (L mol^{-1} s^{-1})	k(298 K) (L mol^{-1} s^{-1})	Reference
PhMe	50% MeCOOH	313			8.32×10^{-3}	223
m-$NO_2C_6H_4Me$	$[HClO_4] = 1\ M$	313			5.89×10^{-3}	223
p-$NO_2C_6H_4Me$	$[HClO_4] = 1\ M$	313			3.55×10^{-4}	223
m-ClC_6H_4Me	$[HClO_4] = 1\ M$	313			1.88×10^{-3}	223
o-ClC_6H_4Me	$[HClO_4] = 1\ M$	313			2.63×10^{-3}	223
p-ClC_6H_4Me	$[HClO_4] = 1\ M$	313			9.55×10^{-3}	223
MeOH	$[HClO_4] = 1\ M$	280–300	51.0	6.08	1.38×10^{-3}	224
MeOH	$[H_2SO_4] = 1\ M$	280–300	91.4	10.74	5.24×10^{-6}	225
EtOH	$[H_2SO_4] = 1\ M$	313–343	78.7	9.10	2.02×10^{-5}	225
EtOH	$[HClO_4] = 3.2\ M$	293			2.85×10^{-2}	226
n-PrOH	$[H_2SO_4] = 1\ M$	313–343	58.0	6.32	1.42×10^{-4}	225
Me_2CHOH	$[HNO_3] = 1\ M$ $[RH] = 0.5\ M$	288			7.00×10^{-5}	227
EtMeCHOH	$[HNO_3] = 1\ M$ $[RH] = 0.5\ M$	288			1.23×10^{-4}	227
$PhCH_2OH$	$[HClO_4] = 1M$ $\kappa = 2.1\ M$	283–293	79.2	13.22	0.22	228
	$[H_2SO_4] = 0.25\ M$, $[HClO_4] = 0.75\ M$	283–303	115.0	16.83	4.70×10^{-4}	229
	$[H_2SO_4] = 1.48\ M$ $\kappa = 0.24$	297–332	92.9	11.85	3.71×10^{-5}	230

(continued overleaf)

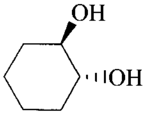
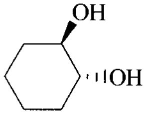
TABLE 15.12 (*continued*)

Substance	Conditions	T (K)	E (kJ mol^{-1})	log A, A (L mol^{-1} s^{-1})	k(298 K) (L mol^{-1} s^{-1})	Reference
	$[HClO_4] = 1$ *M*	288			6.61×10^{-3}	229
	$[HClO_4] = 1$ *M*	323			1.78×10^{-3}	231
	$[H_2SO_4] = 0.25$ *M* $[HClO_4] = 0.75$ *M*	283–303	96.2	16.04	0.15	229
	$[HClO_4] = 1$ *M*	128			0.11	229
	$[H_2SO_4] = 0.25$ *M* $[HClO_4] = 0.75$ *M*	283–303	128.4	18.92	2.59×10^{-4}	229
	$[H_2SO_4] = 0.25$ *M* $[HClO_4] = 0.75$ *M*	283–303	120.9	18.22	1.06×10^{-3}	229

MeCH(OH)CH(OH)Me	$[HNO_3] = 0.5$ *M*	273			7.33×10^{-2}	232
$CH(OH)[CH_2OH]_2$	$[HSO_4] = 0.2$ *M* $[HClO_4] = 0.2$ *M*	293			6.68×10^{-5}	233
$CH(OH)[CH_2OH]_2$	$[HClO_4] = 0.5$ *M* $[NaClO_4] = 0.1$ *M*	293			0.27	233
$Me_2C(OH)C(OH)Me_2$	pH 0.07 $[SO_4^{2-}] = 0.29$ *M*	293–303	94.1	15.09	2.23	234
	$[H_2SO_4] = 0.25$ *M*	283–303	97.5	15.76	4.70×10^{-2}	229
	$[H_2SO_4] = 0.25$ *M* $[HClO_4] = 0.75$ *M*	283–303	97.1	16.62	0.40	229
	$[HClO_4] = 1$ *M*	288			0.74	229
	$[H_2SO_4] = 0.25$ *M* $[HClO_4] = 0.75$ *M*	293			1.78×10^{-3}	229

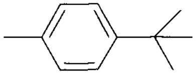
(continued overleaf)

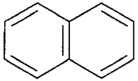
TABLE 15.12 (*continued*)

Substance	Conditions	T (K)	E (kJ mol^{-1})	log A, A (L mol^{-1} s^{-1})	k(298 K) (L mol^{-1} s^{-1})	Reference
	$[HClO_4] = 1$ *M*	288			0.10	229
	$[H_2SO_4] = 0.25$ *M* $[HClO_4] = 0.75$ *M*	293			5.31×10^{-3}	229
$H_2C(OH)_2$	$[HClO_4] = 1$ *M*	283–293	64.0	10.88	0.46	235
MeCH(O)	$[HClO_4] = 1$ *M*	286–298	40.4	5.86	6.07×10^{-2}	235
$CCl_3CH(O)$ (hydrate)	$[HClO_4] = 1$ *M*	313–323	103.4	15.49	2.30×10^{-3}	235
MeC(O)Me	$HClO_4$	298			1.20×10^{2}	236
Arabinose	$[H_2SO_4] = 0.25$ *M*	308			4.95×10^{-2}	237
HO(O)CC(O)OH	$[H_2SO_4] = 1$ *M*	292–308	69.0	13.71	41.3	238
HO(O)CC(O)OH	$[H_2SO_4] = 2$ *M*	292–308	69.0	13.04	8.62	238
HO(O)CC(O)OH	$[H_2SO_4] = 0.78$ *M*	292–308	53.5	8.48	0.13	239
HO(O)CC(O)OH	$[H_2SO_4] = 1.96$ *M*	292–308	74.5	11.32	1.83×10^{-2}	239
$HO(O)CCH_2C(O)OH$	$[HClO_4] = 0.5$ *M*	382–303	38.5	9.29	3.48×10^{2}	240
$HO(O)CCH_2C(O)OH$	$[H_2SO_4] = 0.25$ *M*	382–303	67.4	10.66	7.01×10^{-2}	240
$HO(O)CCH_2C(O)OH$	$[H_2SO_4] = 2$ *M*	293–303	50.2	8.61	0.65	241
$HO(O)CCH_2C(O)OH$	$[HClO_4] = 2.0$ *M*	298			3.7	242

$HO(O)CCH_2C(O)OH$	$[HClO_4] = 2.0$ *M* $[H_2SO_4] = 1$ *M*	298			0.36	242
$HO(O)CCH_2C(O)OH$	$[H_2SO_4] = 1$ *M*	298			0.29	242
$HOCH_2C(O)OH$	$[H_2SO_4] = 1$ *M*	298–323		4.26	10.1	243
$HOCH_2C(O)OH$	$[H_2SO_4] = 1.66$ *M*	300			1.00×10^{-4}	244
$MeCH(OH)C(O)OH$	$[H^+] = 0.53$ *M* $[SO_4^{2-}] = 4 \times 10^{-2}$	300	4.99		9.77×10^{-4}	244
$MeCH(OH)C(O)OH$	$[H_2SO_4] = 0.5$ *M*	298			0.14	245
$MeCH(OH)C(O)OH$	$[HClO_4] = 0.98$ *M*	278–298	57.7	8.61	3.13×10^{-2}	246
$MeCH(OH)C(O)OH$	$[HClO_4] = 0.7$ *M*	298			2.04×10^{-2}	247
$EtCH(OH)C(O)OH$	$[H_2SO_4] = 1$ *M*	298–318	95.4	14.23	3.22×10^{-3}	248
$PhCH(OH)C(O)OH$	$[H_2SO_4] = 1$ *M*	273–323	79.1	13.22	0.23	248
$PhCH(OH)C(O)OH$	$[SO_4^{2-}] = 0.025$ *M* pH 1.36	298	26.8	4.22	0.33	249
$PhCH(OH)C(O)OH$	$[HClO_4] = 0.9$ *M*	278			2.75×10^{-2}	249
$PhCH(OH)C(O)OH$	$[H_2SO_4] = 1.66$ *M*	300			6.84×10^{-2}	244
$Ph_2C(OH)C(O)OH$	$[H_2SO_4] = 1$ *M*	293–308	84.9	14.97	1.23	250
$HO(O)CCH(OH)CH_2CO_2H$	$[H_2SO_4] = 0.5$ *M*	25			0.78	245
$[CH(OH)C(O)OH]_2$	$[H_2SO_4] = 0.25$ *M*	298	103.5	17.32	0.14	251
$[CH(OH)C(O)OH]_2$	$[H_2SO_4] = 0.49$ *M*	284–296	88.7	15.13	0.38	252
$MeC(O)C(O)OH$	$Ce(SO_4)_2$, pH 1.26	273–288	46.0	6.91	6.96×10^{-2}	252

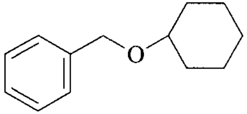
TABLE 15.13 Rate Constants for Oxidation of Organic Compounds by Co(III) Ions

Compound	Conditions	*T* (K)	*E* (kJ mol^{-1})	log *A*, *A* (L mol^{-1} s^{-1})	*k*(298 K) (L mol^{-1} s^{-1})	Reference
		Oxidation in Aqueous Solutions				
H_2O	H_2SO_4	298	140.6	22.9	1.80×10^{-2}	253
$CH_2{=}C(Me)CH_2Me$	$[H_2SO_4] = 0.09\ M$	298	113.4	20.20	2.11	254
$CH_2{=}CH(CH_2)_2Me$	$[H_2SO_4] = 0.09\ M$	298			0.90	254
$CH_2{=}CHCH(Et)_2$	$[H_2SO_4] = 0.09\ M$	298			0.75	254
$CH_2{=}CH(CH_2)_3Me$	$[H_2SO_4] = 0.09\ M$	298	121.3	20.75	0.30	254
$CH_2{=}CH(CH_2)_4Me$	$[H_2SO_4] = 0.09\ M$	298			0.38	254
$CH_2{=}CH(CH_2)_5Me$	$[H_2SO_4] = 0.09\ M$	298	119.2	20.49	0.39	254
$CH_2{=}CHPh$	$[H_2SO_4] = 0.09\ M$	298			7.40	254
$CH_2{=}C(CH_3)CH{=}CH_2$	$[H_2SO_4] = 0.09\ M$	298			6.17	254
PhMe	50% MeCN, $[HClO_4] = 1\ M$	273–304	117.1	18.50	9.23×10^{-3}	255
PhMe	84% MeCN, $[HClO_4] = 1\ M$	273–304	95.0	15.25	4.00×10^{-2}	255
cyclo-C_6H_{12}	50% MeCN, $[HClO_4] = 1\ M$, $\kappa = 1.05\ M$	293			9.77×10^{-3}	255
C_6H_6	$HClO_4$, $\kappa = 2.0$	288	79.5	11.255	2.09×10^{-3}	256
PhEt	70% MeCN, $[HClO_4] = 0.77\ M$, $\kappa = 0.9\ M$	288			2.29×10^{-3}	255
Ph_2CH_2	70% MeCN, $[HClO_4] = 0.77\ M$, $\kappa = 0.9\ M$	128			5.89×10^{-3}	255
	50% MeCN $[HClO_4] = 1\ M$, $\kappa = 1.04\ M$	293			3.80×10^{-2}	255

$(PhCH_2)_2$	60% MeCN $[HClO_4] = 1\ M$, κ = 1.02 M	288			1.99×10^{-3}	255
$(C_6H_5)_2$	50% MeCN $[HClO_4] = 1\ M$, κ = 1.05 M	293			9.12×10^{-2}	255
	50% MeCN $[HClO_4] = 1\ M$, κ = 1.05 M	293			30.2	255
MeOH	$[HClO_4] = 1.57\ M$	288			0.12	257
EtOH	$[HClO_4] = 1.57\ M$	288			0.28	257
n-PrOH	$[HClO_4] = 1.57\ M$	288			0.29	257
Me_2CHOH	$[HClO_4] = 1.57\ M$	288	124.7	22.02	1.45	257
Me_2CHCH_2OH	$[HClO_4] = 1.57\ M$	288			0.34	257
Et_2CHOH	$[HClO_4] = 1.57\ M$	288	124.7	21.62	0.59	257
EtMeCHOH	$[HClO_4] = 1.57\ M$	288			6.31×10^{-2}	257
n-$C_8H_{17}CH(Me)OH$	$[HClO_4] = 1.57\ M$	288			6.31×10^{-2}	257
$Me_2CHCDMeOH$	$[HClO_4] = 1.57\ M$	288			0.25	257
Et_2CDOH	$[HClO_4] = 1.57\ M$	288			0.10	257
cyclo-$C_6H_{11}OH$	$[HClO_4] = 1.57\ M$	288	131.8	22.60	0.31	257
$(Me)_3COH$	$[HClO_4] = 1.57\ M$	288	134.3	21.08	3.45×10^{-3}	258
$EtMe_2COH$	$[HClO_4] = 1.57\ M$	288			5.01×10^{-2}	258
Me_3CCMe_2OH	$[HClO_4] = 1.57\ M$	288			1.12×10^{-2}	258
EtMePrCOH	$[HClO_4] = 1.57\ M$	288			6.46×10^{-2}	258
n-$C_5H_{11}EtMeCOH$	$[HClO_4] = 1.57\ M$	288			8.32×10^{-2}	258
MeOC(O)EtMeCOH	$[HClO_4] = 1.57\ M$	288			8.61×10^{-3}	258

(*continued overleaf*)

TABLE 15.13 (*continued*)

Compound	Conditions	T (K)	E (kJ mol^{-1})	log A, A (L mol^{-1} s^{-1})	k(298 K) (L mol^{-1} s^{-1})	Reference
$MeOCH_2C(OH)Et$	$[HClO_4] = 1.57\ M$	288	1.20		0.16	258
$Et_2C(O)$	$[HClO_4] = 1.57\ M$ $\kappa = 1.5\ M$	283			3.02×10^{-4}	259
$(PhCH_2)_2O$	60% MeCN, $\kappa = 1\ M$, $[HClO_4] = 1\ M$	288			2.40×10^{-2}	260
$PhCH_2OMe$	60% MeCN, $\kappa = 1\ M$, $[HClO_4] = 1\ M$	273–298	114.6	18.77	9.33×10^{-3}	260
	60% MeCN, $\kappa = 1\ M$, $[HClO_4] = 1\ M$	288			3.02×10^{-2}	260
PhOPh	60% MeCN, $\kappa = 1\ M$, $[HClO_4] = 1\ M$	288	2.96		9.12×10^{-2}	260
HC(O)OH	$[H_2SO_4] = 1–5\ N$, $\kappa = 4\ M$	273–303	112.5	17.83	1.26×10^{-2}	261
	Oxidation by Co(III) Acetylacetonate in Nonaqueous Solutions					
Me_2CHOH	n-C_7H_{14}	385–403	108.8	12.20	1.35×10^{-7}	262
Me_2CHOH	C_6H_6	387–403	129.7	13.43	4.96×10^{-10}	262
n-C_4H_9OH	C_6H_5Cl	362–391	164.8	17.175	1.90×10^{-12}	263
cyclo-$C_6H_{11}OH$	C_6H_5Cl	361–391	129.7	13.63	7.86×10^{-10}	263

15.5.3 Oxidation by Copper Ions

The oxidation of carbonyl compounds (aldehydes, ketones, sugars) by copper complexes is limited by the enolization rate and does not depend on the copper ion concentration. One of the exceptions is the oxidation of α-hydroxyacetophenone by copper ions in the presence of pyridine.[264] The oxidation rate is given by the equation

$$v = v_{\mathrm{en}} + k[\mathrm{Cu}^{2+}][\mathrm{PhCOCH_2OH}] \tag{15.12}$$

where v_{en} is the enolization rate. The following oxidation mechanism was postulated:

$$\mathrm{PhC(O)CH_2OH} + \mathrm{Cu}^{2+} \overset{K}{\leftrightarrow} \text{Complex} \xrightarrow{k_1} \mathrm{Cu}^{+} + \text{radical}$$

and $k = k_1K$. At 298 K in 50% pyridine with [pyridine H^+] = 0.02 M and ionic strength = 0.062 M, $k = 2.97 \times 10^{-3}$ L mol^{-1} s^{-1}, $A = 5.89 \times 10^{11}$ L mol^{-1} s^{-1}, and $E = 81.6$ kJ mol^{-1}.

15.5.4 Oxidation by Trivalent Iron

The ions of trivalent iron are weak oxidants. The oxidation of hydroxyketones, hydroquinones, and ascorbic acid by salts and complexes of trivalent iron were studied. The more active form is the hydroxoiron(III) ion and the experimental reaction rate constant $k = k_1K/[\mathrm{H}^+]$, where K is the dissociation constant of the iron(III) ion. For the values of rate constants, see Table 15.14.

15.5.5 Oxidation by Trivalent Manganese

The trivalent manganese ion is a strong oxidizer. Oxidation reactions involving sulfate and pyrophosphate complexes of trivalent manganese were studied in an aqueous solution. Carbonyl compounds, as a rule, are oxidized in the form of enols, and the oxidation rate is often limited by the enolization rate. Acids and hydroxy acids first form a complex with trivalent manganese, within which the oxidation–reduction reaction is accomplished. The most widely accepted scheme for the oxidation is the following:

$$\mathrm{RH} + \mathrm{Mn^{(III)}} \overset{K}{\leftrightarrow} \text{Complex} \xrightarrow{k_1} \text{Products} + \mathrm{Mn^{(II)}}$$

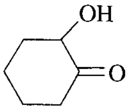
Therefore, the experimental bimolecular rate constants listed in Table 15.9 are close to production k_1K.

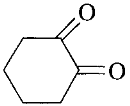
According to Andrulis *et al.*[269] and Andrulis and Dewar,[270] the oxidation of aromatic compounds proceeds through the preliminary formation of a charge transfer complex according to the equilibrium

$$\mathrm{RH} + \mathrm{Mn[O(O)CMe]_3} \overset{K}{\leftrightarrow} \mathrm{RH^+} + \mathrm{MeCOO^-} + \mathrm{Mn(O(O)CMe)_2}$$

$$\mathrm{RH^+} + \mathrm{MeCOO^-} \rightarrow \mathrm{R^\bullet} + \mathrm{MeC(O)OH}$$

TABLE 15.14 Rate Constants for Substrate Oxidation by Trivalent Iron Ions

Compound	Conditions	*T* (K)	*E* (kJ mol^{-1})	log *A*, *A* (L mol^{-1} s^{-1})	*k*(298 K) (L mol^{-1} s^{-1})	Reference
		Oxidation in Aqueous Solutions				
MeCH(OH)C(O)Me	$[HClO_4] = 1\ M$	298–323	103.3	13.56	2.79×10^{-5}	265
H_2NNH_2	$[H^+] = 1\ M$ $\kappa = 3.5\ M$	298			6.03×10^{-2}	266
		Oxidation by (phen)$_3$Fe in Aqueous Solutions				
cyclo-$C_6H_{11}OH$	$[H_2SO_4] = 1.5\ M$	298			6.61×10^{-4}	267
$Me_2C(OH)C(OH)Me_2$	$[H_2SO_4] = 1.5\ M$	298			1.20×10^{-4}	267
MeCH(O)	$[H_2SO_4] = 1.5\ M$	298			8.13×10^{-5}	267
cyclo-$C_6H_{10}O$	$[H_2SO_4] = 1.5\ M$	278–313	53.5	8.72	0.22	267
MeCH(OH)C(O)Me	$[H_2SO_4] = 1.5\ M$	298			1.20×10^{-3}	267
	$[H_2SO_4] = 1.5\ M$	298			6.76×10^{-2}	267

MeC(O)C(O)Me	$[H_2SO_4] = 1.5$ *M*	298	2.09×10^{-3}	267
	$[H_2SO_4] = 1.5$ *M*	298	9.55	267
HO(O)CC(O)OH	$[H_2SO_4] = 1.5$ *M*	298	1.20×10^{-3}	267
$HO(O)CCH_2C(O)OH$	$[H_2SO_4] = 1.5$ *M*	298	2.57×10^{-4}	267
MeC(O)C(O)OH	$[H_2SO_4] = 1.5$ *M*	298	6.61×10^{-3}	267
PhCH(OH)C(O)OH	$[H_2SO_4] = 1.5$ *M*	298	1.00×10^{-4}	267
$MeC(O)CH_2C(O)OEt$	$[H_2SO_4] = 1.5$ *M*	298	6.76×10^{-4}	267
		Oxidation by $Fe[OOC(CH_2)_8Me]$ in Nonaqueous Solutions		
$PhCH_2SH$	MeC_6H_4Me	308	0.75	268
$Me(CH_2)_8CH_2SH$	MeC_6H_4Me	308	0.24	268
$Me(CH_2)_8CH_2SH$	MeC(O)Me	308	5.89×10^{-2}	268

Corresponding to this mechanism, the reaction rate is given by the expression

$$v = \text{const} \times [\text{RH}][\text{Mn}^{(\text{III})}]/[\text{Mn}^{(\text{II})}]. \tag{15.13}$$

In Table 15.15, values are listed for $k = v/[\text{Mn(III)}][\text{RH}]$.

15.5.6 Oxidation by Pentavalent Vanadium

In aqueous solutions, ions of pentavalent vanadium exist in the form $VO_2{}^+$ and $V(OH)_3{}^{2+}$, the ratio between these two forms depends on pH because of the equilibrium.

$$VO_2{}^+ + H_3O^+ \Leftrightarrow V(OH)_3{}^{2+}$$

The oxidation of an alcohol (aldehyde or acid) is preceded by complex formation[220]

$$\text{RH} + VO_2{}^+ \overset{K_1}{\leftrightarrow} \text{Complex} \rightarrow V^{(\text{IV})} + \text{Products}$$

$$\text{RH} + V(OH)_3{}^{2+} \overset{K_2}{\leftrightarrow} \text{Complex} \rightarrow V^{(\text{IV})} + \text{Products}$$

The reaction rate constant measured in an experiment, $k = v/[V(V)][\text{RH}]$, is an overall constant that includes K_1 and k_1 if $VO_2{}^+$ is the oxidant, K_{H+}, K_2, and k_2 if $V(OH)_3{}^{2+}$ is the oxidant, or all five constants if the oxidant consists of both VO_2^+ and $V(OH)_3{}^{2+}$. In the oxidation of malonic acid and formaldehyde, it was established that the observed reaction rate[230,283]

$$v = a[V^V] + b[V^V]^2 \tag{15.14}$$

and it was concluded that these compounds are oxidized in both mononuclear and binuclear complexes:

$$\text{RH} + V(OH)_3{}^{2+} \overset{K_2}{\leftrightarrow} X_1 \overset{k_2}{\rightarrow} \text{Products}$$

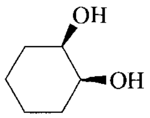
$$X_1 + V(OH)_3{}^{2+} \overset{K_3}{\leftrightarrow} X_2 \overset{k_3}{\rightarrow} \text{Products}$$

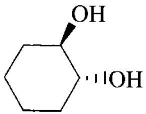
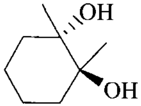
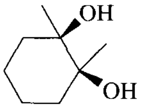
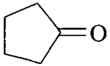
In Table 15.16, experimental values are listed for $k = v/[V^V][\text{RH}]$ and their theoretical treatment within the framework of the scheme set forth above. In the presence of acids with anions that form stable complexes with vanadium, the mechanism of the oxidation is more complicated. For example, in the oxidation of alcohols in the presence of H_2SO_4, it was established[273] that the reaction rate $v \sim [H_2SO_4]^2$ and $v \sim ([NaHSO_4] + [H_2SO_4])^2$, and it was concluded that the alcohols are oxidized by the complex $V(OH)_2(HSO_4)^{2+}$ or $V(OH)(HSO_4)(SO_4)^+$. For the rate constants of organic compounds oxidation, see Table 15.16.

TABLE 15.15 Rate Constants for Substrates Oxidation by Trivalent Manganese Ions in Aqueous Solutions

Compound	Conditions	T (K)	E (kJ mol^{-1})	log A, A (L mol^{-1} s^{-1})	k(298 K) (L mol^{-1} s^{-1})	Reference
cyclo-$C_6H_{11}OH$	$[Mn^{(II)}] = 0.167\ M$ $[H_2SO_4] = 1.97\ M$	297–327	120.9	17.50	2.02×10^{-4}	271
$CH_2(O)$	$[Mn^{(II)}] = 0.20\ M$ $[H_2SO_4] = 2.025\ M$	298–330	105.4	14.81	2.13×10^{-4}	271
Glucose	$[H_2P_2O_7{}^{2-}] = 0.112\ M$, $[H^+] = 4.5\ M$	293–308	97.5	14.33	1.75×10^{-3}	272
HCOOH	$[H_2SO_4] = 4.5\ M$	313			7.76×10^{-6}	273
HO(O)CCH$_2$C(O)OH	$[H_2SO_4] = 2.95\ M$	298			3.76×10^{-2}	274
HOCH$_2$C(O)OH	$[H_2SO_4] = 2.47\ M$	297			5.69×10^{-3}	244
MeCH(OH)C(O)OH	$[H_2SO_4] = 2.47\ M$	297			9.55×10^{-2}	244
PhCH(OH)C(O)OH	$[H_2SO_4] = 3.38\ M$ $[Mn^{(II)}] = 0.43$	296	2.24		1.74×10^{-2}	244
Me$_2$C(OH)C(O)OH	$[H_2SO_4] = 3.35\ M$ $[Mn^{(II)}] = 0.338\ M$	294–309	83.7	14.37	0.50	244

TABLE 15.16 Rate Constants for Organic Compounds Oxidation by V(V) Ions

Reactant	Conditions	T (K)	E (kJ mol^{-1})	log A, A (L mol^{-1} s^{-1})	k(298 K) (L mol^{-1} s^{-1})	Reference
		Oxidation in Aqueous Solutions				
n-PrOH	$[HClO_4] = 1$; $\kappa = 3.1$ *M*	323			2.34×10^{-5}	275
n-PrOH	$[HClO_4] = 2$ *M*	303–333	88.7	8.29	5.53×10^{-8}	276
n-PrOH	$[H_2SO_4] = 2$ *M*	303–333	96.6	10.95	1.04×10^{-6}	276
Me_2CHOH	$[HClO_4] = 1$ *M*; $\kappa = 3.1$ *M*	323			7.60×10^{-6}	275
n-BuOH	$[HClO_4] = 1$ *M*; $\kappa = 3.1$ *M*	323			2.29×10^{-5}	275
cyclo-$C_6H_{11}OH$	$[HClO_4] = 1$ *M*; $\kappa = 3.1$ *M*	323			2.29×10^{-5}	275
cyclo-$C_6H_{11}OH$	$[HClO_4] = 4.77$ *M*	298–333	94.1	10.10	4.04×10^{-7}	230
$CH_2{=}CHCH_2OH$	$[HClO_4] = 1$ *M*, $\kappa = 3.1$ *M*	323			7.08×10^{-4}	275
$MeCH{=}CHCH_2OH$	$[HClO_4] = 1$ *M*, $\kappa = 3.1$ *M*	323			7.24×10^{-4}	275
$PhCH_2OH$	60% MeCOOH	298–318	55.3	5.65	9.06×10^{-5}	277
$PhCH_2OH$	80% MeCOOH	298–318	48.9	5.26	4.88×10^{-4}	277
$HOCH_2CH_2CH_2OH$	$[HClO_4] = 2$ *M*	303–333	112.5	13.28	3.64×10^{-7}	276
$HOCH_2CH_2CH_2OH$	$[H_2SO_4] = 2$ *M*	303–333	95.8	11.11	2.08×10^{-6}	276
$HOCH_2(CH_2)_2CH_2OH$	$[HClO_4] = 2$ *M*	303–333	100.4	11.31	5.15×10^{-7}	276
$HOCH_2(CH_2)_2CH_2OH$	$[H_2SO_4] = 2$ *M*	303–333	90.0	10.08	2.02×10^{-6}	276
$MeCH(OH)CH_2OH$	$[H_2SO_4] = 1$ *M*	333			3.89×10^{-4}	278
$MeCH(OH)CH(OH)Me$	$[H_2SO_4] = 1$ *M*	333			3.80×10^{-4}	278
$Me_2C(OH)CH(OH)Me$	$[H_2SO_4] = 1$ *M*	333			2.57×10^{-4}	278
	$[H_2SO_4] = 1$ *M*	333			4.79×10^{-4}	278

	$[H_2SO_4] = 1\ M$	333	1.41×10^{-4}	278
	$[H_2SO_4] = 1\ M$	333	6.03×10^{-4}	278
	$[H_2SO_4] = 1\ M$	333	1.10×10^{-3}	278
$Me_2C(OH)CMe_2OH$	$[HClO_4] = 0.5–5\ M$, $\kappa = 5\ M$	298	0.33	279
$MeCH_2CH(O)$	$[HClO_4] = 1\ M$, $\kappa = 3.1\ M$	298	3.89×10^{-4}	230
$Me(CH_2)_2CH(O)$	$[HClO_4] = 1\ M$, $\kappa = 3.1\ M$	298	4.47×10^{-4}	280
$Me_2CHCH(O)$	$[HClO_4] = 1\ M$, $= 3.1\ M$	298	9.55×10^{-6}	280
	$[H_2SO]_4] = 2.8\ M$	313	0.12	281
$MeC(O)CHMe(OH)$	$[HClO_4] = 1\ M$, $\kappa = 3.1\ M$	298	3.02×10^{-2}	282

(*continued overleaf*)

TABLE 15.16 (*continued*)

Reactant	Conditions	T (K)	E (kJ mol^{-1})	log A, A (L mol^{-1} s^{-1})	k(298 K) (L mol^{-1} s^{-1})	Reference
$MeC(O)Me_2COH$	$[HClO_4] = 1\ M$, $\kappa = 3.1\ M$	298			6.61×10^{-3}	282
$HC(O)OH$	$[H_2SO_4] = 0.48\ M$	308–331	95.4	9.72	9.96×10^{-8}	283
$HO(O)CCH_2C(O)OH$	$[H_2SO_4] = 1.81\ M$	330			1.10×10^{-5}	283
$HO(O)CCH_2C(O)OH$	$[H_2SO_4] = 1.72\ M$	298–333	82.4	8.92	2.97×10^{-6}	283
$HOCH_2C(O)OH$	$[HClO_4] = 2.13\ M$, $\kappa = 2.5\ M$	311	69.9	9.01	5.79×10^{-4}	284
$HOCH_2C(O)OH$	$[H_2SO_4] = 1.47\ M$	300			7.33×10^{-3}	244
$MeCH(OH)C(O)OH$	$[H_2SO_4] = 1.47\ M$	300			5.19×10^{-3}	244
$MeCH(OH)C(O)OH$	$[HClO_4] = 0.5–4\ M$, $\kappa = 3\ M$	298			6.46×10^{-4}	279
$MeCH(OH)C(O)OH$	$[HClO_4] = 0.67\ M$	303–313	69.0	7.77	4.67×10^{-5}	285
$Me_2C(OH)C(O)OH$	$[HClO_4] = 2\ M$	303–323	92.0	13.02	7.68×10^{-4}	286
$Me_2C(OH)C(O)OH$	$[HClO_4] = 1\ M$, $\kappa = 3.1\ M$	298			6.46×10^{-4}	244
$Me_2C(OH)C(O)OH$	$[HClO_4] = 2–5\ M$, $\kappa = 5\ M$	291–308	91.2	12.85	7.28×10^{-4}	287
$Me_2C(OH)C(O)OH$	$[H_2SO_4] = 2\ M$	293–318	96.2	13.57	5.04×10^{-4}	288
$PhCH(OH)C(O)OH$	$[HClO_4] = 0.5–2.6\ M$; $\kappa = 5.0\ M$	298			3.24×10^{-2}	279

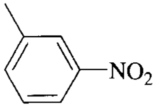
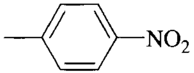
PhCH(OH)C(O)OH	$[H_2SO_4] = 1.47$ *M*	300			0.16	244
HO(O)CCH$_2$CH(SH) C(O)OH	$[HClO_4] = 0.5–4.6$ *M*; $\kappa = 5.0$ *M*	298			8.71×10^{-3}	279
CH(OH)[CH$_2$C(O)OH]$_2$	$[HClO_4] = 1$ *M*	298	88.7	13.78	1.71×10^{-2}	286
CH(OH)[CH$_2$C(O)OH]$_2$	$[H_2SO_4] = 1$ *M*	298	80.3	12.25	1.50×10^{-2}	286
	Oxidation in Nonaqueous Solutions					
PhMe	70% MeCOOH, 30% RH, $[H_2SO_4] = 4$ *M*	333			6.03×10^{-3}	289
	70% MeCOOH, 30% RH, $[H_2SO_4] = 4$ *M*	333			1.29×10^{-5}	289
	70% MeCOOH, 30% RH, $[H_2SO_4] = 4$ *M*	333			8.91×10^{-6}	289

TABLE 15.17 **Rate Constants for the Electron Transfer (*k*) from Radical Anion Donors to Peroxides**[a]

Radical Anion Donors Q	Solvent[b]	T (K)	E (kJ mol^{-1})	log A, A (L mol^{-1} s^{-1})	k(298 K) (L mol^{-1} s^{-1})
		Dicumyl Peroxide			
Anthracene	*N*,*N*-Dimethylformamide	298			6.46×10^4
9,10-Diphenylanthracene	*N*,*N*-Dimethylformamide	298			2.51×10^4
Benzophenone	*N*,*N*-Dimethylformamide	298			3.72×10^3
Fluoranthene	*N*,*N*-Dimethylformamide	298			6.46×10^3
Perylene	*N*,*N*-Dimethylformamide	298			1.95×10^3
Acenaphthylene	*N*,*N*-Dimethylformamide	298			9.33×10^2
Naphthacene	*N*,*N*-Dimethylformamide	298			3.47×10^2
Terephthalonitrile	*N*,*N*-Dimethylformamide	298			4.68×10^2
4-Methyl-4′-ethoxyazobenzene	*N*,*N*-Dimethylformamide	298			42.7
4-Methylazobenzene	*N*,*N*-Dimethylformamide	298			6.61
Anthracene	Acetonitrile	298			9.55×10^4
9,10-Diphenylanthracene	Acetonitrile	298			2.24×10^4
Benzophenone	Acetonitrile	298			
Fluoranthene	Acetonitrile	298			6.76×10^3
Perylene	Acetonitrile	298			1.26×10^3
Acenaphthylene	Acetonitrile	298			9.12×10^2

Terephthalonitrile	Acetonitrile	298			5.37×10^2
4-Methyl-4′-ethoxyazobenzene	Acetonitrile	298			70.8
4-Methylazobenzene	Acetonitrile	298			1.15
	1,1-Dimethylethyl Peroxide				
Chrysene	*N*,*N*-Dimethylformamide/TEAP[b] (0.1 *M*)	243–323	11.7	7.06	1.02×10^5
Isoquinoline	*N*,*N*-Dimethylformamide/TEAP[b] (0.1 *M*)	243–323	17.8	7.47	2.24×10^4
Pyrene	*N*,*N*-Dimethylformamide/TEAP[b] (0.1 *M*)	243–323	23.1	8.08	1.07×10^4
Anthracene	*N*,*N*-Dimethylformamide/TEAP[b] (0.1 *M*)	243–323	26.7	8.15	2.95×10^3
9,10-Diphenylanthracene	*N*,*N*-Dimethylformamide/TEAP[b] (0.1 *M*)	243–323	32.5	8.76	1.16×10^3

[a] See Ref. 293.

[b] TEAP = Tetraethylammonium perchlorate.

15.6 REDUCTION OF PEROXIDES BY RADICAL ANIONS

Radical anions ($Q^{\bullet -}$) are very active reducing agents. They can be generated by electrolysis, radiolysis, or photolysis. Radical anions participate in reactions of electron transfer from a radical anion to a molecule. These reactions are often accompanied by fragmentation of the reduced molecule with the formation of radical anion.

$$Q^{\bullet -} + AB \rightarrow Q + A^{\bullet} + B^{-}$$

This reaction can occur either via a stepwise mechanism with an intermediate radical anion

$$Q^{\bullet -} + AB \Leftrightarrow Q + AB^{\bullet -}$$

or via one elementary step with simultaneous breaking of the A—B bond. The last mechanism was analyzed by Saveant and by German and Kuznetsov.[290–292] Wayner and co-workers[293] studied reactions of line anion radicals with 1,1-dimethylethyl peroxide and dicumyl peroxide in different solvents.

$$Q^{\bullet -} + ROOR \Leftrightarrow Q + RO^{\bullet} + RO^{-}$$

The results of measurements are presented in Table 15.17.

REFERENCES

1. F. Haber and R. Willstatter, *Ber. Deutsch. Chem. Ges.* **64B**, 2844 (1931).
2. F. Haber and J. Weiss, *Naturwissenschaften* **20**, 948 (1932).
3. F. Haber and J. Weiss, *Proc. R. Soc. London, Ser. A* **147**, 332 (1934).
4. J. H. Baxendale, M. G. Evans, and G. S. Park, *Trans. Faraday Soc.* **42**, 155 (1946).
5. W. Shumb, C. N. Satterfield, and R. L. Wentworth, *Hydrogen Peroxide*, Reinhold Publishing Corp., New York, 1955.
6. F. Basolo and R. G. Pearson, *Mechanism of Inorganic Reactions A Study of Metal Complexes in Solution*, John Wiley & Sons, Inc., New York, 1967.
7. A. Ya. Sychev, S. O. Travkin, G. G. Duka, and Yu. I. Skurlatov, *Catalytic Reactions and Protection of Environment* (Russian), Shtiintsa, Kishinev, USSR, 1983.
8. J. H. Baxendale, in *Advances of Catalysis*, W. G. Frankenburg, V. I. Komarewsky, and E. K. Rideal (Eds.), London, 1952, Vol. 4, p. 31.
9. J. Weiss, in *Advances of Catalysis*, W. G. Frankenburg, V. I. Komarewsky, and E. K. Rideal (Eds.), London, 1952, Vol. 4, p. 343.
10. A. Ya. Sychev and V. G. Isak, *Usp. Khim.* **64**, 1183 (1995).
11. C. Walling, *Free Radicals in Solution*, John Wiley & Sons, Inc., New York, 1962.
12. R. Houwink and A. J. Staverman, *Chemie und Technologie der Kunststoffe*, Akademische Verlagsgeselschaft, Leipzig, Germany, 1962, B. 1.
13. G. C. Eastmond, in *Comprehensive Chemical Kinetics*, C. H. Bamford and C. F. H. Tipper (Eds.), Elsevier, Amsterdam, The Netherlands, 1976, Vol. 14A, p. 1.

14. B. A. Dolgoplosk and E. I. Tinyakova, *Generation and Reactions of Free Radicals* (Russian) Nauka, Moscow, 1982.
15. B. Halliwell and J. M. C. Gutteridge, *Free Radicals in Biology and Medicine*, 2nd ed., Clarendon Press, Oxford, U.K., 1989.
16. *The Role of Oxygen in Chemistry and Biochemistry*, W. Ando and Y. Moro-Oka (Eds.), Elsevier, Amsterdam, The Netherlands, 1988.
17. *Biological Oxidation Systems*, C. Reddy, G. A. Hamilton, and K. M. Madyastha (Eds.), Academic Press, New York, 1990.
18. *Bioinorganic Catalysis*, H. Sigel and A. Sigel (Eds.), Marcel Dekker, New York, 1992.
19. *Oxygenases and Model Systems*, T. Funabiki (Ed.), Kluer, Dordrecht, The Netherlands, 1997.
20. A. E. Shilov, *Metal Complexes in Biomimetic Chemical Reactions*, CRC Press, Boca Raton, FL, 1997.
21. W. G. Barb, J. H. Baxendale, P. George, and H. G. Hargrave, *Trans Faraday Soc.* **47**, 591 (1951).
22. M. L. Kremer and G. Stein, *Trans. Faraday Soc.* **55**, 595 (1959).
23. M. L. Kremer, *Int. J. Chem. Kinet.* **17**, 1299 (1959).
24. C. Walling and Amarnath, *J. Am. Chem. Soc.* **104**, 1185 (1982).
25. J. D. Rush and W. H. Koppenol, *J. Am. Chem. Soc.* **110**, 4957 (1988).
26. S. Rahhal and W. H. Richter, *J. Am. Chem. Soc.* **110**, 3126 (1988).
27. S. Groft, B. C. Gilbert, J. R. L. Smith, and A. C. Whitwood, *Free Rad. Res. Comm.* **17**(1), 21 (1992).
28. B. Chance, *J. Franklin Inst.* **229**, 737 (1940).
29. G. Czapski, B. H. J. Bielski, and N. Sutin, *J. Phys. Chem.* **67**, 201 (1963).
30. V. M. Berdnikov, Yu. M. Kozlov, and A. P. Purmal, *Khim. Vysokikh Energiy* **3**, 321 (1969).
31. I. M. Kolthoff and R. Woods, *J. Electroanal. Chem. Interfac. Chem.* **12**, 385 (1966).
32. R. Woods, I. M. Kolthoff, and E. J. Mechan, *J. Am. Chem. Soc.* **85**, 3334 (1963).
33. W. C. Barb, J. H. Baxendale, P. George, and K. R. Hargrave, *Trans. Faraday Soc.* **47**, 462 (1951).
34. C. F. Wells, *J. Chem. Soc.* 2741 (1969).
35. F. S. Dainton and H. C. Sutton, *Trans. Faraday Soc.* **49**, 1011 (1953).
36. J. P. Keene, *Rad. Res.* **22**, 14 (1964).
37. Z. Pospisil, *Coll. Czech. Chem. Commun.* **18**, 337 (1953).
38. T. Rigg, W. Taylor, and J. Weiss, *J. Chem. Phys.* **22**, 575 (1954).
39. T. J. Hardwick, *Can. J. Chem.* **35**, 428 (1957).
40. C. F. Wells and M. A. Salam, *Trans. Faraday Soc.* **63**, 620 (1967).
41. I. A. Kulikov, V. S. Koltunov, V. I. Marchenko, A. S. Milodranova, and L. K. Nikishova, *Zh. Fiz. Khim.* **53**, 647 (1979).
42. H. Po and R. Sutin, *Inorg Chem.* **7**, 621 (1968).
43. T. L. Conochioli, E. L. Hamilton, and R. Sutin, *J. Am. Chem. Soc.* **87**, 926 (1965).
44. C. F. Wells and M. A. Salam, *Nature (London)* **203**, 751 (1964).
45. C. F. Wells and M. A. Salam, *Nature (London)* **205**, 690 (1965).

46. C. Walling, *Acc. Chem. Res.* **8**, 125 (1975).
47. W. C. Barb, J. H. Baxendale, P. George, and K. R. Hargrave, *Trans. Faraday Soc.* **51**, 935 (1955).
48. G. Davies, L. J. Kirschenbaum, and K. Kustin, *Inorg. Chem.* **7**, 146 (1968).
49. F. B. Baker and T. W. Newton, *J. Phys. Chem.* **65**, 1897 (1961).
50. G. Tachiev, I. A. Roth, and A. R. Bowers, *Int. J. Chem. Kinet.* **32**, 24 (2000).
51. N. Uri, in *Autooxidation and Antioxidants*, W. O. Lundberg (Eds.), John Wiley & Sons, Inc., New York, 1961, Vol. 1, p. 55.
52. N. N. Semenov, *Some Problems of Chemical Kinetics and Reactivity*, Pergamon Press, London, 1958, Vol. 1; 1959, Vol. 2.
53. E. T. Denisov, and N. M. Emanuel, *Usp. Khim.* **29**, 1409 (1960).
54. N. M. Emanuel, E. T. Denisov, and Z. K. Maizus, *Liquid-Phase Oxidation of Hydrocarbons*, Plenum Press, New York, 1967.
55. J. M. Tedder, A. Nachvatal, and A. H. Jubb, *Basic Organic Chemistry*, John Wiley & Sons, Inc., London, 1975.
56. I. V. Berezin, E. T. Denisov, and N. M. Emanuel, *The Oxidation of Cyclohexane*, Pergamon Press, Oxford, 1966.
57. R. A. Sheldon and J. K. Kochi, *Metal-Catalysed Oxidation of Organic Compounds*, Academic Press, New York, 1981.
58. D. T. Sawer, *Oxygen Chemistry*, Oxford University Press, Oxford, U.K., 1991.
59. L. I. Simandi (Ed.), *Dioxygen Activation and Homogeneous Catalytic Oxidation*, Elsevier, Amsterdam, The Netherlands, 1991.
60. N. A. Shilov, *About Coupled Reactions of Oxidation*, (Russian), Mamontov, Moscow, 1905.
61. C. Bawn and J. Williamson, *Trans. Faraday Soc.* **47**, 735 (1951).
62. C. Bawn and J. Jolley, *Proc. R. Soc. London, Ser. A*, **273**, 297 (1956).
63. C. Bawn, T. P. Hobin, and L. Rafphael, *Proc. R. Soc. London, Ser. A*, **273**, 313 (1956).
64. C. Bawn, *Disc. Faraday Soc.* N **14**, 181 (1953).
65. M. S. Kharash, F. S. Arimoto, and W. Nudenberg, *J. Org. Chem.* **16**, 1556 (1951).
66. W. H. Richardson, *J. Am. Chem. Soc.* **87**, 247 (1965).
67. K. Omuta, K. Wada, J. Yamashita, and H. Hashimoto, *Bull. Chem. Soc. Jpn.* **40**, 2000 (1967).
68. R. Hiatt, K. C. Irwin, and C. W. Gould, *J. Org. Chem.* **33**, 1430 (1968).
69. W. H. Richardson, *J. Am. Chem. Soc.* **87**, 1096 (1965).
70. H. Hock and H. Kropf, *J. Pract. Chem.* **16**, 113 (1962).
71. H. Kropf, *Ann.* **637**, 111 (1960).
72. M. T. Lisovska, V. I. Timokhin, A. P. Pokutsa, and V. I. Kopylets, *Kinet. Katal.* **41**, 223 (2000).
73. Y. Kamiya, S. Beaton, A. Lafortune, and K. U. Ingold, *Can. J. Chem.* **41**, 2034 (1963).
74. A. G. Korsun, V. Ya. Shlyapintokh, and N. M. Emanuel, *Izv. AN SSSR, OKhN*, 788 (1961).
75. J. Tomiska, *Coll. Czech. Chem. Communs*, **27**, 1549 (1962).

76. W. L. Reynolds and R. J. W. Lumry, *J. Chem. Phys.* **23**, 2460 (1955).
77. I. M. Kolthoff and W. L. Reynolds, *Discuss Faraday Soc.* **17**, 167 (1954).
78. W. L. Reynolds and I. M. Kolthoff, *J. Phys. Chem.* **60**, 969 (1956).
79. J. W. L. Fordham and H. L. Williams, *J. Am. Chem. Soc.* **72**, 1634 (1950).
80. J. W. L. Fordham and H. L. Williams, *J. Am. Chem. Soc.* **72**, 4465 (1950).
81. R. J. Orr and H. L. Williams, *Can. J. Chem.* **30**, 985 (1952).
82. R. J. Orr and H. L. Williams, *J. Phys. Chem.* **57**, 925 (1953).
83. S. Hasegawa and N. Nishimura, *Bull. Chem. Soc. Jpn.* **33**, 775 (1960).
84. S. Hasegawa, N. Nishimura, and K. Miura, *Bull. Chem. Soc. Jpn.* **33**, 1323 (1960).
85. S. Hasegawa, N. Nishimura, S. Mitsumoto, and K. Yokoyama, *Bull. Chem. Soc. Jpn.* **36**, 522 (1963).
86. D. G. Knorre, Z. K. Maizus, M. I. Markin, and N. M. Emanuel, *Zh. Fiz. Khim.* **33**, 398 (1959).
87. E. T. Denisov, in *Itogi Nauki I Tekhniki, Kinetika I Kataliz* (Russian), VINITI, Moscow, 1981, Vol. 9.
88. G. F. Pustarnakova and V. M. Solyanikov, *Neftekhimiya* **15**, 124 (1975).
89. G. F. Pustarnakova and V. M. Solyanikov, *Reaction Kinet. Lett.* **2**, 313 (1975).
90. V. M. Goldberg and L. K. Obukhova, *Progress in Chemistry of Organic Peroxides and Autooxidation* (Russian), Khimiya, Moscow, 1969, p. 160.
91. L. I. Matienko, L. A. Goldina, I. P. Skibida, and Z. K. Maizus, *Izv. AN SSSR, Ser. Khim.* 287 (1975).
92. Z. K. Maizus, I. P. Skibida, and N. M. Emanuel, *Dokl AN SSSR*, **164**, 374 (1965).
93. A. E. Semenchenko, V. M. Solyanikov, and E. T. Denisov, *Zh. Fiz. Khim.* **47**, 1148 (1973).
94. L. N. Denisova, E. T. Denisov, and T. G. Degtyareva, *Izv. AN SSSR, Ser. Khim.* 1095 (1966).
95. I. V. Zakharov, *Kinet. Katal.* **15**, 1457 (1974).
96. I. V. Zakharov and Yu. V. Geletii, *Neftekhimiya* **18**, 615 (1978).
97. R. W. Fisher and F. Rohrscheid, in *Applied Homogeneous Catalysis with Organometallic Compounds*, B. Cornils and W. A. Herrmann (Eds.), VCH, Weinheim, Germany, 1996, p. 439.
98. M. Herustiak, M. Hronec, and J. Ilavsky, *J. Mol. Catal.* **53**, 209 (1989).
99. G. M. Dugmore, G. J. Powels, and B. Zeelie, *J. Mol. Catal. A: Chem.* **99**, 1 (1995).
100. M. F. T. Gomez and O. A. C. Antunes, *J. Mol. Catal. A: Chem.* **121**, 145 (1997).
101. D. A. Shiraldi, in *Applied Homogeneous Catalysis with Organometallic Compounds*, B. Cornils and W. A. Herrmann (Eds.), VCH, Weinheim, Germany, 1996, p. 541.
102. E. T. Denisov, O. M. Sarkisov, and G. I. Likhtenshtein, *Chemical Kinetics* (Russian), Khimiya, Moscow, 2000.
103. E. T. Denisov, *Usp. Khim.* **40**, 43 (1973).
104. J. K. Kochi, in *Free Radicals*, J. K. Kochi (Ed.), John Wiley & Sons, Inc., New York, 1973, Vol. 1, p. 591.
105. W. G. Rothschild and A. O. Allen, *Rad. Res.* **8**, 101 (1958).
106. G. C. Eastmond, in *Comprehensive Chemical Kinetics*, C. H. Bamford and C. F. H. Tipper (Eds.), Elsevier, Amsterdam, The Netherlands, 1976, Vol. 14A, p. 104.

107. R. W. Matthews, *Aust. J. Chem.* **37**, 475 (1984).
108. A. E. Cahill and H. Taube, *J. Am. Chem. Soc.* **74**, 2312 (1952).
109. M. Anbar and P. Neta, *Intern. Appl. Radiat. Isotopes* **18**, 493 (1967).
110. G. V. Buxton, R. M. Sellers, and D. R. McCracken, *J. Chem. Soc., Faraday Trans. 1*, **72**, 1464 (1976).
111. B. Jezowska-Trzebiatowska, E. Kalecinska, and J. Kalecinski, *Bull. Acad. Pol. Sci., Ser. Sci. Chim.* **19**, 265 (1971).
112. H. Boncher, A. M. Sargeson, D. F. Sangster, and J. C. Sullivan, *Inorg. Chem.* **20**, 3719 (1981).
113. K. V. S. Rama Rao, L. V. Shastry, and J. Shankar, *Radiat. Eff.* **2**, 193 (1970).
114. N. L. Sukhov, M. A. Akishin, and B. G. Ershov, *Khim. Vysokikh Energiy* **20**, 392 (1986).
115. G. V. Buxton, C. L. Greenstock, W. P. Helman, and A. B. Ross, *J. Phys. Chem. Ref. Data* **17**, 513 (1988).
116. J. H. Baxendale, E. M. Fielden, and J. P. Keene, *Pulse Radiolysis*, Academic Press, London, 1965, p. 217.
117. A. Samumi, D. Meisel, and G. Czapski, *J. Chem. Soc., Dalton Trans.* 1273 (1972).
118. E. Hayon and M. More, *J. Chim. Phys.* 391 (1965).
119. B. Jezowska-Trzebiatowska, E. Kalecinska, and J. Kalecinski, *Bull. Acad. Pol. Sci., Ser. Sci. Chim.* **17**, 225 (1969).
120. D. M. Brown, E. S. Dainton, D. C. Walker, and J. P. Keene, *Pulse Radiolysis*, Academic Press, London, 1965, p. 221
121. D. Bunn, F. S. Dainton, G. A. Salmon, and T. J. Hardwick, *Trans. Faraday Soc.* **55**, 1760 (1959).
122. H. A. Schwarz, *J. Phys. Chem.* **66**, 255 (1962).
123. A. K. Pikaev, P. Ya. Glazunov, and V. I. Spitsyn, *Izv. AN SSSR, Ser. Khim.* 401 (1965).
124. B. Chutny, *Coll. Czech. Chem. Commun.* **31**, 358 (1966).
125. H. Christensen and K. Schested, *Radiat. Phys. Chem.* **18**, 723 (1981).
126. Z. Stuglik and Z. P. Zagorski, *Radiat. Phys. Chem.* **17**, 229 (1981).
127. G. G. Jayson, B. J. Parsons, and A. J. Swallow, *J. Chem. Soc. Faraday Trans. 1*, **68**, 2053 (1972).
128. D. Zehavi and J. Rabani, *J. Phys. Chem.* **75**, 1738 (1971).
129. J. S. B. Park, P. M. Wood, B. C. Gilbert, and A. C. Whitwood, *J. Chem. Soc., Perkin Trans. 2*, 923 (1999).
130. J. Rabani and G. Stein, *Trans. Faraday Soc.* **58**, 2150 (1962).
131. J. K. Thomas, *Trans. Faraday Soc.* **61**, 702 (1965).
132. R. W. Mattews and D. F. Sangster, *J. Phys. Chem.* **69**, 1938 (1965).
133. I. Kraljie and C. N. Trumbore, *J. Am. Chem. Soc.* **87**, 2547 (1965).
134. J. Rabani and M. S. Matheson, *J. Am. Chem. Soc.* **86**, 3175 (1964).
135. D. M. Brown, E. S. Dainton, D. C. Walker, and J. P. Keene, *Pulse Radiolysis*, Academic Press, London, 1965, p. 221.
136. P. C. Beaumont and E. L. Powers, *Int. J. Radiat. Biol. Relat. Stud. Phys. Chem. Med.* **43**, 485 (1983).

137. J. W. Boyles, S. Weiner, and C. J. Hochanadel, *J. Phys. Chem.* **63**, 892 (1959).
138. J. Rabani and M. S. Mutbeson, *J. Am. Chem. Soc.* **86**, 3175 (1964).
139. T. J. Sworski, *Rad. Res.* **4**, 483 (1956); *J. Am. Chem. Soc.* **79**, 3655 (1957).
140. D. Meisel, Y. A. Ilan, and G. J. Czapski, *J. Phys. Chem.* **78**, 2330 (1974).
141. Yu. N. Kozlov and V. M. Berdnikov, *Russ. J. Phys. Chem.* **47**, 338 (1973).
142. J. H. Baxendale, *Rad. Res.* **17**, 312 (1962).
143. J. Rabani, D. Klug-Roth, and J. J. Lilic, *J. Phys. Chem.* **77**, 1169 (1973).
144. D. Zehavi and J. Rabani, *J. Phys. Chem.* **76**, 3703 (1972).
145. A. D. Nadezhdin, Yu. N. Kozlov, and A. P. Purmal, *Zh. Fiz. Khim.* **50**, 910 (1976).
147. J. D. Rush and B. H. J. Bielski, *J. Phys. Chem.* **89**, 5062 (1985).
148. G. G. Jayson, J. P. Keene, D. A. Stirling, and A. J. Swallow, *Trans. Faraday Soc.* **65**, 2453 (1969).
149. K. Sehested, E. Bjergbukke, O. L. Rasmussen, and H. Fricke, *J. Chem. Phys.* **51**, 3159 (1969).
150. J. Pucheault, C. Ferradini, and A. Buu, *Int. J. J. Radiat Phys. Chem.* **1**, 209 (1969).
151. A. O. Allen, V. D. Hogan, and W. G. Rothschild, *Rad. Res.* **7**, 603 (1957).
152. J. P. Keene, *Rad. Res.* **17**, 14 (1962).
153. M. Pic-Kaplan and J. Rabani, *J. Phys. Chem.* **80**, 1840 (1976).
154. D. E. Cabelli and B. H. J. Bielski, *J. Phys. Chem.* **88**, 311 (1984).
155. B. Cercek, M. Ebert, and A. J. Swallow, *J. Chem. Soc. A*, 612 (1966).
156. E. M. Tochina, L. M. Postnikov, and V. Ya. Shlyapintokh, *Izv. AN SSSR, Ser. Khim.* 1489 (1968).
157. L. M. Postnikov, E. M. Tochina, and V. Ya. Shlyapintokh, *Dokl. AN SSSR* **172**, 651 (1967).
158. V. M. Goldberg and L. K. Obukhova, *Dokl. AN SSSR* **165**, 860 (1965).
159. V. P. Scheredin and E. T. Denisov, *Izv. AN SSSR, Ser. Khim.* 1428 (1967).
160. J. Butler, G. G. Jayson, and A. J. Swallow, *J. Chem. Soc. Faraday Trans. 1*, **70**, 1394 (1974).
161. C. L. Jenkins, and J. K. Kochi, *J. Am. Chem. Soc.* **94**, 843 (1972).
162. J. K. Kochi, A. Bemis, and C. L. Jenkins, *J. Am. Chem. Soc.* **90**, 4616 (1968).
163. V. M. Berdnikov, O. S. Zhuravleva, and L. A. Terentyeva, *Bull. Acad. Sci. USSR, Div. Chem. Sci.* **26**, 2050 (1977).
164. G. V. Buxton and J. C. Green, *J. Chem. Soc., Faraday Trans. 1*, **74**, 697 (1978).
165. A. G. Pribush, S. A. Brusentseva, V. N. Shubin, and P. I. Dolin, *High Energy Chem.* **9**, 206 (1975).
166. E. Collinson, F. S. Dainton, B. Mile, and S. Tazuke, D. R. Smith, *Nature (London)* **198**, 26 (1963).
167. E. Collinson, F. S. Dainton, and G. S. MeNaughton, *Trans. Faraday Soc.* **53**, 189 (1957).
168. E. Collinson, F. S. Dainton, D. R. Smith, G. J. Trudel, and S. Tazuke, *Discuss. Faraday Soc.* **29**, 188 (1960).
169. F. S. Dainton and W. D. Sisley, *Trans. Faraday Soc.* **59**, 1377 (1963).
170. K. W. Chambers, E. Collinson, F. S. Dainton, W. A. Seddon, and F. Wilkiason, *Trans. Faraday Soc.* **63**, 1699 (1967).

171. C. H. Bamford, A. D. Jenkina, and R. Johnston, *Proc. Roy. Soc. A*, **239**, 214 (1957).
172. N. Colebourne, E. Collinson, D. J. Currie, and F. S. Dainton, *Trans. Faraday Soc.* **59**, 1357 (1963).
173. W. I. Bengough and W. H. Fairservice, *Trans. Faraday Soc.* **61**, 1206 (1965).
174. R. M. Dovydov, *Zh. Fiz. Khim.* **42**, 2639 (1968).
175. C. E. H. Bawn and D. Verdin, *Trans. Faraday Soc.* **56**, 519 (1960).
176. R. I. Zusman, Yu. I. Naberukhin, Yu. N. Molin, and V. V. Voevodskii, *Kinet. Katal.* **7**, 414 (1966).
177. V. V. Voevodskii, R. I. Zusman, G. I. Shamovskaya, and Yu. N. Molin, *Izv. SO ANSSSR*, **3**, 127 (1968).
178. A. L. Aleksandrov and E. T. Denisov, *Izv. AN SSSR, Ser. Khim.* 1652 (1969).
179. E. T. Denisov, *Kinet. Katal.* **11**, 312 (1970).
180. E. T. Denisov, *Russ. Chem. Rev.* **65**, 461 (1997).
181. E. T. Denisov and I. V. Khudyakov, *Chem. Rev.* **87**, 1313 (1987).
182. E. T. Denisov and T. G. Denisova, *Handbook of Antioxidants*, CRC Press, Boca Raton, FL, 2000.
183. E. T. Denisov and V. V. Azatyan, *Inhibition of Chain Reactions*, Gordon and Breach, London, 2000.
184. A. L. Aleksandrov, G. I. Solov'ev, and E. T. Denisov, *Izv. Akad. Nauk. SSSR, Ser. Khim.* 1527 (1972).
185. A. L. Aleksandrov, *Negative catalysis in radical-chain reactions of oxidation of N- and O-containing compounds*, Doctor Diss. Thesis (Russian), Inst. Chem. Phys., Chernogolovka, USSR, 1987.
186. G. A. Kovtun, *Mechanism of oxidation of aliphatic amines and regeneration of antioxidants*, Ph.D. Thesis (Russian), Institute of Chemical Physics, Chernogolovka, USSR, 1974.
187. N. G. Zubareva, E. T. Denisov, and A. V. Ablov, *Kinet. Katal.* **14**, 579 (1973).
188. N. G. Zubareva, E. T. Denisov, and A. V. Ablov, *Kinet. Katal.* **14**, 346 (1973).
189. G. A. Kovtun, *Complexes of transition metals as catalysts of chain termination in oxidation*, Doctor Diss. Thesis (Russian), Institute of General and Inorganic Chemistry, Moscow, 1984.
190. A. L. Aleksandrov, E. P. Marchenko, and T. S. Pokidova, *Kinet. Katal.* **36**, 825, 1995.
191. E. M. Pliss, *Oxidation of vinyl compounds: mechanism, elementary reactions, structure and reactivity*, Doctor Diss. Thesis (Russian), Institute of Chemical Physics, Chernogolovka, USSR, 1990.
192. E. M. Pliss and A. L. Aleksandrov, *Izv. Akad. Nauk SSSR, Ser. Khim.* 214 (1978).
193. R. L. Vardanyan and E. T. Denisov, *Izv. Akad. Nauk SSSR, Ser. Khim.* 2818 (1971).
194. U. Ya. Samatov, A. L. Aleksandrov, and I. R. Akhyndov, *Izv. Akad. Nauk SSSR, Ser. Khim.* 2254 (1978).
195. G. A. Kovtun and A. L. Aleksandrov, *Izv. Akad. Nauk SSSR, Ser. Khim.* 2611 (1973).
196. E. M. Pliss, A. L. Aleksandrov, and M. M. Mogilevich, *Izv. Akad. Nauk SSSR, Ser. Khim.* 1441 (1977).
197. E. T. Denisov, *Liquid-Phase Reaction Rate Constants, Plenum*, New York (1974).

198. A. E. Shilov and G. B. Shulpin, *Activation and Catalytic Reactions of Saturated Hydrocarbons in the Presence of Metal Complexes*, Kluer Academic Publishers, Dordrecht, The Netherlands, 2000.
199. E. A. Kutner and B. P. Matseevskii, *Kinet. Katal.* **10**, 997 (1969).
200. H. Mimoun and Seree de Roch, *Tetrahedron* **31**, 777 (1975).
201. I. V. Zakharov, E. I. Karasevich, A. E. Shilov, and A. A. Shteinman, *Kinet. Katal.* **16**, 1151 (1975).
202. Yu. V. Geletii, I. V. Zakharov, E. I. Karasevich, and A. A. Shteinman, *Kinet. Katal.* **20**, 1124 (1979).
203. V. V. Lavrushko, A. M. Klenkin, and A. E. Shilov, *Kinet. Katal.* **21**, 276 (1980).
204. J. Simplicio and R. G. Wilkins, *J. Am. Chem. Soc.* **84**, 6092 (1967).
205. C. Tanford, D. C. Kirk, and M. K. Chantoosi, *J. Am. Chem. Soc.* **76**, 5325 (1954).
206. H. Nord, *Acta Chem. Scand.* **9**, 430 (1955).
207. A. Zuberbuhler, *Helv. Chim. Acta* **50**, 466 (1967).
208. J. Pecht and M. Anbar, *J. Chem. Soc. A*, 1902 (1968).
209. M. Cher and N. Davidson, *J. Am. Chem. Soc.* **77**, 793 (1955).
210. L. K. Lepin and B. P. Matseevskii, *Dokl. AN SSSR* **173**, 1336 (1967).
211. D. I. Metelitsa and E. T. Denisov, *Kinet. Katal.* **9**, 733 (1968).
212. A. M. Posner, *Trans. Faraday Soc.* **49**, 382 (1953).
213. P. George, *J. Chem. Soc.* 4349 (1954).
214. S. Utsumi and K. Murosima, *J. Chem. Soc. Jpn., Pure Chem. Soc.* **86**, 503 (1965).
215. R. E. Huffman and N. Davidson, *J. Am. Chem. Soc.* **78**, 4836 (1956).
216. A. B. Lamb and L. W. Elder, *J. Am. Chem. Soc.* **53**, 137 (1931).
217. G. S. Hammond and Chin-Hun S. Wu, *International oxidations symposium San Francisco*, **2**, 413 (1967).
218. E. A. Kutner, Ph.D. Thesis (Russian), Riga, USSR, 1968.
219. J. B. Ramsey, R. Sugimoto, and H. De Vorkin, *J. Am. Chem. Soc.* **63**, 3480 (1941).
220. W. A. Waters, *Mechanism of Oxidation of Organic Compounds*, John Wiley & Sons, Inc., New York, 1963.
221. R. A. Sheldon and J. K. Kochi, *Metal-Catalyzed Oxidation of Organic Compounds*, Academic Press, New York, 1981.
222. E. S. Rudakov, *Reactions of Alkanes with Oxidants, Metal Complexes, and Radicals in Solution* (Russian), Naukova Dumka, Kiev, USSR, 1985.
223. P. S. R. Murty and K. V. Rao, *Bull. Chem. Soc. Jpn.* **36**, 913 (1963).
224. S. S. Muhammad and K. V. Rao, *Bull. Chem. Soc. Jpn.* **36**, 913 (1963).
225. S. S. Muhammad and K. V. Rao, *Bull. Chem. Soc. Jpn.* **36**, 919 (1963).
226. M. Ardon, *J. Chem. Soc.* 1811 (1957).
227. B. Sethuram and S. S. Muhammad, *Acta Chim. Acad. Sci. Hung.* **16**, 115 (1965).
228. M. Ranguswamy and M. Santappa, *Current Sci. (India)* **34**, 282 (1965); **35**, 332 (1966).
229. H. L. Hintz and D. C. Johnson, *J. Org. Chem.* **32**, 556 (1967).
230. T. J. Kemp and W. A. Waters, *Proc. R. Soc. London, Ser. A*, **274**, 480 (1963).
231. J. S. Littler, *J. Chem. Soc.* 4135 (1959).

232. F. R. Duke and A. A. Forist, *J. Am. Chem. Soc.* **71**, 2790 (1949).
233. G. G. Guilbault and W. H. Mc Curdy, *J. Phys. Chem.* **67**, 283 (1963).
234. G. Mino, S. Kaizerman, and E. Rasmussen, *J. Am. Chem. Soc.* **81**, 1494 (1959).
235. N. Rangaswamy and M. Santappa, *Acta Chim. Sci. Hung.* **56**, 413 (1968).
236. J. Shorter, *J. Chem. Soc.* 1868 (1962).
237. R. N. Mehrotra, *Z. Phys. Chem.* **230**, 221 (1965).
238. V. H. Dodson and A. H. Black, *J. Am. Chem. Soc.* **79**, 3657 (1957).
239. K. K. Sengupta, *J. Proc. Instn. Chem. (India)* **36**, 138 (1964).
240. K. K. Sengupta and S. Aditya, *Z. Phys. Chem.* **38**, 25 (1963).
241. R. L. Yaday and W. V. Bhagwat, *J. Indian. Chem. Soc.* **41**, 389 (1964).
242. H.-D. Forsterling and L. Stuk, *J. Phys. Chem.* **96**, 3067 (1992).
243. A. Mc. Auley, *J. Chem. Soc.* 4054 (1965).
244. T. J. Kemp and W. A. Waters, *J. Chem. Soc.* 1192 (1964).
245. B. Krishna and K. C. Tewari, *J. Chem. Soc.* 3097 (1961).
246. K. K. Sengupta, *Indian J. Chem.* **2**, 267 (1964).
247. K. B. Bhargava, R. Shanker, and S. N. Joshi, *J. Sci. Indian Res. B*, **21**, 573 (1962).
248. A. Mc Auley and C. H. Brubaker, *J. Chem. Soc. A*, 960 (1966).
249. K. K. Sengupta, S. Aditya, and B. N. Ghosh, *J. Indian Chem. Soc.* **40**, 823 (1963).
250. S. K. Misra and R. N. Mehrotra, *J. Indian Chem. Soc.* **44**, 927 (1968).
251. R. N. Mehrotra and S. Gosh, *Z. phys. Chem.* **230**, 231 (1965).
252. K. K. Sengupta, *J. Indian Chem. Soc.* **41**, 423, 427 (1964).
253. C. E. H. Bawn and A. G. White, *J. Chem. Soc.* 331 (1951).
254. C. E. H. Bawn and J. A. Sharp, *J. Chem. Soc.* 1854 (1957).
255. T. A. Cooper and W. A. Waters, *J. Chem. Soc. B*, 687 (1967).
256. C. F. Wells, *Trans. Faraday Soc.* **63**, 156 (1967).
257. D. G. Hoare and W. A. Waters, *J. Chem. Soc.* 2560 (1964).
258. D. G. Hoare and W. A. Waters, *J. Chem. Soc.* 2552 (1964).
259. D. G. Hoare and W. A. Waters, *J. Chem. Soc.* 971 (1962).
260. T. A. Cooper and W. A. Waters, *J. Chem. Soc. B*, 687 (1967).
261. C. E. H. Bawn and A. G. White, *J. Chem. Soc.* 339 (1951).
262. V. M. Solyanikov and E. T. Denisov, *Neftekhimiya* **6**, 97 (1966).
263. V. S. Martemyanov and E. T. Denisov, *Zh. Fiz. Khim.* **40**, 2315 (1966).
264. R. B. Wiberg and W. G. Nigh, *J. Am. Chem. Soc.* **87**, 3849 (1965).
265. J. K. Thomas, G. Trudel, and S. Bywater, *J. Phys. Chem.* **64**, 51 (1960).
266. W. C. E. Higginson and P. Wright, *J. Chem. Soc.* 1551 (1955).
267. J. S. Littler and I. G. Sayce, *J. Chem. Soc.* 2545 (1964).
268. T. J. Walluce, *J. Org. Chem.* **31**, 3071 (1966).
269. P. J. Andrulis, M. J. S. Dewar, R. Dietz, and R. L. Hunt, *J. Am. Chem. Soc.* **88**, 5473 (1966).
270. P. J. Andrulis and M. J. S. Dewar, *J. Am. Chem. Soc.* **88**, 5483 (1966).
271. T. J. Kemp and W. A. Waters, *J. Chem. Soc.* 339 (1964).
272. G. V. Bakore and M. S. Bararia, *Z. Phys. Chem.* **229**, 245 (1965).

273. M. A. Beg and F. Ahmad, *J. Indian. Chem. Soc.* **44**, 947 (1967).
274. T. J. Kemp and W. A. Waters, *J. Chem. Soc.* 1489 (1964).
275. J. R. Jones and W. A. Waters, *J. Chem. Soc.* 2068 (1962).
276. R. N. Mehrotra, *J. Chem. Soc. B*, 1123 (1968).
277. R. Shanker and S. N. Joshi, *Indian J. Chem.* **1**, 289 (1963).
278. J. S. Littler, A. L. Mallet, and W. A. Waters, *J. Chem. Soc.* 2761 (1960).
279. J. R. Jones, W. A. Waters, and J. S. Littler, *J. Chem. Soc.* 630 (1961).
280. J. R. Jones and W. A. Waters, *J. Chem. Soc.* 352 (1963).
281. J. S. Littler and W. A. Waters, *J. Chem. Soc.* 3014 (1959).
282. J. R. Jones and W. A. Waters, *J. Chem. Soc.* 1629 (1962).
283. T. J. Kemp and W. A. Waters, *J. Chem. Soc.* 1610 (1964).
284. G. V. Bakore and R. Shanker, *Can. J. Chem.* **44**, 1717 (1966).
285. G. S. Mahnot, R. Shanker, and S. N. Swami, *Z. Phys. Chem.* **222**, 240 (1963).
286. R. N. Mehrotra, *J. Chem. Soc. B*, 1563 (1968).
287. G. S. Mahnot, R. Shanker, and S. S. Dua, *Z. Phys. Chem.* **236**, 129 (1967).
288. R. N. Mehrotra, *J. Chem. Soc. B*, 642 (1968).
289. P. S. Radhakrishna Murti and S. C. Pati, *J. Indian Chem. Soc.* **45**, 640 (1968).
290. J.-M. Saveant, in *Advances in Electron Transfer Chemistry*, P. S. Mariano (Ed.), JAI Press, Greenwich, CT, 1994, Vol. 4, p. 53.
291. C. P. Andrieux, J.-M. Saveant, and C. Tardy, *J. Am. Chem. Soc.* **120**, 4167 (1998).
292. E. D. German and A. M. Kuznetsov, *J. Phys. Chem.* **98**, 6120 (1994).
293. R. L. Donkers, F. Maran, D. D. M. Wayner, and M. S. Workentin, *J. Am. Chem. Soc.* **121**, 7239 (1999).

Handbook of Free Radical Initiators. E.T. Denisov, T.G. Denisova, T.S. Pokidova
Copyright © 2003 John Wiley & Sons, Inc.
ISBN: 0-471-20753-5

PART III

REACTIONS OF FREE RADICALS

Handbook of Free Radical Initiators. E.T. Denisov, T.G. Denisova, T.S. Pokidova
Copyright © 2003 John Wiley & Sons, Inc.
ISBN: 0-471-20753-5

16

ISOMERIZATION AND DECOMPOSITION OF FREE RADICALS

16.1 INTRAMOLECULAR ABSTRACTION OF HYDROGEN ATOM

16.1.1 Alkyl Radicals

Alkyl radical isomerization accompanied by free-valence transfer from one carbon atom to another:

$$C^{\bullet}H_2(CH_2)_3CH_2R \rightarrow CH_3(CH_2)_3C^{\bullet}HR$$

occurs in the chain cracking and radiolysis of hydrocarbons,[1] radical polymerization and oligomerization of monomers,[2] and the thermal and thermooxidative destruction of polymers.[3,4] These reactions affect both the rate of the overall process and the composition of the resulting products. The rate constants of intramolecular hydrogen-atom abstraction were measured for a few reactions (see Table 16.1).

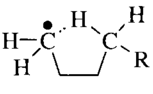
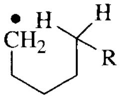
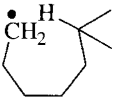
The experimental data on free radical isomerization reactions with H abstraction were analyzed by the IPM method.[5] The kinetic parameters of isomerization were compared with those of the intermolecular hydrogen-atom abstraction (see Chapter 17). The results of analysis and comparison are given in Table 16.2.

It is seen from the activation energy of thermoneutral reactions that the six-membered activated complex is the most favorable for the isomerization of alkyl radicals. Obviously, this configuration is the best for intramolecular radical isomerization involving hydrogen-atom abstraction. The effect of the cycle size on the activation energy was estimated for intramolecular hydrogen-atom abstraction in alkyl radicals. Comparison of the ΔE_e values with the cycle strain energy in *cyclo*-C_nH_{2n} suggests their similarity.

TABLE 16.1 Thermodynamic and Kinetic Parameters for Alkyl Radical Isomerization

Radical $R^{\bullet}$	D_i, (kJ mol^{-1})	D_f, (kJ mol^{-1})	ΔH, (kJ mol^{-1})	E, (kJ mol^{-1})	Cycle	References
$C^{\bullet}Cl_2(CH_2)_3(C-H)HMe$	413.0	388.7	24.3	39.9	6	6
$C^{\bullet}Cl_2(CH_2)_3(C-H)HEt$	414.5	388.7	25.8	39.0	6	6
$C^{\bullet}Cl_2(CH_2)_2Si(CH_2CH_3)_2(C-H)HMe$	413.0	388.7	24.3	44.8	6	7,8
$C^{\bullet}H_2(CH_2)_3(C-H)HC(O)OMe$	398.8	422.0	−23.2	25.1	6	9
$(C-H)(O)CH_2CH[C(CH_3)_3]CH_2C^{\bullet}H_2$	385.6	422.0	−36.4	12.5	6	10
$CH(O)(C-H)HCH_2CH[C(CH_3)_3]CH_2C^{\bullet}H_2$	397.8	422.0	−24.2	17.1	6	10
$C^{\bullet}H_2(CH_2)_4(C-H)HC(O)OMe$	398.8	422.0	−23.2	30.2	7	9
$C^{\bullet}H_2(CH_2)_2(C-H)HC(O)OMe$	398.8	422.0	−23.2	32.4	5	9
2-$[Me_2C(C-H)H_2]$-4,6-$(Me_3C)_2C_6H_2^{\bullet}$	422.0	474.0	−52.0	19.0	5	11–13
2,4,6-$Ad_3C_6H_2^{\bullet}$[a]	408.8	474.0	−65.2	18.0	5	11,13

[a] Ad=Adamantyl-.

Transition State			
E_e(kJ mol^{-1})	59.4	46.6	57.1
ΔE_e (kJ mol^{-1})	11.9	0.0	9.7
E (ring strength) (kJ mol^{-1})	26.4	0.0	26.8

The intramolecular radical hydrogen-atom abstraction proceeds with lower activation energies in comparison with intermolecular (see the values of E_e for both types of reactions in Table 16.2). The values for activation energies of intramolecular radical hydrogen-atom abstraction calculated by the IPM method (see Chapter 9) are in Table 16.3.

16.1.2 Alkoxyl Radicals

Alkoxyl radicals are very active and rapidly enter into the bimolecular reaction:

$$RO^{\bullet} + R^1H \rightarrow ROH + R^{1\bullet}$$

Moreover, alkoxyl radicals with sufficiently long alkyl substituents isomerize into alkyl radicals, for example,[14]

$$R(CH_2)_3Me_2CO^{\bullet} \rightarrow RC^{\bullet}H(CH_2)_2Me_2COH$$

Therefore, the chain chlorination of hydrocarbons with alkyl hypochlorite results in the formation of chlorine-containing alcohols because of a more rapid bimolecular reaction compared to isomerization:[14]

$$RC^{\bullet}H(CH_2)_2Me_2COH + R_1OCl \rightarrow RCHCl(CH_2)_2Me_2COH + R_1O^{\bullet}$$

The isomerization occurs via the formation of a six-membered activated complex and activation energy for the thermally neutral isomerization of alcoxyl radicals is equal to 53.4 kJ mol^{-1}. These parameters were used for the calculation of the activation energies for the isomerization of several alkoxyl radicals (see Table 16.4). The activation energies for the bimolecular reaction of hydrogen-atom abstraction by the alkoxyl radical and intramolecular isomerization are virtually the same (see Chapter 17).

16.1.3 Peroxyl Radicals

Peroxyl radical isomerization

$$RCH(OO^{\bullet})(CH_2)_nCH_2R^1 \rightarrow RCH(OOH)(CH_2)_nC^{\bullet}HR^1$$

TABLE 16.2 IPM Characteristics for Intramolecular H Abstraction Reactions[a]

Radical	br_e (kJ mol^{-1})$^{1/2}$	E_{e0} (kJ mol^{-1})	$r_e \times 10^{11}$ (m)	A_{C-H} (s^{-1})	E_{e0} (bimol.) (kJ mol^{-1})
$R^\bullet \rightarrow R^{1\bullet}$ (six-membered transition state)					
$RC^\bullet H(CH_2)_3(C-H)HY$	14.63	53.5	3.91	1.0×10^{10}	74.8
$RC^\bullet H(CH_2)_3(C-H)HPh$	15.13	57.2	4.04	1.0×10^{9}	79.2
$RC^\bullet H(CH_2)_3(C-H)HCH=CH_2$	15.93	63.4	4.26	1.0×10^{9}	86.5
$R^\bullet \rightarrow R^{1\bullet}$ (five-membered transition state)					
$RC^\bullet H(CH_2)_2(C-H)HY$	16.17	65.4	4.32	3.5×10^{10}	74.8
$RC^\bullet H(CH_2)_2(C-H)HPh$	16.67	69.5	4.45	3.5×10^{9}	79.2
$RC^\bullet H(CH_2)_2(C-H)HCH=CH_2$	17.47	76.3	4.67	3.5×10^{9}	86.5
$Ph^\bullet CMe_2CH_2-H$	14.98	59.3	4.00	3.5×10^{9}	75.3
$R^\bullet \rightarrow R^{1\bullet}$ (seven-membered transition state)					
$RC^\bullet H(CH_2)_4(C-H)HY$	15.90	63.2	4.25	2.8×10^{9}	74.8
$RC^\bullet H(CH_2)_4(C-H)HPh$	16.40	67.2	4.38	2.8×10^{8}	79.2
$RC^\bullet H(CH_2)_4(C-H)HCH=CH_2$	17.20	74.0	4.59	2.8×10^{8}	86.5
$RO^\bullet \rightarrow R^{1\bullet}$ (six-membered transition state)					
$Me_2C(O^\bullet)(CH_2)_2(C-H)HR$	13.13	53.4	3.51	2.0×10^{9}	53.2
$Me_2C(O^\bullet)(CH_2)_2(C-H)HPh$	13.53	56.8	3.61	2.0×10^{8}	56.5
$Me_2C(O^\bullet)(CH_2)_2(C-H)HCH=CH_2$	14.17	62.2	3.79	2.0×10^{8}	62.0
$RO_2{}^\bullet \rightarrow R^{1\bullet}$ (six-membered transition state)					
$RCH(OO^\bullet)Y(C-H)HR$	13.23	53.2	3.53	2.0×10^{9}	56.3
$RCH(OO^\bullet)Y(C-H)HPh$	14.38	62.8	3.84	2.0×10^{8}	62.3
$RCH(OO^\bullet)Y(C-H)HCH=CH_2$	14.82	66.7	3.96	2.0×10^{8}	70.2
$RO_2{}^\bullet \rightarrow R^{1\bullet}$ (seven-membered transition state)					
$RCH(OO^\bullet)YCH_2(C-H)HR$	13.43	54.8	3.59	5.6×10^{8}	56.3
$RCH(OO^\bullet)YCH_2(C-H)HPh$	14.58	64.6	3.90	5.6×10^{7}	62.3
$RCH(OO^\bullet)YCH_2(C-H)HCH=CH_2$	15.02	68.6	4.01	5.6×10^{7}	70.2
$R^{1\bullet} \rightarrow RO_2{}^\bullet$ (six-membered transition state)					
$RCH(OO-H)YC^\bullet HR$	16.25	53.2	3.53	2.0×10^{8}	56.3
$RCH(OO-H)YC^\bullet HPh$	17.67	62.9	3.84	2.0×10^{8}	62.3
$RCH(OO-H)YC^\bullet HCH=CH_2$	18.21	66.8	3.96	2.0×10^{8}	70.2
$R^{1\bullet} \rightarrow RO_2{}^\bullet$ (seven-membered transition state)					
$RCH(OO-H)YCH_2C^\bullet HR$	16.50	54.8	3.59	5.6×10^{7}	56.3
$RCH(OO-H)YCH_2C^\bullet HPh$	17.91	64.6	3.89	5.6×10^{7}	62.3
$RCH(OO-H)YCH_2C^\bullet HCH=CH_2$	18.45	68.6	4.01	5.6×10^{7}	70.2

[a] See Ref. 5.

TABLE 16.3 Enthalpies, Activation Energies, and Rate Constants for Intramolecular Hydrogen Atom Abstraction in Alkyl Radicals (Calculated by IPM Method)[a]

Radical $\mathrm{R^{\bullet}}$	ΔH (kJ mol^{-1})	E (kJ mol^{-1})	k (350 K) (s^{-1})	E (bimol.) (kJ mol^{-1})
$\mathrm{C^{\bullet}H_2(CH_2)_3(C{-}H)HMe}$	−10.0	32.6	2.72×10^5	54.0
$\mathrm{MeC^{\bullet}H(CH_2)_3(C{-}H)HMe}$	0	37.5	5.06×10^4	58.9
$\mathrm{MeC^{\bullet}H(CH_2)_3(C{-}H)Me_2}$	−12.0	31.7	1.86×10^4	53.0
$\mathrm{MeC^{\bullet}H(CH_2)_2NH(C{-}H)HMe}$	−33.4	22.1	1.01×10^7	43.2
$\mathrm{MeC^{\bullet}H(CH_2)_2NMe(C{-}H)HMe}$	−44.9	17.4	5.06×10^7	38.2
$\mathrm{Me_2C^{\bullet}(CH_2)_2NH(C{-}H)Me_2}$	−43.0	18.2	1.92×10^7	39.0
$\mathrm{Me_2C^{\bullet}(CH_2)_2NMe(C{-}H)Me_2}$	−54.5	13.7	9.02×10^7	34.2
$\mathrm{MeC^{\bullet}H(CH_2)_3(C{-}H)HOH}$	−14.6	30.5	5.61×10^5	51.8
$\mathrm{MeC^{\bullet}H(CH_2)_3(C{-}H)MeOH}$	−20.5	27.7	7.35×10^5	49.0
$\mathrm{MeC^{\bullet}H(CH_2)_2C(O)(C{-}H)H_2}$	−2.0	36.5	1.07×10^5	57.9
$\mathrm{MeC^{\bullet}H(CH_2)_2C(O)(C{-}H)HMe}$	−14.2	30.6	5.42×10^5	52.0
$\mathrm{MeC^{\bullet}H(CH_2)_2C(O)(C{-}H)Me_2}$	−19.3	28.3	5.98×10^5	49.6
$\mathrm{MeC^{\bullet}H(CH_2)_3(C{-}H)(O)}$	−26.4	25.1	1.79×10^6	46.3
$\mathrm{MeC^{\bullet}H(CH_2)_3(C{-}H)HPh}$	−43.3	21.6	1.19×10^6	43.1
$\mathrm{Me_2C^{\bullet}(CH_2)_3(C{-}H)MePh}$	−45.3	20.8	7.87×10^5	42.3
$\mathrm{Me_2C^{\bullet}(CH_2)_3(C{-}H)HCH{=}CH_2}$	−50.2	24.8	4.98×10^5	47.3
$\mathrm{Me_2C^{\bullet}(CH_2)_3(C{-}H)MeCH{=}CH_2}$	−60.4	20.8	8.87×10^5	43.0

[a] See Ref. 5.

TABLE 16.4 Enthalpies, Activation Energies, and Rate Constants for Intramolecular Hydrogen Atom Abstraction in Alkoxyl Radicals (Calculated by IPM Method)[a]

Radical $\mathrm{RO^{\bullet}}$	D_i (kJ mol^{-1})	ΔH_e (kJ mol^{-1})	E (kJ mol^{-1})	k (350 K) (s^{-1})	E (bimol.) (kJ mol^{-1})
$\mathrm{Me_2C(O^{\bullet})(CH_2)_2(C{-}H)H_2}$	422.0	−19.5	29.3	2.5×10^5	29.1
$\mathrm{Me_2C(O^{\bullet})(CH_2)_2(C{-}H)HMe}$	412.0	−29.5	25.4	6.4×10^5	25.2
$\mathrm{Me_2C(O^{\bullet})(CH_2)_2(C{-}H)Me_2}$	400.0	−41.5	21.1	1.4×10^6	20.8
$\mathrm{Me_2C(O^{\bullet})CH_2NH(C{-}H)HMe}$	378.6	−62.9	14.0	3.3×10^7	13.7
$\mathrm{Me_2C(O^{\bullet})CH_2NMe(C{-}H)HMe}$	367.1	−74.4	10.5	1.1×10^8	10.3
$\mathrm{Me_2C(O^{\bullet})CH_2NH(C{-}H)Me_2}$	357.0	−84.5	7.7	1.4×10^8	7.5
$\mathrm{Me_2C(O^{\bullet})CH_2NMe(C{-}H)Me_2}$	345.5	−96.0	4.7	4.0×10^8	4.5
$\mathrm{Me_2C(O^{\bullet})(CH_2)_2(C{-}H)HOH}$	397.4	−44.1	20.1	3.9×10^6	19.9
$\mathrm{Me_2C(O^{\bullet})(CH_2)_2(C{-}H)MeOH}$	391.5	−50.0	18.1	3.9×10^6	17.9
$\mathrm{Me_2C(O^{\bullet})CH_2C(O)(C{-}H)H_2}$	410.0	−31.5	24.7	1.2×10^6	24.5
$\mathrm{Me_2C(O^{\bullet})CH_2C(O)(C{-}H)HMe}$	397.8	−43.7	20.3	3.8×10^6	20.1
$\mathrm{Me_2C(O^{\bullet})CH_2C(O)(C{-}H)Me_2}$	392.7	−48.8	18.5	3.4×10^6	18.3
$\mathrm{Me_2C(O^{\bullet})(CH_2)_2(C{-}H)(O)}$	385.6	−55.9	16.2	7.7×10^6	15.9
$\mathrm{Me_2C(O^{\bullet})(CH_2)_2(C{-}H)HPh}$	368.7	−72.8	14.0	3.3×10^6	13.7
$\mathrm{Me_2C(O^{\bullet})(CH_2)_2(C{-}H)MePh}$	354.7	−86.8	9.9	6.6×10^6	9.7
$\mathrm{Me_2C(O^{\bullet})(CH_2)_2(C{-}H)HCH{=}CH_2}$	349.8	−91.7	13.4	4.0×10^6	13.2
$\mathrm{Me_2C(O^{\bullet})(CH_2)_2(C{-}H)MeCH{=}CH_2}$	339.6	−101.9	10.6	5.2×10^6	10.4

[a] See Ref. 5.

via hydrocarbon oxidation results in the formation of bifunctional products (dihydroperoxides, diatomic alcohols, etc.) even at early oxidation stages. These reactions are very important in the oxidation of carbochain polymers.[3,4] The available data on the rates of such reactions are summarized in Table 16.5. The activation energy for isomerization E was calculated from rate constants using the standard preexponential factor $A_{\mathrm{C-H}} = 2.0 \times 10^9\ \mathrm{s^{-1}}$ obtained by averaging the experimental A values for the reactions studied.[5]

Peroxyl radical isomerization involving the formation of a six-membered activated complex is energetically more favorable: The activation energy of a thermally neutral reaction E_e is 53.2 kJ mol^{-1}. For the seven-membered transition state, the E_e, value (54.8 kJ mol^{-1}) is slightly higher. The calculated br_e parameter for the six-membered transition state [13.23 (kJ mol^{-1})$^{1/2}$] is close

TABLE 16.5 Thermodynamic and Kinetic Parameters for Peroxyl Radical Isomerization (C–H Designates the Attacked Bond)

Radical $\mathrm{RO_2^{\bullet}}$	ΔH, (kJ mol^{-1})	E, (kJ mol^{-1})	k(350 K) (s^{-1})	Cycle	References
$\mathrm{PhCH(O_2^{\bullet})O(C{-}H)HPh}$	1.4	44.2	1.01×10^3	6	15–17
$\mathrm{Me_2C(O_2^{\bullet})CH_2(C{-}H)Me_2}$	41.4	57.4	5.43	6	18
$\mathrm{Me_2C(O_2^{\bullet})OC{-}HMe_2}$	32.2	55.2	11.6	6	15,19
$\mathrm{MeCH(O_2^{\bullet})CH_2(C{-}H)HMe}$	47.5	68.9	0.21	6	20
$\mathrm{MeCH(O_2^{\bullet})CH_2(C{-}H)H(CH_2)_9Me}$	50.2	58.8	6.71	6	21
$\mathrm{Me(C{-}H)HCH_2CH(O_2^{\bullet})(CH_2)_{11}Me}$	47.5	62.2	2.09	6	22
$\mathrm{MeCH(O_2^{\bullet})CH_2(C{-}H)(O_2H)(CH_2)_{11}Me}$	26.0	48.3	1.24×10^2	6	22
$\mathrm{Me_2CHCH_2C(O_2^{\bullet})(Me)CH_2(C{-}H)Me_2}$	41.4	54.5	14.72	6	23
$\mathrm{Me_2C(O_2^{\bullet})C(O)(C{-}H)Me_2}$	34.1	59.0	3.13	6	24
$\mathrm{[Me(CH_2)_5C(O)OCH_2]_3CCH_2OC(O)\text{-}CH_2CH(O_2^{\bullet})CH_2(C{-}H)HEt}$	47.5	56.8	13.34	6	25
$\mathrm{[Me(CH_2)_5C(O)OCH_2]_3CCH_2OC(O)\text{-}(CH_2)_3CH(O_2^{\bullet})CH_2(C{-}H)H_2}$	56.5	56.9	19.34	6	25
$\mathrm{Ph(C{-}H)(O_2H)OCH(O_2^{\bullet})Ph}$	1.4	47.7	15.22	6	17,26
$\mathrm{[Me(CH_2)_5C(O)OCH_2]_3CCH_2OC(O)\text{-}(CH_2)_2(C{-}H)HCH_2CH(O_2^{\bullet})Me}$	50.2	56.8	13.34	6	25
$\mathrm{[Me(CH_2)_5C(O)OCH_2]_3CCH_2OC(O)\text{-}CH_2CH(O_2^{\bullet})CH_2(C{-}H)(O_2H)Et}$	26.0	41.9	1.12×10^3	6	25
$\mathrm{MeCH(O_2^{\bullet})(CH_2)_2(C{-}H)H(CH_2)_{10}Me}$	50.2	63.1	1.53	7	22,27
$\mathrm{EtC(O)OCH_2Me_2C\text{-}CH(O_2^{\bullet})OC(O)(C{-}H)HMe}$	33.3	52.5	58.47	7	28
$\mathrm{[EtC(O)OCH_2]_3C\text{-}CH(O_2^{\bullet})OC(O)(C{-}H)HMe}$	33.3	53.5	41.47	7	28
$\mathrm{Me(C{-}H)H(CH_2)_2CH(O_2^{\bullet})(CH_2)_{10}Me}$	47.5	62.3	2.02	7	22
$\mathrm{MeCH(O_2^{\bullet})(CH_2)_2(C{-}H)(O_2H)(CH_2)_{10}Me}$	26.0	52.7	27.29	7	22
$\mathrm{[EtC(O)OCH_2]_2Et\text{-}CCH(O_2^{\bullet})OC(O)(C{-}H)HMe}$	33.3	53.4	42.92	7	28
$\mathrm{[Me(CH_2)_5C(O)OCH_2]_3CCH_2OC(O)\text{-}CH_2CH(O_2^{\bullet})(CH_2)_2(C{-}H)(O_2H)Me}$	26.0	46.2	2.55×10^2	7	25
$\mathrm{[Me(CH_2)_5C(O)OCH_2]_3CCH_2OC(O)\text{-}CH_2(C{-}H)(O_2H)(CH_2)_2CH(O_2^{\bullet})Me}$	26.0	47.0	1.93×10^2	7	25

TABLE 16.6 Enthalpies, Activation Energies, and Rate Constants for Intramolecular Hydrogen Atom Abstraction in Peroxyl Radicals (Calculated by the IPM Method)[a,b]

Radical $RO_2^\bullet$	ΔH (kJ mol^{-1})	$\Delta E\mu$ (kJ mol^{-1})	E (kJ mol^{-1})	k(350 K), (s^{-1})	E(bimol.) (kJ mol^{-1})
$CH_2(OO^\bullet)CMe_2CH_2{-}H$	56.5	0	64.3	1.5	67.2
$MeCH(OO^\bullet)CH_2(C{-}H)HMe$	46.5	0	58.7	7.0	61.6
$Me_2C(OO^\bullet)CH_2(C{-}H)Me_2$	41.4	0	55.9	9.2	58.9
$MeCH(OO^\bullet)NH(C{-}H)HMe$	13.1	0	41.6	2.5×10^3	44.7
$MeCH(OO^\bullet)NMe(C{-}H)HMe$	1.6	0	36.3	1.5×10^4	39.4
$Me_2C(OO^\bullet)NH(C{-}H)Me_2$	−1.6	0	34.9	1.2×10^4	38.0
$Me_2C(OO^\bullet)NMe(C{-}H)Me_2$	−13.1	0	30.0	6.6×10^4	33.1
$CH(OH)(OO^\bullet)CH_2(C{-}H)HOH$	25.8	−2.2	45.5	6.4×10^2	48.6
$MeC(OH)(OO^\bullet)CH_2(C{-}H)MeOH$	19.9	−2.2	42.6	8.7×10^2	45.7
$CH_2(OO^\bullet)C(O)(C{-}H)H_2$	44.5	−15.4	42.2	3.1×10^3	45.1
$MeCH(OO^\bullet)C(O)(C{-}H)HMe$	32.3	−15.4	35.7	1.9×10^4	38.7
$Me_2C(OO^\bullet)C(O)(C{-}H)Me_2$	34.1	−15.7	36.3	7.7×10^3	39.3
$C(O)(OO^\bullet)CH_2(C{-}H)(O)$	−20.5	−8.8	18.3	3.8×10^6	21.3
$PhCH(OO^\bullet)CH_2(C{-}H)HPh$	−1.4	0	44.6	8.7×10^1	44.1
$PhC(OO^\bullet)CH_2(C{-}H)MePh$	−3.9	0	43.5	6.3×10^1	43.0
$CH_2{=}CHCH(OO^\bullet)CH_2\text{-}(C{-}H)HCH{=}CH_2$	−15.7	0	42.4	1.9×10^2	45.9
$CH_2{=}CHC(OO^\bullet)MeCH_2\text{-}(C{-}H)MeCH{=}CH_2$	−19.0	0	41.2	1.5×10^2	44.5

[a] $\Delta E\mu$ is increment of polar interaction in transition state.
[b] See Ref. 5.

to the br_e value [13.62 (kJ mol^{-1})$^{1/2}$] for bimolecular hydrogen-atom abstraction from the aliphatic C—H bond by the peroxyl radical. Therefore, the kinetic parameters for isomerization are close to those for bimolecular hydrogen-atom abstraction by the peroxyl radical. This allows the estimation of the kinetic parameters for peroxyl radical isomerization. Relevant results of calculation are presented in Table 16.6. Data from this table shows that the activation energy for peroxy radical isomerization ranges from 18.3 to 64.3 kJ mol^{-1}, whereas the rate constant k(350 K) varies from 1.5 to 3.8×10^6 s^{-1}.

16.2 CYCLIZATION OF FREE RADICALS

Alkyl radicals possessing the double bond react with the intramolecular free-valence attack on this bond with formation of cyclic free radicals, for example,

$$C^\bullet H_2(CH_2)_nCH{=}CH_2 \rightarrow \textit{cyclo}\text{-}[(CH_2)_{n+1}CH(C^\bullet H_2)]$$

$$C^\bullet H_2(CH_2)_nCH{=}CHR \rightarrow \textit{cyclo}\text{-}[(CH_2)_{n+1}C^\bullet HCHR]$$

These reactions found numerous applications in synthetic chemistry and were intensively studied during the last two decades.[29–34] They are widely used in various kinetic experiments as "o'clock—reactions" as well since the rate constants of such reactions do not depend on the used solvent. The reactions of intramolecular addition are known to produce products with the ring structure contains 3, 4, 5, 6, 7, and 8 atoms. The values for rate constants and the activation energies of various reactions with ring formation are compiled in Table 16.7.

The analysis of experimental data on the preexponential factor of these reactions showed that this factor depends on the size of the formed ring, and the dependence has the following form (n is the number of atoms in the ring):[34]

$$\log(A/\mathrm{s}^{-1}) = 13.10 - 0.55 \times n \tag{16.1}$$

This dependence was used to calculate the activation energy from the rate constant value using the Arrhenius equation.

$$E = RT\ln(A/k) \tag{16.2}$$

Activation entropy of cyclization $\Delta S^{\neq}$ was found to be exactly equal to the difference of entropies of subsequent linear and cyclic hydrocarbons.[34]

$$\Delta S^{\#} = [S^0(cyclo\text{-}\mathrm{C}_n\mathrm{H}_{2n}) - S^0(\mathrm{C}_n\mathrm{H}_{2n+2})] \tag{16.3}$$

The values of activation energy were analyzed in the IPM model (see Chapter 9). The following factors influencing on E were found to be very important.

The first is the reaction enthalpy that depends on the enthalpy of free-valence addition to the double bond and the ring strain energy E_{rsc}. As well as $E_{\mathrm{rsc}} \approx 0$ for the six-membered cycle, the minimal values of ΔH are observed for the six-membered cyclization.

The second factor is the influence of ring strain energy E_{rsc} on the thermoneutral activation energy of cyclization (see Table 16.8). The thermoneutral activation energy E_{e0} (see Chapter 9) characterizes the height of the activation barrier for the reaction with $\Delta H_{\mathrm{e}} = 0$. The value of E_{e0} was found to be dependent on the ring strain energy E_{rsc}^{34}.

$$E_{\mathrm{e0}}(n) = E_{\mathrm{e0}}(n = 6) - 0.44E_{\mathrm{rsc}}(n) \tag{16.4}$$

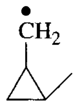
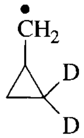
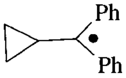
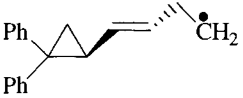
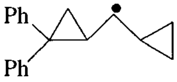
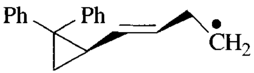
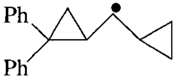
The values of $E_{\mathrm{e0}}(n)$ and $E_{\mathrm{rsc}}(n)$ are given in the Table 16.8.

As a result, the following simple empirical equation for the activation energy of the cyclization of alkyl radicals possessing the double bond was drawn:[34]

$$\sqrt{E + 8.5} = 3.28 \times \sqrt{194.5 - E_{\mathrm{rsc}}}\left\{1.202\sqrt{1 + \frac{0.208(\Delta H + 1.7)}{194.5 - E_{\mathrm{rsc}}}} - 1\right\} \tag{16.5}$$

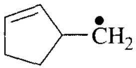
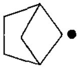
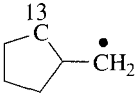
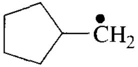
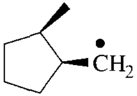
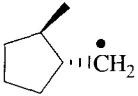
The third important factor is the force constant of the reacting bond. It was found that the thermoneutral activation energy of the intramolecular addition to the triple bond is higher than that to the double bond (for designations see Chapter 9).

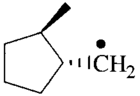
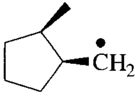
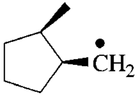
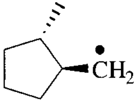
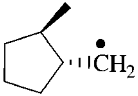
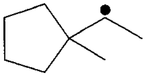
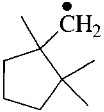
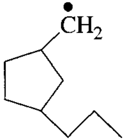
TABLE 16.7 Rate Constants and Activation Energies for Alkyl Radicals Cyclization

$R_i^\bullet$ (Reactant)	$R_f^\bullet$ (Product)	ΔH (kJ mol^{-1})	T (K)	k(298 K) (s^{-1})	E (kJ mol^{-1})	References
	$n = 3$, log $[A(s^{-1})] = 11.6$					
$CH_2{=}CHCHMeC^\bullet H_2$		23.0	333–379	4.94×10^4	39.4	35
$CH_2{=}CHCH_2C^\bullet D_2$		23.4	252–276	5.37×10^3	44.9	36
$Ph_2C{=}CHCH_2C^\bullet H_2$			277–309	2.01×10^7	24.5	37
$PhCH{=}CHCH_2C^\bullet H_2$			280–321	6.53×10^6	27.3	37
			292–331	6.05×10^4	38.9	38
			293–322	8.43×10^4	38.1	38

(*continued overleaf*)

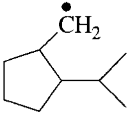
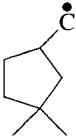
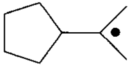
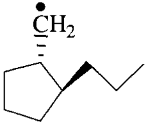
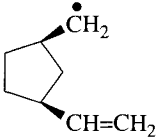
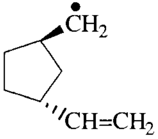
TABLE 16.7 (*continued*)

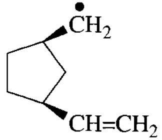
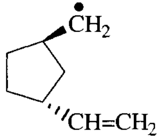
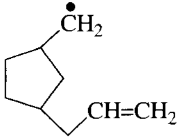
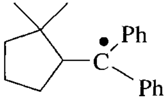
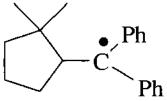
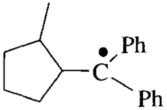
$R_i^\bullet$ (Reactant)	$R_f^\bullet$ (Product)	ΔH (kJ mol^{-1})	T (K)	k(298 K) (s^{-1})	E (kJ mol^{-1})	References
	$n = 4$, $\log[A(s^{-1})] = 11.3$					
		−104.8	338	8.3×10^4	34.8	39
	$n = 5$, $\log[A(s^{-1})] = 10.2$					
$CH_2{=}CH(CH_2)_3C^\bullet H_2$		−64.4	313	1.8×10^5	29.7	40
$CH_2{=}CH(CH_2)_3C^\bullet H_2$		−64.4	188–373	3.75×10^4	32.1	41–44
$CH_2{=}CH(CH_2)_2CHMeC^\bullet H_2$		−66.7	318–373	4.57×10^5	25.9	45–47
$CH_2{=}CHCHMe(CH_2)_2C^\bullet H_2$		−66.3	298–373	7.74×10^4	30.3	45–47
$CH_2{=}CHCHMe(CH_2)_2C^\bullet H_2$		−69.8	298–373	3.74×10^5	26.4	45–47

$CH_2=CHCH_2CHMeCH_2C^{\bullet}H_2$		−66.7	318–373	2.40×10^5	27.5	45–47
$CH_2=CHCH_2CHMeCH_2C^{\bullet}H_2$		−63.2	318–373	2.40×10^5	27.5	45–47
$CH_2=CH(CH_2)_2CHMeC^{\bullet}H_2$		−63.2	318–373	2.40×10^5	27.5	45–47
$CH_2=CMe(CH_2)_3C^{\bullet}H_2$		−65.3	298–338	2.22×10^4	33.4	41,47,48
$CH_2=CH(CH_2)_3C^{\bullet}HMe$		−66.8	298–338	1.03×10^5	29.6	41,47
$MeCH=CMe(CH_2)_3C^{\bullet}H_2$		−61.7	338	3.3×10^5	30.3	41
$CH_2=CMe(CH_2)_3C^{\bullet}Me_2$		−43.8	313	6.2×10^4	32.4	48
$CH_2=CHCH_2CH(CH_2C^{\bullet}H_2)Pr$		−64.4	353	6.6×10^6	22.8	45,49

(continued overleaf)

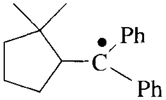
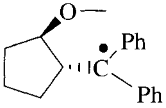
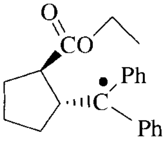
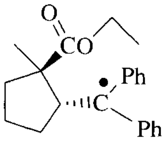
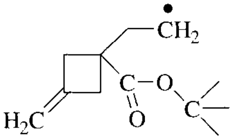
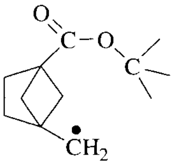
TABLE 16.7 (*continued*)

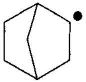
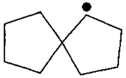
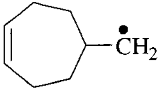
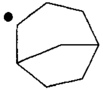
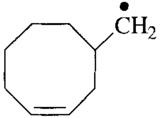
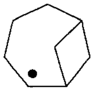
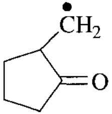
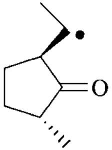
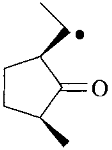
$R_i^{\bullet}$ (Reactant)	$R_f^{\bullet}$ (Product)	ΔH (kJ mol^{-1})	T (K)	k(298 K) (s^{-1})	E (kJ mol^{-1})	References
$CH_2{=}C(CHMe_2)(CH_2)_3C^{\bullet}H_2$		−61.6	338	2.5×10^4	37.5	45
$CH_2{=}CH(CH_2)_2CMe_2C^{\bullet}H_2$		−64.4	298–353	2.81×10^6	21.4	49–51
$Me_2C{=}CH(CH_2)_3C^{\bullet}H_2$		−69.3	338	2.6×10^6	24.5	41
$CH_2{=}CH(CH_2)_3C^{\bullet}HPr$		−66.8	338	8.5×10^5	27.6	41
$CH_2{=}CH(CH_2)_2CH(C^{\bullet}H_2)CH{=}CH_2$		−60.9	353	7.8×10^5	29.1	45
$CH_2{=}CH(CH_2)_2CH(C^{\bullet}H_2)CH{=}CH_2$		−64.4	353	1.4×10^6	27.3	45

$CH_2{=}CHCH_2CH(CH{=}CH_2)CH_2C^{\bullet}H_2$		−60.9	353	2.2×10^{6}	26.1	45
$CH_2{=}CHCH_2CH(CH{=}CH_2)CH_2C^{\bullet}H_2$		−64.4	353	6.6×10^{5}	29.6	45
$C^{\bullet}H_2CH_2CH(CH_2CH{=}CH_2)_2$		−65.4	303−357	1.88×10^{6}	22.4	52
$N{\equiv}CCH{=}CH(CH_2)_3C^{\bullet}H_2$		−107.4	223−324	1.72×10^{8}	11.2	53
$Ph_2C{=}CH(CH_2)_3C^{\bullet}H_2$		−112.5	226−317	5.35×10^{7}	14.1	54
$Ph_2C{=}CH(CH_2)_3C^{\bullet}H_2$		−112.5	236−317	4.08×10^{7}	14.8	55
$Ph_2C{=}CH(CH_2)_3C^{\bullet}HMe$			234−325	2.36×10^{7}	16.1	55

(*continued overleaf*)

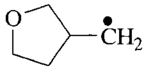
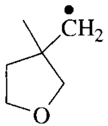
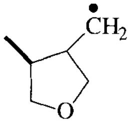
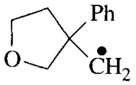
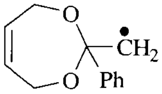
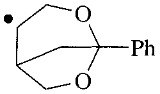
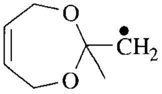
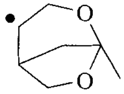
TABLE 16.7 (*continued*)

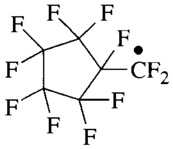
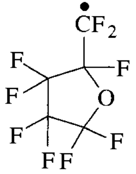
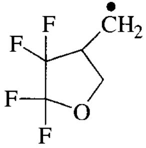
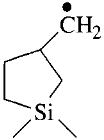
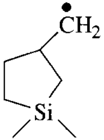
$R_i^\bullet$ (Reactant)	$R_f^\bullet$ (Product)	ΔH (kJ mol^{-1})	T (K)	k(298 K) (s^{-1})	E (kJ mol^{-1})	References
$Ph_2C{=}CH(CH_2)_3C^\bullet Me_2$			263–326	1.22×10^7	17.8	55
$Ph_2C{=}CH(CH_2)_3C^\bullet HOMe$		−106.7	273–313	3.87×10^7	14.9	56
$Ph_2C{=}CH(CH_2)_3C^\bullet HC(O)OEt$		−98.1	273–313	6.55×10^7	13.6	57
$PH_2C{=}CH(CH_2)_3C^\bullet MeC(O)OEt$		−87.6	273–333	4.39×10^5	26.0	57
		−61.6	274–383	2.71×10^5	27.2	58

		−51.2	366–403	3.91×10^3	37.7	59
		−61.9	338	1.2×10^5	33.0	41
		−53.8	280–470	1.67×10^5	28.4	60
		−56.4	280–470	6.86×10^4	30.6	60
$CH_2{=}CH(CH_2)_3C^{\bullet}(O)$			298	2.2×10^5		61
$MeCH{=}CH(CH_2)_2CHMeC^{\bullet}(O)$			298	1.8×10^5	25.1	61
$MeCH{=}CH(CH_2)_2CHMeC^{\bullet}(O)$			298	1.3×10^5	25.5	61

(continued overleaf)

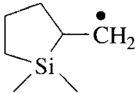
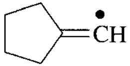
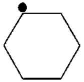
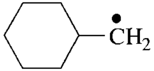
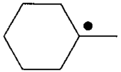
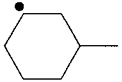
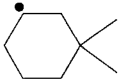
TABLE 16.7 (*continued*)

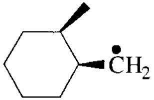
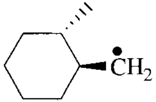
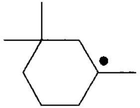
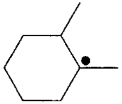
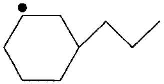
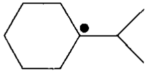
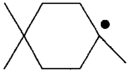
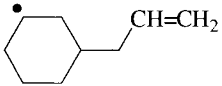
$R_i^\bullet$ (Reactant)	$R_f^\bullet$ (Product)	ΔH (kJ mol^{-1})	T (K)	k(298 K) (s^{-1})	E (kJ mol^{-1})	References
$CH_2{=}CH(CH_2)_2OC^\bullet H_2$		−65.7	180−220	3.32×10^4	32.4	50,62
$CH_2{=}CMeCH_2OCH_2C^\bullet H_2$		−62.9	313	2.0×10^5	29.3	63
$CH_2{=}CHCH_2OCH_2C^\bullet HMe$		−96.1	338	8.8×10^6	21.1	64
$CH_2{=}CPhCH_2OCH_2C^\bullet H_2$		−61.6	313	1.7×10^5	29.7	63
		−92.7	298−423	4.96×10^5	25.7	65
		−92.7	272−394	8.38×10^5	24.4	65

$F_2C{=}CF(CF_2)_3C^{\bullet}F_2^{\bullet}$		−136.8	231−353	4.22×10^5	26.1	66
$F_2C{=}CFO(CF_2)_2C^{\bullet}F_2$		−137.9	303	3.5×10^6	21.2	67
$H_2C{=}CHCH_2OCF_2C^{\bullet}F_2$			298	3.8×10^7	15.0	68
$CH_2{=}CHCH_2SiMe_2CH_2C^{\bullet}H_2$		−64.4	298	1.0×10^3	36.6	43
$CH_2{=}CH(CH_2)_2SiMe_2C^{\bullet}H_2$		−64.4	298	7.5×10^3	38.7	43

(*continued overleaf*)

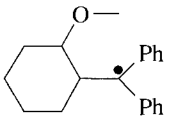
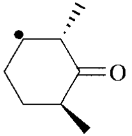
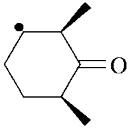
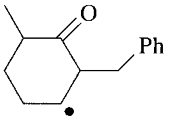
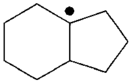
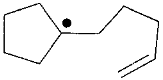
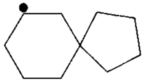
TABLE 16.7 (*continued*)

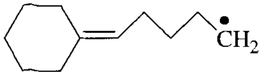
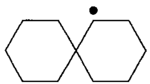
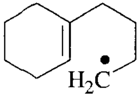
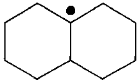
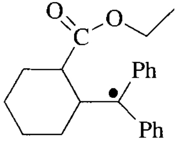
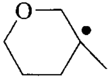
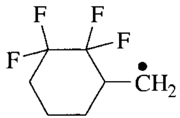
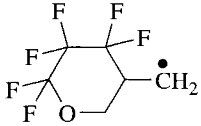
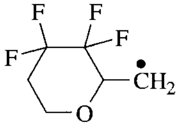
$R_i^•$ (Reactant)	$R_f^•$ (Product)	ΔH (kJ mol^{-1})	T (K)	k(298 K) (s^{-1})	E (kJ mol^{-1})	References
$CH_2{=}CHSiMe_2(CH_2)_2C^•H_2$		−64.4	298	7.5×10^4	34.9	43,51,69
$HC{\equiv}C(CH_2)_3C^•H_2$		−75.9	298	2.8×10^4	32.8	47
	$n = 6$, $\log(A/s^{-1}) = 9.7$					
$CH_2{=}CH(CH_2)_3C^•H_2$		−75.3	188−396	1.78×10^2	42.5	41,42,43,46,50
$CH_2{=}CH(CH_2)_4C^•H_2$		−92.5	338	2.5×10^4	34.3	70
$CH_2{=}CMe(CH_2)_3C^•H_2$		−108.3	298−338	8.57×10^3	32.9	41,47
$CH_2{=}CH(CH_2)_3C^•HMe$		−97.6	338	9.7×10^3	36.9	41
$CH_2{=}CH(CH_2)_3C^•Me_2$		−87.6	298−338	9.68×10^3	32.6	41,47,71

$CH_2{=}CH(CH_2)_4C^{\bullet}HMe$		−82.7	298	2.1×10^3	33.9	47
$CH_2{=}CH(CH_2)_4C^{\bullet}HMe$		−90.5	298	5.7×10^3	36.4	47
$CH_2{=}CMe(CH_2)_3C^{\bullet}Me_2$		−105.1	313	5.4×10^4	29.7	41,48
$MeCH{=}CMe(CH_2)_3C^{\bullet}H_2$		−92.2	338	6.0×10^4	31.8	41
$CH_2{=}CH(CH_2)_3C^{\bullet}H(CH_2)_2Me$		−97.6	338	4.1×10^3	39.4	41
$CH_2{=}C(CHMe_2)(CH_2)_3C^{\bullet}H_2$		−103.9	338	8.0×10^4	31.0	45
$CH_2{=}CMe(CH_2)_2CMe_2C^{\bullet}H_2$		−105.0	318−373	2.17×10^4	30.6	49
$(CH_2{=}CHCH_2)_2CHCH_2C^{\bullet}H_2$		−95.3	333	2.3×10^5	27.6	52

(continued overleaf)

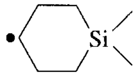
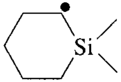
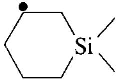
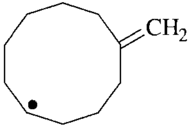
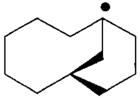
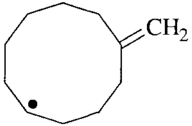
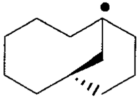
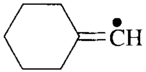
TABLE 16.7 (*continued*)

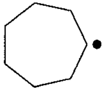
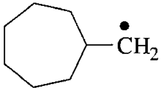
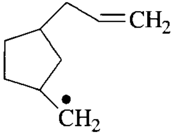
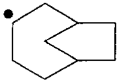
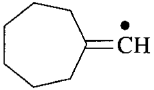
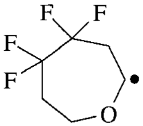
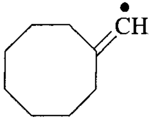
$R_i^\bullet$ (Reactant)	$R_f^\bullet$ (Product)	ΔH (kJ mol^{-1})	T (K)	k(298 K) (s^{-1})	E (kJ mol^{-1})	References
$Ph_2C{=}CH(CH_2)_4C^\bullet HOMe$		−133.0	283–323	1.51×10^5	25.8	56
$MeCH{=}CH(CH_2)_2CHMeC^\bullet(O)$			298	2.0×10^4	26.8	61
$MeCH{=}CH(CH_2)_2CHMeC^\bullet(O)$			298	5.2×10^3	28.4	61
$PhCH_2CH{=}CH(CH_2)_2CHMeC^\bullet(O)$		−84.8	353	2.0×10^5	29.7	72
		−89.3	338	3.0×10^4	33.7	41
		−76.8	338	6.7×10^4	31.5	41

		−89.5	338	1.0×10^6	23.8	41
		−89.4	338	5.3×10^4	32.2	41
$Ph_2C{=}CH(CH_2)_4C^{\bullet}HC(O)OEt$		−124.5	273–313	1.99×10^7	13.7	57
$CH_2{=}CMeCH_2OCH_2C^{\bullet}H_2$		−80.0	313	4.6×10^3	36.2	63
$H_2C{=}CH(CH_2)_3CF_2C^{\bullet}F_2$			298	1.44×10^7	14.5	68
$H_2C{=}CHCH_2O(CF_2)_2C^{\bullet}F_2$			298	1.21×10^6	20.6	68
$H_2C{=}CHO(CH_2)_2CF_2C^{\bullet}F_2$			298	9.4×10^6	15.6	68

(continued overleaf)

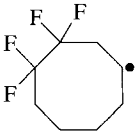
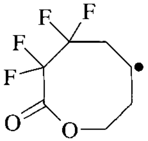
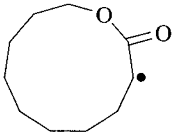
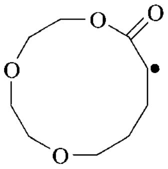
TABLE 16.7 (*continued*)

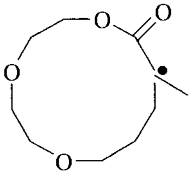
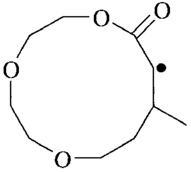
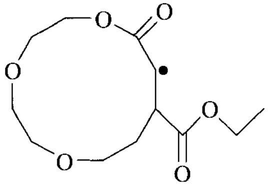
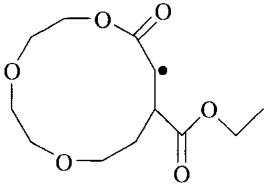
$R_i^{\bullet}$ (Reactant)	$R_f^{\bullet}$ (Product)	ΔH (kJ mol^{-1})	T (K)	k(298 K) (s^{-1})	E (kJ mol^{-1})	References
$CH_2{=}CH(CH_2)_2SiMe_2C^{\bullet}H_2$		−95.3	298	1.6×10^4	34.0	43
$CH_2{=}CHSiMe_2(CH_2)_2C^{\bullet}H_2$		−95.3	298	7.5×10^4	34.7	43
$CH_2{=}CHCH_2SiMe_2CH_2C^{\bullet}H_2$		−95.3	298	1.4×10^4	34.9	51
		−136.2	313–396	9.97×10^8	4.0	73
		−149.6	313–396	3.21×10^9	1.1	73
$HC{\equiv}C(CH_2)_4C^{\bullet}H_2$		−58.9	333	4.6×10^4	32.1	44

	$n = 7$, $\log(A/s^{-1}) = 9.1$					
$CH_2{=}CH(CH_2)_4C^{\bullet}H_2$		−53.5	338	4.8 × 10^3	35.0	70
$CH_2{=}CH(CH_2)_5C^{\bullet}H_2$		−64.6	338	8.3 × 10^2	39.9	70
		−73.4	338	3.0 × 10^3	37.7	52
$HC{\equiv}C(CH_2)_5C^{\bullet}H_2$		−85.3	333	2.5 × 10^3	36.3	44
$H_2C{=}CHO(CH_2)_2CF_2C^{\bullet}F_2$			298	3.4 × 10^6	14.2	68
	$n = 8$, $log[A(s^{-1})] = 8.8$					
$HC{\equiv}C(CH_2)_6C^{\bullet}H_2$		−58.5	333	1.2 × 10^2	42.8	44

(*continued overleaf*)

TABLE 16.7 (*continued*)

$R_i^{\bullet}$ (Reactant)	$R_f^{\bullet}$ (Product)	ΔH (kJ mol^{-1})	T (K)	k(298 K) (s^{-1})	E (kJ mol^{-1})	References
$H_2C{=}CH(CH_2)_4CF_2C^{\bullet}F_2$			298	2.0×10^4	25.7	68
$H_2C{=}CH(CH_2)_2OC(O)CF_2C^{\bullet}F_2$			298	3.6×10^4	24.2	68
	$n = 11$, $log[A(s^{-1})] = 7.1$					
$H_2C{=}CHC(O)O(CH_2)_6C^{\bullet}H_2$			353	2.8×10^3	20.5	74
	$n = 12$, $log[A(s^{-1})] = 6.5$					
$H_2C{=}CHC(O)O(CH_2CH_2O)_2$- $CH_2C^{\bullet}H_2$			353	1.5×10^5	7.4	74

$H_2C{=}CCH_3C(O)O(CH_2CH_2O)_2$- $CH_2C^{\bullet}H_2$		353	7.0×10^4	9.3	74
(*E*)-$CH_3CH{=}CHC(O)O(CH_2CH_2O)_2$- $CH_2C^{\bullet}H_2$		353	6.6×10^3	15.0	74
(*Z*)-$(CH_3CH_2OC(O))CH{=}CHC(O)O$- $(CH_2CH_2O)_2CH_2C^{\bullet}H_2$		353	6.0×10^3	15.3	74
(*E*)-$(CH_3CH_2OC(O))CH{=}CHC(O)O$- $(CH_2CH_2O)_2CH_2C^{\bullet}H_2$		353	9.4×10^4	8.6	74

(*continued overleaf*)

TABLE 16.7 (*continued*)

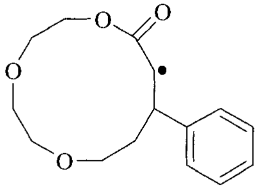
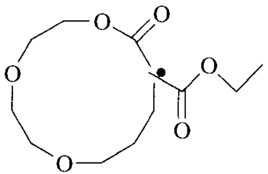
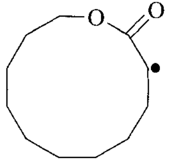
$R_i^\bullet$ (Reactant)	$R_f^\bullet$ (Product)	ΔH (kJ mol^{-1})	T (K)	k(298 K) (s^{-1})	E (kJ mol^{-1})	References
(E)-$(C_6H_5)CH{=}CHC(O)O$- $(CH_2CH_2O)_2CH_2C^\bullet H_2$			353	2.9×10^3	17.0	74
$CH{=}C[C(O)OCEt]$- $CH_2O(CH_2CH_2O)_2CH_2C^\bullet H_2$			353	1.4×10^5	7.6	74
$H_2C{=}CHC(O)O(CH_2)_7C^\bullet H_2$			353	4.8×10^3	15.8	74

TABLE 16.8 Comparison of Activation Energies and Preexponential Factors of Alkyl Radicals Cyclization with Ring Formation Stress Energy (E_{rsc}) and Entropy of Ring Formation

Number of Atoms in the Formed Ring	3	5	6	7
E_{e0} (kJ mol^{-1})	36.4	69.7	85.7	78.0
E_{rsc} (kJ mol^{-1})	115.1	26.7	0.7	26.3
$E_{e0}(6)$ - $E_{e0}(n)$ (kJ mol^{-1})	49.3	16.0	0	7.7
$\log(A/s^{-1})$	11.60	10.20	9.90	9.10
$\Delta S^{\neq}$ (J mol^{-1} K^{-1})	−32.5	−59.3	−65.2	−80.5
S^0(cycle) (J mol^{-1} K^{-1})	237.4	293.1	298.6	342.6
$S^0(C_nH_{2n+2})$ (J mol^{-1} K^{-1})	270.0	348.9	388.1	427.9
$\Delta S^0 = S^0(\text{cycle}) - S^0(C_nH_{2n+2})$ (J mol^{-1} K^{-1})	−32.6	−55.8	−89.5	−85.3

Bond	br_e (kJ mol^{-1})$^{1/2}$	E_{e0} (kJ mol^{-1})	$b \times 10^{-11}$ (kJ mol^{-1}) m^{-1}	$r_e \times 10^{11}$, (m)
C=C	18.39	69.7	5.39	3.41
C≡C	22.98	81.7	6.91	3.32

The values for the parameter r_e (sum of valence vibration amplitudes of reacting bonds) are close and the difference in values of E_{e0} is the result of the difference in the values of coefficients b ($2b^2$ is the force constant of the attacked double or triple bond, respectively). The rate constants values of intramolecular cyclization through addition of alkyl and aminyl radicals to double C=N, N=N, and C=O bonds are in Table 16.9.

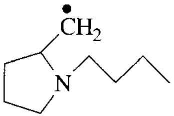
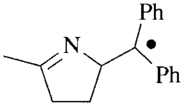
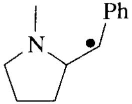
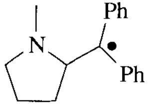
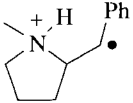
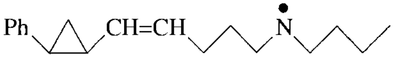
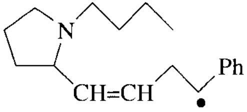
16.3 DECYCLIZATION OF CYCLIC RADICALS

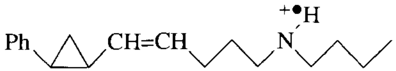
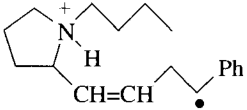
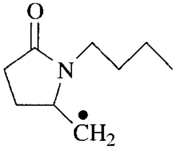
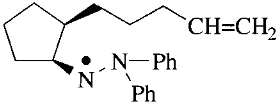
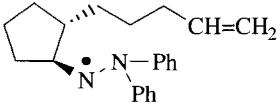
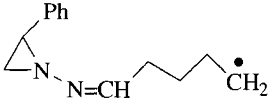
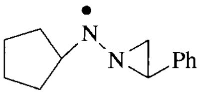
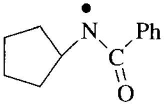
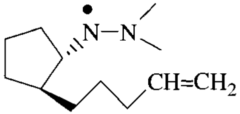
Cyclic alkyl radicals react with the break of the ring and formation of linear radicals with the double bond.

$$cyclo\text{-}[(CH_2)_{n-1}CH(C^{\bullet}H_2)] \rightarrow CH_2{=}CH(CH_2)_{n-2}C^{\bullet}H_2$$

When the number of atoms in the cycle $n = 3$ or 4, reactions with ring opening are exothermic and occur fast. Decay of three-membered cyclic alkyl radicals occurs with preexponential factor $A = 3.0 \times 10^{13\pm0.6}$ s^{-1} and activation energies $E =$ 7–53 kJ mol^{-1} (see Table 16.10). The four-membered cyclic alkyl radicals are decomposed very rapidly also. Their preexponential factor $A = 6.0 \times 10^{13.0\pm1.2}$ (number of measurements $n = 17$) and activation energies varies from 39 to 58 kJ mol^{-1} (see Table 16.10). Among five-membered cyclic radicals, reactions

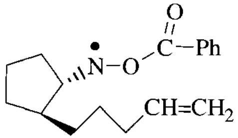
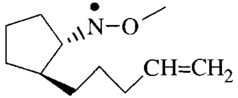
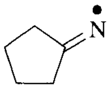
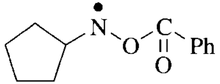
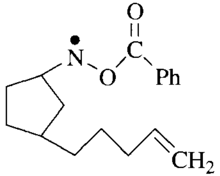
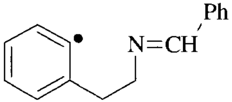
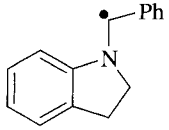
TABLE 16.9 Rate Constants of Cyclization of Iminoalkyl and Aminyl Radicals

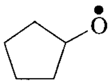
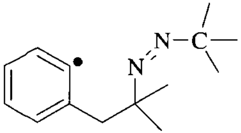
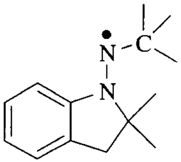
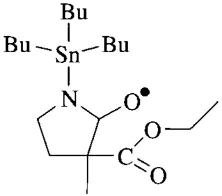
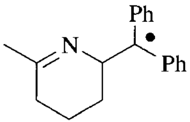
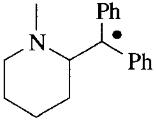
$R_i^\bullet$	$R_f^\bullet$	*T* (K)	*k* (s^{-1})	References
	Formation of Five-Membered Cycle			
$CH_2{=}CH(CH_2)_3N^\bullet Bu$		323	5.0×10^4	75
$Ph_2C{=}CH(CH_2)_2MeC{=}N^\bullet$		298	2.2×10^6	76
$PhCH{=}CH(CH_2)_3N^\bullet Me$		293	1.9×10^5	77
$Ph_2C{=}CH(CH_2)_3N^\bullet Me$		293	3.2×10^5	77
$Ph_2C{=}CH(CH_2)_3N^\bullet H^+Me$		293	1.0×10^{10}	78
		323	1.0×10^4	79

		283	1.0×10^8	79
$CH_2{=}CH(CH_2)_2C(O)N^{\bullet}Bu$		323	1.0×10^4	80
$Ph_2NN{=}CH(CH_2)_3C^{\bullet}H(CH_2)_3CH{=}CH_2$		353	1.1×10^8	81
$Ph_2NN{=}CH(CH_2)_3C^{\bullet}H(CH_2)_3CH{=}CH_2$		353	4.6×10^7	81
		353	2.5×10^8	82
$PhC(O){-}N{=}CH(CH_2)_3C^{\bullet}H_2$		353	6.0×10^6	83
$Me_2NN{=}CH(CH_2)_3C^{\bullet}H(CH_2)_3CH{=}CH_2$		353	2.4×10^7	84

(*continued overleaf*)

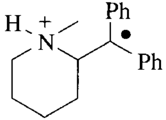
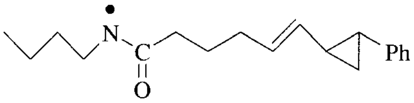
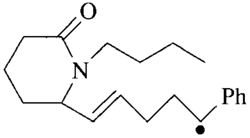
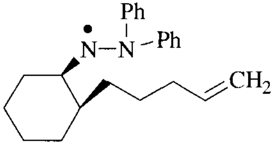
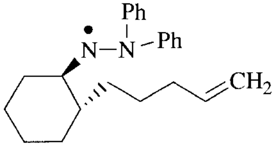
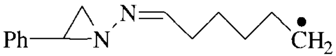
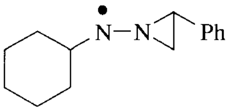
TABLE 16.9 (*continued*)

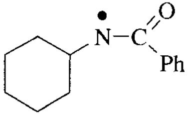
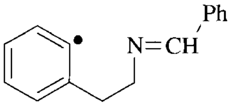
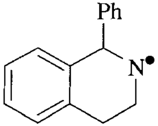
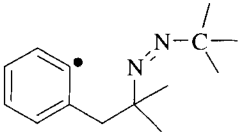
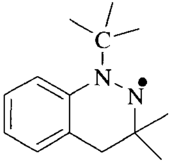
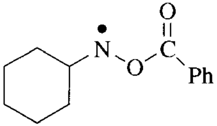
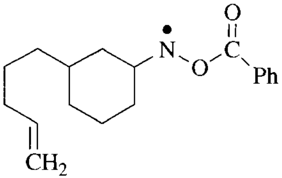
$R_i^•$	$R_f^•$	T (K)	k (s^{-1})	References
$PhCOON{=}CH(CH_2)_3C^•H(CH_2)_3CH{=}CH_2$		353	3.3×10^7	84
$MeON{=}CH(CH_2)_3C^•H(CH_2)_3CH{=}CH_2$		353	2.4×10^7	84
$N{\equiv}C(CH_2)_3C^•H_2$		353	4.0×10^4	85
$PhC(O)ON{=}CH(CH_2)_3C^•H_2$		353	4.2×10^7	84
$PhC(O)ON{=}CH(CH_2)_2CH(C^•H_2)(CH_2)_3CH{=}CH_2$		353	6.8×10^7	84
		353	3.8×10^7	86

$CH(O)(CH_2)_3C^{\bullet}H_2$		353	8.6 × 10^5	87
		353	1.5 × 10^9	88,89
$Me(EtOC(O))(CHO)C(CH_2)_2N^{\bullet}SnBu_3$		298	3.1 × 10^4	84
	Formation Six-Membered Cycle			
$Ph_2C{=}CH(CH_2)_3CMe{=}N^{\bullet}$		298	1.0 × 10^4	76
$Ph_2C{=}CH(CH_2)_3N^{\bullet}Me$		293	7.0 × 10^3	77

(*continued overleaf*)

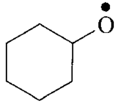
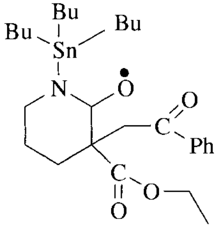
TABLE 16.9 (*continued*)

$R_i^\bullet$	$R_f^\bullet$	*T* (K)	*k* (s^{-1})	References
$Ph_2C{=}CH(CH_2)_4N^{\bullet+}HMe$		293	9.0×10^7	78
		298	1.2×10^7	79
$Ph_2NN{=}CH(CH_2)_4C^\bullet H(CH_2)_3CH{=}CH_2$		353	9.4×10^5	81
$Ph_2NN{=}CH(CH_2)_4C^\bullet H(CH_2)_3CH{=}CH_2$		353	9.4×10^5	81
		353	4.7×10^6	82

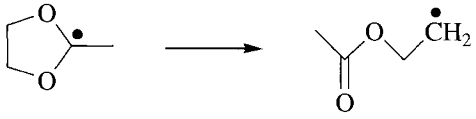
$PhC(O)N{=}CH(CH_2)_4C^{\bullet}H_2$		353	6.7×10^5	83
		355	1.6×10^8	86
		355	2.3×10^9	88,89
$PhC(O)ON{=}CH(CH_2)_4C^{\bullet}H_2$		353	2.4×10^6	84
$PhC(O)ON{=}CH(CH_2)_3CH(C^{\bullet}H_2)(CH_2)_3CH{=}CH_2$		353	4.1×10^6	84

(continued overleaf)

TABLE 16.9 (*continued*)

$R_i^\bullet$	$R_f^\bullet$	*T* (K)	*k* (s^{-1})	References
$HC(O)(CH_2)_4C^\bullet H_2$		353	4.7×10^8	87
$PhC(O)(EtOC(O))(CHO)C(CH_2)_3N^\bullet SnBu_3$		298	6.5×10^8	90

of radicals with oxygen-containing rings were studied, for example,



Activation energies for such reactions were found to be equal to 64–67 kJ mol^{-1} and the preexponential factor $A = 10^{13}\ s^{-1}$ (see Table 16.10). Cyclic alkoxyl radicals with five- and six-membered cycles are decomposed with formation of radicals with a carbonyl group.

$$cyclo\text{-}[(CH_2)_{n-1}CH(O^\bullet)] \rightarrow C^\bullet H_2(CH_2)_{n-2}CH(O)$$

The decay occurs with high values of rate constants (300 K) $k \approx 10^7–10^8\ s^{-1}$ (see Table 16.10).

16.4 FRAGMENTATION OF FREE RADICALS

In addition to reactions of isomerization, many free radicals undergo reactions of decomposition with production of a molecule and a new free radical. The enthalpy of such decomposition is the main factor that determines the activation energy and the rate constant of decomposition.

16.4.1 Alkyl Radicals

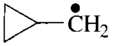
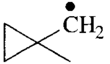
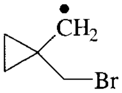
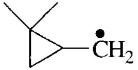
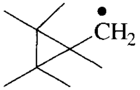
Alkyl radicals are generated in reactions for the decomposition of diacyl peroxides, peresters (see Chapter 5), and azo compounds (Chapter 7), as well as in reactions of alkoxyl, hydroxyl, and aminyl radicals with solvent (see Chapter 18). Alkyl radicals undergo unimolecular fragmentation by the scission of the β-C—H bond with formation of an olefin and hydrogen atom.[134] Such reactions are very endothermic. For example, the reaction of ethyl radical fragmentation into ethylene and a hydrogen atom occurs with enthalpy equal to 150 kJ mol^{-1}. Such high endothermic reactions play an important role in high temperature thermolysis of hydrocarbons at $T > 800$ K.[1] For the values of ΔH for these reactions, see Table 9.6, Chapter 9.

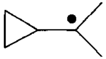
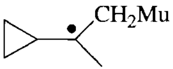
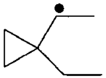
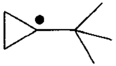
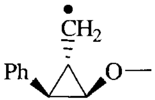
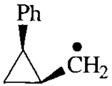
Another reaction of alkyl radical decomposition is the scission of β-C—C bond,[130] for example,

$$CH_3CH_2C^\bullet H_2 \rightarrow C^\bullet H_3 + CH_2{=}CH_2$$

These reactions are very endothermic as well. The enthalpy of *n*-propyl radical decay is equal to 99 kJ mol^{-1}. These reactions are important in gas-phase thermolysis of hydrocarbons[1] and occur very slowly at moderate temperatures 300–450 K.

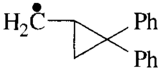
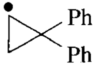
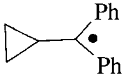
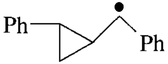
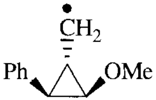
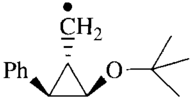
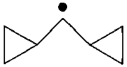
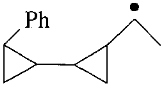
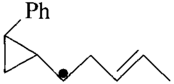
TABLE 16.10 Rate Constants and Activation Energies of Decyclization of Alkyl, Aminyl, and Alcoxyl Radicals

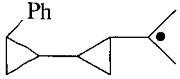
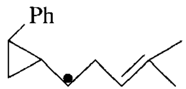
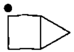
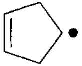
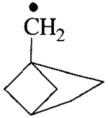
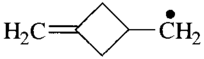
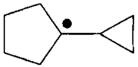
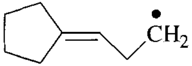
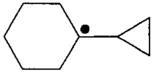
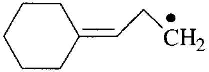
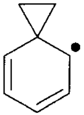
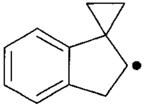
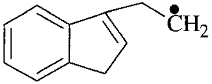
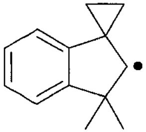
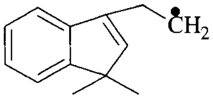
$R_i^\bullet$ (Reactant)	$R_f^\bullet$ (Product)	T (K)	E, (kJ mol^{-1})	log A, A (s^{-1})	k (298 K) (s^{-1})	References
			Radicals with Three-Membered Cycle			
	$CH_2{=}CHCH_2C^\bullet H_2$	128–362	28.4	13.0	1.05×10^8	91–96
	$CH_2{=}CMeCH_2C^\bullet H_2$	310–358	31.0	13.15	5.20×10^7	96
	$CH_2{=}CHCH_2C^\bullet HMe$	310–378	25.5	13.00	3.39×10^8	96,97
	$CH_2{=}CHCH_2C^\bullet HMe$	333–379	31.4	13.50	9.91×10^7	96,97
	$CH_2{=}C(CH_2Br)CH_2C^\bullet H_2$	318			2.6×10^8	98
	$CH_2{=}CHCH_2C^\bullet Me_2$	195–379	30.1	13.2	8.39×10^7	96,99
	$CH_2{=}CMeCH_2C^\bullet Me_2$	310–358	26.8	12.85	1.42×10^8	96
	$CH_2{=}CMeCMe_2C^\bullet Me_2$	310–358	20.5	13.15	3.60×10^9	96

	$MeCH{=}CHCH_2C^{\bullet}H_2$	310–353	32.2	13.2	3.60 × 10^7	96,100
	$Me_2C{=}CHCH_2C^{\bullet}H_2$	298–358	32.8	13.4	4.47 × 10^7	96,100,101
	$Me(CH_2Mu)C{=}CHCH_2C^{\bullet}H_2$	233–382	42.1	14.5	1.31 × 10^7	102
	$MeCH{=}CEtCH_2C^{\bullet}H_2$	310	32.1	13.15	5.4 × 10^7	96
	$MeCH{=}CH(C^{\bullet}H_2)Et$	310	28.0	12.85	1.4 × 10^8	96
	$MeCH{=}CHCH_2C^{\bullet}HEt$	310	23.4	12.85	8.6 × 10^8	96
	$Me_3CCH{=}CHC^{\bullet}H_2$	243			1.0 × 10^3	103
	$CH_2{=}CHCH(OMe)C^{\bullet}HPh$	225–298	14.0	13.94	3.06 × 10^{11}	104,105
	$CH_2{=}CHCH_2C^{\bullet}HPh$	225–298	13.0	13.90	4.18 × 10^{11}	104
	$PhCH{=}CHCH_2C^{\bullet}H_2$	315–353	52.7	14.0	5.79 × 10^4	100,106
	$PhCH{=}CHCH_2C^{\bullet}H_2$	280–321	47.7	13.3	8.69 × 10^4	37

(continued overleaf)

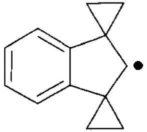
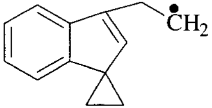
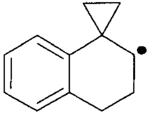
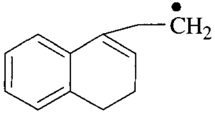
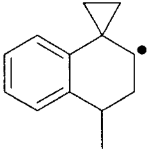
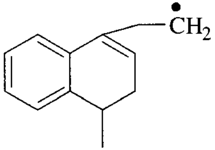
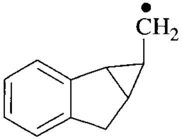
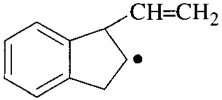
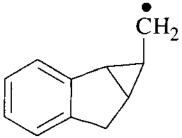
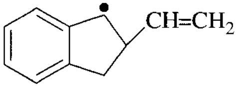
TABLE 16.10 (*continued*)

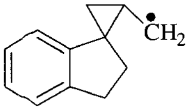
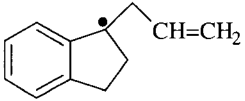
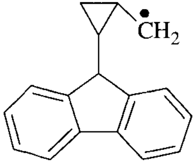
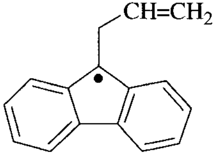
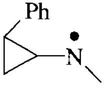
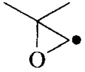
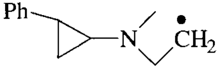
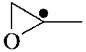
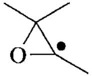
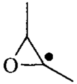
$R_i^\bullet$ (Reactant)	$R_f^\bullet$ (Product)	T (K)	E, (kJ mol^{-1})	log A, A (s^{-1})	k (298 K) (s^{-1})	References
	$CH_2{=}CHCH_2C^{\bullet}Ph_2$	225–298	8.4	13.10	4.24×10^{11}	105
	$Ph_2C^{\bullet}CH{=}CH_2$	351			4.0×10^{6}	107
	$C^{\bullet}H_2CH_2CH{=}CPh_2$	277–309	51.9	12.3	1.6×10^{3}	37
	$PhC^{\bullet}HCH_2CH{=}CHPh$	313			3.8×10^{8}	108
	$PhC^{\bullet}HCH(OMe)CH{=}CH_2$	252–311	15.2	14.55	7.70×10^{11}	109
	$PhC^{\bullet}HCH(OCMe_3)CH{=}CH_2$	257–311	16.4	14.54	4.63×10^{11}	109
		333–353	36.0	13.6	1.95×10^{7}	100
		284			5.6×10^{7}	110

		283			3.0×10^7	110
		200–303	22.2	13.1	2.1×10^9	96,111
		161–333	29.7	12.3	1.24×10^7	112,113
		298–331	29.3	12.3	1.46×10^7	114
		298			1.1×10^7	114
	$PhCH_2C^{\bullet}H_2$	108–198	11.7	9.2	1.41×10^7	115
		348			2.1×10^9	116
		348			8.6×10^9	116

(continued overleaf)

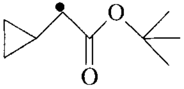
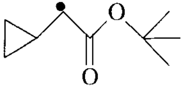
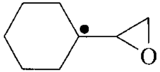
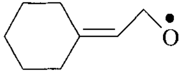
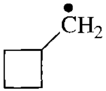
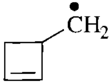
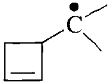
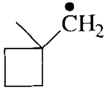
TABLE 16.10 (*continued*)

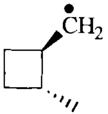
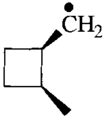
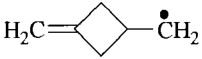
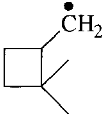
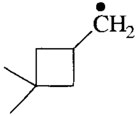
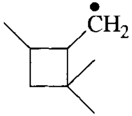
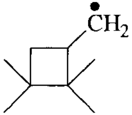
$R_i^\bullet$ (Reactant)	$R_f^\bullet$ (Product)	T (K)	E, (kJ mol^{-1})	log A, A (s^{-1})	k (298 K) (s^{-1})	References
		348			5.3×10^8	116
		348			3.0×10^9	116
		348			3.6×10^9	116
		228–326	13.4	13.6	1.78×10^{11}	117
		195–327	14.2	13.9	2.58×10^{11}	117

		195–298	7.1	13.0	5.70×10^{11}	117
		193–296	8.8	14.3	5.72×10^{12}	117
	$PhC^{\bullet}HCH_2CH{=}NMe$	227–323	15.0	14.5	7.43×10^{11}	118
	$Me_2C^{\bullet}HCH(O)$	193			1.0×10^{3}	103
	$MeN{=}CH(CH_2)_3C^{\bullet}HPh$	300			9.0×10^{4}	119
	$MeC(O)C^{\bullet}H_2$	273			1.0×10^{3}	103
	$Me_2C^{\bullet}C(O)Me$	228			1.0×10^{3}	103
	$MeC^{\bullet}HC(O)Me$	238			1.0×10^{3}	103

(*continued overleaf*)

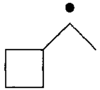
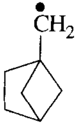
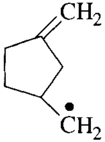
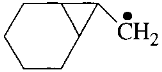
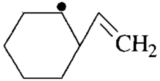
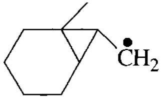
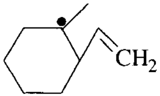
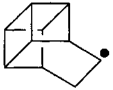
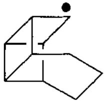
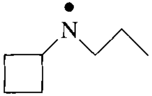
TABLE 16.10 (*continued*)

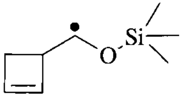
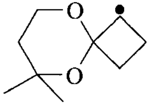
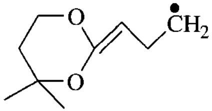
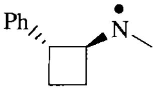
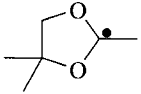
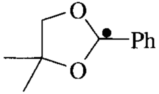
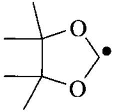
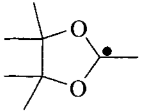
$R_i^\bullet$ (Reactant)	$R_f^\bullet$ (Product)	T (K)	E, (kJ mol^{-1})	log A, A (s^{-1})	k (298 K) (s^{-1})	References
	(Z)-$Me_3COC(O)CH{=}CH\ CH_2C^\bullet H_2$	284–332	51.9	14.0	8.00×10^4	100
	(E)-$Me_3COC(O)CH{=}CH\ CH_2C^\bullet H_2$	284–332	44.8	13.7	7.04×10^5	100
		298			3.2×10^{10}	120
	Radicals with Four-Membered Cycle					
	$CH_2{=}CH(CH_2)_2C^\bullet H_2$	148–363	48.3	13.43	9.20×10^4	121–123
	$CH_2{=}CHC^\bullet HCH{=}CH_2$	214–298	42.2	12.23	6.81×10^4	112,113
	$Me_2C{=}CH(CH_2)_2C^\bullet H_2$	273–333	58.1	13.63	2.79×10^3	121,123
	$CH_2{=}CMe(CH_2)_2C^\bullet H_2$	333	54.4	14.90	2.30×10^6	121

	$CH_2{=}CH(CH_2)_2C^{\bullet}HMe$	333–363	48.5	15.06	3.62×10^6	121
	$CH_2{=}CH(CH_2)_2C^{\bullet}HMe$	333–363	44.8	15.26	2.55×10^7	121
	$CH_2{=}CHCH_2C(C^{\bullet}H_2){=}CH_2$	211–400	48.1	12.9	2.94×10^4	123,124
	$Me_2C^{\bullet}(CH_2)_2CH{=}CH_2$	333–363	39.3	15.27	2.41×10^8	121
	$CH_2{=}CHCH_2CMe_2C^{\bullet}H_2$	333–363	56.9	14.88	8.06×10^4	121
	$CH_2{=}CHCHMeCH_2C^{\bullet}Me_2$	333–363	38.9	15.32	3.17×10^8	121
	$CH_2{=}CHCH_2CMe_2C^{\bullet}Me_2$	333–363	42.2	15.37	9.40×10^7	121

(*continued overleaf*)

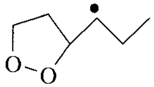
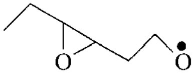
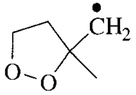
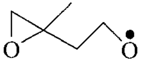
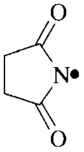
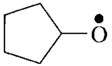
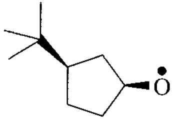
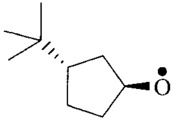
TABLE 16.10 (*continued*)

$R_i^\bullet$ (Reactant)	$R_f^\bullet$ (Product)	T (K)	E, (kJ mol^{-1})	log A, A (s^{-1})	k (298 K) (s^{-1})	References
	E – MeCH=CH(CH$_2$)$_2$C$^\bullet$H$_2$	333–363	54.4	14.54	1.01×10^5	121
		195–228	38.9	12.0	1.52×10^5	111
		298			3.0×10^8	92
		273			5.0×10^7	92
		413–493	56.5	13.6	4.97×10^3	125
	C$^\bullet$H$_2$(CH$_2$)$_2$CH=NPr	198–247	43.9	12.8	1.27×10^5	126

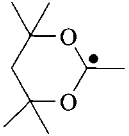
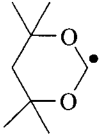
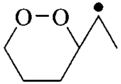
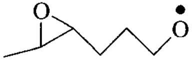
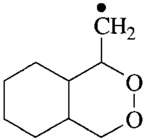
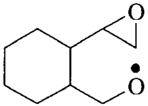
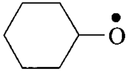
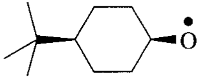
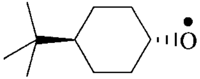
	$CH_2{=}CHC^{\bullet}HCH{=}CHOSiMe_3$	214–247	45.1	12.23	2.11 × 10^4	122
		199–224	43.9	12.5	6.38 × 10^4	127
	$PhC^{\bullet}H(CH_2)_2CH{=}NMe$	227–323	24.7	13.2	7.42 × 10^8	118
		Radicals with Five-Membered Cycle				
	$MeC(O)OCH_2C^{\bullet}Me_2$	279–348	61.1	13.0	1.93 × 10^2	127,128
	$PhC(O)OCH_2C^{\bullet}Me_2$	328–363	66.9	13.0	0.19	127
	$Me_2C^{\bullet}CMe_2OCH(O)$	345			9.0 × 10^3	128
	$Me_2C^{\bullet}CMe_2OCH(O)$	345			5.25 × 10^3	128

(*continued overleaf*)

TABLE 16.10 (*continued*)

$R_i^\bullet$ (Reactant)	$R_f^\bullet$ (Product)	T (K)	E, (kJ mol^{-1})	log A, A (s^{-1})	k (298 K) (s^{-1})	References
		298			1.8×10^5	129
		298			2.0×10^4	129
	$C(O){=}NC(O)CH_2C^\bullet H_2$	298			8.0×10^4	130
	$CH(O)(CH_2)_3C^\bullet H_2$	279–353	26.2	12.55	9.07×10^7	131
	$CH(O)(CH_2)_2CH(CMe_3)C^\bullet H_2$	353			7.8×10^7	132
	$CH(O)(CH_2)_2CH(CMe_3)C^\bullet H_2$	353			1.2×10^8	132

Radicals with Six-Membered Cycle

	$\mathrm{MeC(O)OCMe_2CH_2C^{\bullet}Me_2}$	313–349	33.4	8.7	7.00×10^2	128
	$\mathrm{CH(O)OCMe_2CH_2C^{\bullet}Me_2}$	304–348	31.4	9.4	7.87×10^3	128
		298			2.10×10^6	129
		298			2.4×10^4	129
	$\mathrm{CH(O)(CH_2)_4C^{\bullet}H_2}$	353	38.5	6.7	1.1×10^7	133
	$\mathrm{CH(O)(CH_2)_2CH(CMe_3)CH_2C^{\bullet}H_2}$	353			8.2×10^6	132
	$\mathrm{CH(O)(CH_2)_2CH(CMe_3)CH_2C^{\bullet}H_2}$	353			3.1×10^6	132

16.4.2 Acetyl Radicals

Acetyl radicals are produced as a result of the following reactions. They are produced in the reactions of free radicals with aldehydes, for example,

$$R^1O^{\bullet} + RC(O)H \rightarrow RC^{\bullet}(O) + R^1OH$$

and in reactions of the addition of alkyl radicals to carbon monoxide.[61] Fragmentation of acetyl radicals:[61]

$$RC^{\bullet}(O) \rightarrow R^{\bullet} + CO$$

occurs with a sufficient rate at moderate temperatures (see Table 16.11). Endothermicity of acyl radical fragmentation is not as high as that of alkyl radicals. For example, acetyl radical splits into methyl radical and carbon monoxide with $\Delta H = 47\ \mathrm{kJ\,mol^{-1}}$.

16.4.3 Alkoxyl Radicals

Alkoxyl radicals are generated by decompositions of alkyl peroxides, peresters, and alkyl nitrites (see Chapters 4, 6, and 8) and from hypochlorites via the reaction[135]

$$ROCl + R^{1\bullet} \rightarrow RO^{\bullet} + R^1Cl$$

They are very active in reactions of hydrogen-atom abstraction from different organic compounds (see Chapter 18). Alkoxyl radicals are unstable at elevated temperatures and are decomposed by splitting of α-C−C bond with formation of a carbonyl compound and an alkyl radical, for example,[134]

$$(CH_3)_3CO^{\bullet} \rightarrow C^{\bullet}H_3 + CH_3C(O)CH_3$$

The enthalpy of this reaction is equal to $65\ \mathrm{kJ\,mol^{-1}}$. For rate constants and activation energies for decay of alkoxyl radicals, see Table 16.11.

16.4.4 Carboxyl Radicals

Carboxyl (acetoxyl) radicals are produced as a result of the decomposition of peresters and diacyl peroxides (see Chapter 5). Decomposition of acetyloxyl radicals is exothermic and occurs very rapidly (see Table 16.11). Reaction

$$CH_3C(O)O^{\bullet} \rightarrow C^{\bullet}H_3 + CO_2$$

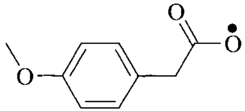
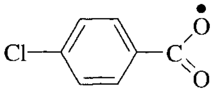
occurs with $\Delta H = -35\ \mathrm{kJ\,mol^{-1}}$ and the rate constant $k(298\ \mathrm{K}) = 2 \times 10^9\ \mathrm{s^{-1}}$.

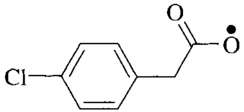
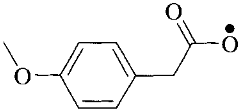
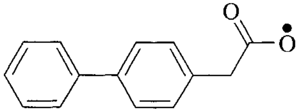
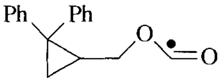
TABLE 16.11 Rate Constants for Decompositions of Free Radicals

$\mathrm{R^1R^2R^3CO^\bullet}$	Solvent	T (K)	E ($\mathrm{kJ\,mol^{-1}}$)	log A, A ($\mathrm{s^{-1}}$)	k(298 K) ($\mathrm{s^{-1}}$)	References
$R^1R^2R^3CO^\bullet \rightarrow R^1C(O)R^2 + R^{3\bullet}$						
$\mathrm{EtCH_2O^\bullet}$	Trichloroethylene	303–343	30.4	13.53	1.59×10^8	135
$\mathrm{EtMeCHO^\bullet}$	Trichloroethylene	303–343	22.8	12.74	5.54×10^8	135
$\mathrm{Me_2CHCH_2O^\bullet}$	Trichloroethylene	303–343	19.3	11.16	5.98×10^7	135
$\mathrm{Me_3CCH_2O^\bullet}$	Trichloroethylene	303–343	19.3	11.16	5.98×10^7	135
$\mathrm{(Me_2CH)MeCHO^\bullet}$	Trichloroethylene	303–343	20.3	12.96	2.52×10^9	135
$\mathrm{Me_3CO^\bullet}$	Water	298			1.36×10^6	136
$\mathrm{EtMe_2CO^\bullet}$	Trichloroethylene	303–343	21.6	13.17	2.42×10^9	135
$\mathrm{(Me_2CH)Me_2CO^\bullet}$	Trichloroethylene	303–323	19.3	13.26	7.53×10^9	135
$\mathrm{Me_2(CN)CO^\bullet}$	Chlorobenzene	353			1.6×10^5	137
$\mathrm{PhMe_2CO^\bullet}$	Chlorobenzene	303–373	36.0	12.36	1.12×10^6	138
$\mathrm{PhMe_2CO^\bullet}$	Carbon tetrachloride	303			2.63×10^5	139
$\mathrm{PhMe_2CO^\bullet}$	Benzene	303			3.75×10^5	139
$\mathrm{PhMe_2CO^\bullet}$	Chlorobenzene	303			5.54×10^5	139
$\mathrm{PhMe_2CO^\bullet}$	*tert*-Butanol	303			5.84×10^5	139
$\mathrm{PhMe_2CO^\bullet}$	Acetonitrile	303			6.33×10^5	139
$\mathrm{PhMe_2CO^\bullet}$	Acetic acid	303			1.96×10^6	139
$\mathrm{PhCH_2CH_2O^\bullet}$	Chlorobenzene	234–308	20.2	10.89	2.23×10^7	135,140
$\mathrm{HOCH_2CH(O^\bullet)CH{=}CH_2}$	Gas phase	298			3.10×10^6	141
$\mathrm{HOCH_2CMe(O^\bullet)CH{=}CH_2}$	Gas phase	298			9.30×10^6	141
$\mathrm{{}^\bullet OCH_2CH(OH)CH{=}CH_2}$	Gas phase	298			2.70×10^8	141
$\mathrm{{}^\bullet OCH_2CMe(OH)CH{=}CH_2}$	Gas phase	298			6.30×10^8	141

(continued overleaf)

TABLE 16.11 (*continued*)

$R^1R^2R^3CO^\bullet$	Solvent	T (K)	E (kJ mol^{-1})	log A, A (s^{-1})	k(298 K) (s^{-1})	References
		$RC(O)O^\bullet \rightarrow R^\bullet + CO_2$				
$MeCO_2^\bullet$	Octadecane	313–373	27.6	13.54	5.0×10^8	142
$MeCO_2^\bullet$	Acetyl isobutyryl peroxide	333			2.6×10^9	143
$MeCO_2^\bullet$	Hexachloro-2-propanone	383			3.0×10^9	144
$EtCO_2^\bullet$	Carbon tetrachloride	343			3.3×10^{10}	145
$EtCO_2^\bullet$	Methanol	293			2.0×10^9	146
$Me_2CHCO_2^\bullet$	Methanol	293			6.5×10^9	146
$Me_3CCO_2^\bullet$	Methanol	293			1.1×10^{10}	146
$MeCC{\equiv}CCO_2^\bullet$	Acetonitrile	293			5.0×10^5	147
(E)-$PhCH{=}CHCO_2^\bullet$	Acetonitrile	293			1.0×10^6	148
$PhCO_2^\bullet$	Carbon tetrachloride	259–293	21.0	10.3	4.16×10^6	147
$PhCO_2^\bullet$	Carbon tetrachloride	252–326	36.0	12.6	1.95×10^6	149
$PhCO_2^\bullet$	Freon-113	328			1.0×10^5	150
	Carbon tetrachloride	294–329	38.5	12.3	3.56×10^5	151
	Carbon tetrachloride	297			1.4×10^6	151

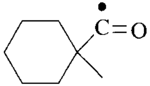
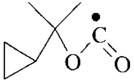
$PhC\equiv CCO_2^\bullet$	Acetonitrile	293			2.0 × 10^5	148
$PhCH_2CO_2^\bullet$	Methanol	293			5.5 × 10^9	146
	Water	298			1.6 × 10^9	152
	Water	298			1.5 × 10^9	152
	Water	298			1.5 × 10^9	152
$PhCH_2CH_2CO_2^\bullet$	Methanol	293			2.3 × 10^9	146
$Ph_2CHCO_2^\bullet$	Water	298			6.1 × 10^9	153
$Ph_2C(OH)CO_2^\bullet$	Water	296			8.0 × 10^{11}	153
	Tetrahydrofuran	276–321	40.2	12.2	1.42 × 10^5	154

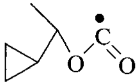
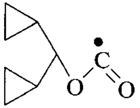
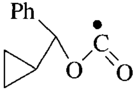
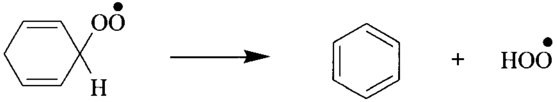
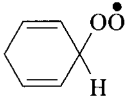
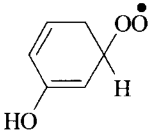
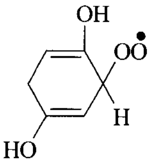
$$R^1OOCH_2C^\bullet HR \rightarrow R^1O^\bullet + cyclo\text{-}[OCH_2CHR]$$

$Me_3COOCH_2C^\bullet H_2$	Benzene	298			2.0 × 10^3	155
$Me_3COOCHMeC^\bullet H_2$	Benzene	298			4.0 × 10^4	155
$Me_3COOCMe_2C^\bullet H_2$	Benzene	298			7.0 × 10^5	155

(*continued overleaf*)

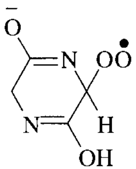
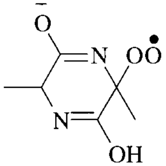
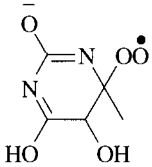
TABLE 16.11 (*continued*)

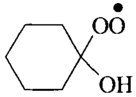
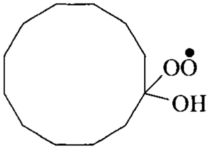
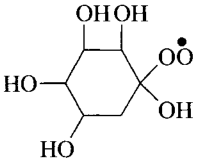
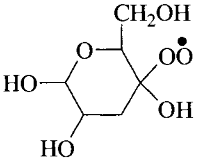
$R^1R^2R^3CO^\bullet$	Solvent	T (K)	E (kJ mol^{-1})	log A, A (s^{-1})	k(298 K) (s^{-1})	References
			$RC^\bullet(O) \rightarrow R^\bullet + C{=}O$			
$CH_3C^\bullet(O)$	Gas		62.8	10.3	0.29	134
$EtC^\bullet\ (O)$	Gas		61.1	13.1	2.46×10^2	156
$EtPrCHC^\bullet(O)$	Toluene		50.2	12.0	1.59×10^3	157
	Hexane		41.8	13.1	5.93×10^3	157
$Me_3CC^\bullet(O)$	Hexane	297			7.0×10^5	158
$Me_2CHC^\bullet(O)$	Tetraethylsilane	313–353	54.5	14.0	2.80×10^4	159
$HOCH_2C^\bullet(O)$	Acetonitrile/water	268–313	37.0	11.0	3.27×10^4	160
$PhCH_2C^\bullet(O)$	Isooctane	245–331	37.2	12.0	8.1×10^8	161
$PhCH_2C^\bullet(O)$	Cyclopropane	157			9.0×10^2	162
$PhMeCHC^\bullet(O)$	Isooctane	223–251	25.9	12.2	4.2×10^7	163
$C_{11}H_{24}C^\bullet(O)$	Toluene	323–433	61.1	13.1	2.46×10^2	157
$PhMe_2CC^\bullet(O)$	Isooctane	178–203	17.1	11.2	1.5×10^8	163
			$ROC^\bullet(O) \rightarrow R^\bullet + CO_2$			
$Me_3COC^\bullet(O)$	Heptane	240			1.3×10^3	164
$Me_3COC^\bullet(O)$	*tert*-Butyl peroxide	240–286	45.2	13.2	1.89×10^5	165
$PhOC^\bullet(O)$	Cyclohexane	315	23.8	11.9	5.35×10^7	166
$PhCH_2OC^\bullet(O)$	Tetrahydrofuran	274–304	29.3	13.0	7.3×10^7	154
	Cyclohexane	298–353	32.6	12.9	1.53×10^7	166

	Cyclohexane	353			1.6×10^7	166
	Cyclohexane	333–353	36.8	13.2	5.62×10^6	166
	Cyclohexane	315–353	21.8	12.9	1.20×10^9	166
						
	Water	298			8.0×10^5	167
	Water, pH = 1	292			2.0×10^8	168
	Water, pH = 3.9	292			8.0×10^3	168

(continued overleaf)

TABLE 16.11 (*continued*)

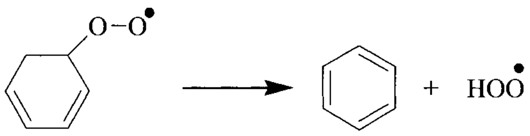
$R^1R^2R^3CO^\bullet$	Solvent	T (K)	E (kJ mol^{-1})	log A, A (s^{-1})	k(298 K) (s^{-1})	References
	Water, pH = 11.7	298			1.6×10^5	169
	Water, pH = 11.7	298			3.7×10^6	170
	Water, pH = 8–11	298			8.3×10^8	170
		$RCH(OH)OO^\bullet \rightarrow RCH(O) + HO_2^\bullet$				
$CH_2(OH)OO^\bullet$	Methanol/water	295			10.0	171
$MeCH(OH)OO^\bullet$	Ethanol/water	295			52.0	171
$Me_2C(OH)OO^\bullet$	Isopronanol/water	295			6.6×10^2	171
$Me_2C(OD)OO^\bullet$	Isopropanol(OD)/water	295			1.9×10^2	171

	Cyclohexanol	299–387	42.9	10.7	1.5×10^3	172
	Dodecanol	368–408	54.0	11.2	54.0	172
$(CO_2^-)_2C(OH)OO^\bullet$	Water, pH = 5.6	293			1.1×10^4	173
$CH_2(OH)CH(OH)OO^\bullet$	Water	295			1.9×10^2	174
$HOCH_2CH(OH)CH(OH)OO^\bullet$	Water	295			2.1×10^2	174
	Water, pH = 5.5	295			4.7×10^2	174
$HOCH_2(CHOH)_2CH(OH)OO^\bullet$	Water, pH = 5.5	295			1.9×10^2	174
$HOCH_2(CHOH)_3CH(OH)OO^\bullet$	Water, pH = 5.5	295			2.2×10^2	174
$HOCH_2(CHOH)_4CH(OH)OO^\bullet$	Water, pH = 5.5				2.1×10^2	174
$HOCH_2CH(O)(CHOH)_3CH(OH)OO^\bullet$	Water, pH = 5.5	295			4.0×10^2	174
	Water, pH = 5.5	295			4.0×10^2	174

16.4.5 Peroxyl Radicals

Peroxyl radicals are produced in the result of dioxygen addition to alkyl radicals. The formed C—O bond has the BDE > 100 kJ mol^{-1} and alkyl radicals are stable at moderate temperatures ($T < 450$ K).[176] In the case of allyl and benzyl radicals, the C—O bond is weaker (60–80 kJ mol^{-1}) and these $RO_2^\bullet$ are unstable at elevated temperatures ($T > 360$ K).

Peroxyl radicals formed from cyclohexadienyl compounds are unstable and decomposed with elimination of the hydroperoxyl radical.[175]



For rate constants for such reactions of elimination, see Table 16.11.

A similar reaction for $HO_2^\bullet$ elimination occurs with α-hydroxyperoxyl radicals formed as the result of alcohol oxidation.[175]

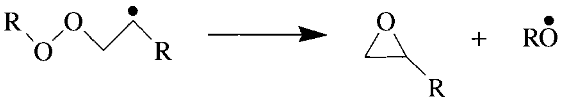
$$Me_2C(OH)OO^\bullet \rightarrow MeC(O)Me + HO_2^\bullet$$

The reaction to substitute the peroxyl radicals by hydroperoxyl radicals in oxidized alcohol occurs rapidly at elevated temperatures. The same reaction takes place with α-aminoperoxyl radicals.

$$RNHCH(OO^\bullet)R^1 \rightarrow RN{=}CHR^1 + HO_2^\bullet$$

The values of rate constants of these reactions are in Table 16.11.

The β-peroxyalkyl radicals are decomposed with splitting of the O—O bond and elimination of epoxide.[175]



The rate constants of two such reactions are in Table 16.11.

REFERENCES

1. K. J. Laidler and L. F. Loucks, in *Comprehensive Chemical Kinetics*, C. H. Bamford and C. F. H. Tipper (Eds.), Elsevier, Amsterdam, The Netherlands, 1972, Vol. 5, p. 1.
2. G. C. Eastmond, in *Comprehensive Chemical Kinetics*, C. H. Bamford and C. F. H. Tipper (Eds.), Elsevier, Amsterdam, The Netherlands, 1976, Vol. 14, p. 104.
3. E. T. Denisov, in *Handbook of Polymer Degradation*, S. H. Hamid (Ed.), Marcel Dekker, New York, 2000, p. 383.

4. E. T. Denisov and V. V. Azatyan, *Inhibition of Chain Reactions*, Gordon and Breach, London, 2000.
5. T. G. Denisova and E. T. Denisov, *Kinet. Catal.* **42**, 620 (2001).
6. N. V. Blinova, L. V. Il'inskaya, N. V. Kruglova, and R. G. Gasanov, *Kinet. Katal.* **31**, 1314 (1990).
7. N. V. Blinova and R. G. Gasanov, *Kinet. Katal.* **31**, 524 (1990).
8. R. G. Gasanov and N. V. Blinova, *Izv. AN SSSR, Ser. Khim.* 2512 (1988).
9. R. G. Gasanov, L. V. Ivanova, and R. Kh. Freidlina, *Izv. AN SSSR, Ser. Khim.* 2810 (1979).
10. A. L. J. Beckwith and K. D. Raner, *J. Org. Chem.* **57**, 4954 (1992).
11. G. Brunton, D. Griller, L. R. C. Barclay, and K. U. Ingold, *J. Am. Chem. Soc.* **98**, 6803 (1976).
12. P. R. Marriott and D. Griller, *J. Am. Chem. Soc.* **103**, 1521 (1981).
13. J. A. Howard and J. C. Scaiano, in *Radical Reaction Rates in Liquids*, Landolt-Bornstein New series, Group 2 (Atomic and Molecular Physics), H. Fischer (Ed.), Springer-Verlag, Berlin, 1984, Vol. 13, subvolume (d).
14. J. K. Kochi, in *Free Radicals*, J. K. Kochi (Ed.), John Wiley & Sons, Inc. New York, 1973, Vol. 2, p. 665.
15. J. A. Howard and K. U. Ingold, *Can. J. Chem.* **48**, 873 (1970).
16. N. A. Kravchuk, *Reactivity of oxygen- and nitrogen-containing compounds in mono- and bimolecular reactions of chain propagation*, Ph.D. Thesis (Russian), Institute of Physical Chemistry, L'vov, USSR, 1987.
17. S. G. Voronina, L. V. Krutskaya, A. L. Perkel', and B. G. Freidin, *Zh. Prikl. Khim.* **63**, 1376 (1990).
18. T. Mill and G. Montorsi, *Int. J. Chem. Kinet.* **5**, 119 (1973).
19. M. N. Schuchmann and C. von Sonntag, *Z. Naturforsch. B, Chem. Sci.* **42**, 495 (1987).
20. D. E. Van Sickle, T. Mill, and F. R. Mayo, *J. Org. Chem.* **38**, 4435 (1973).
21. I. N. Demidov and V. M. Solyanikov, *Neftekhimiya* **24**, 406 (1986).
22. R. K. Jensen, S. Korcek, L. R. Mahoney, and M. Zinbo, *J. Am. Chem. Soc.* **103**, 1742 (1981).
23. D. E. Van Sickle, *J. Org. Chem.* **37**, 755 (1972).
24. I. A. Opeida, V. I. Timokhin, and V. F. Galat, *Teor. Eksp. Khim.* **14**, 554 (1978).
25. E. J. Hamilton, S. Korcek, L. R. Mahoney, and M. Zinbo, *Int. J. Chem. Kinet.* **12**, 577 (1980).
26. A. L. Perkel', *Degradation of oxygen-containing aliphatic and aromatic compounds in oxidative processes*, Doctor Diss. Thesis (Russian), Technological Institute, St. Petersburg, Russia, 1992.
27. R. K. Jensen, S. Korcek, and M. Zinbo, *J. Am. Chem. Soc.* **114**, 7742 (1992).
28. Z. F. Sharafutdinova, V. S. Martem'yanov, and I. M. Borisov, *Kinet. Katal.* **29**, 553 (1988).
29. J. W. Wilt, in *Free Radicals*, J. K. Kochi (Ed.), John Wiley & Sons, Inc. New York, 1973, Vol. 1, p. 333.
30. D. P. Curran, N. A. Porter, and B. Giese, *Stereochemistry of Radical Reactions*, CH, Weinheim, Germany, 1995.

31. A. L. J. Beckwith and C. H. Schiesser, *Tetrahedron* **41**, 3925 (1985).
32. D. C. Spellmeyer and K. N. Houk, *J. Org. Chem.* **52**, 959 (1987).
33. C. Chatgilialoglu and P. Renaud, in *General Aspects of the Chemistry of Radicals*, Z. B. Alfassi (Ed.), John Wiley & Sons, Inc., Chichester, 1999, p. 501.
34. T. G. Denisova and E. T. Denisov, *Russ. Chem. Bull.* 949 (2002).
35. A. L. J. Beckwith and V. W. Bowry, *J. Org. Chem.* **54**, 2681 (1989).
36. A. Effio, D. Griller, K. U. Ingold, A. L. J. Beckwith, and A. K. Serelis, *J. Am. Chem. Soc.* **102**, 1734 (1980).
37. T. A. Halgren, J. D. Roberts, J. H. Horner, F. N. Martinez, Ch. Tronche, and M. Newcomb, *J. Am. Chem. Soc.* **122**, 2988 (2000).
38. E. Furxhi, J. H. Horner, and M. Newcomb, *J. Org. Chem.* **64**, 4064 (1999).
39. E. C. Friedrich and R. L. Holmstead, *J. Org. Chem.* **37**, 2550 (1972).
40. P. Schmid and K. U. Ingold, *J. Am. Chem. Soc.* **100**, 2493 (1978).
41. A. L. J. Beckwith, I. A. Blair, and G. Phillipou, *Tetrahedron Lett.* **N. 26**, 2251 (1974).
42. D. Lal, D. Griller, S. Husband, and K. U. Ingold, *J. Am. Chem. Soc.* **96**, 6355 (1974).
43. J. W. Wilt, J. Lusztyk, M. Peeran, and K. U. Ingold, *J. Am. Chem. Soc.* **110**, 281 (1988).
44. A. L. J. Beckwith, *Tetrahedron.* **37**, 3073 (1981).
45. A. L. J. Beckwith, T. Lawrence, and A. K. Serelis, *J. Chem. Soc., Chem. Commun.* **N. 11**. 484 (1980).
46. A. L. J. Beckwith, C. J. Easton, T. Lawrence, and A. K. Serelis, *Aust. J. Chem.* **36**, 545 (1983).
47. A. L. J. Beckwith and C. H. Schiesser, *Tetrahedron* **41**, 3925 (1985).
48. C. Walling and A. Cioffari, *J. Am. Chem. Soc.* **94**, 6064 (1972).
49. A. L. J. Beckwith and T. Lawrence, *J. Chem. Soc., Perkin Trans. 2*, 1535 (1979).
50. A. L. J. Beckwith and V. W. Bowry, *J. Org. Chem.* **53**, 1632 (1988).
51. J. W. Wilt, *Tetrahedron* **41**, 3979 (1985).
52. A. L. J. Beckwith and G. Moad, *J. Chem. Soc., Perkin Trans. 2*, 1726 (1975).
53. M. Newcomb, T. R. Varick, C. Ha, M. B. Manek, and X. Yue, *J. Am. Chem. Soc.* **114**, 8158 (1992).
54. C. Ha, J. H. Horner, M. Newcomb, T. R. Varick, B. R. Arnold, and J. Lusztyk, *J. Org. Chem.* **58**, 1194 (1993).
55. M. Newcomb and S. Y. Choi, *J. Org. Chem.* **64**, 1225 (1999).
56. C. C. Johnson, J. H. Horner, C. Tronche, and M. Newcomb, *J. Am. Chem. Soc.* **117**, 1684 (1995).
57. M. Newcomb, J. H. Horner, M. A. Filipkowski, C. Ha, and Seung-Un Park. *J. Am. Chem. Soc.* **117**, 3674 (1995).
58. P. E. Pigou, *J. Org. Chem.* **54**, 4943 (1989).
59. J. W. Wilt, S. N. Massie, and R. B. Dabek, *J. Org. Chem.* **35**, 2803 (1970).
60. F. MacCorquodale and J. C. Walton, *J. Chem. Soc., Perkin Trans. 1*, 347 (1989).
61. C. Chatgilialoglu, D. Chrich, M. Komatsu, and I. Ryu, *Chem. Rev.* **99**, 1991 (1999).
62. A. L. J. Beckwith and S. A. Glover, *Aust. J. Chem.* **40**, 157 (1987).
63. T. W. Smith and G. B. Butter, *J. Org. Chem.* **43**, 6 (1978).

64. A. L. J. Beckwith, I. A. Blair, and G. Phillipou, *J. Am. Chem. Soc.* **96**, 1613 (1974).
65. A. C. Hindson, F. MacCorquodale, and J. C. Walton, *J. Chem. Soc., Perkin Trans. 2*, 871 (1993).
66. C. F. Sturino and A. G. Fallis, *J. Org. Chem.* **59**, 6514 (1994).
67. W. R. Dolbier, *Chem. Rev.* **96**, 1557 (1996).
68. A. Li, A. B. Shtarev, B. E. Smart, Z.-Y. Yang, J. Lusztyk, K. U. Ingold, A. Bravo and W. R., Jr. Dolbier, *J. Org. Chem.* **64**, 5993 (1999).
69. J. W. Wilt, *J. Am. Chem. Soc.* **103**, 5251 (1981).
70. A. L. J. Beckwith and G. Moad, *J. Chem. Soc., Chem. Commun.* 472 (1974).
71. J. Lusztyk, B. Maillard, S. Deycard, D. A. Lindsay, and K. U. Ingold, *J. Org. Chem.* **52**, 3509 (1987).
72. C. Chatgilialoglu, C. Ferreri, and A. Sommazzi, *J. Am. Chem. Soc.* **118**, 7223 (1996).
73. A. L. J. Beckwith, V. W. Bowry, and C. H. Schiesser, *Tetrahedron* **47**, 121 (1991).
74. A. Phillippon, M. Degueil-Castaing, A. L. J. Beckwith, and B. Maillard, *J. Org. Chem.* **63**, 6814 (1998).
75. M. Newcomb, O. M. Musa, F. N. Martines, and J. H. Horner, *J. Am. Chem. Soc.* **119**, 4569 (1997).
76. Le Tadic-Biadatti, A.-C. Callier-Dublanchet, J. H. Horner, B. Quidet-Sire, S. Z. Zard, and M. Newcomb, *J. Org. Chem.* **62**, 559 (1997).
77. O. M. Musa, J. H. Horner, H. E. Shahin, and M. Newcomb, *J. Am. Chem. Soc.* **118**, 3862 (1996).
78. J. H. Horner, F. N. Martinez, O. M. Musa, M. Newcomb, and H. E. Shahin, *J. Am. Chem. Soc.* **117**, 11124 (1995).
79. M. Newcomb, N. Takana, A. Bouvier, C. Tronche, J. H. Horner, O. M. Musa, and F. N. Martinez, *J. Am. Chem. Soc.* **118**, 8505 (1996).
80. M. Newcomb. and J. L. Esker, *J. Org. Chem.* **58**, 34933 (1993).
81. C. F. Sturino and A. G. Fallis, *J. Org. Chem.* **59**, 6514 (1994).
82. S. Kim and I. S. Kee, *Tetrahedron Lett.* **34**, 4213 (1993).
83. S. Kim, K. S. Yoon and Y. S. Kim, *Tetrahedron Lett.* **38**, 73 (1997).
84. A. G. Fallis and M. Brinza, *Tetrahedron* **53**, 17543 (1997).
85. D. Griller, P. Schmid, and K. U. Ingold, *Can J. Chem.* **57**, 831 (1979).
86. A. L. J. Beckwith and B. P. Hay, *J. Am. Chem. Soc.* **111**, 2674 (1989).
87. M. J. Tomaszewski and J. Warkentin, *Tetrahedron Lett.* **33**, 2123 (1992).
88. A. L. J. Beckwith, S. Wang, and J. Warkentin, *J. Am. Chem. Soc.* **109**, 5289 (1987).
89. C. P. A. Kunka and J. Warkentin, *Can. J. Chem.* **68**, 575 (1990).
90. S. Kim, K. S. Yoon, and S. S. Kim, *Tetrahedron* **51**, 8437 (1995).
91. M. Newcomb and A. G. Glenn, *J. Am. Chem. Soc.* **111**, 275 (1989).
92. A. L. J. Beckwith and G. Moad, *J. Chem. Soc., Perkin Trans. 2*, 1473 (1980).
93. R. Kaptein, *J. Am. Chem. Soc.* **94**, 6262 (1972).
94. B. Maillard, D. Forrest, and K. U. Ingold, *J. Am. Chem. Soc.* **98**, N. 22, 1026 (1976).
95. L. Mathew and J. Warkentin, *J. Am. Chem. Soc.* **108**, 7981 (1986).
96. V. W. Bowry, J. Lusztyk, and K. U. Ingold, *J. Am. Chem. Soc.* **113**, 5687 (1991).
97. A. L. J. Beckwith and V. W. Bowry, *J. Org. Chem.* **54**, 2681 (1989).

98. A. J. Kennedy, J. C. Walton, and K. U. Ingold, *J. Chem. Soc., Perkin Trans. 2*, 751 (1982).
99. M. Newcomb, A. G. Glenn, and W. G. Williams, *J. Org. Chem.* **54**, 2675 (1989).
100. A. L. J. Beckwith and V. Bowry, *J. Am. Chem. Soc.* **116**, 2710 (1994).
101. P. S. Engel, S.-L. He, J. T. Banks, K. U. Ingold, and J. Lusztyk, *J. Org. Chem.* **62**, 1210 (1997).
102. P. Burkhard, E. Roduner, J. Hochmann, and H. Fischer, *J. Phys. Chem.* **88**, 773 (1984).
103. H. Itzel and H. Fischer, *Helv. Chim. Acta* **59**, 880 (1976).
104. M. Newcomb and M. B. Manek, *J. Am. Chem. Soc.* **112**, 9662 (1990).
105. M. Newcomb, C. Johnson, M. B. Manek, and T. R. Varick, *J. Am. Chem. Soc.* **114**, 10915 (1992).
106. J. Masnov, E. G. Samsel, and R. M. Bullock, *J. Chem. Soc., Chem. Commun.* 1044 (1989).
107. L. J. Johnston, J. Lusztyk, D. D. M. Wayner, A. N. Abeywickreyma, A. L. J. Beckwith, J. C. Scaiano, and K. U. Ingold, *J. Am. Chem. Soc.* **107**, 4594 (1985).
108. R. Hollis, L. Hughes, V. W. Bowry, and K. U. Ingold, *J. Am. Chem. Soc.* **57**, 4284 (1992).
109. M.-H. Le Tadic-Biadatti and M. Newcomb, *J. Chem. Soc., Perkin Trans. 2*, 1467 (1996).
110. M. Newcomb, N. Tanaka, A. Bouvier, C. Tronche, J. H. Horner, O. M. Musa, and F. N. Martinez, *J. Am. Chem. Soc.* **118**, 8505 (1996).
111. M. Newcomb, M. B. Manek, and A. G. Glenn, *J. Am. Chem. Soc.* **113**, 949 (1991).
112. E. W. Della, C. H. Shiesser, D. K. Taylor, and J. C. Walton, *J. Chem. Soc., Perkin Trans. 2*, 1329 (1991).
113. B. P. Branchaud, A. G. Glenn and H. C. Stiasny, *J. Org. Chem.* **56**, 6656 (1991).
114. P. S. Engel and A. M. Culotta, *J. Am. Chem. Soc.* **113**, 2686 (1991).
115. A. Effio, D. Griller, K. U. Ingold, J. C. Scaiano, and S. J. Sheng, *J. Am. Chem. Soc.* **102**, 6063 (1980).
116. R. P. Lemieux and P. Beak, *J. Org. Chem.* **55**, 5454 (1990).
117. A. A. Martin-Esker, C. C. Johnson, J. H. Horner, and M. Newcomb, *J. Am. Chem. Soc.* **116**, 9174 (1994).
118. O. M. Musa, J. H. Horner, H. Shahin, and M. Newcomb, *J. Am. Chem. Soc.* **118**, 3862 (1996).
119. M. Newcomb, O. M. Musa, F. N. Martinez, and J. H. Horner, *J. Am. Chem. Soc.* **119**, 4569 (1997).
120. V. Krishnamurthy and V. H. Rawal, *J. Org. Chem.* **62**, 1572 (1997).
121. A. L. J. Beckwith and G. Moad, *J. Chem. Soc., Perkin Trans. 2*, 1083 (1980).
122. K. U. Ingold, B. Maillard, and J. C. Walton, *J. Chem. Soc., Perkin Trans. 2*, 970 (1981).
123. F. MacCorquodale and J. C. Walton, *J. Chem. Soc., Faraday Trans. 1*, **84**, 3233 (1988).
124. J. C. Walton, *J. Chem. Soc. Perkin Trans. 2*, **N. 2**, 231 (1987).

125. G. T. Binmore, E. W. Della, G. M. Elsey, N. J. Head, and J. C. Walton, *J. Am. Chem. Soc.* **116**, 2759 (1994).
126. Y. Maeda and K. U. Ingold, *J. Am. Chem. Soc.* **102**, 328 (1980).
127. L. R. C. Barclay, D. Griller, and K. U. Ingold, *J. Am. Chem. Soc.* **104**, 4399 (1982).
128. J. M. Perkins, and B. P. Roberts, *J. Chem. Soc., Perkin Trans. 2*, 77 (1975).
129. A. J. Bloodworth, J. L. Courtneidge, and A. Davies, *J. Chem. Soc., Perkin Trans. 2*, 523 (1984).
130. J. Lind, M. Jonsson, T. Eriksen, J. Merenyi, and L. Eberson, *J. Phys. Chem.* **97**, 1610 (1993).
131. A. L. J. Beckwith and B. P. Hay *J. Am. Chem. Soc.* **111**, 230 (1989).
132. A. L. J. Beckwith and K. D. Raner, *J. Org. Chem.* **57**, 4954 (1992).
133. A. L. J. Beckwith and B. P. Hay, *J. Am. Chem. Soc.* **111**, 2674 (1989).
134. S. W. Benson and H. E. O'Neal, *Kinetic Data on Gas Phase Unimolecular Reactions*, NSRDS, Washington, D.C., 1970.
135. C. Walling and R. T. Clark, *J. Am. Chem. Soc.* **96**, 4530 (1974).
136. M. Erben-Russ, C. Michel, W. Bors, and M. Saran, *J. Phys. Chem.* **91**, 2362 (1987).
137. G. Vasvari, E. M. Kuramshin, S. Holly, T. Vidoczy, and D. Gal, *J. Phys. Chem.* **92**, 3810 (1988).
138. A. Baignee, J. A. Howard, L. C. Scaiano, and L. C. Stewart, *J. Am. Chem. Soc.* **105**, 6120 (1983).
139. D. V. Avila, C. E. Brown, K. U. Ingold, and J. Lusztyk, *J. Am. Chem. Soc.* **115**, 466 (1993).
140. G. D. Mendenhall, L. C. Stewart, and J. C. Scaiano, *J. Am. Chem. Soc.* **104**, 5109 (1982).
141. R. Atkinson, *J. Phys. Chem. Ref. Data.* **26**, 215 (1997).
142. W. Braun, L. Rajbenbach, and F. R. Eirich, *J. Phys. Chem.* **66**, 1591 (1962).
143. Yu. V. Glazkov, Ye. A. Turetskaya, and Ye. D. Skakovskii, *Zh. Prikl. Spektrosk.* **28**, 891 (1978).
144. R. Kaptein, J. Brokken-Zijp, and J. J. de Kanter, *J. Am. Chem. Soc.* **94**, 6280 (1972).
145. Ye. A. Turetskaya, Ye. D. Skakovskii, S. V. Rykov, Yu. V. Glazkov, and Yu. A. Oldekop, *Dokl. Akad. Nauk BSSR* **24**, 57 (1980).
146. J. W. Hilborn and J. A. Pincock, *J. Am. Chem. Soc.* **113**, 2683 (1991).
147. S. Yamauchi and N. Hirota, *J. Am. Chem. Soc.* **107**, 5021 (1985).
148. H. G. Korth, J. Chateauneuf, J. Lusztyk, and K. U. Ingold, *J. Org. Chem.* **56**, 2405 (1991).
149. J. Chateauneuf, J. Lusztyk, and K. U. Ingold, *J. Am. Chem. Soc.* **110**, 2877 (1988).
150. L. Grossi, K. U. Ingold, and J. Lusztyk, *J. Org. Chem.* **50**, 5882 (1985).
151. J. Chateauneuf, J. Lusztyk, and K. U. Ingold, *J. Am. Chem. Soc.* **110**, 2886 (1988).
152. T. M. Bockman, S. M. Hubig, and J. K. Kochi, *J. Org. Chem.* **62**, 2210 (1997).
153. T. M. Bockman, S. M. Hubig, and J. K. Kochi, *J. Am. Chem. Soc.* **118**, 4502 (1996).
154. P. A. Simakov, F. N. Martinez, J. H. Horner, and M. Newcomb, *J. Org. Chem.* **63**, 1226 (1998).
155. A. J. Bloodworth, A. G. Davies, I. M. Griffin, B. Muggleton, and B. P. Roberts, *J. Am. Chem. Soc.* **96**, 7599 (1974).

156. J. A. Kerr and A. C. Lloid, *Trans. Faraday Soc.* **63**, 2480 (1967).
157. C. Chatgilialoglu, C. Ferreri, M. Lucarini, P. Pedrielli, and G. F. Pedulli, *Organometallics* **14**, 2672 (1995).
158. I. G. Neville, C. E. Brown, D. M. Rayner, J. Lusztyk, and K. U. Ingold, *J. Am. Chem. Soc.* **113**, 1869 (1991).
159. J. Lipscher and H. Fischer, *J. Phys. Chem.* **88**, 2555 (1984).
160. J. K. Vollenweider and H. Paul, *Int. J. Chem. Kinet.* **18**, 791 (1986).
161. L. Lunazzi, K. U. Ingold, and J. C. Scaiano, *J. Phys. Chem.* **87**, 529 (1983).
162. G. Brunton, H. C. McBay, and K. U. Ingold, *J. Am. Chem. Soc.* **99**, 4447 (1977).
163. N. J. Turro, I. R. Gold, and B. H. Baretz, *J. Phys. Chem.* **87**, 531 (1983).
164. H. Fischer and H. Paul, *Acc. Chem. Res.* **20**, 200 (1987).
165. J. A. Baban, J. P. Goddard, and B. P. Roberts, *J. Chem. Soc., Perkin Trans. 2*, 1269 (1986).
166. A. L. J. Beckwith and V. Bowry, *J. Am. Chem. Soc.* **116**, 2710 (1994).
167. X. M. Pan, M. N. Schuchmann, and C. von Sonntag, *J. Chem. Soc., Perkin Trans. 2*, 1021 (1993).
168. O. I. Micic and M. T. Nenadovic, *J. Phys. Chem.* **80**, 940 (1976).
169. P. Neta, R. E. Huie, and A. B. Ross, *J. Phys. Chem. Ref. Data* **19**, 413 (1990).
170. M. I. Al-Sheikhly, A. Hissung, H. P. Schuchmann, M. N. Schuchmann, C. von Sonntag, A. Garner, and G. Scholes, *J. Chem. Soc., Perkin Trans.* 2, 601 (1984).
171. E. Bothe, G. Behrens, and D. Schulte-Frohlinde, *Z. Naturforsch. B.* **32**, 886 (1977).
172. B. Ya. Ladygin and A. A. Revina, *Izv. AN SSSR, Ser. Khim.* 282 (1985).
173. X. Zhang, N. Zhang, H. P. Schuchmann, and C. von Sonntag, *J. Phys. Chem.* **98**, 6541 (1994).
174. E. Bothe, D. Schulte-Frohlinde, and C. von Sonntag, *J. Chem. Soc., Perkin Trans. 2*, 416 (1978).
175. T. Mill and D. G. Hendry, in *Comprehensive Chemical Kinetics*, C. H. Bamford and C. F. H. Tipper (Eds.), Elsevier, Amsterdam, The Netherlands, 1980, Vol. 16, p. 1.
176. E. T. Denisov and T. G. Denisova, *Handbook of Antioxidants*, CRC Press, Boca Raton, FL, 2000.

Handbook of Free Radical Initiators. E.T. Denisov, T.G. Denisova, T.S. Pokidova
Copyright © 2003 John Wiley & Sons, Inc.
ISBN: 0-471-20753-5

17

FREE RADICAL ABSTRACTION REACTIONS

Bimolecular radical abstraction reactions participate in many chemical processes such as combustion, liquid-phase oxidation of hydrocarbons, halogenation and cracking of hydrocarbons, degradation of polymers, photolysis and radiolysis of organic compounds, etc. These reactions began to be investigated vigorously as early as the 1920s. The experimental data on the abstraction reactions in the gas and liquid phase are collected in handbooks and databases.[1-9] According to the transition state theory, three atoms ($X\cdots H\cdots Y$) at the reaction center of the abstraction reaction $X^{\bullet} + HY \rightarrow XH + Y^{\bullet}$ are placed on a nearly straight line.[10,11] The last quantum chemical calculations proved that small deviation from the straight line are observed in reactions with an unsymmetrical reaction center.[12] The interatomic distances and angles in the reaction center ($X\cdots H\cdots Y$) of a few reactions are given below.[12]

Reaction	$X\cdots H\cdots Y$	$r(X\cdots H) \times 10^{10}$ (m)	$r(Y\cdots H) \times 10^{10}$ (m)	$\varphi(X\cdots H\cdots Y)$ (°)
$C^{\bullet}H_3 + CH_4$	$C\cdots H\cdots C$	1.347	1.347	180
$N^{\bullet}H_2 + H_2$	$N\cdots H\cdots H$	1.335	0.881	161
$HO^{\bullet} + H_2$	$O\cdots H\cdots H$	1.429	0.804	163
$HO^{\bullet} + CH_4$	$O\cdots H\cdots C$	1.325	1.216	174

17.1 CLASSIFICATION OF RADICAL ABSTRACTION REACTIONS

A great number of kinetic data on radical abstraction reactions were analyzed in the framework of IPM (see Chapter 9).[13-16] Parameters for free radical reactions introduced by this method opened the way for us to build up a new classification of abstraction reactions.

The BDE is an individual characteristic of the molecule entered into the reaction or formed. The force constants for the stretching vibration of bonds ($2\pi^2\nu^2\mu$) of each type (C—H, O—H, etc.) are virtually identical for the entire class of isotypical compounds. This important factor makes it possible to classify radical abstraction reactions in terms of the type of reacting bonds and the coefficients b characterizing them ($2b^2$ is the force constant of the reacting bond). A pair of coefficients, b_i and b_f or $b = b_i$ and $\alpha = b_i/b_f$, corresponds to each class of such reactions. In the calculation of the activation energy E_e from E and conversely, the zero-point vibration energy of the cleaved bond also becomes important. The quantities α, br_e, E_{e0}, $0.5hL(\nu - \nu_f)$, and the preexponential factor A for the studied radical abstraction reactions of different classes are listed in Table 17.1.

The class of radical abstraction reactions may include a single reaction (e.g., $H^\bullet + HCl$), one group of reactions (e.g., $R^\bullet + NH_3$, where $R^\bullet$ is any alkyl radical), or several such groups (e.g., the class of reactions $RO^\bullet + R'H$, where $R'H$ is a hydrocarbon, consists of three groups of reactions: $RO^\bullet + HR^1$, $RO^\bullet + HR^2$, and $RO^\bullet + HR^3$, where R^1H, R^2H, and R^3H are any aliphatic, unsaturated, and aromatic alkyl-substituted hydrocarbons, respectively. All of the reactions belonging to one group are characterized by a single parameter r_e or br_e. By knowing the parameter br_e, it is possible to calculate an important characteristic of the reactivity of each group of reactions such as the activation energy for a thermally neutral reaction E_{e0}. The energies E_{e0} may differ significantly for reactions of different classes (see Table 17.1). Knowing these parameters, it is easy to find the analogous characteristics of the reverse reactions. For a reverse reaction, to which the index f corresponds, we have $\alpha_f = \alpha^{-1}$, $b_f = b/\alpha$, and $0.5hL\nu_f = 0.5hL\nu_i/\alpha$. The classification of radical reactions carried out in this way makes it possible to observe empirically (on the basis of the parameter br_e) structural differences between reactants within one class, to compare the classes and groups of reactions in terms of reactivity (in terms of the parameter br_e or E_{e0}), and to identify the physical and structural factors determining the reactivities of groups of reactants. The activation energy for any individual reaction within the limits of a given group of reactions may be calculated correctly from the parameters α, br_e, and the enthalpy of reaction (equations for calculations are given in Chapter 9). These parameters were used for the calculation of activation energies and rate constants of various free radical reactions. The results of the calculation are presented in Tables 17.2–17.8.

17.2 ENTHALPY OF REACTION

A clear-cut dependence of the activation energy on the heat (enthalpy) of reaction was established for radical abstraction reactions almost 60 years ago when Evans

TABLE 17.1 Parameters of the IPM Method for Reactions of Hydrogen-Atom Abstraction[a,b]

Reaction	α	br_e $(\mathrm{kJ\,mol^{-1}})^{1/2}$	E_{e0} $(\mathrm{kJ\,mol^{-1}})$	$0.5hL(\nu_i - \nu_f)$ $(\mathrm{kJ\,mol^{-1}})$	A $(\mathrm{L\,mol^{-1}\,s^{-1}})$
$R^{1\bullet} + R^1H$	1.00	17.30	74.8	0.0	1.0×10^9
$R^{1\bullet} + R^2H$	1.00	18.60	86.5	0.0	1.0×10^8
$R^{1\bullet} + R^3H$	1.00	17.80	79.2	0.0	1.0×10^8
$R^{2\bullet} + R^2H$	1.00	19.25	92.6	0.0	1.0×10^8
$R^{2\bullet} + R^3H$	1.00	18.45	85.1	0.0	1.0×10^8
$R^{3\bullet} + R^3H$	1.00	18.05	81.4	0.0	1.0×10^8
$N^{\bullet}H_2 + R^1H$	0.869	13.70	53.7	−2.6	5.0×10^8
$N^{\bullet}H_2 + R^2H$	0.869	15.01	64.5	−2.6	5.0×10^7
$N^{\bullet}H_2 + R^3H$	0.869	14.46	59.9	−2.6	5.0×10^7
$RO^{\bullet} + R^1H$	0.796	13.10	53.2	−4.3	1.0×10^9
$RO^{\bullet} + R^2H$	0.796	14.14	62.0	−4.3	1.0×10^8
$RO^{\bullet} + R^3H$	0.796	13.50	56.5	−4.3	1.0×10^8
$RO_2^{\bullet} + R^1H$	0.814	13.61	56.3	−3.8	1.0×10^8
$RO_2^{\bullet} + R^2H$	0.814	15.20	70.2	−3.8	1.0×10^7
$RO_2^{\bullet} + R^3H$	0.814	14.32	62.3	−3.8	1.0×10^7
$R_3Si^{\bullet} + R^1H$	1.358	17.91	57.7	4.8	1.0×10^9
$R_3Si^{\bullet} + R^2H$	1.358	19.18	66.2	4.8	1.0×10^8
$R_3Si^{\bullet} + R^3H$	1.358	18.40	60.9	4.8	1.0×10^8
$R^{1\bullet} + R_2N{-}H$	1.150	18.07	70.6	2.6	1.2×10^8
$R^{1\bullet} + H{-}OR$	1.256	16.46	53.2	4.3	1.0×10^8
$R^{1\bullet} + H{-}OOR$	1.229	16.73	56.3	3.8	1.0×10^7
$R^{1\bullet} + H{-}SiR_3$	0.736	13.18	57.6	−4.8	1.0×10^9
$R^{1\bullet} + H{-}SR$	0.808	11.80	42.6	−3.6	2.0×10^7
$N^{\bullet}H_2 + H{-}NR_2$	1.000	19.86	98.6	0.0	5.0×10^8
$N^{\bullet}H_2 + H{-}OR$	1.092	11.77	31.6	1.7	2.0×10^8
$N^{\bullet}H_2 + H{-}OOR$	1.068	11.11	28.9	1.2	2.0×10^7
$N^{\bullet}H_2 + H{-}SiR_3$	0.640	10.57	41.5	−7.4	1.5×10^8
$N^{\bullet}H_2 + H{-}SR$	0.703	8.78	26.6	−6.2	2.0×10^7
$RO^{\bullet} + H{-}NR_2$	0.916	12.36	41.6	−1.7	5.0×10^8
$RO^{\bullet} + H{-}OR$	1.000	13.62	46.4	0.0	1.0×10^9
$RO^{\bullet} + H{-}OOR$	0.978	14.13	51.0	−0.5	1.0×10^9
$RO^{\bullet} + H{-}SiR_3$	0.586	10.13	40.8	−9.1	1.0×10^9
$RO^{\bullet} + H{-}SR$	0.644	10.39	39.9	−7.9	1.0×10^9
$RO_2^{\bullet} + H{-}NR_2$	0.936	11.93	38.0	−1.2	5.0×10^7
$RO_2^{\bullet} + H{-}OR$	1.022	14.45	51.1	0.5	1.0×10^9
$RO_2^{\bullet} + H{-}OOR$	1.000	13.13	43.1	0.0	1.0×10^8
$RO_2^{\bullet} + H{-}SiR_3$	0.599	12.41	60.2	−8.6	1.0×10^8
$RO_2^{\bullet} + H{-}SR$	0.658	10.39	39.3	−7.4	3.2×10^7
$R_3Si^{\bullet} + H{-}NR_2$	1.562	18.78	53.7	7.4	5.0×10^7
$R_3Si^{\bullet} + H{-}OR$	1.706	17.29	40.8	9.1	1.0×10^9
$R_3Si^{\bullet} + H{-}OOR$	1.669	20.72	60.3	8.6	1.0×10^8
$R_3Si^{\bullet} + H{-}SiR_3$	1.000	13.69	46.8	0.0	2.0×10^9
$R_3Si^{\bullet} + H{-}SR$	1.098	12.73	36.8	1.2	1.0×10^8

---

[a] For designation, see Chapter 9.

[b] See Refs. 13–25.

TABLE 17.2 Activation Energies for Alkyl Radical Reactions with C−H Bonds of Organic Compounds $R^\bullet + R_iH \rightarrow RH + R_i^\bullet$ (Calculated by the IPM Method)[a]

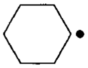
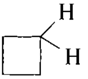
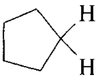
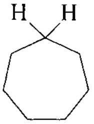
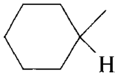
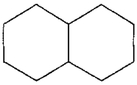
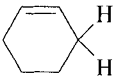
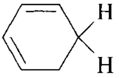
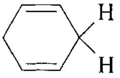
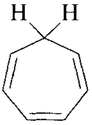
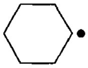
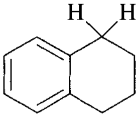
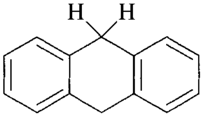
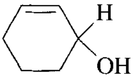
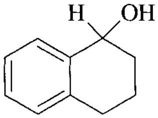
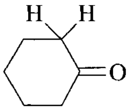
	E (kJ mol^{-1})					
R_iH	$C^\bullet H_3$	$MeC^\bullet H_2$	$Me_2C^\bullet H$	$Me_3C^\bullet$		
EtMeCH−H	45.8	54.3	59.2	65.4	50.9	67.7
Me_3C-H	40.1	48.1	52.8	58.7	44.9	70.0
	48.4	57.0	62.0	68.3	53.5	70.7
	43.8	52.1	56.9	63.0	48.8	65.3
	41.8	50.0	54.7	60.7	46.7	63.0
	38.1	46.1	50.7	56.5	42.9	58.7
	34.8	42.5	47.0	52.6	39.5	54.8
$CH_2{=}CHCH_2-H$	38.1	46.0	49.8	55.1	42.6	57.2
$CH_2{=}CHCH-HMe$	31.2	38.1	42.1	47.1	35.3	49.0
$CH_2{=}CHC-HMe_2$	27.5	34.1	38.0	42.8	31.5	44.7
(Z)-MeCH=CHCH−HMe	29.0	35.8	39.7	44.7	33.1	46.6
$Me_2{=}CHCH-HMe$	24.8	31.2	35.0	39.7	28.7	41.5
$Me_2C{=}CMeC-HMe_2$	21.7	27.9	31.5	36.1	25.4	37.9
$CH_2{=}CHCMe-HCH{=}CH_2$	16.7	22.5	25.9	30.2	20.2	31.9
	28.2	34.8	38.7	43.6	32.2	45.5
	24.4	30.8	34.6	39.3	28.3	41.1
	18.4	24.3	27.8	32.2	22.0	33.9
	14.8	20.5	23.8	28.0	18.2	29.6

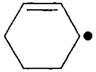
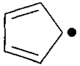
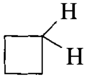
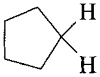
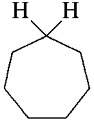
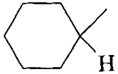
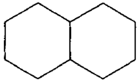
TABLE 17.2 (*continued*)

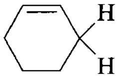
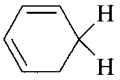
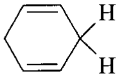
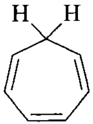
R_iH	E (kJ mol^{-1})					
	$C^{\bullet}H_3$	$MeC^{\bullet}H_2$	$Me_2C^{\bullet}H$	$Me_3C^{\bullet}$		
$MeC\equiv CC-HMe_2$	23.9	30.3	34.0	38.7	27.8	40.5
$PhMeCH-H$	29.7	36.9	41.0	46.2	34.0	48.2
$PhMe_2C-H$	26.2	33.0	37.0	42.1	30.3	44.0
	22.9	29.5	33.4	38.3	26.9	40.1
	15.1	21.0	24.5	28.9	18.6	30.6
Me_2NH_2C-H	31.5	39.0	43.4	48.8	36.0	50.9
$(CH_2=CHCH_2)_3N$	29.6	36.4	40.4	45.3	33.7	47.2
$Me_2(HO)C-H$	36.0	43.8	48.4	54.0	40.7	56.2
	24.0	30.4	34.1	38.8	27.9	40.6
$MeCH=CMeC-HMeOH$	22.5	28.8	32.4	37.0	26.3	38.8
	20.2	26.5	30.2	34.9	24.0	36.8
$PhC(O)-H$	23.8	30.4	34.3	39.2	27.8	41.1
	37.5	45.4	50.0	55.8	42.3	58.0
$Me_2CHOC-HMe_2$	36.1	43.9	48.5	54.2	40.8	56.4
$(CH_2=CHCH-H)_2O$	35.0	42.2	46.3	51.6	39.3	53.6
$Ph_2C-HOMe$	26.0	32.8	36.8	41.9	30.1	43.8

[a] See Eqs. (9.12), (9.15), and (9.16) and the parameters in Table 17.1.

and Polanyi found the linear relation between the changes in the activation energy ΔE and the heat of reaction Δq in a series of reactions of atomic sodium and alkyl halides.[26] Later, Semenov[27] demonstrated, in relation to extensive experimental data, that the linear relation $\Delta E \sim \Delta q$, where q is the heat of the reaction, holds in other radical abstraction reactions.

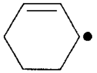
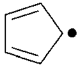
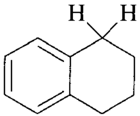
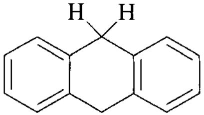
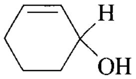
TABLE 17.3 Activation Energies for Allyl Radical Reactions with C–H Bonds of Organic Compounds $R^{\bullet} + R_iH \rightarrow RH + R_i^{\bullet}$ (Calculated by the IPM Method)[a]

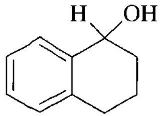
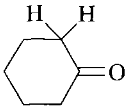
	E (kJ mol^{-1})					
R_iH	$CH_2{=}CHC^{\bullet}H_2$	$CH_2{=}CHC^{\bullet}HMe$	$Me_2C{=}CH$ $C^{\bullet}HMe$	$Me_2C{=}CMe$ $C^{\bullet}Me_2$		
EtMeCH–H	94.3	104.9	115.6	121.4	109.8	124.4
Me_3C–H	87.1	97.3	107.7	113.3	102.1	116.2
	97.5	108.2	119.0	124.9	113.2	127.9
	91.8	10.2	112.8	118.5	107.1	121.5
	89.3	99.5	110.1	115.7	104.4	118.7
	84.7	94.8	105.1	110.6	99.5	113.5
	80.5	90.3	100.4	105.8	95.0	108.7

$CH_2{=}CHCH_2{-}H$	76.5	85.9	95.4	100.5	90.3	103.2
$CH_2{=}CHCH{-}HMe$	67.7	76.5	85.7	90.5	80.7	93.1
$CH_2{=}CHC{-}HMe_2$	62.9	71.5	80.4	85.1	75.6	87.7
(Z)-$MeCH{=}CHCH{-}HMe$	64.9	73.7	82.6	87.4	77.8	90.0
$Me_2{=}CHCH{-}HMe$	59.4	67.9	76.5	81.2	71.8	83.7
$Me_2C{=}CMeC{-}HMe_2$	55.3	63.5	72.0	76.5	67.4	79.0
$CH_2{=}CHCMe{-}HCH{=}CH_2$	48.6	56.5	64.6	68.9	60.2	71.2
	63.8	72.4	81.4	86.1	76.5	88.7
	58.9	67.3	76.0	80.6	71.3	83.1
	50.9	58.9	67.1	71.5	62.7	73.9
	46.1	53.8	61.7	66.0	57.4	68.2

(continued overleaf)

TABLE 17.3 (*continued*)

	E (kJ mol^{-1})					
R_iH	$CH_2{=}CHC^{\bullet}H_2$	$CH_2{=}CHC^{\bullet}HMe$	$Me_2C{=}CH$ $C^{\bullet}HMe$	$Me_2C{=}CMe$ $C^{\bullet}Me_2$		
$MeC{\equiv}CC{-}HMe_2$	58.3	66.6	75.3	79.9	70.6	82.3
$PhMeCH{-}H$	67.1	76.3	85.8	90.9	80.7	93.6
$PhMe_2C{-}H$	62.5	71.5	80.7	85.7	75.7	88.3
	58.2	66.9	75.9	80.8	71.1	83.4
	48.0	55.7	64.1	68.6	59.5	71.0
$Me_2NH_2C{-}H$	76.2	85.9	95.8	101.1	90.4	103.9
$(CH_2{=}CHCH_2)_3N$	65.7	74.5	83.5	88.3	78.6	90.9
$Me_2(HO)C{-}H$	82.0	91.9	102.1	107.6	96.6	110.4
	58.4	66.8	75.4	80.0	70.7	82.5
$MeCH{=}CMeC{-}HMeOH$	56.4	64.7	73.2	77.7	68.6	80.2

	54.4	63.0	71.8	76.5	67.0	79.0
PhC(O)−H	59.3	68.1	77.2	82.1	72.3	84.7
	83.9	94.0	104.2	109.7	98.7	112.6
$Me_2CHOC{-}HMe_2$	82.2	92.1	102.3	107.7	96.8	110.6
$(CH_2{=}CHCH{-}H)_2O$	72.6	81.7	91.1	96.1	86.0	98.7
$Ph_2C{-}HOMe$	62.2	71.2	80.5	85.4	75.5	88.1

---

[a] See Eqs. (9.12), (9.15), and (9.16) and the parameters in Table 17.1.

TABLE 17.4 Activation Energies for Reactions of the Benzyl Type of Radicals with C–H Bonds of Organic Compounds $R^\bullet + R_iH \rightarrow RH + R_i^\bullet$ (Calculated by the IPM Method)[a]

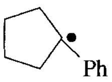
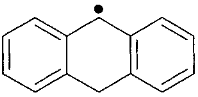
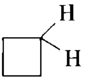
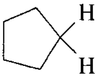
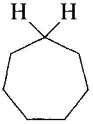
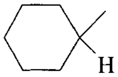
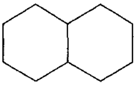
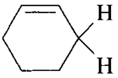
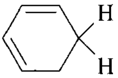
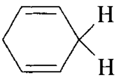
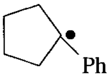
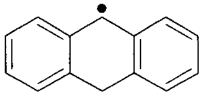
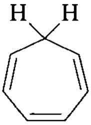
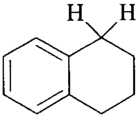
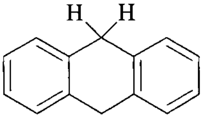
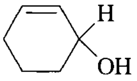
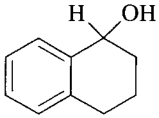
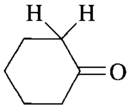
	E (kJ mol^{-1})				
R_iH	$PhC^\bullet H_2$	$PhMe_2C^\bullet$	$Ph_3C^\bullet$		
EtMeCH–H	83.3	94.9	100.2	98.3	115.1
Me_3C–H	76.1	87.4	92.4	90.6	106.9
	86.4	98.2	103.5	101.6	118.7
	80.7	92.2	97.4	95.5	112.2
	78.2	89.6	94.7	92.9	109.4
	73.7	84.8	89.8	88.0	104.1
	69.5	80.4	85.3	83.5	99.3
CH_2=$CHCH_2$–H	65.5	75.8	80.4	78.7	93.6
CH_2=CHCH–HMe	56.9	66.6	70.9	69.4	83.5
CH_2=CHC–HMe_2	52.2	61.6	65.8	64.3	78.0
(Z)-MeCH=CHCH–HMe	54.2	63.7	68.0	66.5	80.4
Me_2C=CHCH–HMe	48.9	58.0	62.1	60.7	74.1
Me_2C=CMeC–HMe_2	44.9	53.8	57.8	56.4	69.4
CH_2=CHCMe–HCH=CH_2	38.5	46.9	50.7	49.3	61.8
	53.1	62.5	66.8	65.2	79.0
	48.4	57.5	61.6	60.1	73.5
	40.7	49.3	53.1	51.7	64.4

TABLE 17.4 (*continued*)

	E (kJ mol^{-1})				
R_iH	$PhC^{\bullet}H_2$	$PhMe_2C^{\bullet}$	$Ph_3C^{\bullet}$		
	36.0	44.3	48.0	46.7	58.8
$MeC{\equiv}CC{-}HMe_2$	47.7	56.8	60.9	59.4	72.7
$PhMeCH{-}H$	60.0	70.1	74.7	73.0	87.8
$PhMe_2C{-}H$	55.5	65.4	69.8	68.2	82.5
	51.3	60.9	65.2	63.6	77.6
	41.0	49.8	53.8	52.4	65.4
$Me_2NH_2C{-}H$	65.4	76.0	80.8	79.0	94.5
$(CH_2{=}CHCH_2)_3N$	54.9	64.5	68.8	67.3	81.2
$Me_2(HO)C{-}H$	71.0	82.0	86.9	85.2	101.1
	55.3	64.5	68.6	67.1	80.4
$MeCH{=}CMeC{-}HMeOH$	45.9	54.9	58.9	57.5	70.6
	47.7	57.0	61.2	59.7	73.3
$PhC(O){-}H$	52.4	62.0	66.4	64.8	78.9
	73.0	84.0	89.0	87.2	103.3
$Me_2CHOC{-}HMe_2$	71.2	82.2	87.1	85.3	101.2
$(CH_2{=}CHCH{-}H)_2O$	69.2	79.2	83.7	82.1	96.5
$Ph_2C{-}HOMe$	55.3	65.1	69.5	67.9	82.3

---

[a] See Eqs. (9.12), (9.15), and (9.16) and the parameters in Table 17.1.

TABLE 17.5 Rate Constants and Activation Energies for the Aminyl ($N^{\bullet}H_2$) Radical Reactions with C−H Bonds of Organic Compounds[a]

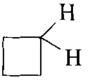
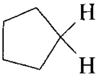
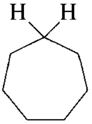
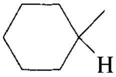
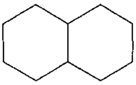
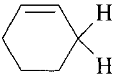
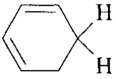
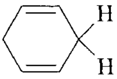
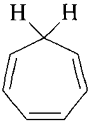
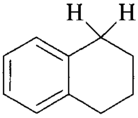
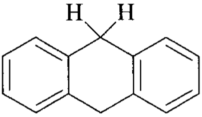
RH	n	ΔH_e (kJ mol^{-1})	E (kJ mol^{-1})	A (L mol^{-1} s^{-1})	k (300 K) (L mol^{-1} s^{-1})
EtMeCH−H	4	−39.0	21.1	2.0×10^9	4.24×10^5
Me_3C−H	1	−52.0	16.4	5.0×10^8	7.00×10^5
	8	−33.5	23.2	4.0×10^9	3.62×10^5
	1	−43.6	19.4	5.0×10^9	2.10×10^6
	1	−48.1	17.8	7.0×10^9	5.65×10^6
	1	−56.5	14.8	5.0×10^8	1.31×10^6
	2	−64.4	12.2	1.0×10^9	7.52×10^6
CH_2=$CHCH_2$−H	3	−84.0	15.7	1.5×10^8	2.71×10^5
CH_2=CHCH−HMe	2	−102.2	10.3	1.0×10^8	1.59×10^6
CH_2=CHC−HMe_2	1	−112.4	7.5	5.0×10^7	2.45×10^6
(*Z*)-MeCH=CHCH−HMe	2	−108.0	8.7	1.0×10^8	3.04×10^6
Me_2C=CHCH−HMe	2	−120.0	5.6	1.0×10^8	1.08×10^7
Me_2C=CMeC−HMe_2	1	−129.2	3.3	5.0×10^7	1.34×10^7
CH_2=CHCMe−HCH=CH_2	1	−144.8	1.0	5.0×10^7	3.35×10^7
	4	−110.5	8.0	1.0×10^9	7.98×10^7
	4	−121.1	5.3	2.0×10^9	2.42×10^8
	4	−139.4	1.2	2.0×10^9	1.24×10^9
	2	−151.0	1.0	1.0×10^9	6.70×10^8

TABLE 17.5 (*continued*)

RH	n	ΔH_e (kJ mol^{-1})	E (kJ mol^{-1})	A (L mol^{-1} s^{-1})	k (300 K) (L mol^{-1} s^{-1})
$MeC\equiv CC{-}HMe_2$	1	−122.6	4.9	5.0×10^7	7.02×10^6
$PhMeCH{-}H$	2	−87.9	10.4	1.0×10^8	1.53×10^6
$PhMe_2C{-}H$	1	−97.3	7.7	5.0×10^7	2.25×10^6
	4	−106.4	5.3	2.0×10^9	2.42×10^8
	4	−130.0	1.0	2.0×10^9	1.34×10^9
$Me_2NCH_2{-}H$	1	−72.5	9.6	5.0×10^8	1.05×10^7
$(CH_2{=}CHCH_2)_3N$	6	−106.4	5.3	3.0×10^8	3.63×10^7

[a] See Eqs. (9.12), (9.15), and (9.16) and the parameters in Table 17.1.

The IPM model[13–16] opens the way for us to evaluate the contribution of reaction enthalpy to the activation energy of any radical abstraction reaction. As noted above, all radical abstraction reactions can be divided into groups and the activation energy E_{e0} for a thermally neutral reaction can be calculated in each group. The possibility of calculating the activation energy for any reaction of the given series (group) from the value of E_{e0} (or br_e) and of estimating the contribution of the enthalpy to the activation energy follows from this important factor. The contribution of ΔE_H represents the difference between the activation energies for the given (ith) reaction and a thermally neutral reaction characterized by the quantity E_{e0}

$$\Delta E_H = E_e - E_{e0} \tag{17.1}$$

As an example, Table 17.9 presents the values of ΔH, E, and ΔE_H for the reactions of different classes. It follows from this table that the ratio $\Delta E_H/\Delta H$ for these groups of reactions is close to 0.5 at low values of ΔH.

In terms of the parabolic model, it is possible to obtain simple and physically clear equations for the estimation of ΔE_H as a function of α, br_e, and ΔH_e. The following simple expressions follow from the combination of Eqs. (17.2) and (9.12)–(9.14):

for $\alpha = 1$

$$\Delta E_H = 0.5\Delta H_e + 0.25(br_e)^{-2}\Delta H_e^2 \tag{17.2}$$

for $\alpha \neq 1$

$$(1-\alpha^2)\Delta E_H = 2\alpha(br_e)^2 - \alpha^2\Delta H_e - 2\alpha(br_e)^2[1-(1-\alpha^2)(br_e)^{-2}\Delta H_e]^{1/2} \tag{17.3}$$

TABLE 17.6 Rate Constants and Activation Energies for the 1-Methyl-1-phenylethoxyl Radical ($Me_2PhCO^{\bullet}$) Reactions with C–H Bonds of Organic Compounds[a]

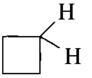
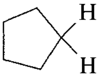
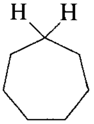
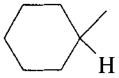
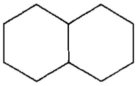
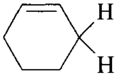
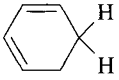
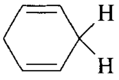
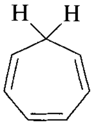
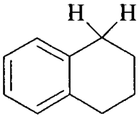
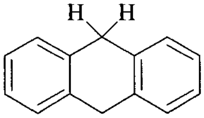
RH	n	ΔH_e (kJ mol^{-1})	E (kJ mol^{-1})	A (L mol^{-1} s^{-1})	k (300 K) (L mol^{-1} s^{-1})
EtMeCH–H	4	−31.6	24.1	4.0×10^9	2.53×10^5
Me_3C–H	1	−44.6	19.4	1.0×10^9	4.13×10^5
	8	−26.1	26.2	8.0×10^9	2.19×10^5
	1	−36.2	22.4	10×10^{10}	1.25×10^6
	1	−40.7	20.8	1.4×10^{10}	3.34×10^6
	1	−49.1	17.9	1.0×10^9	7.65×10^5
	2	−57.0	15.3	2.0×10^9	4.35×10^6
CH_2=$CHCH_2$–H	3	−76.6	17.3	3.0×10^8	2.92×10^5
CH_2=CHCH–HMe	2	−94.8	12.0	2.0×10^8	1.62×10^6
CH_2=CHC–HMe_2	1	−105.0	9.3	1.0×10^8	2.42×10^6
(*Z*)-MeCH=CHCH–HMe	2	−100.6	10.4	2.0×10^8	3.05×10^6
Me_2C=CHCH–HMe	2	−112.6	7.3	2.0×10^8	1.05×10^7
Me_2C=CMeC–HMe_2	1	−121.8	5.1	1.0×10^8	1.28×10^7
CH_2=CHCMe–HCH=CH_2	1	−137.4	1.6	1.0×10^8	5.20×10^7
	4	−103.1	9.8	4.0×10^8	7.95×10^7
	4	−113.7	7.1	4.0×10^9	2.35×10^8
	4	−132.0	2.8	4.0×10^9	1.30×10^9
	2	−143.6	1.0	2.0×10^9	1.34×10^9

TABLE 17.6 (*continued*)

RH	n	ΔH_e (kJ mol^{-1})	E (kJ mol^{-1})	A (L mol^{-1} s^{-1})	k (300 K) (L mol^{-1} s^{-1})
$MeC{\equiv}CC{-}HMe_2$	1	−115.2	6.7	1.0×10^8	6.81×10^6
$PhMeCH{-}H$	2	−80.5	11.1	2.0×10^8	2.26×10^6
$PhMe_2C{-}H$	1	−89.9	8.6	1.0×10^8	3.23×10^6
	4	−99.0	6.2	4.0×10^9	3.36×10^8
	4	−122.6	1.0	4.0×10^9	2.68×10^9
$Me_2NH_2C{-}H$	1	−65.1	12.8	1.0×10^9	6.03×10^6
$(CH_2{=}CHCH_2)_3N$	6	−99.0	10.9	6.0×10^8	7.69×10^6

[a] See Eqs. (9.13), (9.15), and (9.16) and the parameters in Table 17.1.

for $\Delta H_e(1 - \alpha^2) \ll (br_e)^2$

$$\Delta E_H = \alpha(1+\alpha)^{-1}\Delta H_e + 0.25\alpha(br_e)^{-2}\Delta H_e^2 \tag{17.4}$$

It is seen from Eqs. (17.2)–(17.4) that, for low values of the enthalpy of reaction, ΔE_H is directly proportional to ΔE_e, which agrees with the Polanyi–Semenov equation. The slope of the linear plot of ΔE_H as a function of ΔH_e depends on α, that is, on the force constants of the bonds. The ratio $\Delta E_H/\Delta H_e = \alpha(1+\alpha)^{-1}$ at low ΔH_e may serve as a parameter for the sensitivity of ΔE_e to ΔH_e for low values of the latter. For reactions of different classes, the coefficient α varies in the range 0.6–1.7 and the coefficient $\alpha(1+\alpha)^{-1}$ therefore varies from 0.38 to 0.63. The ratio $\Delta E_H/\Delta H_e$ increases with increasing reaction enthalpy and tends to unity. Here are the values of ratio $\Delta E_H/\Delta H_e$ at $br_e = 15.0$ (kJ/mol)$^{1/2}$ and different α and ΔH_e (kJ mol^{-1}):

	ΔH_e(kJ mol^{-1})					
α	10	20	40	70	100	120
			$\Delta E_H/\Delta H_e$			
0.667	0.405	0.410	4.200	4.346	4.494	4.593
1.000	0.511	0.522	0.544	0.578	0.611	0.633
1.500	0.625	0.650	0.700	0.775	0.850	0.900

TABLE 17.7 Rate Constants and Activation Energies for the Benzoyloxyl Radical ($PhCO_2^\bullet$) Reactions with C–H Bonds of Organic Compounds[a]

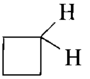
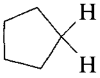
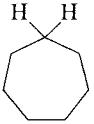
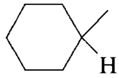
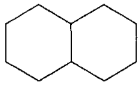
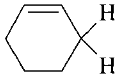
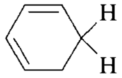
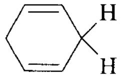
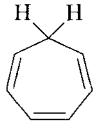
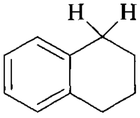
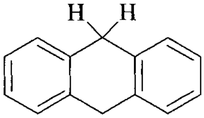
RH	n	ΔH_e ($kJ\,mol^{-1}$)	E ($kJ\,mol^{-1}$)	A ($L\,mol^{-1}\,s^{-1}$)	k (300 K) ($L\,mol^{-1}\,s^{-1}$)
EtMeCH–H	4	−34.8	22.9	8.0×10^9	8.24×10^5
Me_3C–H	1	−47.8	18.3	2.0×10^9	1.30×10^6
	8	−29.3	25.0	1.6×10^{10}	7.10×10^5
	1	−39.4	21.3	2.0×10^{10}	3.96×10^6
	1	−43.9	19.7	2.8×10^{10}	1.05×10^7
	1	−52.3	16.8	2.0×10^9	2.35×10^6
	2	−60.2	14.3	4.0×10^9	1.31×10^7
CH_2=$CHCH_2$–H	3	−79.8	16.3	6.0×10^8	8.60×10^5
CH_2=CHCH–HMe	2	−98.0	11.1	4.0×10^8	4.60×10^6
CH_2=CHC–HMe_2	1	−108.2	8.5	2.0×10^8	6.75×10^6
(Z)-MeCH=CHCH–HMe	2	−103.8	9.6	4.0×10^8	8.55×10^6
Me_2C=CHCH–HMe	2	−115.8	6.6	4.0×10^8	2.89×10^7
Me_2C=CMeC–HMe_2	1	−125.0	4.4	2.0×10^8	3.46×10^7
CH_2=CHCMe–HCH=CH_2	1	−140.6	1.0	2.0×10^8	1.36×10^8
	4	−106.3	8.9	8.0×10^9	2.22×10^8
	4	−116.9	6.3	8.0×10^9	6.43×10^8
	4	−135.2	2.1	8.0×10^9	3.44×10^9
	2	−146.8	1.0	4.0×10^9	2.68×10^9

TABLE 17.7 (***continued***)

RH	n	ΔH_e (kJ mol^{-1})	E (kJ mol^{-1})	A (L mol^{-1} s^{-1})	k (300 K) (L mol^{-1} s^{-1})
$MeC{\equiv}CC{-}HMe_2$	1	−118.4	5.9	2.0×10^8	1.86×10^7
$PhMeCH{-}H$	2	−83.7	10.3	4.0×10^8	6.51×10^6
$PhMe_2C{-}H$	1	−93.1	7.7	2.0×10^8	9.10×10^6
	4	−102.2	5.4	8.0×10^9	9.29×10^8
	4	−125.8	1.0	8.0×10^9	5.36×10^9
$Me_2NH_2C{-}H$	1	−68.3	11.8	2.0×10^9	1.78×10^7
$(CH_2{=}CHCH_2)_3N$	6	−102.2	10.0	1.2×10^9	2.17×10^7

[a]See Eqs. (9.13), (9.15), and (9.16) and the parameters in Table 17.1.

The activation energy increases with an increase in ΔH_e and diminishes with an increase in $|\Delta H_e|$ for $\Delta H_e < 0$. On the other hand, according to the law of conservation of energy, $E > 0$ for exothermic reactions and $E > \Delta H_e$ for endothermic reactions. This follows from the law of conservation of energy and Eq. (9.5).[28] The parameter br_e for one group of reactions is constant, while ΔH_e varies in the range $\Delta H_{e,\max} < \Delta H_e < \Delta H_{e,\min}$. For highly endothermic reactions with $\Delta H_e > \Delta H_{e,\max}$ the activation energy is $E = \Delta H + 0.5RT$, while for exothermic reactions with $\Delta H_e < \Delta H_{e,\min}$ it is $0.5RT$ (see Chapter 9). The limiting values of enthalpies of one class of radical reactions $\Delta H_{e,\min}$ and $\Delta H_{e,\max}$ are related to the parameters br_e and α in the following way:[28]

$$\Delta H_{e,\max} = (br_e)^2 - 2\alpha br_e(0.5hL\nu_f)^{1/2} + 0.5(\alpha^2 - 1)hL\nu_f \tag{17.5}$$

$$\Delta H_{e,\min} = -(br_e/\alpha)^2 + 2\alpha^{-2} br_e(0.5hL\nu_i)^{1/2} + 0.5(1 - \alpha^{-2})hL\nu_i \tag{17.6}$$

As seen from Eqs. (17.5) and (17.6), the range of variation of ΔH_e in which $br_e = \text{const}$ is wider the greater the parameter br_e. For the reactions of alkyl radicals with aliphatic hydrocarbons ($\alpha = 1$, $br_e = 17.23$ (kJ/mol)$^{1/2}$), we have $\Delta H_{e,\max} = |\Delta H_{e,\min}| = 153.1$ kJ mol^{-1}, that is, the range of enthalpies ΔH_e, where $br_e = \text{const}$ is 306 kJ mol^{-1}. For the values of the enthalpy limits $\Delta H_{e,\max} - \Delta H_{e,\min}$ see Table 17.10. The question of the preexponential factor for the very exothermic and very endothermic reactions has been recently examined.[28] The preexponential factor for such reactions appeared to be a function of reaction enthalpy. For the equations of the preexponential factor at high values of $|\Delta H|$, see Chapter 9.

TABLE 17.8 Rate Constants and Activation Energies for the Cyclohexylperoxyl Radical Reactions with C−H Bonds of Organic Compounds[a]

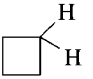
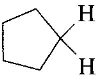
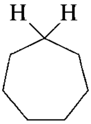
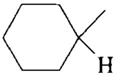
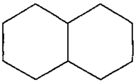
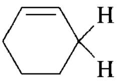
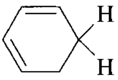
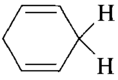
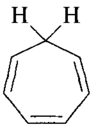
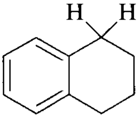
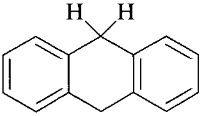
RH	n	ΔH_e (kJ mol^{-1})	E (kJ mol^{-1})	A (L mol^{-1} s^{-1})	k (300 K) (L mol^{-1} s^{-1})
EtMeCH−H	4	43.7	61.9	4.0×10^8	6.68×10^{-3}
Me_3C−H	1	30.7	54.9	1.0×10^8	2.73×10^{-2}
	8	49.2	65.0	8.0×10^8	3.92×10^{-3}
	1	39.1	59.4	1.0×10^9	4.58×10^{-2}
	1	34.6	57.0	1.4×10^9	0.17
	1	26.2	52.6	1.0×10^8	6.89×10^{-2}
	2	18.3	48.7	2.0×10^8	0.67
CH_2=$CHCH_2$−H	3	−1.3	53.4	3.0×10^7	1.49×10^{-2}
CH_2=CHCH−HMe	2	−19.5	45.6	2.0×10^7	0.23
CH_2=CHC−HMe_2	1	−29.7	41.5	1.0×10^7	0.61
(*Z*)-MeCH=CHCH−HMe	2	−25.3	43.2	2.0×10^7	0.60
Me_2C=CHCH−HMe	2	−37.3	38.5	2.0×10^7	4.01
Me_2C=CMeC−HMe_2	1	−46.5	35.0	1.0×10^7	8.09
CH_2=CHCMe−HCH=CH_2	1	−62.1	29.4	1.0×10^7	76.1
	4	−27.8	42.2	4.0×10^8	17.9
	4	−38.4	38.0	4.0×10^8	95.1
	4	−56.7	31.3	4.0×10^8	1.43×10^3
	2	−68.3	27.3	2.0×10^8	3.56×10^3

TABLE 17.8 (*continued*)

RH	n	ΔH_e (kJ mol^{-1})	E (kJ mol^{-1})	A (L mol^{-1} s^{-1})	k (300 K) (L mol^{-1} s^{-1})
$\mathrm{MeC{\equiv}CC{-}HMe_2}$	1	−39.9	37.5	1.0×10^7	3.0
$\mathrm{PhMeCH{-}H}$	2	−5.2	43.8	2.0×10^7	0.48
$\mathrm{PhMe_2C{-}H}$	1	−14.6	39.8	1.0×10^7	1.19
	4	−23.7	36.0	4.0×10^8	2.13×10^2
	4	−47.3	27.0	4.0×10^8	7.86×10^3
$\mathrm{Me_2NH_2C{-}H}$	1	−10.2	44.8	1.0×10^8	1.59
$\mathrm{(CH_2{=}CHCH_2)_3N}$	6	−23.7	43.9	6.0×10^7	1.38

[a] See Eqs. (9.12), (9.15), and (9.16) and the parameters in Table 17.1.

17.3 FORCE CONSTANTS OF REACTING BONDS

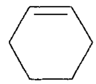
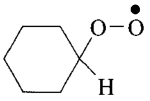
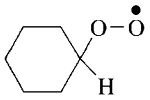
The force constants of the cleaved and generated bonds are yet another important characteristic of radical abstraction reactions.[13–15] The dependence of the activation energy for reactions of the type $R^\bullet + RX \rightarrow RX + R^\bullet$, where X = H, Cl, Br, or I, on the coefficients b_i and b_f was demonstrated experimentally.[29] It was found that the parameter r_e = const in these reactions, while the square root of the activation energy for a thermally neutral reaction is directly proportional to the force constant of the ruptured bond. The smaller the force constant of the C−X bond, the lower is E_{e0} and the relation $E_{e0}^{1/2}$ to $b(1+\alpha)^{-1}$ is linear. The same result was obtained for reactions of the hydrogen atoms with RCl, RBr, and RI (see Table 17.11).[29] These results confirm the important role of the force constant of the reacting bonds in the formation of the activation barrier. The activation energies for the $R^\bullet + RX$ reactions can easily be estimated from the empirical formula

$$[E_{e0}(\mathrm{kJ\,mol^{-1}})]^{1/2} = 4.80 \times 10^{-11} b(1+\alpha)^{-1} \tag{17.7}$$

17.4 TRIPLET REPULSION

The hydrogen atom migrates from Y to X in the $X^\bullet + HY$ reaction. The transition state of this reaction can be regarded conventionally as a labile formation

TABLE 17.9 Enthalpies, Activation Energies, and Values of ΔE_H for Different Free Radical Abstraction Reactions

Reaction	ΔH_e (kJ mol^{-1})	E_e (kJ mol^{-1})	E_{e0} (kJ mol^{-1})	ΔE_H (kJ mol^{-1})	$\Delta E_H/\Delta H_e$
$C^{\bullet}H_3 + Me_2C{=}CMeCHMe_2$	−100.4	43.7	86.5	−42.8	0.43
$CH_3C^{\bullet}H_2 + Me_2C{=}CHCH_2Me$	−72.2	54.3	86.5	−32.2	0.45
$CH_3C^{\bullet}H_2$ + 	−80.5	51.0	86.5	−35.5	0.44
$Me_2C^{\bullet}H + PhMe_2CH$	−57.3	53.2	79.2	−26.0	0.45
$N^{\bullet}H_2 + Me_3CH$	−52.0	32.6	53.7	−21.1	0.40
$N^{\bullet}H_2 + EtMeCH_2$	−39.0	37.3	53.7	−16.4	0.42
$Me_2PhCO^{\bullet} + EtMeCH_2$	−31.6	40.3	53.2	−12.9	0.41
$Et_3Si^{\bullet} + CH_2{=}CHCH_2Me$	−23.4	53.2	66.2	−13.0	0.55
$Et_3Si^{\bullet} + PhMeCH_2$	−9.1	55.7	60.9	−5.2	0.57
$Ph_3C^{\bullet} + CH_2{=}CHCH_2Me$	3.8	87.1	85.1	2.0	0.53
 $+ Me_3CH$	30.7	71.1	56.3	14.8	0.48
 $+ EtMeCH_2$	43.7	78.1	56.3	21.8	0.50
$Ph_3C^{\bullet} + Me_3CH$	54.0	108.6	79.2	29.4	0.54
$Ph_3C^{\bullet} + EtMeCH_2$	67.0	116.4	79.2	37.2	0.55
$PhC^{\bullet}H_2 + Me_2CHOCHMe_2$	15.8	87.4	79.2	8.2	0.52

containing the X···H···Y pseudobond. The characteristics of this bond may influence the activation energy. This influence can be observed with the aid of the IPM model,[13-16] since it makes it possible for us to convert the activation energy for an individual reaction into the activation energy for a thermally neutral reaction (see Chapter 9) and also to take into account the influence of the force constants of the X—H and Y—H bonds on E_{e0} [Eq. (9.6)]. When the hydrogen abstraction reactions are compared in relation to different classes of compounds, it is useful to employ the parameter r_e, in which the influence of ΔH_e, b_i, and b_f on the activation energy for the reaction has already been taken into account.

In the X···H···Y transition state, the X···Y pseudobond is formed by three electrons. According to the Pauli principle, one molecular orbital may be occupied by only two electrons with opposite spins. Two molecular orbitals therefore participate in the transition state: The bonding orbital of the X—Y bond, in which two electrons are accommodated, and its nonbonding orbital containing the third electron. The energy of the nonbonding orbital D_T is higher the stronger the

TABLE 17.10 The Limits $\Delta H_{e\,min}, \Delta H_{e\,max}$ for Different Classes of Free Radical Abstraction Reactions

Reaction	$0.5hL\nu_f$ (kJ mol^{-1})	br_e (kJ/mol)$^{1/2}$	$-\Delta H_{e\,min}$ (kJ mol^{-1})	$\Delta H_{e\,max}$ (kJ mol^{-1})	References
$R^{1\bullet} + R^1H$	17.4	17.30	155.0	155.0	15
$R^{1\bullet} + R^2H$	17.4	18.60	190.8	190.8	15
$R^{1\bullet} + R^3H$	17.4	17.80	168.3	168.3	15
$R^{2\bullet} + R^2H$	17.4	19.25	210.0	210.0	15
$R^{2\bullet} + R^3H$	17.4	18.45	186.5	186.5	15
$R^{3\bullet} + R^3H$	17.4	18.05	175.2	175.2	15
$N^\bullet H_2 + R^1H$	20.0	13.70	102.8	76.3	24
$N^\bullet H_2 + R^2H$	20.0	15.01	137.9	103.9	24
$N^\bullet H_2 + R^3H$	20.0	14.46	122.6	91.8	24
$RO^\bullet + R^1H$	21.7	13.10	108.5	66.6	15,17
$RO^\bullet + R^2H$	21.7	14.14	139.4	87.1	15,17
$RO^\bullet + R^3H$	21.7	13.50	120.0	74.2	15,17
$RO_2{}^\bullet + R^1H$	21.2	13.61	117.2	76.1	15,18
$RO_2{}^\bullet + R^2H$	21.2	15.20	166.4	110.1	15,18
$RO_2{}^\bullet + R^3H$	21.2	14.32	138.0	90.6	15,18
$R_3Si^\bullet + R^1H$	12.6	17.91	84.8	158.6	22
$R_3Si^\bullet + R^2H$	12.6	19.18	107.4	193.7	22
$R_3Si^\bullet + R^3H$	12.6	18.40	92.2	171.6	22
$N^\bullet H_2 + HNR_2$	20.0	19.86	218.8	216.8	24
$RO^\bullet + HOR$	21.7	13.62	61.3	61.3	15
$RO_2{}^\bullet + HOOR$	21.2	13.13	51.5	51.5	15
$R_3Si^\bullet + HSiR_3$	12.6	13.69	90.2	90.2	22

X−Y bond; its value is described by the Sato formula[30]

$$D_T = D_e\{\exp(-brD_e^{-1/2}) + 0.5\exp(-2brD_e^{-1/2})\} \tag{17.8}$$

where D_e and D_T are the energies of the bonding and nonbonding X−Y orbitals, respectively, $2b^2$ is the force constant, and r is the amplitude of the vibration of this bond. In any given case, $r = r_{XH} + r_{YH} - r_{XY} + r_e$. The involvement of the nonbonding orbital of the X−Y bond in the formation of the activation barrier has come to be referred to as a triplet repulsion. This effect constitutes the basis of three semiempirical methods for the calculation of the activation energies for radical substitution reactions: the "bond energy–bond order" (BEBO) method,[31] the "bond energy–bond length" (BEBL) method,[32] and the Zavitsas method.[33,34] In all of these methods, the activation energy corresponds to the maxima on the BEBO curves or the BEBL, Zavitsas method, curves while the potential energy curve represents a superposition of two Morse curves corresponding to the Y−H and X−H reacting bonds and the curve for the nonbonding orbital of the X−Y bond [Eq. (17.8)].

TABLE 17.11 Values of br_e, E_{e0}, and r_e for the Reactions $R^\bullet + R^1X \rightarrow RX + R^{1\bullet}$ and $H^\bullet + RX \rightarrow HX + R^{\bullet}$[a]

Reaction	$b \times 10^{-11}$ (kJ mol^{-1}) m^{-1}	br_e[a] (kJ mol^{-1})$^{1/2}$	α	E_{e0} (kJ mol^{-1})	$r_e \times 10^{11}$ (m)
$R^\bullet + RCl$	3.288	16.70	1.00	69.7	5.079
$R^\bullet + RBr$	2.364	12.00	1.00	36.0	5.076
$R^\bullet + RI$	1.542	8.90	1.00	19.8	5.772
$H^\bullet + RCl$	3.288	16.26	0.835	78.5	4.945
$H^\bullet + RBr$	2.364	11.33	0.672	45.9	4.793
$H^\bullet + RI$	1.542	7.30	0.502	23.6	4.734

[a] See Ref. 29.

The role of triplet repulsion in radical abstraction can clearly be traced to comparing reactions in which the energies of the X—Y bonds differ significantly. The values of E_{e0} and r_e for a series of radical abstraction reactions found by the IPM method as well as the energies D_e of the X—Y bond are presented below.[15,25]

X···H···Y	E_{e0} (kJ mol^{-1})	$r_e \times 10^{11}$ (m)	D_e (kJ mol^{-1})
R···H···R	68.2	4.414	382
$\mathrm{R\cdots H\cdots N}\begin{smallmatrix}/\\ \backslash\end{smallmatrix}$	60.2	3.862	361
ArO···H···OAm	41.8	2.772	~0
RO_2···H···O_2R	43.1	2.854	88
RO_2···H···OAr	45.3	2.885	~0
RO_2···H···OAm	45.6	2.895	~0

The difference between the reactions with a high X—Y (C—C and C—N) bond energy, for which $E_{e0} \sim 60–70$ kJ mol^{-1}, and the reactions with a very low energy for this bond (O—O), for which $E_{e0} \sim 40–45$ kJ mol^{-1} can clearly be traced. Within the limits of the error of the measurement, the parameter r_e for the last four reactions is constant: $r_e = (2.85 \pm 0.05) \times 10^{-11}$ m. This value is characteristic of reactions with zero triplet repulsion in the transition state. On substituting this quantity into Eq. (9.6), we obtain Eq. (17.9) for the estimation of the contribution of triplet repulsion ΔE_T to the activation energy E_{e0}:[15,19,20]

$$\Delta E_T = (b_i b_f)^2 (b_i + b_f)^{-2} (r_e^2 - 2.852 \times 10^{-22}) \qquad (17.9)$$

For reactions of the $R^\bullet + RH$ class, this contribution is 40.0 kJ mol^{-1}, that is, a considerable proportion of the activation energy $\Delta E_{e0} = 68 - 40 = 28$ kJ mol^{-1}

is due precisely to the triplet repulsion in the transition state. Between parameter r_e and the dissociation energy X—Y bond there exists an empirical correlation (D_{HH} is BDE of hydrogen molecule)[16]

$$[\Delta r_e(m)^2] = 13.7 \times 10^{-22}(D_{XY}/D_{HH}) \qquad (17.10)$$

17.5 ELECTRON AFFINITY OF ATOMS IN REACTION CENTER

Another important characteristic of the X—Y bond is its polarity induced by the different electron affinities of the atoms or radicals X and Y. The greater the difference, the greater the polarity of the bond, its strength, and its dipole moment. According to Pauling,[35] the polarity of the X—Y bond may be characterized by the extent to which its strength differs from one-half of the sum of the BDE of the XX and YY molecules by virtue of the different electronegativities of the atoms X and Y.

$$\Delta EA(XY) = D_{XY} - 0.5(D_{XX} + D_{YY}) \qquad (17.11)$$

The question arises whether the polarity of the X—Y bond affects the $X^{\bullet} + YH$ abstraction reactions.

We shall compare two reactions:[20]

$$H^{\bullet} + H_2 \rightarrow H_2 + H^{\bullet}$$

$$Cl^{\bullet} + H_2 \rightarrow ClH + H^{\bullet}$$

Reaction	E_{e0} (kJ mol^{-1})	$r_e \times 10^{11}$ (m)	D_{XY} (kJ mol^{-1})
$H^{\bullet} + H_2$	58.2	3.69	436.0
$Cl^{\bullet} + H_2$	36.7	3.04	431.6

Evidently, the dissociation energies of the H—H and Cl—H bonds are very close and the triplet repulsion in the transition states of these reactions is therefore almost identical. Nevertheless, the quantities E_{e0} and r_e in these two reactions differ considerably. The reason for this is that the H—H bond is nonpolar, while the Cl—H bond is polarized and $\Delta EA = 92.3$ kJ mol^{-1} [Eq. (17.11)] for the latter. As in the HCl molecule, in the transition state there is evidently a strong attraction between Cl and H, which in fact induces a decrease in r_e and E_{e0}. If the $Cl^{\bullet} + H_2$ reaction was characterized by the same parameter $r_e = 3.69 \times 10^{-11}$ m as the $H^{\bullet} + H_2$ reaction, the activation energy $E_{e0} = 56.5$ kJ mol^{-1} [Eq. (9.6)] would have been obtained for it. The difference between the observed and expected activation energies ($\Delta E_{EA} = 36.7 - 56.5 = -19.8$ kJ mol^{-1}) must be attributed to the influence of the unequal electronegativities of the hydrogen and chlorine atoms on E_{e0} in the $Cl^{\bullet} + H_2$ reaction.

The $R^\bullet + RH$ and $RO^\bullet + RH$ reactions may serve as another example.[17]

Reaction	E_{e0}, (kJ mol^{-1})	$r_e \times 10^{11}$ (m)	D_{XY} (kJ mol^{-1})
$R^\bullet + R^1H$	74.8	4.622	376
$RO^\bullet + R^1H$	53.2	2.787	361

In this case, the similarity of the R—R and RO—R bond dissociation energies also leads to the similarity in the triplet repulsion energies in the $R \cdots H \cdots R$ and $RO \cdots H \cdots R$ transition states. However, in these reactions the quantities E_{e0} and r_e also differ appreciably. The polarity of the O—C bond in the RO + HR reaction is manifested here. On substituting the dissociation energies $D(CH_3{-}CH_3)$, $D(CH_3O{-}OCH_3)$, and $D(CH_3{-}OCH_3)$ in Eq. (17.11), we obtain $\Delta EA = 80$ kJ mol^{-1}. Calculation of the contribution of the electronegativities of the O and C atoms to the activation energy for the $RO^\bullet + RH$ reaction yields $\Delta EA = 26.1$ kJ mol^{-1}, which should be regarded as very considerable bearing in mind that $E_{e0} = 54.8$ kJ mol^{-1}. The higher is the difference in electron affinity of atoms in reaction $X^\bullet + HY \rightarrow XH + Y^\bullet$, the lower is the activation energy E_{e0}. The empirical dependence of parameter r_e on ΔEA has the following form:[13–15]

$$[\Delta r_e(m)^2] = -22.4 \times 10^{-22}[\Delta EA(XY)/D_{HH}] \qquad (17.12)$$

17.6 REPULSION OF ATOMS FORMING THE REACTION CENTER

When the fragments X and Y approach one another in the $X \cdots H \cdots Y$ transition state, their outer electron shells begin to repel one another. The larger the radii of the atoms X and Y, the stronger the repulsion becomes. The examples presented below confirm this conclusion. We shall compare the $R^\bullet + RH$, $R^\bullet + HSiR_3$, and $R_3Si^\bullet + HSiR_3$ reactions.[22]

Reaction	$r_e \times 10^{11}$ (m)	$r_{X-Y} \times 10^{11}$ (m)	D_{XY} (kJ mol^{-1})	ΔEA (kJ mol^{-1})
$R^\bullet + RH$	4.414	15.13	376	0.0
$R^\bullet + HSiR'_3$	4.782	18.70	376	11.0
$R_3Si^\bullet + HSiR'_3$	4.967	23.59	354	0.0

An evident parallel variation of the increment in r_e and in the bond length r_{XY} is observed. On the other hand, the strengths of the X—Y bonds in this series are

TABLE 17.12 Comparison of r_e Parameters with Bond Length r_{E-X} for the Reactions of Hydrogen Atom and Alkyl Radicals with EH_n and $R_{n-1}EH$ Compounds, where E = C, Si, Ge, Sn, P, Se, in the Gas and Liquid Phase[a]

Reactant	$r_e \times 10^{11}$ (m)	$r_{E-X} \times 10^{10}$ (m)	D_e(E−X) (kJ mol^{-1})	$r_e^2 \times 10^{22} - 137 \times (D_{E-X} - D_{H-H})$ (m)^2
		$H^\bullet + EH_4 \rightarrow H_2 + E^\bullet H_3$		
CH_4	3.87	1.091	457.4	1.42
SiH_4	4.09	1.480	408.0	4.64
GeH_4	4.28	1.525	380.4	7.04
PH_3	4.09	1.420	364.9	5.91
SeH_2	4.06	1.470	348.9	6.14
GeH_4	4.28	1.525	380.4	7.04
		$R^\bullet + R^1_3EH \rightarrow RH + R^1_3E^\bullet$		
R^1_2PH	4.16	1.858	306.6	8.22
R^1_3CH	4.62	1.536	384.2	9.96
R^1_3SiH	4.77	1.870	381.3	11.45
R^1_3GeH	4.93	1.945	350.4	10.92
R^1_3SnH	5.07	2.144	300.2	16.81

[a] See Eq. (17.13) and Refs. 15, 22, and 36.

similar, so that an increase in r_e is not caused by a change in the triplet repulsion. The electron affinities of the C and Si atoms are also similar and in the first and third reactions $\Delta EA = 0$. The same situation was observed for the reactions of hydrogen atoms and alkyl radicals with several organometallic hydrides (see Table 17.12).[36]

The empirical dependence of the parameter r_e on X−Y bond length r_{XY} in the reactions $X^\bullet + HY$ obeys the linear equation.[36]

$$[\Delta r_e(m)^2] = 9.4(r_{XY}/r_{HH}) \times 10^{-22} \tag{17.13}$$

The rate constant reactions of triethylsilyl radicals with different compounds are in Table 17.13.

The general dependence of the r_e parameter in the interaction of radicals carrying a free valence on the D_{XY} and r_{XY} of reacting bonds and ΔEA of X and Y atoms has the following form:[15,36]

$$[r_e(m)^2] \times 10^{22} = 13.7(D_{XY}/D_{HH}) - 22.4(\Delta EA/D_{HH}) + 9.4(r_{XY}/r_{HH}) - 12.4 \tag{17.14}$$

These formulas make it possible to estimate the contribution of each factor, namely, triplet repulsion ΔE_T, electronegativity, ΔE_{EA}, and repulsion of the electron shells of the X and Y atoms ΔE_R in the transition state, to the activation barrier E_{e0} for each class of radical abstraction reactions. Since

TABLE 17.13 Rate Constants and Activation Energies for the Triethylsilyl Radical Reactions with C–H Bonds of Organic Compounds[a]

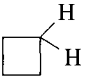
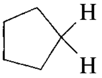
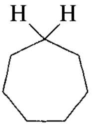
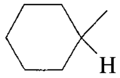
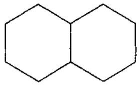
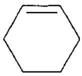
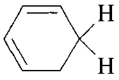
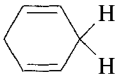
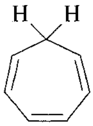
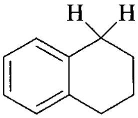
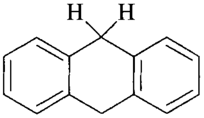
RH	n	ΔH_e (kJ mol^{-1})	E (kJ mol^{-1})	A (L mol^{-1} s^{-1})	k (300 K) (L mol^{-1} s^{-1})
EtMeCH–H	4	39.8	66.0	4.0×10^9	1.29×10^{-2}
Me_3C–H	1	26.8	57.7	1.0×10^9	8.99×10^{-2}
	8	45.3	69.6	8.0×10^9	6.02×10^{-3}
	1	35.2	63.0	1.0×10^{10}	0.11
	1	30.7	60.1	1.4×10^{10}	0.47
	1	22.3	54.8	1.0×10^9	0.28
	2	14.4	50.0	2.0×10^9	3.9
CH_2=$CHCH_2$–H	3	−5.2	47.0	3.0×10^8	2.0
CH_2=CHCH–HMe	2	−23.4	37.0	2.0×10^8	72.1
CH_2=CHC–HMe_2	1	−33.6	31.7	1.0×10^8	3.03×10^2
(*Z*)-MeCH=CHCH–HMe	2	−29.2	34.0	2.0×10^8	2.44×10^2
Me_2C=CHCH–HMe	2	−41.2	27.9	2.0×10^8	2.80×10^3
Me_2C=CMeC–HMe_2	1	−50.4	23.4	1.0×10^8	8.34×10^3
CH_2=CHC–HMeCH=CH_2	1	−66.0	16.3	1.0×10^8	1.45×10^5
	4	−31.7	32.7	4.0×10^9	8.20×10^3
	4	−42.3	27.3	4.0×10^9	6.95×10^4
	4	−60.6	18.7	4.0×10^9	2.21×10^6
	2	−72.2	13.6	2.0×10^9	8.44×10^6
MeC≡CC–HMe_2	1	−43.8	26.6	1.0×10^8	2.33×10^3

TABLE 17.13 (*continued*)

RH	n	ΔH_e (kJ mol^{-1})	E (kJ mol^{-1})	A (L mol^{-1} s^{-1})	k (300 K) (L mol^{-1} s^{-1})
PhMeCH–H	2	−9.1	39.5	2.0×10^8	26.2
$PhMe_2C$–H	1	−18.5	34.4	1.0×10^8	1.03×10^2
	4	−27.6	29.6	4.0×10^9	2.82×10^4
	4	−51.2	18.0	4.0×10^9	2.92×10^6
Me_2NH_2C–H	1	6.3	45.2	1.0×10^9	13.7
$(CH_2{=}CHCH_2)_3N$	6	−27.6	34.8	6.0×10^8	5.25×10^2

[a] See Eqs. (9.13), (9.15), and (9.16) and the parameters in Table 17.1.

$E_{e0} = br_e(1 + \alpha)^{-1}$, it follows that, by employing the corresponding increment from Eqs. (17.9), (17.12), and (17.13), it is possible to calculate the contribution of a particular factor. Table 17.14 presents the results of such calculation for 21 classes of radical abstraction reactions.

It is seen from the data presented in Table 17.14 that the triplet repulsion ΔE_T makes an additional contribution to the activation energy E_{e0}. The difference between the electronegativities of the fragments X and Y decreases the activation energy. When the discrepancy between the electron affinities is large, this decrease may be considerable. For example, $\Delta E_{EA} = -45$ kJ mol^{-1} for the $HO^{\bullet} + SiH_4$ reaction and $\Delta E_{EA} = -43$ kJ mol^{-1} in the hydrogen atom reaction with water.

The repulsion of the electron orbitals for the atoms forming the reaction center ΔE_R plays an important role in all radical abstraction reactions. In the interaction of radicals with molecules, the contribution of this repulsion ranges from 25 to 46 kJ mol^{-1}. In reactions of molecules with hydrogen atoms, the contribution is naturally smaller, varying from 8 to 16 kJ mol^{-1}.

17.7 INFLUENCE OF π-BONDS IN THE VICINITY OF THE REACTION CENTER

An aromatic ring and a double or triple bond in the α-position relative to a C–H bond weaken the latter by virtue of the delocalization of the unpaired electron in its interaction with the π-bond. The weakening of the C–H bond is very considerable: for example, D(C–H) is 422 kJ mol^{-1} in ethane, 368 kJ mol^{-1} in

TABLE 17.14 The Contribution of Triplet Repulsion (ΔE_T), the Electron Affinity of the Fragments X and Y (ΔE_{EA}), and the Repulsion of the Atoms Forming the X–Y Bond (ΔE_R) to the Activation Energy E_{e0} for the $X^\bullet + HY \rightarrow XH + Y^\bullet$ Reaction[a]

Reaction	$b(1+\alpha)^{-1} \times 10^{-11}$ $(\mathrm{kJ\,mol^{-1}})\mathrm{m^{-1}}$	$r_e \times 10^{11}$ (m)	ΔE_T $(\mathrm{kJ\,mol^{-1}})$	ΔE_{EA} $(\mathrm{kJ\,mol^{-1}})$	ΔE_R $(\mathrm{kJ\,mol^{-1}})$
$R^\bullet + HR^1$	1.87	4.41	41	0	25
$R^\bullet + H_2NR^1$	2.05	3.84	45	−8	32
$R^\bullet + HOOR^1$	2.06	3.80	37	−7	29
$R^\bullet + HOAr$	2.08	3.80	35	−19	26
$R^\bullet + HSiR^1_3$	1.60	4.78	30	−3	27
$R^\bullet + HSR^1$	2.13	4.09	44	0	46
$HO^\bullet + HR$	2.09	3.67	53	−22	30
$HO^\bullet + SiH_4$	1.79	3.30	55	−45	28
$RO^\bullet + HR^1$	2.08	3.55	49	−20	30
$RO^\bullet + HSiR^1_3$	1.74	3.68	45	−34	26
$RO_2^\bullet + HR^1$	2.06	3.80	37	−7	29
$RO_2^\bullet + HOOR^1$	2.30	2.85	15	0	28
$RO_2^\bullet + HOAr$	2.33	2.88	0	0	45
$AmO^\bullet + HR$	2.08	3.66	28	−23	26
$AmO^\bullet + HOAr$	2.33	2.77	0	0	42
$R_3Si^\bullet + HSiR^1_3$	1.38	4.97	18	0	27
$H^\bullet + HR$	1.96	3.76	53	−8	10
$H^\bullet + NH_3$	2.11	3.45	63	−21	9
$H^\bullet + H_2O$	2.20	3.91	76	−43	8
$H^\bullet + SiH_4$	1.69	4.09	34	−2	15
$H^\bullet + H_2S$	1.88	3.60	42	−5	16

[a] See Refs. 15, 25, 37, and 38.

the methyl group of propene ($\Delta D = -54\ \mathrm{kJ\,mol^{-1}}$), and 375 $\mathrm{kJ\,mol^{-1}}$ in the methyl group of toluene ($\Delta D = -47\ \mathrm{kJ\,mol^{-1}}$). Such a decrease in the strength of the C–H bond diminishes the enthalpy of the radical abstraction reaction and, hence, its activation energy. This effect is illustrated below in relation to the reactions of the methyl radical with hydrocarbons.

Hydrocarbon	C_2H_6	$MeCH{=}CH_2$	PhMe
ΔH $(\mathrm{kJ\,mol^{-1}})$	−18.0	−72.0	−65.0
E $(\mathrm{kJ\,mol^{-1}})$	52.4	37.4	39.3
ΔE $(\mathrm{kJ\,mol^{-1}})$	0.0	−15.0	−13.1

Comparative analysis of the kinetics of the reactions of atoms and radicals with paraffinic (R^1H), olefinic (R^2H), and aromatic alkyl-substituted (R^3H) hydrocarbons within the framework of the IPM model permitted a new and important

TABLE 17.15 The Influence of the π-C—C Bond on the Activation Energy E_{e0} for the Radical Abstraction Reaction[a]

Radical	RH	br_e $(kJ\,mol^{-1})^{1/2}$	E_{e0} $(kJ\,mol^{-1})$	ΔE_{π} $(kJ\,mol^{-1})$
$H^{\bullet}$	R^1H	14.49	57.9	0.0
$H^{\bullet}$	R^2H	15.58	66.9	9.0
$H^{\bullet}$	R^3H	15.34	64.9	7.0
$R^{\bullet}$	R^1H	17.23	74.2	0.0
$R^{\bullet}$	R^2H	18.86	88.9	14.7
$R^{\bullet}$	R^3H	18.11	82.0	7.8
$RO^{\bullet}$	R^1H	13.37	55.2	0.0
$RO^{\bullet}$	R^2H	14.41	64.1	8.9
$RO^{\bullet}$	R^3H	14.16	61.9	6.7
$RO_2^{\bullet}$	R^1H	14.23	61.5	0.0
$RO_2^{\bullet}$	R^2H	15.68	74.7	13.2
$RO_2^{\bullet}$	R^3H	14.74	66.0	4.5
$AmO^{\bullet}$	R^1H	13.72	58.0	0.0
$AmO^{\bullet}$	R^2H	15.66	75.5	17.5
$AmO^{\bullet}$	R^3H	14.42	64.0	6.0

[a] See Refs. 13, 15, 17, 18, and 37.

conclusion.[15–18] It was found that the π-C—C bond occupying the α-position relative to the attacked C—H bond increases the activation energy for thermally neutral reaction. The corresponding results are presented in Table 17.15. Evidently, the activation energy for a thermally neutral reaction with participation of a hydrogen atom or a radical (alkyl, alkoxyl, etc.) is higher in those cases where there is a π bond or an aromatic ring next to the attacked C—H bond. Evidently, this effect is a property of the structures themselves and the π bond exerts a dual effect on the reaction center. On the one hand, by weakening the C—H bond the π bond in the α-position decreases the enthalpy, and hence the activation energy for the reaction. On the other hand, by interacting with the electrons of the reacting bonds, the π-orbital increases the strength of the C—Y bond in the $Y^{\bullet} + HR$ reaction, which increases the energy of the nonbonding C—Y orbital and intensifies triplet repulsion.

17.8 STERIC EFFECT

The influence of bulky substituents, for example, tertiary alkyl groups, on the kinetics of diverse chemical reactions is well known. A steric effect also occurs in radical reactions. Such substituents usually influence both the enthalpy of the reaction and its activation energy. The IPM model makes it possible to separate these effects and to estimate the contribution of steric hindrance to the activation energy. Radical reactions in which a radical attacks the O—H bond of a sterically hindered phenol (Ar^2OH) containing two *tert*-butyl groups in the ortho position relative to the phenolic group were thoroughly investigated. Comparison of the energies E_{e0} for isotypical reactions involving both sterically unhindered (Ar^1OH) and sterically hindered (Ar^2OH) phenols makes it possible to estimate the contribution of steric hindrance ΔE_S to the activation energy.[38]

$$\Delta E_S = E_{e0}(Ar_2OH) - E_{e0}(Ar_1OH) \tag{17.15}$$

The results of the comparison are presented in Table 17.16. The steric hindrance increases the activation energy for a thermally neutral reaction by 8.2, and 24 kJ mol^{-1} when oxygen-centered, nitrogen-centered, and alkyl radicals are involved, respectively. The data were obtained with the aid of the IPM model. The steric effect is manifested similarly in the reactions of sterically hindered ($Ar^2O^{\bullet}$) phenoxyl radicals with various substrates (Table 17.16). The reactions of the sterically hindered diphenylpicryl radical ($DPPH^{\bullet}$) and the unhindered diphenylaminyl radical may serve as another example (Table 17.16). In the reactions of $DPPH^{\bullet}$ with phenols, the contribution of the steric effect to E_{e0} ranges from 23 to 30 kJ mol^{-1}, that is, it is very considerable.

TABLE 17.16 The Contribution of the Steric Effect (ΔE_S) on the Activation Energy E_{e0} for the $X^{\bullet} + HY \rightarrow XH + Y^{\bullet}$ Reactions[a]

Reaction[b]	br_e (kJ mol^{-1})$^{1/2}$	E_{e0} (kJ mol^{-1})	ΔE_S (kJ mol^{-1})
$C^{\bullet}H_3 + Ar_1OH$	17.38	59.8	0.0
$C^{\bullet}H_3 + Ar_2OH$	18.92	84.2	24.4
$RO_2^{\bullet} + Ar_1OH$	13.76	45.3	0.0
$RO_2^{\bullet} + Ar_2OH$	14.40	51.8	6.5
$Ar_1O^{\bullet} + Ar_1OH$	12.61	39.7	0.0
$Ar_1O^{\bullet} + Ar_2OH$	13.31	44.3	4.6
$Am^{\bullet} + Ar_1OH$	10.93	27.6	0.0
$Am^{\bullet} + Ar_2OH$	12.15	34.2	6.6
$AmO^{\bullet} + Ar_1OH$	12.93	41.8	0.0
$AmO^{\bullet} + Ar_2OH$	14.54	52.9	11.1
$Ar_1O^{\bullet} + HOOR$	13.46	45.3	0.0
$Ar_2O^{\bullet} + HOOR$	14.40	51.8	6.5
$Ar_2O^{\bullet} + Ar_2OH$	14.37	51.6	7.3
$Ar_1O^{\bullet} + AmH$	10.13	27.6	0.0
$Ar_2O^{\bullet} + AmH$	11.59	36.2	8.6
$Am^{\bullet} + RH$	16.87	81.7	0.0
$DPPH^{\bullet} + RH$	18.59	99.3	17.6
$Am^{\bullet} + Ar_1OH$	10.93	27.6	0.0
$DPPH^{\bullet} + Ar_1OH$	14.85	51.0	23.4
$Ar_2O^{\bullet} + Ar_2OH$	12.15	34.2	0.0
$DPPH^{\bullet} + Ar_2OH$	16.74	64.8	30.6

[a] See Refs. 25 and 28.

[b] DPPH = 2,2′-Diphenyl-1-picrylhydrazyl.

17.9 POLAR EFFECT IN RADICAL REACTIONS

An extensive literature was devoted to polar effects in chemical reactions. The IPM model permit a fresh approach to this important problem. The introduction of a functional group into a hydrocarbon molecule alters the dissociation energy of the neighboring C—H bonds, which is indicated by the examples presented below.

Compound	C_2H_5–H	MeCH–H(OH)	MeC–H(O)	EtOCH–HMe
D (kJ mol^{-1})	422	400	338	399

The change in the C—H bond strength affects the enthalpies and through them the activation energies for radical abstraction reactions. If a molecule is attacked by a nonpolar group (hydrogen atom or alkyl radical), then the influence of the polar group on the activation energy is confined to a change in ΔH. This was confirmed by data on the reactions of the methyl radical with the C—H bonds of hydrocarbons and their derivatives (alcohols, ethers, etc.), which are characterized by a virtually identical parameter $br_e = 17.23$ (kJ mol^{-1})$^{1/2}$. Thus a polar group (OH, OR, etc.) influences only the enthalpy of reaction and not the energy for the reaction center of a transition state of the type $C\cdots H\cdots C$ and $H\cdots H\cdots C$.

A different picture is observed when a polar radical reacts with a C—H bond of a polar molecule. For example, the reaction of an oxygen atom with a methane C—H bond is characterized by the parameter $br_e = 13.11$(kJ mol^{-1})$^{1/2}$ while the reaction with a C—H bond of methanol is characterized by the corresponding parameter of 12.55 (kJ mol^{-1})$^{1/2}$.[39] For these values of br_e the difference between the activation energies is equal to 4.6 kJ mol^{-1}. The decrease in activation energy can be explained by the fact that the polar O—H group in the $O\cdots H\cdots C{-}OH$ transition state interacts with the $O\cdots H\cdots C$ polar reaction center.

The IPM model makes it possible for us to isolate, from the overall effect of the substituent, its contribution to E. In the calculation, use is made of the values for ΔH and the activation energy for a thermally neutral reaction of the given group (reaction series) because the activation energy can be represented by the sum $E_e = E_{e0} + \Delta E_H$ (see above), where the second term takes into account only the influence of enthalpy. The polar interaction in the transition state may be inferred by comparing the values of E_{e0} in various reactions of the same radical involving a hydrocarbon and the corresponding polar molecule. The contribution of the polar interaction to the activation energy (ΔE_μ) can be estimated from the formula[15–18]

$$\Delta E_\mu = [(br_e)^2_\mu - (br_e)^2_{RH}](1+\alpha)^{-2} \qquad (17.16)$$

where the parameters $(br_e)^2_\mu$ and $(br_e)^2_{RH}$ refer to reactions involving a polar compound YH with dipole moment μ and a reference hydrocarbon RH, respectively.

The results of the calculation of the energy ΔE_{μ} (in kJ mol^{-1}) for the $X^{\bullet}$ + HY gas-phase reactions are presented below.[39]

$X^{\bullet}$/HY	MeOH	$CH_2(O)$	RCH(O)	MeC(O)Me	Me_2O
O	4.6	−4.6	−7.9	−9.4	−5.1
$HO^{\bullet}$	2.4	1.8	1.5	−11.4	2.8
$MeO^{\bullet}$	−6.0	0	−12.2		
$Me_3CO^{\bullet}$		−4.2	−3.1	−17.8	

Extensive data concerning the influence of polar groups on the activation energies for abstraction reactions were obtained by analyzing experimental data on reactions with participation of alkoxyl and peroxyl radicals in the liquid phase. These data are presented in Table 17.17. As seen from the table, the interaction of a polar group with a $O\cdots H\cdots C$ or $O{-}O\cdots H\cdots C$ polar reaction center can both diminish and increase the activation energy. A very marked decrease in activation energy (from −11 to −19 kJ mol^{-1}) was observed in the reactions of $RO^{\bullet}$ and $RO_2^{\bullet}$ with aldehydes and ketones. The alcoholic group diminishes the height of the activation barrier slightly (by 1–3 kJ mol^{-1}), with the reaction of $RO^{\bullet}$ with benzyl alcohol being an exception. An increase in activation energy is observed in reactions with ethers.

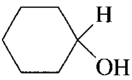
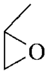
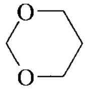
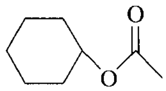
17.10 EFFECT OF MULTIDIPOLE INTERACTION

Yet another effect, namely, multidipole interaction, is manifested in the reactions of polar radicals with polyfunctional compounds. This effect consists of the unequal reactivities of the same group, for example, $R_2CH(OH)$, in compounds with one or several functional groups. The corresponding kinetic data were analyzed within the framework of the IPM model.[42] The multidipole interaction is manifested, in particular, in the reactions of peroxyl radicals $RO_2^{\bullet}$, containing functional groups, with oxygen-containing compounds YH (Table 17.17). The magnitude of this effect in the transition state may be inferred from the change in the activation energy for a thermally neutral reaction on passing from a monofunctional compound YH to a polyfunctional compound ZH.

$$\Delta\Delta E_{\mu} = [(br_e)^2_{ZH} - (br_e)^2_{YH}](1+\alpha)^{-2} \qquad (17.17)$$

As can be seen from Table 17.18, the highest values of $\Delta\Delta E_{\mu}$ correspond to the transition from $RO_2^{\bullet}$ to $YO_2^{\bullet}$ containing a carbonyl or ester group. Apparently this effect is induced by the dipole–dipole interaction in the transition state. Table 17.19 presents data concerning the influence of an ester groups on the reactivity of the CH_2 groups in reactions with peroxyl radicals. The multidipole effect always reduces the activation energy for reactions of this group and, in

TABLE 17.17 The Contribution of the Polar Effect (ΔE_{μ}) on the Activation Energy E_{e0} for the Reactions of the Alkoxyl and Peroxyl Radicals with C−H Bonds of Oxygen-Containing Compounds (YH)[a]

Radical YH	$RO^{\bullet}$ ΔE_{μ} ($kJ\,mol^{-1}$)	$RO_2^{\bullet}$ ΔE_{μ} ($kJ\,mol^{-1}$)	$YO_2^{\bullet}$ ΔE_{μ} ($kJ\,mol^{-1}$)	$YO_2^{\bullet}$ $\Delta\Delta E_{\mu}$ ($kJ\,mol^{-1}$)
R^1OH	−1.5	−2.2	−5.8	−3.6
	−1.1	−2.2	−5.6	−3.4
$PhCH_2OH$	−8.8	−2.8	−12.7	−9.9
PhCH(O)	−19.0	−8.2	−15.8	−7.6
$R^1CH(O)$	−12.2	−8.8	−15.8	−7.0
$R^1C(O)CH_2R$	−10.6	−15.4	−13.0	−2.4
$R^1C(O)CHR$		−15.7	−21.2	−5.5
$PhCH_2C(O)R$	−5.2	−11.2	−12.9	−1.7
$(R^1CH_2)_2O$	−1.7	3.4	5.7	2.3
$(R_2CH)_2O$	2.3	6.3	3.5	−2.8
$(PhCH_2)_2O$		−1.4		
$(PhR^1CH)_2O$		6.1	3.7	−2.4
$(R^1O)_2CH_2$	−3.9	1.8	1.4	−0.4
$(R^1O)_2CHCH_3$	−0.4	6.2	3.8	−2.4
		−3.8	−3.8	0.0
		−3.4	−5.3	−1.9
		−2.4	−0.2	2.2
$CH_3OC(O)R^1$	6.3	8.7		
$R^1CH_2OC(O)R$	8.0	8.9	−11.2	−20.1
	−6.1	8.8		
$PhCH_2OC(O)R^1$	−2.7	4.5	−17.6	−22.1
MeC(O)OH		11.5		
$R^1CH_2C(O)OH$		7.9		
$Me_2CHC(O)OH$		10.6		
$RCH_2C(O)OR^1$		−2.7		
Me_2CHOR^1		2.7		
$PhCH_2C(O)OR$	−3.1	−7.6		

[a] See Refs. 25 and 39–42.

TABLE 17.18 The Contribution of the Polar Effect (ΔE_{μ}) and the Effect of Multidipole Interaction ($\Delta\Delta E_{\mu}$) on the Activation Energy E_{e0} for the Reactions of the Peroxyl Radicals with the C–H Bonds of Esters[a]

Ester	ΔH_e (kJ mol^{-1})	E_e (kJ mol^{-1})	ΔE_{μ} (kJ mol^{-1})	$\Delta\Delta E_{\mu}$ (kJ mol^{-1})
$[CH_3OC(O)]_2$	31.7	72.5	−3.6	−12.3
$[Me(CH_2)_4C(O)OCH_2]_2$	23.7	71.0	0.3	−8.6
$[Me(CH_2)_4C(O)OCH_2CH_2]_2$	23.7	68.8	−0.4	−9.3
$MeO(O)C(CH_2)_3C(O)OCH_2Me$	23.7	74.8	2.2	−6.7
$CH[CH_2C(O)O(CH_2)_2Me]_3$	23.7	76.6	6.0	−2.9
$CH[CH_2C(O)O(CH_2)_3Me]_3$	23.7	76.1	5.5	−3.4
$[MeCH_2C(O)OCH_2])_2C(Me)_2$	23.7	78.6	8.0	−0.9
$[Me(CH_2)_3C(O)OCH_2]_4C$	23.7	76.8	6.2	−2.7
$[Me(CH_2)_6C(O)OCH_2CH_2]_2O$	23.7	77.3	6.5	−2.4
$[MeC(O)OCH_2]_4C$	23.7	77.6	7.0	−1.9
$[MeCH_2C(O)OCH_2]_4C$	23.7	75.8	5.1	−3.8
$[Me(CH_2)_8C(O)OCH_2]_4C$	23.7	69.6	−1.1	−10
$[MeCH_2C(O)OCH_2]_3CCH_2Me$	23.7	77.4	6.8	−2.1

[a] See Ref. 42.

certain cases, the decrease is extremely significant (down to −10 kJ mol^{-1} and even less).

17.11 SOLVATING EFFECT

An important effect, observed when reactions take place in the liquid phase, is associated with the solvation of the reactants. Theoretical comparison showed that the collision frequencies of the species in a gas and in a liquid are different, the difference being due to the difference between the free volumes. In a gas, the free volume is virtually equal to the volume occupied by the gas species ($V_f \approx V$), while in a liquid it is much smaller than the volume of the liquid species ($V_f \ll V$). Since the motion and collision of the species occurs in the free volume, the collision frequency in a liquid is higher than in a gas by the value $(V/V_f)^{1/3}$. The activation energies for the reactions of radicals and atoms with hydrocarbon C–H bonds in a gas and in a liquid are virtually identical, with those in a liquid being independent of the solvent polarity. This also applies to the parameter br_e, which can be seen from the following examples referring to the interaction of the hydroxyl radical with hydrocarbons:

RH	C_2H_6	C_3H_8
br_e (kJ mol^{-1})$^{1/2}$ (gas)	13.74	13.52
br_e (kJ mol^{-1})$^{1/2}$ (H_2O)	13.48	13.40

A different picture is observed when a polar molecule is attacked by a polar radical ($HO^•$, $RO^•$, $RO_2^•$, etc.).[39] The reaction in a polar solvent is slower than in a nonpolar hydrocarbon solution or in the gas phase. From the change in the parameter br_e, it is possible to estimate the extent to which the activation energy increases as a result of the solvation of the polar reactants.[39]

$$\Delta E_{sol} = [(br_e)_l^2 - (br_e)_g^2] \times (1 + \alpha)^{-2} \qquad (17.18)$$

The subscripts l and g in Eq. (17.18) refer to the liquid and gas phases, respectively. The results of the comparison are presented in Table 17.19. It is seen that the activation energy of the reaction $HO^• + YH$ is higher in aqueous solution in comparison with the gas phase. This is associated with the solvation of the reactants and the need to overcome the solvation shell by the reacting component in order to effect the elementary step. The contribution of ΔE_{sol} is particularly large in the reaction of the hydroxyl radical with aldehydes.

When a radical or atom attacks a polar O—H or N—H bond, the polar solvent Y forms a hydrogen bond of the type $O{-}H \cdots Y$ or $N{-}H \cdots Y$.[43]

$$XH + Y \Leftrightarrow XH \cdots Y$$

Free radicals attack the free X—H bonds of polar XH molecules. The effective rate constant of any free radical with XH depends on the concentration of the polar

TABLE 17.19 The Contribution of Solvation to the Activation Energies for Radical Reactions[a]

RH	$(br_e)_g$ (kJ mol^{-1})$^{1/2}$	$(br_e)_l$ (kJ mol^{-1})$^{1/2}$	ΔE_{sol} (kJ mol^{-1})
	$HO^• + HR \rightarrow HOH + R^•$ (water)		
MeOH	13.91	14.26	3.1
EtOH	13.48	14.01	4.6
Me_2CHOH	13.31	14.12	7.1
Me_3COH	13.39	14.13	6.5
MeOMe	13.95	14.70	6.8
Et_2O	13.47	14.33	7.6
$CH_2(O)$	13.84	14.98	10.4
MeCH(O)	13.81	14.99	10.8
MeC(O)Me	13.81	14.50	6.3
MeC(O)OMe	14.38	14.97	5.5
	$Me_3CO^• + HR \rightarrow Me_3COH + R^•$ (acetone)		
MeC(O)Me	12.67	13.17	7.2

[a] See Ref. 39.

TABLE 17.20 Rate Constants for the 1,1-Dimethylethyloxyl and Cumyloxyl Radicals with Phenols in Different Solvents at $T = 295$ K[a]

Solvent	k ($\mathrm{L\,mol^{-1}\,s^{-1}}$)	Solvent	k ($\mathrm{L\,mol^{-1}\,s^{-1}}$)
$Me_3CO^{\bullet} + PhOH$[44]		*$Me_3CO^{\bullet} + 4\text{-}BrC_6H_4OH$*[b]	
Benzene	3.3×10^8	Benzene	3.4×10^8
Toluene	3.3×10^8	Toluene	3.0×10^8
Methanol	2.2×10^7	Methanol	1.8×10^7
1,1-Dimethylethanol	1.5×10^7	1,1-Dimethylethanol	7.7×10^6
Pyridine	4.7×10^6	Pyridine	2.4×10^6
	$Me_2PhCO^{\bullet} + PhOH$[c]		
Carbon tetrachloride	8.6×10^8	Methyl 1,1-dimethylpropionate	1.3×10^7
Benzene	2.8×10^8	Methyl formate	1.0×10^7
Chlorobenzene	2.2×10^8	Trimethylacetonitrile	9.8×10^6
Anisole	5.6×10^7	Methyl acetate	9.5×10^6
Benzonitrile	1.9×10^7	Ethyl acetate	7.5×10^6
Acetic acid	1.8×10^7	Acetonitrile	5.8×10^6
1,1-Dimethylethyl acetate	1.4×10^7	1,1-Dimethylethanol	3.6×10^6

[a] See Refs. 44 and 45.

[b] See Ref. 44.

[c] See Ref. 45.

compound Y and the equilibrium constant K for the formation of a hydrogen bond between XH and Y.

$$K_{\mathrm{eff}} = k[\mathrm{Y}](1 + K[\mathrm{Y}])^{-1} \tag{17.19}$$

The hydrogen bond shields the reactant and slows down the reaction regardless of what kind of radical, polar or nonpolar, attacks it. The values of rate constants for the reaction of 1,1-dimethylethoxyl and cumyloxyl radicals with phenols in different solvents illustrate this shielding effect (see Table 17.20).[44–50]

REFERENCES

1. V. N. Kondratiev and E. E. Nikitin, *Gas-Phase Reactions*, Springer-Valley, Berlin, 1981.
2. E. T. Denisov, *Liquid-Phase Reaction Rate Constants*, Plenum, New York, 1974.
3. J. A. Kerr, in *Comprehensive Chemical Kinetics*, C. H. Bamford and C. F. H. Tipper (Eds.), Elsevier, Amsterdam, The Netherlands, 1976, Vol. 18, p. 39.
4. K. U. Ingold, in *Free Radicals*, J. K. Kochi (Ed.), John Wiley & Sons, Inc., New York, 1973, Vol. 1, p. 37.

5. W. G. Mallard, F. Westley, J. T. Herron, and R. F. Hampson, *NIST Chemical Kinetics Database*, Version 6.0, NIST Standard Reference Data, Gaithersburg, MD, 1994.
6. H. Fischer (Ed.), *Radical Reaction Rates in Liquids*, Landolt-Bornstein New series, Group 2 (Atomic and Molecular Physics), Springer-Verlag, Berlin, 1984–1985, Vol. 13, subvolumes (a)–(e).
7. H. Fischer (Ed.), *Radical Reaction Rates in Liquids*, Landolt-Bornstein New series, Group 2 (Atomic and Molecular Physics), Springer-Verlag, Berlin, Suppl. 1997, Vol. 13, subvolumes (a)–(e).
8. G. V. Buxton, C. L. Greenstock, W. P. Helman, and A. B. Ross. *J. Phys. Chem. Ref. Data* **17**, 513 (1988).
9. W. G. Mallard, A. B. Ross, and W. P. Helman, *NDRL/NIST Solution Kinetics Database*, Version 2, NIST Standard Reference Data, Gaithersburg, MD, 1994.
10. K. J. Laidler, *Chemical Kinetics*, Harper and Row, New York, 1987.
11. M. W. Hanna, *Quantum Mechanics in Chemistry*, Benjamin / Cummings, Menlo Park, CA, 1981.
12. S. Skokov and R. A. Wheeler, *Chem. Phys. Lett.* **271**, 251 (1997).
13. E. T. Denisov, *Kinet. Catal.* **32**, 406 (1991).
14. E. T. Denisov, *Mendeleev Commun.* **2**, 1 (1992).
15. E. T. Denisov, *Russ. Chem. Rev.* **66**, 859 (1997).
16. E. T. Denisov, in *General Aspects of the Chemistry of Radicals*, Z. B. Alfassi (Ed.), John Wiley & Sons, Inc., Chichester, 1999.
17. E. T. Denisov and T. G. Denisova, *Zh. Fiz. Khim.* **65**, 1208 (1991).
18. E. T. Denisov and T. G. Denisova, *Kinet. Catal.* **34**, 173 (1993).
19. E. T. Denisov, *Kinet. Catal.* **35**, 293 (1994).
20. E. T. Denisov, *Russ. J. Phys. Chem.* **68**, 1089 (1994).
21. E. T. Denisov, *Kinet. Catal.* **35**, 617 (1994).
22. E. T. Denisov, *Russ. Chem. Bull.* **47**, 1274 (1998).
23. E. T. Denisov and S. L. Khursan, *Russ. J. Phys. Chem.* **74**, Suppl. 3, 5491 (2000).
24. E. T. Denisov, *Khim. Fizika* **20**, 37 (2001).
25. E. T. Denisov and T. G. Denisova, *Handbook of Antioxidants*, CRC Press, Boca Raton, FL, 2000.
26. M. G. Evans and M. Polany. *Trans. Faraday Soc.* **34**, 11 (1938).
27. N. N. Semenov, *Some Problems of Chemical Kinetics and Reactivity*, Pergamon Press, London, 1958, Vol. 1; 1959, Vol. 2.
28. E. T. Denisov, *Kinet. Catal.* **37**, 519 (1996).
29. E. T. Denisov, *Kinet. Catal.* **35**, 299 (1994).
30. S. Sato, *J. Chem. Phys.* **23**, 2456 (1995).
31. H. S. Johnston, *Gas Phase Reaction Rate Theory*, Ronald Press, New York, 1996.
32. T. Berces and J. Dombi, *Int. J. Chem. Kinet.* **12**, 123, 183 (1980).
33. A. A. Zavitsas, *J. Am. Chem. Soc.* **94**, 2779 (1972).
34. A. A. Zavitsas and A. A. Melikian. *J. Am. Chem. Soc.* **97**, 2757 (1975).
35. L. Pauling, *General Chemistry*, W. H. Freeman & Co., San Francisco, CA, 1970.
36. T. I. Drozdova and E. T. Denisov, *Kinet. Catal.* **43**, 14 (2002).
37. E. T. Denisov, *Kinet. Catal.* **36**, 351 (1995).

38. E. T. Denisov and T. I. Drozdova, *Kinet. Catal.* **35**, 155 (1994).
39. E. T. Denisov and T. G. Denisova, *Russ. Chem. Bull.* **43**. 29 (1994).
40. E. T. Denisov and T. G. Denisova, *Kinet. Catal.* **34**. 738 (1993).
41. E. T. Denisov and T. G. Denisova, *Kinet. Catal.* **34**. 883 (1993).
42. T. G. Denisova and E. T. Denisov, *Kinet. Catal.* **35**. 305 (1994).
43. N. M. Emanuel, G. E. Zaikov, and Z. K. Maizus, *Oxidation of Organic Compounds*, Pergamon Press, Oxford, U.K., 1984.
44. P. K. Das, M. V. Encinas, S. Steenken, and J. C. Scaiano, *J. Am. Chem. Soc.* **103**, 4162 (1981).
45. D. V. Avila, K. U. Ingold, J. Lusztyk, W. H. Green, and D. R. Procopio, *J. Am. Chem. Soc.* **117**, 2929 (1995).
46. L. Valgimigli, J. T. Banks, K. U. Ingold, and J. Lusztyk, *J. Am. Chem. Soc.* **117**, 9966 (1995).
47. J. T. Banks, K. U. Ingold, and J. Lusztyk, *J. Am. Chem. Soc.* **118**, 6790 (1996).
48. L. Valgimigli, K. U. Ingold, and J. Lusztyk, *J. Org. Chem.* **61**, 7947 (1996).
49. J. T. Banks, K. U. Ingold, and J. Lusztyk, *J. Am. Chem. Soc.* **118**, 12485 (1996).
50. P. A. Macfaul, K. U. Ingold, and J. Lusztyk, *J. Org. Chem.* **61**, 1316 (1996).

Handbook of Free Radical Initiators. E.T. Denisov, T.G. Denisova, T.S. Pokidova
Copyright © 2003 John Wiley & Sons, Inc.
ISBN: 0-471-20753-5

18

FREE RADICAL REACTIONS FOR HYDROGEN TRANSFER AND SUBSTITUTION

18.1 REACTIONS OF HYDROGEN ATOM TRANSFER FROM A FREE RADICAL TO A MOLECULE

Reactions of hydrogen atom abstraction by a free radical from a molecule are widely abundant and well studied (see Chapter 17). The majority of these reactions occur rapidly with heat release ($\Delta H < 0$) and low activation energies. Reverse reactions, in which a free radical acts as the donor of the hydrogen atom and a molecule as its acceptor, are less known and poorly studied. These are, in particular, reactions of ketyl and alkyl radicals with carbonyl compounds.

$$R^1R^2C^{\bullet}OH + R^3R^4C{=}O \rightarrow R^1R^2C{=}O + R^3R^4C^{\bullet}OH$$

$$RCH_2C^{\bullet}H_2 + R^3R^4C{=}O \rightarrow RCH{=}CH_2 + R^3R^4C^{\bullet}OH$$

These transformations occur during photolysis and radiolysis of alcohols and carbonyl compounds[1] and are also intermediate stages in the chain reactions of thermolysis, oxidation, and polymerization in the presence of alcohols, carbonyl compounds, and quinones.[2–4] For empirical rate constants for these reactions, see Table 18.1.

A parabolic model is an efficient method for analysis of the reactivity of radicals and molecules in bimolecular reactions (see Chapter 9), which makes it possible to classify reactions of radical abstraction, divide them into groups, and calculate and compare parameters characterizing the reactivity of each group. This method was used to characterize and analyze the following processes:[9]

$$R^1R^2C^{\bullet}OH + {>}C{=}O \rightarrow R^1R^2C{=}O + {>}C^{\bullet}OH$$

$$RCH_2C^{\bullet}H_2 + {>}C{=}O \rightarrow RCH{=}CH_2 + {>}C^{\bullet}OH$$

$$R^1R^2C^{\bullet}OH + CH_2{=}CHR^3 \rightarrow R^1R^2C{=}O + CH_3C^{\bullet}HR^3$$

$$R^1CH_2C^{\bullet}H_2 + CH_2{=}CHR^2 \rightarrow R^1CH{=}CH_2 + CH_3C^{\bullet}HR^2$$

Since ketyl radicals possess a pronounced reduction activity, it can be expected that they react rather rapidly with olefins to reduce them to alkyl radicals.

$$R^1R^2C^{\bullet}OH + CH_2{=}CHR^3 \rightarrow R^1R^2C{=}O + CH_3C^{\bullet}HR^3$$

Alkyl radicals are well known to react readily at the double bond of an olefin. This results in polymerization, oligomerization, or dimerization of olefins.[3] At the same time, there are reactions in which alkyl radicals act as donors of hydrogen atoms, such as disproportionation reactions in which one alkyl radical serves as the acceptor and the second radical is the hydrogen donor. Similar reaction can occur between the alkyl radical and olefin, for example,

$$CH_2{=}CH_2 + {}^{\bullet}CH_2CH_2Me \rightarrow MeC^{\bullet}H_2 + CH_2{=}CHMe$$

Here olefin acts as the acceptor, the alkyl radical acts as the donor of the hydrogen atom, and the $C\cdots H\cdots C$ reaction center is formed, which is similar to those in the reactions of alkyl radicals with C—H bonds of hydrocarbons. These reactions are known in polymerization as reactions of chain transfer to a monomer.[3] Their activation energies for reactions of different radicals can be estimated using the equations and parameters of the parabolic model of bimolecular reactions (see Chapter 9). Kinetic parameter values for reactions of hydrogen atom abstraction by molecules from radicals are presented in Table 18.2. Values calculated by the IPM model for enthalpies and activation energies of this type of reaction are in Tables 18.3–18.5.

TABLE 18.1 Enthalpies, Activation Energies, and Rate Constants for Ketyl Radical Reactions with Carbonyl Compounds

Reaction	Solvent	ΔH (kJ mol^{-1})	k(298 K) (L mol^{-1} s^{-1})	E (kJ mol^{-1})	Reference
$Me_2C^{\bullet}OH + Me(CH_2)_7CH(O)$	Isopropyl alcohol	0.0	3.0×10^3	20.2	5
$Me_2C^{\bullet}OH + PhCH(O)$	Isopropyl alcohol	−28.6	1.8×10^5	10.0	5
$PhMeC^{\bullet}OH + PhC(O)Pr$	Acetonitrile	0.0	3.7×10^3	20.8	6
$PhC^{\bullet}HOH + PhCH(O)$	Benzene	0.0	8.0×10^4	22.9	7
$4\text{-}Me_3CC_6H_4C^{\bullet}(OH)Ph + Ph_2C(O)$	Acetonitrile	0.0	1.3×10^4	17.7	8

TABLE 18.2 Kinetic Parameters for the Hydrogen Atom Exchange in Free Radical Reactions[a]

Acceptor	α	br_e (kJ/mol)$^{1/2}$	E_{e0} (kJ mol^{-1})	$0.5hL(\nu_i - \nu_f)$ (kJ mol^{-1})	$0.5hL\nu$ (kJ mol^{-1})	A (L mol^{-1} s^{-1})
			$RC^{\bullet}HCH_2{-}H$			
$RCH{=}CH_2$	1.000	17.30	74.8	0.0	17.4	1.0×10^9
$RCH{=}CHCH{=}CH_2$	1.000	18.60	89.0	0.0	17.4	1.0×10^9
$PhCH{=}CH_2$	1.000	17.80	79.2	0.0	17.4	1.0×10^9
$R_2C{=}O$	0.796	13.10	53.2	−4.3	17.4	1.0×10^9
OC_6H_4O	0.802	14.13	61.5	−4.1	17.4	1.0×10^9
O_2	0.814	13.61	56.3	−3.8	17.4	1.0×10^9
			$RCH{=}CHC^{\bullet}HCH_2{-}H$			
$RCH{=}CH_2$	1.000	18.60	86.5	0.0	17.4	1.0×10^8
$RCH{=}CHCH{=}CH_2$	1.000	19.25	92.6	0.0	17.4	1.0×10^8
$PhCH{=}CH_2$	1.000	18.45	85.1	0.0	17.4	1.0×10^8
$R_2C{=}O$	0.796	14.14	62.0	−4.3	17.4	1.0×10^8
OC_6H_4O	0.802	15.96	78.4	−4.1	17.4	1.0×10^8
O_2	0.814	15.20	57.8	−3.8	17.4	1.0×10^8
			$PhC^{\bullet}HCH_2{-}H$			
$RCH{=}CH_2$	1.000	17.80	79.2	0.0	17.4	1.0×10^8
$RCH{=}CHCH{=}CH_2$	1.000	18.45	85.1	0.0	17.4	1.0×10^8
$PhCH{=}CH_2$	1.000	18.05	81.4	0.0	17.4	1.0×10^8
$R_2C{=}O$	0.796	13.50	56.5	−4.3	17.4	1.0×10^8
OC_6H_4O	0.802	15.02	69.5	−4.1	17.4	1.0×10^8
O_2	0.814	14.32	62.3	−3.8	17.4	1.0×10^8
			$R_2C^{\bullet}O{-}H$			
$RCH{=}CH_2$	1.256	16.46	53.2	4.3	21.7	1.0×10^8
$RCH{=}CHCH{=}CH_2$	1.256	17.76	62.0	4.3	21.7	1.0×10^8
$PhCH{=}CH_2$	1.256	16.96	56.5	4.3	21.7	1.0×10^8
$R_2C{=}O$	1.000	12.88	41.5	0.0	21.7	1.0×10^9
OC_6H_4O	1.008	14.10	49.3	0.2	21.7	2.0×10^9
O_2	1.022	13.13	42.2	0.5	21.7	6.4×10^8
			$H{-}OC_6H_4O^{\bullet}$			
$RCH{=}CH_2$	1.246	17.61	61.5	4.1	21.5	1.0×10^8
$RCH{=}CHCH{=}CH_2$	1.246	19.89	78.4	4.1	21.5	1.0×10^8
$PhCH{=}CH_2$	1.246	18.73	69.5	4.1	21.5	1.0×10^8
$R_2C{=}O$	0.992	14.16	50.5	−0.2	21.5	1.0×10^9

(*continued overleaf*)

TABLE 18.2 (*continued*)

Acceptor	α	br_e (kJ/mol)$^{1/2}$	E_{e0} (kJ mol^{-1})	$0.5hL(\nu_i - \nu_f)$ (kJ mol^{-1})	$0.5hL\nu$ (kJ mol^{-1})	A (L mol^{-1} s^{-1})
OC_6H_4O	1.000	12.61	39.7	0.0	21.5	1.0×10^9
O_2	1.014	13.16	42.7	0.3	21.5	3.2×10^8
			$H{-}O_2^{\bullet}$			
$RCH{=}CH_2$	1.229	16.73	56.3	3.8	21.2	1.0×10^8
$RCH{=}CHCH{=}CH_2$	1.229	18.68	70.2	3.8	21.2	1.0×10^7
$PhCH{=}CH_2$	1.229	17.59	62.3	3.8	21.2	1.0×10^7
$R_2C{=}O$	0.978	14.13	51.0	−0.5	21.2	1.0×10^9
OC_6H_4O	0.986	12.98	42.7	−0.3	21.2	3.2×10^8
O_2	1.000	13.13	43.1	0.0	21.2	1.0×10^9

[a] See Ref. 9.

TABLE 18.3 Enthalpies (ΔH) and Activation Energies (E) for the Hydrogen Transfer Reactions from Ketyl Radicals to Carbonyl Compounds (Calculated by the IPM Method)[a]

	$CH_2(O)$		$MeCH(O)$		$Me_2C(O)$	
$R^1R^2C\,OH$	ΔH (kJ mol^{-1})	E (kJ mol^{-1})	ΔH (kJ mol^{-1})	E (kJ mol^{-1})	ΔH (kJ mol^{-1})	E (kJ mol^{-1})
$H_2C^{\bullet}OH$	0.0	21.0	5.6	23.8	9.7	26.0
$MeC^{\bullet}HOH$	−5.6	18.2	0.0	21.0	4.1	23.0
$Me_2C^{\bullet}OH$	−9.7	16.3	−4.1	18.9	0.0	21.0
$PhC^{\bullet}HOH$	22.5	33.0	28.1	36.2	32.2	38.6
$PhMeC^{\bullet}OH$	20.0	31.6	25.6	34.8	29.7	37.1
$Ph_2C^{\bullet}OH$	39.8	43.3	45.4	46.8	49.5	49.4
$HOC_6H_4O^{\bullet}$	116.1	117.3	121.7	123.0	125.8	127.0
	$PhCH(O)$		$Ph_2C(O)$		p-OC_6H_4O	
$H_2C^{\bullet}OH$	−22.5	10.5	−39.8	3.5	−116.1	1.2
$McC^{\bullet}HOH$	−28.1	8.1	−45.1	1.5	−121.7	1.2
$Me_2C^{\bullet}OH$	−32.2	6.4	−49.5	1.2	−125.8	1.2
$PhC^{\bullet}HOH$	0.0	21.0	−17.3	12.8	−93.6	1.2
$PhMeC^{\bullet}OH$	−2.5	19.7	−19.8	11.7	−96.18	1.2
$Ph_2C^{\bullet}OH$	17.3	30.1	0.0	21.0	−76.3	1.2
$HOC_6H_4O^{\bullet}$	93.6	94.8	76.3	77.5	0.0	28.8

[a] See Chapter 9 and Ref. 9.

TABLE 18.4 Enthalpies (ΔH) and Activation Energies (E) for the Reactions of Hydrogen Transfer from Ketyl Radicals to Olefins (Calculated by the IPM Method)[a]

	$C^{\bullet}H_2OH$		$MeC^{\bullet}HOH$		$Me_2C^{\bullet}H$	
Olefin	ΔH (kJ mol^{-1})	E (kJ mol^{-1})	ΔH (kJ mol^{-1})	E (kJ mol^{-1})	ΔH (kJ mol^{-1})	E (kJ mol^{-1})
$CH_2{=}CH_2$	−40.2	12.3	−45.8	9.8	−49.8	8.0
$CH_2{=}CHMe$	−38.5	13.1	−44.1	10.5	−48.2	8.7
(E)-$MeCH{=}CHMe$	−27.1	18.5	−32.7	15.8	−38.6	13.9
$CH_2{=}CMe_2$	−43.4	10.9	−49.0	8.4	−53.1	6.6
$CH_2{=}CHPh$	−80.1	1.2	−85.7	1.2	−89.8	1.2
$CH_2{=}CPh_2$	140.5	1.2	−146.1	1.2	−150.2	1.2
C_6H_6	28.6	66.3	−5.7	62.9	18.9	60.4
	$PhC^{\bullet}HOH$		$PhMeC^{\bullet}OH$		$Ph_2C^{\bullet}OH$	
$CH_2{=}CH_2$	−17.7	23.2	−20.2	22.0	−0.4	32.5
$CH_2{=}CHMe$	−16.0	24.1	−18.5	22.8	−1.3	33.5
(E)-$MeCH{=}CHMe$	−4.6	30.2	−7.1	28.8	12.7	40.0
$CH_2{=}CMe_2$	−20.9	21.6	−23.4	20.4	−3.6	30.7
$CH_2{=}CHPh$	−57.6	7.8	−60.1	6.8	−40.3	15.4
$CH_2{=}CPh_2$	−118.0	1.2	−120.5	1.2	−100.7	1.2
C_6H_6	51.1	80.7	48.6	79.0	68.4	92.4

[a] See Chapter 9 and Ref. 9.

TABLE 18.5 Enthalpies (ΔH) and Activation Energies (E) for the Reactions of Hydrogen Transfer from Alkyl Radicals to Olefins (Calculated by IPM Method)[a]

	$MeC^{\bullet}H_2$		$MeEtC^{\bullet}H$		$Me_2CHC^{\bullet}H_2$	
Olefin	ΔH (kJ mol^{-1})	E (kJ mol^{-1})	ΔH (kJ mol^{-1})	E (kJ mol^{-1})	ΔH (kJ mol^{-1})	E (kJ mol^{-1})
$CH_2{=}CH_2$	0.0	58.6	−13.1	52.2	3.2	60.2
$CH_2{=}CHMe$	1.7	59.5	−11.4	53.0	4.9	61.1
(E)-$MeCH{=}CHMe$	13.1	65.3	0.0	58.6	16.3	67.0
$CH_2{=}CMe_2$	−3.2	57.0	−16.3	50.7	0.0	58.6
$CH_2{=}CHPh$	−39.9	44.3	−53.0	38.7	−36.7	45.7
$CH_2{=}CPh_2$	−100.3	20.8	−113.4	16.5	−97.1	21.9
C_6H_6	68.8	101.1	55.7	93.3	72.0	103.1
	$PhC^{\bullet}HOH$		$PhMeC^{\bullet}OH$		$Ph_2C^{\bullet}OH$	
$CH_2{=}CH_2$	39.9	84.2	40.4	84.5	100.3	121.1
$CH_2{=}CHMe$	41.6	85.2	42.1	85.5	102.0	122.2
(E)-$MeCH{=}CHMe$	53.0	91.7	53.5	92.0	113.4	129.9
$CH_2{=}CMe_2$	36.7	82.4	37.2	82.7	97.1	119.0
$CH_2{=}CHPh$	0.0	65.2	0.6	65.5	60.4	98.2
$CH_2{=}CPh_2$	−60.4	37.8	−59.9	38.0	0.0	65.2
C_6H_6	108.7	128.7	109.2	129.0	169.1	171.7

[a] See Chapter 9 and Ref. 9.

18.2 FREE RADICAL SUBSTITUTION REACTIONS

In addition to well-known reactions of atom abstraction (see Chapter 17), the reactions of radical substitution are known where a free radical attacks the weak Y—Y bond and abstracts radical Y.[10]

$$R^{\bullet} + YY \rightarrow RY + Y^{\bullet}$$

Such reactions can be treated as reactions of Y abstraction from a YY molecule or as the addition of the radical to a YY molecule accompanied by scission of Y—Y bond. These substitution reactions were discovered by Bartlett and Nozaki in their study of benzoyl peroxide decomposition in different solvents.[11,12] When the benzoyl peroxide is decomposed, the formed benzoyloxyl radical attacks the solvent (RH) and alkyl radical ($R^{\bullet}$) formed induces the chain decomposition of the peroxide (see Chapter 1).

$$PhC(O)OOC(O)Ph \rightarrow PhCO_2{}^{\bullet} + PhCO_2{}^{\bullet}$$

$$PhCO_2{}^{\bullet} + RH \rightarrow PhC(O)OH + R^{\bullet}$$

$$R^{\bullet} + PhC(O)OOC(O)Ph \rightarrow ROC(O)Ph + PhCO_2{}^{\bullet}$$

The chain decomposition of the peroxide decreases the effectiveness of initiation. Hydrogen atoms also react with the O—O bond of any peroxide, for example, with hydrogen peroxide.[13–15]

$$H^{\bullet} + H_2O_2 \rightarrow H_2O + HO^{\bullet}$$

This reaction is very exothermic and, therefore, is very fast. For the rate constants of these reactions see Table 18.6. Decomposition of peroxides in the presence of stannum hydride is accompanied by the chain decomposition of peroxide.[10] The chain propagation occurs by the reaction of substitution.

$$ROOR \rightarrow RO^{\bullet} + RO^{\bullet}$$

$$RO^{\bullet} + Bu_3SnH \rightarrow ROH + Bu_3Sn^{\bullet}$$

$$Bu_3Sn^{\bullet} + ROOR \rightarrow Bu_3SnOR + RO^{\bullet}$$

Rate constants for these reactions are in Table 18.6.

When radical polymerization is initiated by a peroxide, the latter reacts with macroradicals ($P^{\bullet}$). This reaction does not break the chain of polymerization but stops the growth of a macroradical and is known as the chain-transfer reaction.[3]

$$P^{\bullet} + PhC(O)OOC(O)Ph \rightarrow POC(O)Ph + PhCO_2{}^{\bullet}$$

The rate constants of polystyrene radical reactions with different substituted benzoyl peroxides are collected in Table 18.7.

TABLE 18.6 Rate Constants for the Free Radical Substitution Reactions of the Hydrogen Atom, Alkyl, and Stannyl Radicals with Peroxides: $R^{\bullet} + R^1OOR^1 \rightarrow ROR^1 + R^1O^{\bullet}$

Reaction	Solvent	T (K)	k ($L\,mol^{-1}\,s^{-1}$)	Reference
$H^{\bullet} + H_2O_2$	Water	298	2.35×10^7	13
$H^{\bullet} + H_2O_2$	Water	298	2.44×10^7	14
$H^{\bullet} + H_2O_2$	Water	298	2.93×10^7	15
$C^{\bullet}H_3 + [PhC(O)O]_2$	Acetic acid	353	1.93×10^3	11
$MeC^{\bullet}H_2 + [PhC(O)O]_2$	Ethyliodide	353	6.81×10^2	11
cyclo-$C_6H_{11}^{\bullet}$	Cyclohexane	353	3.32×10^3	11
$PhC^{\bullet}H_2 + [PhC(O)O]_2$	Toluene	353	4.50×10^2	11
$PhMeC^{\bullet}H + [PhC(O)O]_2$	Ethylbenzene	353	1.27×10^3	11
$PhMe_2C^{\bullet} + [PhC(O)O]_2$	Cumene	353	1.17×10^3	11
$PhCMe_2C^{\bullet}H_2 + [PhC(O)O]_2$	2-Methyl-2-phenylpropane	353	1.36×10^3	11
$C^{\bullet}H_3 + [PhC(O)O]_2$	*p*-Xylene	353	9.81×10^2	11
$Ph_3C^{\bullet} + [PhC(O)O]_2$	Benzene	298	1.2	16
$(4\text{-}MeOC_6H_4)_2PhC^{\bullet} + [PhC(O)O]_2$	Benzene	298	0.2	16
$(4\text{-}MeC_6H_4)_2PhC^{\bullet} + [PhC(O)O]_2$	Benzene	298	0.4	16
$(3\text{-}MeC_6H_4)_2PhC^{\bullet} + [PhC(O)O]_2$	Benzene	298	0.7	16
$(3\text{-}MeOC_6H_4)_2PhC^{\bullet} + [PhC(O)O]_2$	Benzene	298	1.5	16
$(4\text{-}FC_6H_4)_2PhC^{\bullet} + [PhC(O)O]_2$	Benzene	298	2.3	16
$(4\text{-}ClC_6H_4)_2PhC^{\bullet} + [PhC(O)O]_2$	Benzene	298	5.9	16
$(3\text{-}ClC_6H_4)_2PhC^{\bullet} + [PhC(O)O]_2$	Benzene	298	15.0	16
$Bu_3Sn^{\bullet} + EtOOEt$	Benzene	283	2.5×10^4	17
$Bu_3Sn^{\bullet} + AcOOAc$	Benzene	283	7.0×10^4	17
$Bu_3Sn^{\bullet} + AcOOCMe_3$	Benzene	283	4.0×10^4	17
$Bu_3Sn^{\bullet} + PhC(O)OOCMe_3$	Benzene	283	1.4×10^5	17

Experimental data on substitution reactions of free radicals with peroxides were analyzed by the IPM method.[23] The calculated parameters are collected in Table 18.8. Activation energies, enthalpies, and rate constants of radical substitution reactions calculated by the IPM method are presented in Table 18.9.

The free radicals studied form the following consequence according to the values of thermoneutral activation energy: $R_3Sn^{\bullet}$ ($E_{e0} = 75$ kJ mol^{-1}), $H^{\bullet}$ ($E_{e0} = 94$ kJ mol^{-1}), and $R^{\bullet}$ ($E_{e0} = 120$ kJ mol^{-1}).[23] The comparison of E_{e0} with the electronegativity of atoms in a reaction center of the reaction proved the following empirical dependence:[23]

$$br_e/(\text{kJ mol}^{-1})^{1/2} = 25.63 - 6.89 \times 10^{-2}[\Delta EA(\text{kJ mol}^{-1})] \qquad (18.1)$$

that is, the greater the difference in the electron affinity of R (H, R^1, $R_3Sn^{\bullet}$), the lower is the thermoneutral activation energy.

TABLE 18.7 Enthalpies and Rate Constants for the Free Radical Substitution Reactions in Styrene Polymerization: $R^{\bullet} + R^1OOR^1 \rightarrow ROR^1 + R^1O^{\bullet}$

Peroxide	$-\Delta H_e$ (kJ mol^{-1})	T (K)	k (L mol^{-1} s^{-1})	Reference
$[PhC(O)O]_2$	184.1	343	34	18
$[PhC(O)O]_2$	184.1	343	54	18
$[PhC(O)O]_2$	184.1	343	81	18
$[4\text{-}MeC_6H_4C(O)O]_2$	190.7	343	1×10^2	19
$[4\text{-}MeC_6H_4C(O)O]_2$	190.7	323	34	19
$[4\text{-}MeOC_6H_4C(O)O]_2$	195.1	343	33	20
$[4\text{-}ClC_6H_4C(O)O]_2$	188.6	343	97	19
$[4\text{-}CNC_6H_4C(O)O]_2$	185.6	343	3×10^2	19
$[4\text{-}MeC(O)OC_6H_4C(O)O]_2$	181.1	343	84	21
$[3\text{-}ClC_6H_4C(O)O]_2$	187.3	343	1.56×10^2	19
$[2\text{-}CH_3C_6H_4C(O)O]_2$	189.4	343	79	19
$[2\text{-}ClC_6H4C(O)O]_2$	192.8	343	8.61×10^2	19
$[Me(CH_2)_2C(O)O]_2$	206.6	343	8.11	22
$[Me(CH_2)_2C(O)O]_2$	206.6	343	74.8	22
$[Me(CH_2)_{10}C(O)O]_2$	222.5	343	10.8	22

TABLE 18.8 Kinetic Parameters for the Free Radical Substitution Reactions: $R^{\bullet} + YY \rightarrow RY + Y^{\bullet a}$

Radical	α	br_e (kJ/mol)$^{1/2}$	E_{e0} (kJ mol^{-1})	$0.5hL(\nu_i - \nu_f)$ (kJ mol^{-1})	$0.5hL\nu$ (kJ mol^{-1})	A (L mol^{-1} s^{-1})
			YY=ROOH			
$H^{\bullet}$	0.682	16.06	91.2	−16.7	5.1	1.0×10^{10}
$R^{\bullet}$	0.889	18.85	99.6	−1.1	5.1	1.0×10^9
$R_3Sn^{\bullet}$	0.651	12.90	61.0	−0.9	5.1	1.0×10^9
			YY=ROOR			
$H^{\bullet}$	0.689	17.84	111.6	−16.6	5.1	2.0×10^{10}
$R^{\bullet}$	0.826	20.23	122.7	−1.6	5.1	2.0×10^9
$R_3Sn^{\bullet}$	0.651	14.27	74.7	−0.9	5.1	2.0×10^9

[a] See Ref. 23.

Disulfides have a weak S—S bond (see Chapter 9) and react with alkyl radicals with splitting of the S—S bond.[3]

$$R^{\bullet} + R^1SSR^1 \rightarrow RSR^1 + R^1S^{\bullet}$$

TABLE 18.9 Enthalpies, Activation Energies, and Rate Constants for the Substitution Reactions $R^{\bullet} + R^1OOR^1 \rightarrow ROR^1 + R^1O^{\bullet}$ in Hydrocarbon Solution (Calculated by the IPM Method)[a]

Reaction	$-\Delta H$ (kJ mol^{-1})	E (kJ mol^{-1})	A (L mol^{-1} s^{-1})	k(350 K) (L mol^{-1} s^{-1})
$C^{\bullet}H_3 + H_2O_2$	173.1	31.8	1.0×10^9	1.79×10^4
$C^{\bullet}H_3 + Me_3COOH$	205.5	23.6	5.0×10^8	1.50×10^5
$C^{\bullet}H_3 + Me_3COOCMe_3$	183.5	51.4	1.0×10^9	21.3
$C^{\bullet}H_3 + MeC(O)OOC(O)Me$	217.9	42.1	2.0×10^9	1.04×10^3
$C^{\bullet}H_3 + PhC(O)OOC(O)Ph$	242.7	36.0	2.0×10^9	8.48×10^3
$MeC^{\bullet}H_2 + H_2O_2$	178.1	30.4	1.0×10^9	2.90×10^4
$MeC^{\bullet}H_2 + Me_3COOH$	210.5	22.5	5.0×10^8	2.19×10^5
$MeC^{\bullet}H_2 + Me_3COOCMe_3$	190.3	49.5	1.0×10^9	41.0
$MeC^{\bullet}H_2 + MeC(O)OOC(O)Me$	234.3	38.0	2.0×10^9	4.26×10^3
$MeC^{\bullet}H_2 + PhC(O)OOC(O)Ph$	249.5	34.4	2.0×10^9	1.47×10^4
$Me_2C^{\bullet}H + H_2O_2$	188.1	27.8	1.0×10^9	7.10×10^4
$Me_2C^{\bullet}H + Me_3COOH$	220.5	20.2	5.0×10^8	4.83×10^5
$Me_2C^{\bullet}H + Me_3COOCMe_3$	198.6	47.2	1.0×10^9	90.3
$Me_2C^{\bullet}H + MeC(O)OOC(O)Me$	232.9	38.4	2.0×10^9	3.72×10^3
$Me_2C^{\bullet}H + PhC(O)OOC(O)Ph$	257.8	32.5	2.0×10^9	2.82×10^4
$Me_3C^{\bullet} + H_2O_2$	185.1	28.6	1.0×10^9	5.39×10^4
$Me_3C^{\bullet} + Me_3COOH$	207.5	23.2	5.0×10^8	1.72×10^5
$Me_3C^{\bullet} + Me_3COOCMe_3$	165.1	58.8	1.0×10^9	1.68
$Me_3C^{\bullet} + MeC(O)OOC(O)Me$	208.6	44.5	2.0×10^9	4.57×10^2
$Me_3C^{\bullet} + PhC(O)OOC(O)Ph$	233.8	38.1	2.0×10^9	4.13×10^3
$PhC^{\bullet}H_2 + H_2O_2$	132.1	43.7	1.0×10^9	3.01×10^2
$PhC^{\bullet}H_2 + Me_3COOH$	164.5	34.1	5.0×10^8	4.07×10^3
$PhC^{\bullet}H_2 + MeC(O)OOC(O)Me$	177.8	53.0	2.0×10^9	24.6
$PhC^{\bullet}H_2 + PhC(O)OOC(O)Ph$	202.6	46.1	2.0×10^9	2.64×10^2

[a] See Table 18.8 and Eqs. (9.2), (9.3), (9.13), and (9.16).

Such reactions occur in free radical polymerization of monomers and are used for the regulation of the molecular mass of the formed polymer. The values of rate constants for these reactions are collected in Table 18.10.

Experimental data on radical substitution in disulfides were analyzed using the IPM method. The resulting parameters of these reactions are presented in Table 18.11.

It is seen from the values of br_e and E_{e0} that the steric effect is observed in reactions of alkyl and phenyl radicals with primary, secondary, and tertiary alkyl substituted disulfides. The steric effect is sufficiently stronger in reactions of disulfides with a phenyl radical in comparison with alkyl (see ΔE_s values). The effect of α substituents with π bonds is observed as well (see values of ΔE_{π}).

Stannyl radicals also react with disulfides.

$$R_3Sn^{\bullet} + R^1SSR^1 \rightarrow R_3SnSR^1 + R^1S^{\bullet}$$

TABLE 18.10 Enthalpies, Rate Constants and Activation Energies for the Radical Substitution Reactions of Disulfides

R^1SSR^1	$-\Delta H$ (kJ mol^{-1})	T (K)	k (L mol^{-1} s^{-1})	E (kJ mol^{-1})
$R^\bullet = {\sim}CH_2CH^\bullet Ph$[a]				
$[MeS]_2$	35.0	333	2.9	58.3
$[EtS]_2$	29.0	372	5.7	63.0
$[PhS]_2$	29.0	333	0.7	62.2
$[Me(CH_2)_3S]_2$	29.0	333	0.8	61.8
$[Me(CH_2)_3S]_2$	29.0	372	8.6	61.7
$[Me(CH_2)_5S]_2$	29.0	372	13.1	60.4
$[Me(CH_2)_{17}S]_2$	29.0	372	30.2	57.8
$[Me_2CHCH_2S]_2$	29.0	333	0.6	62.6
$[Me_2CHS]_2$	29.0	333	0.2	65.7
$[Me_3CS]_2$	24.0	333	4.2×10^{-2}	70.0
$[PhCH_2S]_2$	29.0	333	3.0	58.2
$[PhCH_2S]_2$	31.9	372	1.4	67.3
$[PhS]_2$	65.8	323	12.0	47.2
$R^\bullet = Me(CH_2)_9C^\bullet H_2$[b]				
$[MeS]_2$	29.0	298	6.0×10^4	27.5
$[MeS]_2$	65.8	298	2.0×10^5	24.5
$R^\bullet = (C_6H_5)^\bullet$[c]				
$[MeS]_2$	113.3	333	2.3×10^8	7.9
$[EtS]_2$	110.3	333	1.3×10^8	9.5
$[PrS]_2$	110.3	333	1.2×10^8	9.7
$[Me_2CHS]_2$	116.3	333	2.4×10^7	14.2
$[Me_3CS]_2$	121.3	333	1.7×10^6	21.5
$R^\bullet = (n\text{-}C_4H_9)_3Sn^\bullet$[d]				
$[Me(CH_2)_3S]_2$	48.1	303	5.1×10^5	24.0
$[Me_2CHCH_2S]_2$	48.1	303	5.1×10^5	24.0
$[PhCH_2S]_2$	48.1	303	3.5×10^5	24.9

[a] See Refs. 3 and 24.
[b] See Ref. 25.
[c] See Ref. 26.
[d] See Ref. 27.

This reaction is exothermic and occurs rapidly (see Table 18.10). Thermoneutral activation energy E_{e0} for this reaction ($E_{e0} = 40$ kJ mol^{-1}) is close to that for alkyl radicals ($E_{e0} = 38$ kJ mol^{-1}). Apparently, the factors have an important influence on the E_{e0} of stannyl radicals: triplet repulsion, difference in electron

TABLE 18.11 Kinetic Parameters for the Alkyl, Phenyl, and Stannyl Radical Reactions with Disulfides

Reaction	br_e $(kJ\,mol^{-1})^{1/2}$	E_{e0} $(kJ\,mol^{-1})$	ΔE_s $(kJ\,mol^{-1})$	ΔE_π $(kJ\,mol^{-1})$
$R^{\bullet} + (RCH_2S)_2$	11.93	38.0	0.0	0.0
$R^{\bullet} + (Me_2CHS)_2$	12.85	44.0	6.0	0.0
$R^{\bullet} + (Me_3CS)_2$	13.18	46.3	8.3	0.0
$C_6H_5^{\bullet} + (RCH_2S)_2$	11.27	33.9	0.0	0.0
$C_6H_5^{\bullet} + (Me_2CHS)_2$	12.75	43.4	9.5	0.0
$C_6H_5^{\bullet} + (Me_3CS)_2$	15.31	62.5	28.6	0.0
$R^{\bullet} + PhSSPh$	12.85	44.0	0.0	6.0
$\sim CH_2C^{\bullet}HPh + PhSSPh$	14.40	55.3	0.0	17.3
$R_3Sn^{\bullet} + R_1SSR_1$	10.19	39.7	0.0	0.0

affinity of Sn and S atoms (ΔEA), and force constants of S—S and Sn—S bonds (coefficient α).

Organoboranes can enter into various radical substitution reactions where one radical ($Y^{\bullet}$) reacts with BR_3 to displace another radical ($R^{\bullet}$). These reactions involve alkyl,[28-30] alkoxyl[31-34] and thiyl radicals[35-37]

$$Y^{\bullet} + BR_3 \rightarrow YBR_2 + R^{\bullet}$$

($Y^{\bullet} = R^{1\bullet}, R^1O^{\bullet}, R^1S^{\bullet}$).

Organoboranes are oxidized via the chain mechanism

$$ROO^{\bullet} + BR_3 \rightarrow ROOBR_2 + R^{\bullet}$$

$$R^{\bullet} + O_2 \rightarrow ROO^{\bullet}$$

According to this, the first step of chain propagation is the radical substitution reaction.[38-40]

It has been proved using various procedures[32-34,38-40] that the radical substitution at the boron atom in trialkylboranes involves oxygen-centered radicals

$$Me_3CO^{\bullet} + BR_3 \rightarrow Me_3COBR_2 + R^{\bullet}$$

$$ROO^{\bullet} + BR_3 \rightarrow ROOBR_2 + R^{\bullet}$$

(R is alkyl, and R in the radical corresponds to R in trialkylborane).

Trialkylboranes react with butane-l-thiol via the free radical chain mechanism in which the chain propagation stage is the homolytic substitution of the alkyl radical at the boron atom by the butylthiyl radical[37]

$$BuS^{\bullet} + BR_3 \rightarrow BuSBR_2 + R^{\bullet}$$

TABLE 18.12 Rate Constants, Enthalpies, and Activation Energies for the Reaction: $Y^{\bullet} + BR_3 \rightarrow YBR_2 + R^{\bullet}$[a]

BR_3	T (K)	$k \times 10^{-6}$ ($L\,mol^{-1}\,s^{-1}$)	E ($kJ\,mol^{-1}$)	$-\Delta H$ ($kJ\,mol^{-1}$)
		$Y^{\bullet} = Me_3CO^{\bullet}$		
BBu_3	313	10	10.2	147.0
$B(CHEtMe)_3$	313	0.40	18.6	152.0
$B(CHEtMe)_3$	313	0.30	19.3	147.0
$B(CH_2CMe_3)_3$	313	0.04	24.5	147.0
$B(CH_2Ph)_3$	313	30	7.3	183.2
		$Y^{\bullet} = ROO^{\bullet}$ (*R coincides with R in* BR_3)		
BBu_3	303	2.0	13.9	79.0
$B(CH_2CMe_3)_3$	303	0.08	22.0	84.0
$B(CH_2Ph)_3$	303	5.0	11.6	133.0
		$Y^{\bullet} = BuS^{\bullet}$		
BBu_3	323	780	2.5	29.7
BBu_3	323	11	14.0	34.7
$B(CH_2CHMe_2)_3$	323	33	8.9	29.6
		$Y^{\bullet} = Me^{\bullet}$		
BEt_3	298	0.05	21.0	19.0

[a] See Refs. 32–34, 38, and 40.

The activation energies for the reactions (see Tables 18.12 and 18.13) were calculated by the kinetic data by using the preexponential factor $A = 2 \times 10^9$ L mol^{-1} s^{-1}.[41]

The following factors were found to be important in the reactivity of trialkylboranes:[41]

1. *Energy of the nonbonding orbital of the formed bond (triplet repulsion).* In radical elimination reactions

$$X^{\bullet} + HY \rightarrow X \cdots H \cdots Y \rightarrow XH + Y^{\bullet}$$

the H atom in the transition state moves from Y to X along the line of the X $\cdots$ Y bond. Since three electrons participating in the rearrangement of bonds cannot dispose on the bonding orbital of X $\cdots$ Y (Pauli exclusion principle), the X $\cdots$ Y bond participates in the formation of the transition state. The stronger this bond, the higher the energy of the nonbonding orbital and the activation energy of the thermoneutral reaction (see Chapter 17). The same interrelation

TABLE 18.13 Rate Constants and Activation Energies for Substitution Reactions in Cycloboranes[a]

Compound	k (L mol^{-1} s^{-1})	E (kJ mol^{-1})
$tert\text{-}Bu^tO^\bullet + cyclo\text{-}(RBO)_3 \rightarrow cyclo\text{-}t\text{-}BuOR_2$		
B*n*-Bu$_3$	1×10^7	10.2
cyclo-(*n*-BuBO)$_3$	1×10^6	19.0
cyclo-(*s*-BuBO)$_3$	6×10^5	20.4
cyclo-(*t*-BuBO)$_3$	1×10^6	19.0
$ROO^\bullet + cyclo\text{-}(RBO)_3 \rightarrow cyclo\text{-}ROOR_2(BO)_3 + R^\bullet$		
B*n*-Bu$_3$	2×10^6	11.3
cyclo-(*n*-BuBO)$_3$	1×10^3	35.8
cyclo-(*s*-BuBO)$_3$	5×10^4	26.0
B(CH$_2$Ph)$_3$	5×10^6	11.6
cyclo-(PhCH$_2$BO)$_3$	1×10^6	18.4
$ROO^\bullet + RB(OR)_n \rightarrow ROOB(OR)_n + R^\bullet$		
Bu$_2$BOOBu	3×10^4	24.5
(CHEtMe)$_2$BOOCHEtMe	1.5×10^4	26.2
Bu$_2$BOEt	5×10^3	29.0
(CHEtMe)$_2$BOCHEtMe	2×10^3	31.3
BuB(OEt)$_2$	4.0	47.0
PhCH$_2$B(OMe)$_2$	21	42.8
PhCH$_2$B(OCH$_2$)$_2$	20	42.9
PhCH$_2$B(OBu)$_2$	18	43.8

[a] See Refs. 32 and 38.

was established for the addition of atoms and radicals at multiple bonds (see Chapter 19). Does triplet repulsion manifest in radical substitution reactions? Compare the r_e values for two classes of reactions with the same O··· B··· C reaction center and that differ from one another only by the strength of the forming bond.

Reaction	E_{e0} (kJ mol^{-1})	D(B−O) (kJ mol^{-1})	$r_e \times 10^{11}$ (m)	$r_e/D \times 10^{13}$ (m mol kJ^{-1})
BuO$^\bullet$+ BBu$_3$	60.7	501.7	3.92	0.781
BuOO$^\bullet$+ BBu$_3$	46.0	433.7	3.41	0.786

It can be seen that the strength of the forming bond has an effect on the r_e parameter and, hence, on E_{e0}. Therefore, it is more correct to consider the r_e/D

ratios rather than r_e values. It is seen from the above data that the r_e/D ratio remains almost unchanged: $r_e/D = 0.78 \times 10^{-13}$ m mol kJ^{-1}. Thus, the triplet repulsion also affects the activation energy of substitution. As in the case of addition reactions (see Chapter 19), the r_e/D ratio remains unchanged.

2. *Influence of* π *bonds on the activation energy.* The comparison of the br_e and E_{e0} parameters for the reactions of $R^1O^•$ and $R^1OO^•$ with tributylborane and tribenzylborane, proves that the replacement of the butyl radical by benzyl increases the activation energy of the thermoneutral reaction. The same effect is observed in radical reactions (abstraction, addition, and substitution). Their E_{e0} (kJ mol^{-1}) are presented below.

Reaction	E_{e0} (kJ mol^{-1}) R = Alk	R = Ph	ΔE_π (kJ mol^{-1})
$R^1O^• + B(CH_2R)_3$	60.7	70.2	9.5
$R^1OO^• + B(CH_2R)_3$	46.0	58.5	12.5
$R^{1•} + RSSR$	44.0	50.0	6.0
$R^{1•} + HCH_2R$	74.2	82.0	7.8
$CH_3^• + CH_2{=}CHR$	82.6	90.0	7.4

The increment $\Delta E_\pi = E_{e0}(R = Ph) - E_{e0}(R = Alk)$ stipulated by the influence of the benzyl ring in the α-position to the reaction center is a magnitude of the same order for all reaction types listed and ranges within 6–12 kJ mol^{-1}.

The benzyl group at the boron atom has a dual effect on the activation energy. On the one hand, the B—C bond in tribenzylborane is weaker than that in tributylborane, and this decreases the enthalpy of the reaction (cf. ΔH_e). On the other hand, when R is replaced by $PhCH_2$ the delocalization of π electrons enhances the bond between the atoms of the reaction center, which increases the energy of the nonbonding orbital and, correspondingly, the activation energy. Below we present the energy balance (E/kJ mol^{-1}) for the reactions t-BuO$^•$ + BBu_3 and t-BuO$^•$ + $B(CH_2Ph)_3$.

Reagent	$-\Delta H_e$ (kJ mol^{-1})	$-\Delta E_H$ (kJ mol^{-1})	ΔE_π (kJ mol^{-1})	E_{e0} (kJ mol^{-1})	E_e (kJ mol^{-1})
BBu_3	145.7	45.1	0.0	60.7	15.6
$B(CH_2Ph)_3$	181.9	57.5	9.5	70.2	12.7

3. *Electron affinity of atoms of the reaction center.* The difference in electron affinity for the atoms of the reaction center (ΔEA) also affects radical elimination reactions: The greater the difference, the lower the activation barrier. This factor is also manifested for substitution at the O—O bond. Does it affect

the activation energy of the radical substitution of organoboranes? Compare the parameters of the substitution reactions $Y^{\bullet} + BR_3 (Y = Me^{\bullet}, BuO^{\bullet})$.

$Y^{\bullet}$	$r_e \times 10^{11}$ (m)	D(Y-B) (kJ mol^{-1})	r_e/D(Y-B) $\times 10^{13}$ (m mol kJ^{-1})	ΔEA, (eV)
$Me^{\bullet}$	3.32	375.1	0.885	0.97(C-B)
n-$BuO^{\bullet}$	3.92	501.7	0.781	1.18(O-B)

The comparison of the parameters (see above) shows that the $r_e/D(Y-B)$ ratio for the reaction of the alkoxyl radical is lower than that for the methyl radical. The difference in electronegativities (EA) for the couple of B and O atoms is much greater than for the B and C couple. The difference in $r_e/D(Y-B)$ is most likely the result of the influence from the electronegativity of the atoms of the reaction center on the activation energy of the substitution reactions of organoboranes.

4. *Steric effect.* As seen from the data in Table 18.12, the E_{e0} values differ for the reactions of alkoxyl and peroxyl radicals with boranes bearing linear and branched alkyl substituents. The introduction of a methyl group into the α- and β- positions of the boron atom increases br_e and, correspondingly, E_{e0}. The contribution (increment) of the steric influence on the activation reaction can be estimated from the difference in E_{e0}.

$$\Delta E_s = E_{e0}(\text{branched}) - E_{e0}(\text{linear}). \qquad (18.2)$$

Obtained values are presented in Table 18.14.

The steric effect (ΔE_s) is of the same order of magnitude in all cases (for the branched substituent with one methyl group in the α- or β- positions relative to the B atom and for two methyl groups in the β-position). A similar effect was also observed for substitution at the S—S bond.[25]

5. *Force constants.* The force constants of reacting bonds also contribute to the activation energy of the thermoneutral reaction, which is seen from the comparison

TABLE 18.14 Activation Energy (E_{e0}) and Contributions of the Steric Effect (ΔE_s) for the Reactions of Boranes BR_3 with the $R^1O^{\bullet}$, $R^1OO^{\bullet}$, and $R^1S^{\bullet}$ Radicals[a]

Compound		E_{e0} (kJ mol^{-1})			ΔE_s (kJ mol^{-1})	
BR_3	$R^1O^{\bullet}$	$R^1OO^{\bullet}$	$R^1S^{\bullet}$	$R^1O^{\bullet}$	$R^1OO^{\bullet}$	$R^1S^{\bullet}$
BBu_3	60.7	46.0	19.9	0	0	0
$B(CHEtMe)_3$	73.2	56.9	34.5	12.5	10.9	14.6
$B(CH_2CHMe_2)_3$	72.6		26.9	11.9		7.0
$B(CH_2CMe_3)_3$	78.9			18.2		

[a] See Ref. 41.

of the $b^2(1+\alpha)^{-2}$ coefficients for three reaction centers [see e.g. (9.6) for E_{e0} in Chapter 9].

Reaction Center	$b^2(1+\alpha)^{-2} \times 10^{22}$ (kJ m^2 mol^{-1})	E_{e0} (kJ mol^{-1})
O··· B··· C	3.95	60.7
C··· B··· C	3.14	34.7
S··· B··· C	2.98	19.9

18.3 REACTION OF PEROXIDES WITH KETYL RADICALS

The ketyl radicals ($R^1R^2C^{\bullet}OH$) are very active reducing agents. They have a weak O–H bond (see Chapter 9) and react as donors of hydrogen atoms with carbonyl compounds, nitro compounds, alkyl chlorides, olefins (see 18.1), dioxygen, and free radicals.

$$R^1R^2C^{\bullet}OH + CCl_4 \rightarrow R^1R^2C{=}O + HCl + C^{\bullet}Cl_3$$

$$R^1R^2C^{\bullet}OH + O_2 \rightarrow R^1R^2C{=}O + HO_2^{\bullet}$$

$$R^1R^2C^{\bullet}OH + R^{\bullet} \rightarrow R^1R^2C{=}O + RH$$

Ketyl radicals reduce peroxides with splitting of the O–O bond.[11,42–44]

$$R^1R^2C^{\bullet}OH + ROOR \rightarrow R^1R^2C{=}O + ROH + RO^{\bullet}$$

This reaction is the chain propagating step in the chain decomposition of peroxides in an alcohol solution. For the kinetics of this chain reaction, see Chapter 1. Ketyl radicals react with hydrogen peroxide to form water and the hydroxyl radical.

$$R^1R^2C^{\bullet}OH + H_2O_2 \rightarrow R^1R^2C{=}O + H_2O + HO^{\bullet}$$

For the rate constants of this reaction see Table 18.15. Bartlett and Nozaki[42] discovered the chain reaction of benzoyl peroxide decomposition in the presence of alcohols where the chain propagating step is the reaction of the ketyl radical with peroxide (see Chapter 1).

$$R^1R^2C^{\bullet}OH + PhC(O)OOC(O)Ph \rightarrow R^1R^2C{=}O + PhCOOH + PhCO_2^{\bullet}$$

For the rate constants of these reactions see Table 18.15. These reactions are very exothermic and occur with high rate constants ((7–14) × 10^5 L mol^{-1} s^{-1}).

The experimental data for the reactions of ketyl radicals with hydrogen and benzoyl peroxides were analyzed in the framework of IPM.[46] The elementary step

TABLE 18.15 Rate Constants for the Reducing Reactions of Ketyl Radicals with Peroxides

Reaction	Solvent	T (K)	k ($L\,mol^{-1}\,s^{-1}$)	Reference
$H_2C^{\bullet}OH + H_2O_2 \rightarrow H_2C(O) + H_2O + HO^{\bullet}$	Water	298	1.75×10^5	45
$MeC^{\bullet}HOH + H_2O_2 \rightarrow MeCH(O) + H_2O + HO^{\bullet}$	Water	298	2.80×10^5	45
$Me_2C^{\bullet}OH + H_2O_2 \rightarrow Me_2C(O) + H_2O + HO^{\bullet}$	Water	298	2.30×10^5	45
$Me_2CHC^{\bullet}HOH + H_2O_2 \rightarrow Me_2C(O) + H_2O + HO^{\bullet}$	Water	298	2.20×10^5	45
$H_2C^{\bullet}OH + [PhC(O)O]_2 \rightarrow H_2C(O) + PhCO_2H + PhC(O)O^{\bullet}$	Methanol	353	3.84×10^5	42
$MeC^{\bullet}HOH + [PhC(O)O]_2 \rightarrow MeCH(O) + PhCO_2H + PhC(O)O^{\bullet}$	Ethanol	353	1.38×10^6	42
$Me_2C^{\bullet}OH + [PhC(O)O]_2 \rightarrow Me_2C(O) + PhCO_2H + PhC(O)O^{\bullet}$	Isopropyl alcohol	353	8.82×10^6	42
$PrC^{\bullet}HOH + [PhC(O)O]_2 \rightarrow PrCH(O) + PhCO_2H + PhC(O)O^{\bullet}$	Butanol	353	7.12×10^5	42

was treated as a reaction with dissociation of the O—H bond of the ketyl radical and formation of the same bond of acid (from acyl peroxide), alcohol (from alkyl peroxide), and water (from hydrogen peroxide). The hydroperoxyl radical also possess reducing activity and reacts with hydrogen peroxide by the reaction

$$HO_2^{\bullet} + H_2O_2 \rightarrow O_2 + H_2O + HO^{\bullet}$$

A semiquinone radical should have a similar reducing activity and attack the O—O bond.

$$HOC_6H_4O^{\bullet} + H_2O_2 \rightarrow OC_6H_4O + H_2O + HO^{\bullet}$$

The parameters calculated for these reactions are in Table 18.16.

The comparison of E_{e0} values for reactions of ketyl radicals with peroxides with those for the reactions $R^1R^2C^{\bullet}OH + R_2C(O)$ show that the reaction of the ketyl radical with peroxide occurs with sufficiently higher E_{e0} (see Table 18.2). Obviously, that is the result of strong additional repulsion in the nonlinear polyatomic transition state of the ketyl radical reaction with peroxide

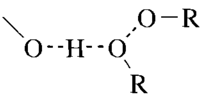


TABLE 18.16 Kinetic Parameters for the Reducing Reactions of Ketyl and Alkyl Radicals with Peroxides[a]

Reaction	α	br_e (kJ/mol)$^{1/2}$	E_{e0} (kJ mol^{-1})	A (L mol^{-1} s^{-1})
$R^1R^2C^•OH + H_2O_2$	1.000	21.24	112.8	2.0×10^9
$R^1R^2C^•OH + ROOR$	1.000	21.51	115.7	2.0×10^9
$RC^•HMe + H_2O_2$	0.778	20.70	135.7	2.0×10^9
$RC^•HMe + ROOR$	0.796	20.90	135.4	2.0×10^9
$RC^•HCH_3 + ROOH$	0.778	20.70	135.7	1.0×10^9
$RCH{=}CHC^•HCH_3 + H_2O_2$	0.778	22.16	155.3	2.0×10^9
$RCH{=}CHC^•HCH_3^• + ROOR$	0.796	22.36	155.0	2.0×10^9
$RCH{=}CHC^•HCH_3^• + ROOH$	0.778	22.16	155.3	1.0×10^9
$PhC^•HMe + H_2O_2$	0.778	21.18	141.9	2.0×10^9
$PhC^•HMe + ROOR$	0.796	21.40	142.0	2.0×10^9
$PhC^•HMe + ROOH$	0.778	21.18	141.9	1.0×10^9
$HOC_6H_4O^• + H_2O_2$	0.982	21.24	112.3	1.0×10^8
$HOC_6H_4O^• + ROOR$	0.992	21.51	126.4	1.0×10^8
$HOC_6H_4O^• + ROOH$	0.982	21.00	112.3	5.0×10^7
$HO_2^• + H_2O_2$	0.969	21.24	116.4	1.0×10^8
$HO_2^• + ROOR$	0.978	21.51	118.3	1.0×10^8
$HO_2^• + ROOH$	0.969	21.24	116.4	5.0×10^7

[a] See Ref. 46.

in comparison with the linear transition state: —O··· H··· O··· of the ketyl radical reaction with a carbonyl compound. The increase in activation energy due to the additional repulsion in the transition state of the ketyl radical reaction with hydrogen peroxide is $104.6 - 41.5 = 63.1$ kJ mol^{-1} and 78.8 kJ mol^{-1} in the reaction of ketyl radical with peroxide (ROOR). The activation energies and rate constants of reactions for different ketyl radicals and $HO_2^•$ with peroxides calculated by the IPM method are presented in Table 18.17.

The alkyl radicals possess reducing activity as well. In the reaction of disproportionation (see Chapter 20) one radical reacts as an acceptor and another as a donor of a hydrogen atom. That is why one can expect the reducing action of alkyl radicals in reactions with peroxides.

$$RCH_2C^•H_2 + R^1OOR^1 \rightarrow RCH{=}CH_2 + R^1OH + R^1O^•$$

The activation energies and rate constants of such reactions were calculated by the IPM method[46] (see Table 18.18). For the parameters used for calculations, see Table 18.18.

As we have seen earlier, alkyl radicals react with peroxides in two different ways: in the substitution reaction (see Section 18.1) and in the reduction reaction. The comparison of both reactions is presented in Table 18.19. It is seen that alkyl

TABLE 18.17 Enthalpies, Activation Energies and Rate Constants for the Peroxide Reduction by Ketyl, Semiquinone and Hydroperoxyl Radicals (Calculated by IPM Model)[a]

Reaction	$-\Delta H$ (kJ mol^{-1})	E (kJ mol^{-1})	log A, A (L mol^{-1} s^{-1})	k(350 K) (L mol^{-1} s^{-1})
$MeC^{\bullet}HOH + H_2O_2$	178.5	20.7	8.78	4.91×10^5
$MeC^{\bullet}HOH + Me_3COOH$	210.9	11.5	8.62	8.01×10^6
$MeC^{\bullet}HOH + EtOOEt$	173.9	24.6	8.72	1.12×10^5
$MeC^{\bullet}HOH + Me_3COOCMe_3$	178.7	23.1	8.75	2.01×10^5
$MeC^{\bullet}HOH + PhC(O)OOC(O)Ph$	180.1	22.6	8.76	7.44×10^5
$Me_2C^{\bullet}OH + H_2O_2$	182.6	19.5	8.79	7.58×10^5
$Me_2C^{\bullet}OH + Me_3COOH$	215.0	10.4	8.63	1.20×10^7
$Me_2C^{\bullet}OH + EtOOEt$	178.0	23.3	8.75	1.87×10^5
$Me_2C^{\bullet}OH + Me_3COOCMe_3$	182.8	21.8	8.66	2.55×10^5
$Me_2C^{\bullet}OH + PhC(O)OOC(O)Ph$	184.2	21.4	8.76	3.68×10^5
$PhC^{\bullet}HOH + H_2O_2$	150.4	29.6	8.70	1.92×10^4
$PhC^{\bullet}HOH + Me_3COOH$	182.8	19.4	8.50	4.02×10^5
$PhC^{\bullet}HOH + EtOOEt$	145.8	33.8	8.66	4.13×10^3
$PhC^{\bullet}HOH + Me_3COOCMe_3$	150.6	32.1	8.67	7.57×10^3
$PhC^{\bullet}HOH + PhC(O)OOC(O)Ph$	152.0	31.6	8.68	9.20×10^3
$PhMeC^{\bullet}OH + H_2O_2$	152.9	28.8	8.70	2.52×10^4
$PhMeC^{\bullet}OH + Me_3COOH$	185.3	18.7	8.51	5.24×10^5
$PhMeC^{\bullet}OH + EtOOEt$	148.3	32.9	8.67	5.75×10^3
$PhMeC^{\bullet}OH + Me_3COOCMe_3$	153.1	31.3	8.62	8.89×10^3
$PhMeC^{\bullet}OH + [PhC(O)O]_2$	154.5	30.8	8.69	1.24×10^4
$4\text{-}HOC_6H_4O^{\bullet} + H_2O_2$	56.8	68.1	7.21	1.13×10^{-3}
$4\text{-}HOC_6H_4O^{\bullet} + Me_3COOH$	89.2	54.7	6.96	6.26×10^{-2}
$4\text{-}HOC_6H_4O^{\bullet} + EtOOEt$	52.2	71.8	7.21	3.13×10^{-4}
$4\text{-}HOC_6H_4O^{\bullet} + Me_3COOCMe_3$	57.0	69.7	7.21	6.56×10^{-4}
$4\text{-}HOC_6H_4O^{\bullet} + [PhC(O)O]_2$	58.4	69.0	7.21	8.13×10^{-4}
$HO_2^{\bullet} + H_2O_2$	63.1	67.4	7.22	1.43×10^{-3}
$HO_2^{\bullet} + Me_3COOH$	95.5	54.2	6.97	0.15
$HO_2^{\bullet} + EtOOEt$	58.5	71.1	7.21	3.90×10^{-4}
$HO_2^{\bullet} + Me_3COOCMe_3$	63.3	69.1	7.21	8.05×10^{-4}
$HO_2^{\bullet} + PhC(O)OOC(O)Ph$	64.7	68.5	7.22	9.93×10^{-4}

[a] See Ref. 46.

radicals (primary and secondary) react with hydrogen peroxide, hydroperoxide, and dibenzoyl peroxide rapidly (by 100–1000 times) as substitution rather than as reducing agents.

Ketyl radicals are more active reducing agents than alkyl radicals, which is seen from the comparison of rate constants and activation energies for reactions of ketyl and alkyl radicals with hydrogen peroxide.[46]

Radical	k(350 K) ($\mathrm{L\,mol^{-1}\,s^{-1}}$)	E ($\mathrm{kJ\,mol^{-1}}$)	$-\Delta H$ ($\mathrm{kJ\,mol^{-1}}$)	E_{e0} ($\mathrm{kJ\,mol^{-1}}$)
$MeC^\bullet HOH$	1.4×10^7	11.8	185.6	104.6
$EtMeC^\bullet H$	3.7	54.1	147.0	125.5

TABLE 18.18 Enthalpies, Activation Energies and Rate Constants for the Peroxide Reduction by Alkyl Radicals Calculated by IPM Model[a]

Reaction	$-\Delta H$ ($\mathrm{kJ\,mol^{-1}}$)	E ($\mathrm{kJ\,mol^{-1}}$)	log A, A ($\mathrm{L\,mol^{-1}\,s^{-1}}$)	k(350 K) ($\mathrm{L\,mol^{-1}\,s^{-1}}$)
$Et^\bullet + H_2O_2$	132.8	68.8	9.00	5.40×10^{-2}
$M_2C^\bullet H + H_2O_2$	144.4	65.0	9.31	0.40
$MeEtC^\bullet H + H_2O_2$	145.8	64.6	8.83	0.15
$Me_3C^\bullet + H_2O_2$	129.5	69.9	9.47	0.11
$PhC^\bullet HMe + H_2O_2$	92.8	88.7	8.94	5.04×10^{-5}
$PhC^\bullet HEt + H_2O_2$	104.6	84.5	8.77	1.47×10^{-4}
$Et^\bullet + Me_3COOH$	165.1	55.3	8.74	6.12
$Me_2C^\bullet H + Me_3COOH$	176.8	51.8	9.05	42.3
$MeEtC^\bullet H + Me_3COOH$	178.2	51.4	8.58	16.3
$Me_3C^\bullet + Me_3COOH$	161.9	56.3	9.21	13.0
$PhMeC^\bullet H + Me_3COOH$	125.2	74.0	8.67	8.58×10^{-3}
$PhEtC^\bullet H + Me_3COOH$	137.0	70.0	8.51	2.29×10^{-2}
$Et^\bullet + EtOOEt$	128.1	69.5	8.99	4.09×10^{-2}
$Me_2C^\bullet H + EtOOEt$	139.8	65.7	9.30	0.32
$MeEtC^\bullet H + EtOOEt$	141.2	65.2	8.83	0.12
$Me_3C^\bullet + EtOOEt$	124.9	70.6	9.46	8.42×10^{-2}
$PhMeC^\bullet H + EtOOEt$	88.2	89.9	8.93	3.24×10^{-5}
$PhEtC^\bullet H + EtOOEt$	100.0	85.6	8.77	9.76×10^{-5}
$Et^\bullet + Me_3COOCMe_3$	132.9	67.9	9.00	7.18×10^{-2}
$Me_2C^\bullet H + Me_3COOCMe_3$	144.6	64.1	9.31	0.55
$MeEtC^\bullet H + Me_3COOCMe_3$	146.0	63.7	8.83	0.21
$Me_3C^\bullet + Me_3COOCMe_3$	129.7	69.0	9.47	0.15
$PhMeC^\bullet H + Me_3COOCMe_3$	93.0	88.2	8.94	6.01×10^{-5}
$PhEtC^\bullet H + Me_3COOCMe_3$	104.8	83.9	8.77	1.78×10^{-4}
$Et^\bullet + PhC(O)OOC(O)Ph$	134.3	67.5	9.00	8.44×10^{-2}
$Me_2C^\bullet H + PhC(O)OOC(O)Ph$	146.0	63.7	9.31	0.64
$MeEtC^\bullet H + PhC(O)OOC(O)Ph$	147.4	63.2	8.34	0.25
$Me_3C^\bullet + PhC(O)OOC(O)Ph$	131.1	68.5	9.47	0.17
$PhMeC^\bullet H + PhC(O)OOC(O)Ph$	94.4	87.7	8.94	7.19×10^{-5}
$PhEtC^\bullet H + PhC(O)OOC(O)Ph$	106.2	83.4	8.77	2.12×10^{-4}

[a] See Ref. 46.

TABLE 18.19 Comparison of Thermodynamic and Kinetic Characteristics for the Substitution and Reduction of Peroxides by Alkyl Radicals

Reactants	Reaction	$-\Delta H$ (kJ mol^{-1})	E (kJ mol^{-1})	k(350 K) (L mol^{-1} s^{-1})
$Et^•$, H_2O_2	Substitution	178.1	30.4	2.9×10^4
$Et^•$, H_2O_2	Reduction	132.8	68.8	5.3×10^{-2}
$Me_2C^•H$, H_2O_2	Substitution	188.1	27.8	4.8×10^5
$Me_2C^•H$, H_2O_2	Reduction	144.4	65.0	0.40
$Me_3C^•$, H_2O_2	Substitution	185.1	28.6	5.4×10^4
$Me_3C^•$, H_2O_2	Reduction	129.5	69.9	0.11
$Et^•$, Me_3COOH	Substitution	210.5	22.5	2.2×10^5
$Et^•$, Me_3COOH	Reduction	165.1	55.3	6.1
$Me_2C^•H$, Me_3COOH	Substitution	220.5	20.2	4.8×10^5
$Me_2C^•H$, Me_3COOH	Reduction	176.8	51.8	42
$Me_3C^•$, Me_3COOH	Substitution	207.5	23.2	1.7×10^5
$Me_3C^•$, Me_3COOH	Reduction	161.9	56.3	13
$Et^•$, PhCOOOCOPh	Substitution	249.5	34.4	1.5×10^4
$Et^•$, PhCOOOCOPh	Reduction	134.3	67.5	8.4×10^{-2}
$Me_2C^•H$, PhCOOOCOPh	Substitution	257.8	32.5	2.8×10^4
$Me_2C^•H$, PhCOOOCOPh	Reduction	146.0	63.7	0.6
$Me_3C^•$, PhCOOOCOPh	Substitution	233.8	38.1	4.1×10^3
$Me_3C^•$, PhCOOOCOPh	Reduction	131.1	68.5	0.2

There are two reasons for such a great difference:

1. Reaction of a ketyl radical is more exothermic (-186 vs -147 kJ mol^{-1}).
2. The triplet repulsion is greater for the reaction of the alkyl radical ($E_{e0} =$ 125 kJ mol^{-1}) in comparison with the ketyl radical ($E_{e0} = 105$ kJ mol^{-1}).

REFERENCES

1. H. R. Ward, in *Free Radicals*, J. K. Kochi (ed.), John Wiley & Sons, Inc., New York, 1973 Vol. 1, p. 239.
2. *Decomposition and Isomerization of Organic Compounds, Comprehensive Chemical Kinetics Kinetics*, C. H. Bamford and C. F. H. Tipper (Eds.), Elsevier, Amsterdam, The Netherlands 1972, Vol. 5.
3. *Free Radical Polymerization, Comprehensive Chemical Kinetics Kinetics*, C. H. Bamford and C. F. H. Tipper (Eds.), Elsevier, Amsterdam, The Netherlands 1976, Vol. 14A.
4. E. T. Denisov, N. I. Mitskevich, and V. E. Agabekov, *Liquid-Phase Oxidation of Oxygen-Containing Compounds*, Consultans Bureau, New York, 1977.

5. D. M. Camaioni, W. J. Shaw, S. T. Autrey, and J. A. Frans, *Abstrs. of 7th Intern. Symposium on Organic Free Radicals*, Bardolino, Italy, 48, 1996.
6. P. J. Wagner, Y. Zhang, and A. E. Puchalski, *J. Phys. Chem.* **97**, 13368 (1993).
7. G. L. Class and D. R. Paulson, *J. Am. Chem. Soc.* **92**, 7229 (1970).
8. M. A. Nagieb, C. Steel, and S. G. Cohen, *J. Phys. Chem.* **92**, 6574 (1988).
9. E. T. Denisov, *Russ. Chem. Bull.* **47**, 2110 (1998).
10. K. U. Ingold and B. P. Roberts, *Free-Radical Substitution Reactions*, John Wiley & Sons, Inc., New York, 1971.
11. K. Nozaki and P. D. Bartlett, *J. Am. Chem. Soc.* **68**, 1686 (1946).
12. K. Nozaki and P. D. Bartlett, *J. Am. Chem. Soc.* **68**, 2377 (1946).
13. J. Warnats, in *Combustion Chemistry*, W. C. Gardiner (ed.), Springer-Verlag, New York, 1984 p. 197.
14. D. L. Baulen, C. J. Cobos, and R. A. Cox, *J. Phys. Chem. Ref. Data* **21**, 411 (1992).
15. W. Tsang and R. F. Hampson, *J. Phys. Chem. Ref. Data* **15**, 1087 (1986).
16. T. Suehiro, A. Konoya, H. Hara, T. Nakahama, M. Omori, and T. Komori, *Bull. Chem. Soc. Jpn.* **40**, 668 (1967).
17. J. L. Brokenshire and K. U. Ingold, *Int. J. Chem. Kinet.* **3**, 343 (1971).
18. E. T. Denisov, *Liquid-Phase Reaction Rate Constants*, Plenum, New York, 1974.
19. A. T. Blomquist and A. J. Buselli, *J. Am. Chem. Soc.* **73**, 3883 (1951).
20. C. G. Swain, W. H. Stockmayer, and J. T. Clarke, *J. Am. Chem. Soc.* **72**, 5426 (1950).
21. M. Levy, M. Steinberg, and M. Szwarc, *J. Am. Chem. Soc.* **76**, 5978 (1954).
22. I. S. Voloshanskii and S. S. Ivanchev, *Zh. Obsch. Khim.* **44**, 892 (1974).
23. T. S. Pokidova and E. T. Denisov, *Neftekhimiya* **38**, 269 (1998).
24. W. A. Pryor and T. L. Pickering, *J. Am. Chem. Soc.* **84**, 2705 (1962).
25. D. P. Curran, A. A. Martin-Esker, Ko S-B., and M. Newcomb, *J. Org. Chem.* **58**, 4691 (1993).
26. R. G. Kryger, J. P. Lorand, N. R. Stevens, and N. R. Herron, *J. Am. Chem. Soc.* **99**, 7589 (1977).
27. J. L. Brokenshire and K. U. Ingold, *Int. J. Chem. Kinet.* **3**, 343 (1971).
28. J. Grotewold and E. A. Lissi, *Chem. Commun.* 21 (1965).
29. J. Grotewold and E. A. Lissi, *J. Chem. Soc. B*, 264 (1968).
30. T. N. Bell and A. E. Platt, *Chem. Commun.* 325 (1970).
31. A. G. Davies and B. P. Roberts, *J. Organomet. Chem.* **19**, 17 (1969).
32. A. G. Davies, T. Maki, and B. P. Roberts, *J. Chem. Soc., Perkin. Trans. 2*, **6**, 744 (1972).
33. A. G. Davies, D. Griller, B. P. Roberts, and R. Tudor, *Chem. Commun.* **11**, 640 (1970).
34. A. G. Davies, D. Griller, and B. P. J. Robers, *J. Chem. Soc. B*, 1823 (1971).
35. B. M. Mikhailov and Yu. N. Bubnov, *Zh. Obshch. Khim.* **31**, 160 (1961).
36. B. M. Mikhailov and F. B. Turovskaya, *Zh. Obshch. Khim.* **32**, 833 (1962).
37. A. G. Davies and B. P. Roberts. *J. Chem. Soc. B*, **9**, 1830 (1971).
38. A. G. Davies, K. U. Ingold, B. P. Roberts, and R. Tudor, *J. Chem. Soc. B*, **4**, 698 (1971).

39. A. G. Davies, D. Griller, B. P. Roberts, and J. C. Scaiano, *Chem. Commun.* **4**, 196 (1971).
40. S. Korcek, G. B. Watts, and K. U. Ingold, *J. Chem. Soc., Perkin Trans. 2*, **3**, 242 (1972).
41. T. S. Pokidova and E. T. Denisov, *Russ. Chem. Bull.* **50**, 390 (2001).
42. P. D. Bartlett and K. Nozaki, *J. Am. Chem. Soc.* **69**, 2299 (1947).
43. B. Barnett and W. E. Vaughan, *J. Phys. Chem.* **51**, 942 (1947).
44. M. L. Poutsma, in *Free Radicals*, J. K. Kochi (ed.), John Wiley & Sons, Inc., New York, 1973 Vol. 2, p. 159.
45. K. Kishore, P. N. Moorthy, and K. N. Rao, *Rad. Phys. Chem.* **39**, 309 (1987).
46. E. T. Denisov, *Neftekhimiya* **39**, 434 (1999).

Handbook of Free Radical Initiators. E.T. Denisov, T.G. Denisova, T.S. Pokidova
Copyright © 2003 John Wiley & Sons, Inc.
ISBN: 0-471-20753-5

19

FREE RADICAL ADDITION

Radical addition to unsaturated compounds underlies modern technology for production of polymers, copolymers, and oligomers.[1-6] These reactions occur during pyrolysis of hydrocarbons,[7] photolysis and radiolysis of organic compounds,[7] halogenation of alkenes,[6] and oxidation of olefins.[8-10] They are widely used in the synthesis of organic compounds and medicines.[11-15] The problem of the reactivity of compounds in reactions of free radical addition to nonsaturated compounds has been widely discussed and is still in debate.[16-25]

19.1 ENTHALPY AND ENTROPY OF FREE RADICAL ADDITION

The radical addition reactions

$$X^{\bullet} + CH_2{=}CHY \rightarrow XCH_2C^{\bullet}HY$$

involve the rupture of the C=C bond and the formation of a C−X σ bond. A σ bond is normally stronger than a π bond; hence, radical addition is an exothermic reaction. This reaction can be clearly seen when comparing the reaction enthalpies ΔH and the strengths of the bonds being formed D(Et−X) (see Table 19.1); the stronger the Et−X bond, the larger the $-\Delta H$ value. Yet another important factor influencing the reaction enthalpy is the energy of stabilization of the radical $XCH_2C^{\bullet}HY$ formed: the higher this energy, the greater the heat of the addition of the $X^{\bullet}$ radical to an alkene. Stabilization energy can be characterized as the difference between the strengths of the C−H bonds in Pr−H and EtYHC−H. Below the data characterizing the contribution to the enthalpy of the stabilization energy of this reaction for the $MeCH_2C^{\bullet}HY$ radical, which results from the addition of a methyl radical to the monomer $CH_2{=}CHY$ are presented.

Y	H	C(O)OMe	Cl	CN	Ph
$D_{Pr-H} - D_{EtYHC-H}$(kJ mol^{-1})	0.0	23.2	24.1	33.6	57.9
$-\Delta H$(kJ mol^{-1})	95.8	102.0	104.3	129.7	143.0

It can be seen that the greater the energy of radical stabilization, the smaller the reaction enthalpy.

All the addition reactions are accompanied by a decrease in entropy (two species are combined to give one specie, see Table 19.1). Therefore, for addition reactions, $\Delta G < \Delta H$ (ΔG is the Gibbs energy) and, when the temperature is sufficiently high, exothermic addition is reversible because $\Delta G = \Delta H - T\Delta S$. Free radical addition can be considered to be reversible if the equilibrium concentration of the X$^{\bullet}$ radicals is commensurate with the concentration of the $XCH_2C^{\bullet}HY$ radicals formed, that is, if the $[X^{\bullet}]/[XCH_2C^{\bullet}HY]$ ratio in the equilibrium state is not <0.05. When $[CH_2{=}CHY] = 10$ mol L^{-1} and $T = 300$ K, this condition results in the inequality $K \geq 200$ (K is the equilibrium constant) and $\Delta G \geq -RT \ln 200 = -13$ kJ mol^{-1}. For addition reactions, $\Delta S \approx -100$; therefore, the enthalpy for irreversible addition of a free radical to an alkene should be smaller than -43 kJ mol^{-1} (at $T = 300$ K). The ΔH values for radical addition reactions listed in Table 19.1 comply with this condition. Naturally, as the temperature rises, the boundary value of ΔH increases in absolute magnitude.

19.2 EMPIRICAL CORRELATION EQUATIONS

A line of empirical equations were proposed for systematization of data on the kinetics of radical addition.

TABLE 19.1 Bond Strength (kJ mol^{-1}), Enthalpy (kJ mol^{-1}), Entropy (J mol^{-1} K^{-1}), and Gibbs Energy (kJ mol^{-1}) for the Addition of Atoms and Radicals to Ethylene (T = 298 K)

X$^{\bullet}$	D(Et–X) (kJ mol^{-1})	$-\Delta H$ (kJ mol^{-1})	$-\Delta S$ (J mol^{-1} K^{-1})	$-\Delta G$(298 K) (kJ mol^{-1})
H$^{\bullet}$	422	150	84	125
Cl$^{\bullet}$	352	82	88	56
$C^{\bullet}H_3$	370	100	122	64
$Me_2C^{\bullet}H$	364	92	134	52
$PhC^{\bullet}H_2$	318	63	122	27
$N^{\bullet}H_2$	353	81	109	49
HO$^{\bullet}$	343	122	100	93
MeO$^{\bullet}$	352	82	118	46
$HO_2^{\bullet}$	327	63	134	23

19.2.1 Activation Energy and Heat of Reaction

A linear correlation between the change in the activation energy (ΔE) of the monomer addition to a macroradical and the change in the heat of the reaction (Δq) for the type

$$\Delta E = -\alpha' \Delta q \tag{19.1}$$

where α' is an empirical factor of proportionality, was found by Evans *et al.*[26] Later, Semenov[16] confirmed this correlation and extended it to a wider range of addition reactions. However, even for a narrow series of reactions, for example, for the addition of the methyl radical to $CH_2{=}CHY$, this correlation is nothing but a trend. Indeed, the correlation coefficient for the variation of $\Delta \log k$ as a function of Δq is 0.85 (k is the reaction rate constant of methyl radical addition to monomers).[27] Evidently, apart from the heat of reaction, other factors also influence the activation energy.

19.2.2 $Q - e$ Scheme

The Alfrey and Price $Q - e$ scheme[28] takes account of two factors affecting activation energy, namely, the energy of stabilization of the radical formed in the reaction and the interaction between polar groups in the radical and the monomer. This scheme was based on the analysis of empirical rate constants for copolymerization. The rate constant for the reaction of a radical with a monomer is postulated to have the following form:

$$k_{AB} = P_A Q_B \exp(-e_A e_B) \tag{19.2}$$

where the factors P_1 and Q_2 reflect the reactivity and e_1 and e_2 are the charges of the radical (1) and the monomer (2), respectively. The Q and e parameters are calculated from the corresponding rate constants for copolymerization. When developing the $Q - e$ scheme, the researchers assumed that the charges on the molecule and on the radical are equal and constant (polarization in the transition state was not taken into account) and that the copolymerization rate constants do not depend on the dielectric constant of the medium. Subsequently, these assumptions have been criticized. The $Q - e$ scheme made it possible to systematize the vast experimental information on radical copolymerization of various monomers. It permits rough prediction of the rate constants for copolymerization. The Q and e values for monomers in radical polymerization are listed in Table 19.2.

19.2.3 The Bamford and Jenkins $\alpha - \beta$ Scheme

These researchers suggested[29,30] that the reactivities of a radical and a monomer should be described by three parameters. (a) The rate constant for the reaction of the macroradical (e.g., $R^{1\bullet}$) with toluene (k_T):

$$R^{1\bullet} + PhCH_3 \rightarrow R^1H + PhC^{\bullet}H_2$$

TABLE 19.2 Correlation Parameters for the Reactivity of Monomers Toward Radical Polymerization in Terms of the Alfrey–Price (Q, e), Bamford–Jenkins (α, β), and Ito–Matsuda (K, P) Schemes[a]

Monomer	Q	e	α	β	K	P
$CH_2{=}CHPh$	1.00	−0.80	0.00	4.85	2.28	1.00
$CH_2{=}CHSEt$	0.27	−1.33	−0.50	4.21	1.30	2.78
$CH_2{=}CHSO_2Et$	0.07	1.29	−4.0	4.62	−1.40	−0.26
$CH_2{=}CHCO_2Me$	0.45	0.60	−3.0	5.20	0.00	0.58
$CH_2{=}CHOCOMe$	0.03	−0.88	0.0	3.00	−1.36	0.81
$CH_2{=}CHCN$	0.48	0.12	−3.0	5.30	0.89	−1.00
$CH_2{=}CHOEt$	0.02	−1.17	0.0	2.97	−0.59	1.63
$CH_2{=}CMePh$	0.98	−0.81	−1.0	4.72	1.30	1.69
$CH_2{=}CMeCO_2Me$	0.78	0.40	—	4.90	1.89	0.25
$CH_2{=}CHCH{=}CH_2$	1.70	−0.50	0.0	5.03		1.00
$CH_2{=}CMeCH{=}CH_2$	1.99	−0.55	0.0	4.92		1.09
$CH_2{=}CClCH{=}CH_2$	10.52	1.20	−1.5	5.82		0.10
$CH{\equiv}CPh$	0.45	0.5	0.5	4.41		1.00

[a] See Ref. 34.

(b) The product of coefficient α with the Hammett constant σ, which takes into account the polar effect. (c) The coefficient β, reflecting the difference between the radical reactivities toward the monomer and toluene. Thus the equation for the rate constant of the addition of $R^{1\bullet}$ to the monomer M_l is represented as follows:

$$\ln k_{1l} = \ln k_T + \alpha_l \sigma_l + \beta_l \tag{19.3}$$

the coefficients σ_l and β_l are calculated from the dependence of $\ln(k_{1l}/k_T)$ on σ, and the rate constant k_T is determined experimentally at $T = 333$ K. The values of α and β for a number of monomers are listed in Table 19.2.

19.2.4 The Ito and Matsuda $K - P$ Scheme

In terms of this scheme,[31–34] the activation energy of an addition reaction is represented as the sum of two terms, E_1 and E_2. The first term E_1 is proportional to the change in the Gibbs energy in the reversible addition of the thiyl radical $XC_6H_4S^\bullet$ to the monomer, $E_1 \sim \lg K$, where K is the equilibrium constant of the reaction.

$$PhS^\bullet + CH_2{=}CHY \Leftrightarrow PhSCH_2C^\bullet HY$$

The second term E_2 reflects the contribution of the polar interaction between the radical and the monomer to the activation energy. The contribution of the Gibbs energy to the activation energy is determined by the coefficient present in the linear dependence on log K of the logarithm of the rate constant (k_X) for the addition of the $XC_6H_4S^\bullet$ radical to the monomer $CH_2{=}CHY$.

$$\Delta \log k = \alpha_Y \Delta \log K \tag{19.4}$$

The α_Y value depends on the nature of the substituent Y in the monomer. This dependence is used to estimate the contribution of the polar effect to the activation energy. This contribution is characterized by the increment P.

$$P = \alpha_Y + 2(\alpha_Y - \alpha_{\text{styrene}}) \tag{19.5}$$

The parameters K and P are listed in Table 19.2.

All the above schemes include, in essence, different variants of empirical linear equations in which the rate constants for chain propagation in the free radical polymerization are brought into correlation with thermodynamic [heat, Hammett constant (σ), and the change in the Gibbs energy in the equilibrium reaction] and kinetic (logarithms of the rate constants of the reference reaction and the reaction under study) characteristics of the addition reaction.

19.3 QUANTUM CHEMICAL CALCULATIONS FOR THE ACTIVATION ENERGY

Quantum chemical methods are widely used to study addition reactions. The results obtained, in particular, the activation energies, depend significantly on the program chosen for calculations. For example, Radom and co-workers[35–38] calculated the activation energy of the methyl radical addition to ethylene using the QCISD(T) program package. The results of calculations by this program are in good agreement with experimental data.

When C atoms of an alkyl radical approach C atoms of a double bond and a transition state is formed, the bond angles at the carbon atom attacked by an atom or radical substantially change. The geometry of the transition state is characterized by the distance $r(C{-}C)$, the angle of attack $\varphi_{at}(C{-}C{-}C)$, and the pyramidal angle $\varphi_{pyr} = \varphi(H{-}C{-}C)$. The last-mentioned parameter is the angle of deviation for the two C–H bonds of ethylene from the plane in which they have been located in the initial molecule (the four hydrogens and both carbons of ethylene lie in one plane). Table 19.3 presents the values for the three above parameters and the activation energies for the addition of methyl radicals and the $C^\bullet H_2OH$ and $C^\bullet H_2CN$ radicals to ethylene.

The energy profile for the addition reaction is calculated using specific quantum chemical programs as a superposition of four different electron configurations of the reactants, namely,[35–38]

$$\text{DA}[\text{YCH}_2^\bullet(\uparrow)\text{CH}_2{=}\text{CHX}(\uparrow\downarrow)] \qquad \text{D}^3\text{A}^*[\text{YCH}_2^\bullet(\downarrow)\text{CH}_2{=}\text{CHX}(\uparrow\uparrow)]$$

$$\text{D}^+\text{A}^-[\text{YCH}_2(+)\text{CH}_2{=}\text{CHX}(\uparrow -)] \quad \text{and} \quad \text{D}^-\text{A}^+[\text{YCH}_2(-)\text{CH}_2{=}\text{CHX}(\uparrow +)]$$

where D is the radical, A is the molecule, the arrows mark the orientation of the electrons involved in the reorganization, and (+) and (−) are the charges

TABLE 19.3 Interatomic Distances and Bond Angles in the Reaction Center and the Activation Energies for the Addition of the $XC^{\bullet}H_2$ Radicals to Ethylene (Quantum Chemical Calculations)[a]

X	H	OH	CN
$r(C{-}C) \times 10^{10}$(m)	2.246	2.226	2.173
$\varphi_{att}(^{\circ})$	109.9	108.2	109.3
$\varphi_{pyr}(^{\circ})$	25.0	25.9	28.0
$E(\mathrm{kJ\,mol^{-1}})$	39.8	35.0	42.3

[a] See Refs. 35–38.

on the radical and on the molecule. The results (the activation energies) thus obtained are considered with allowance for the influence of two values, namely, the reaction enthalpy and the polar effect.

19.4 PARABOLIC MODEL OF RADICAL ADDITION

Within the framework of the parabolic model,[39–52] radical addition

$$X^{\bullet} + CH_2{=}CHY \rightarrow XCH_2C^{\bullet}HY$$

is represented as a result of intersection of two potential curves, each of them describing the potential energy of the stretching vibrations of atoms as a parabolic function of the amplitudes of vibrations of atoms in the outgoing (i) and incoming (f) bonds. In terms of the parabolic model, radical addition can be characterized by the following parameters: (**1**) reaction enthalpy ΔH_e; (**2**) activation energy E_e; (**3**) distance r_e, which is equal to the sum of the amplitudes of vibrations of the atoms of the reacting bonds in the transition state; and (**4**) parameters b_i and b_f, which are the dynamic characteristics ($2b^2$ is the force constant) of the outgoing and the incoming bond (detailed description of IPM model see Chapter 9).

As a rule, each reaction within one group is characterized by the same pre-exponential factor A (determined in relation to one reaction center). This allows the activation energy to be expressed in terms of the rate constant k using the Arrhenius equation.

$$E = RT\ln(A/k) \tag{19.6}$$

Since for any elementary reaction, $E > 0$, when $\Delta H_e > \Delta H_{e,\min}$, whereas for $\Delta H_e < \Delta H_{e,\min}$, the activation energy is very small and amounts to $0.5RT$ (see Chapter 9). In accordance with the parabolic model, $\Delta H_{e,\min}$ is related to br_e and α by the expression

$$\alpha^2\Delta H_{e,\min} = -(br_e)^2 + 2br_e(0.5hL\nu_i)^{1/2} + 0.5hL\nu_i(\alpha^2 - 1) \tag{19.7}$$

The physical, thermodynamic, and kinetic parameters for 15 classes of reactions involving addition of atoms and radicals to carbon–carbon and carbon–oxygen multiple bonds are listed in Table 19.4.

TABLE 19.4 Parameters of Various Classes of Addition of Atoms and Radicals to Multiple Bonds Used in the Parabolic Model[a]

Reaction	α	$b \times 10^{-11}$ $(\mathrm{kJ\,mol^{-1}})^{1/2}\,\mathrm{m^{-1}}$	$0.5hL\nu$ $(\mathrm{kJ\,mol^{-1}})$	$0.5hL(\nu_i - \nu_f)$ $(\mathrm{kJ\,mol^{-1}})$	$A \times 10^{-10}$ $(\mathrm{L\,mol^{-1}\,s^{-1}})$
$H^{\bullet} + CH_2{=}CHR$	1.440	5.389	9.9	−7.5	10
$H^{\bullet} + CH{\equiv}CR$	1.847	6.912	12.7	−4.7	40
$H^{\bullet} + O{=}CR^1R^2$	1.600	5.991	10.3	−11.4	10
$D^{\bullet} + CH_2{=}CHR$	1.461	5.389	9.9	−2.7	10
$Cl^{\bullet} + CH_2{=}CHR$	1.591	5.389	9.9	4.8	9
$Br^{\bullet} + CH_2{=}CHR$	1.844	5.389	9.9	5.8	5
$R^{\bullet} + CH_2{=}CHR$	1.202	5.389	9.9	1.7	0.1
$R^{\bullet} + CH{\equiv}CR$	1.542	6.912	12.7	3.8	0.1
$R^{\bullet} + O{=}CR^1R^2$	1.570	5.991	10.3	3.7	0.05
$N^{\bullet}H_2 + CH_2{=}CHR$	1.410	5.389	9.9	3.1	0.008
$RO^{\bullet} + CH_2{=}CHR$	1.413	5.389	9.9	3.3	0.05
$RO_2{}^{\bullet} + CH_2{=}CHR$	1.737	5.389	9.9	4.6	0.1
$R_3Si^{\bullet} + CH_2{=}CHR$	2.012	5.389	9.9	4.1	0.1
$R_3Si^{\bullet} + O{=}CR^1R^2$	2.518	5.991	10.3	7.0	0.08
$PhS^{\bullet} + CH_2{=}CHR$	2.282	5.389	9.9	6.3	0.07

[a] See Refs. 40 and 44–49.

The parabolic model makes it possible to develop an empirical hierarchy of addition reactions. All the known addition reactions are divided a priori into classes in accordance with the atomic structure of the reaction center in the transition state. Each class is characterized by a pair of force constants of the outgoing and incoming bonds or by the parameters $b = b_i$ and $\alpha = b_i/b_f$ (see above). Subclasses are distinguished in each class. Each subclass is characterized by $r_e = \mathrm{const}$ or $br_e = \mathrm{const}$, which is confirmed by analysis of a large array of experimental results. Each subclass of reactions can be described additionally by the energy of the thermally neutral reaction E_{e0} (see Chapter 9) and by the threshold value $\Delta H_{e,\min}$, for which $E = 0.5RT$ provided that $\Delta H_e < \Delta H_{e,\min}$ (see Chapter 9). The kinetic parameters for various subclasses of addition reactions are listed in Table 19.5. It can be seen that each subclass is characterized by individual values of these parameters. For example, E_{e0} varies from 31.4 kJ mol^{-1} for the addition of $PhS^{\bullet}$ to 105.3 kJ mol^{-1} for the addition of the phenyl radical to an alkene double bond.

19.5 CONTRIBUTION OF ENTHALPY FOR AN ADDITION REACTION TO ITS ACTIVATION ENERGY

The parabolic model postulates a nonlinear relationship between the activation energy and the enthalpy of a reaction (see Chapter 9). The contribution of enthalpy to the activation energy ΔE_H can be estimated as the difference $\Delta E_{e0} = E_e - E_{e0}$.

TABLE 19.5 Kinetic Parameters E_{e0}, $b(1+\alpha)^{-1}$, r_e, $(r^{\#}/r_e)_0$, and $-\Delta H_{e,\min}$ Calculated From Eqs. (9.10) and (9.12) for Addition Reactions of Various Subclasses[a]

$Y^{\bullet}$	E_{e0} (kJ mol^{-1})	$b(1+\alpha)^{-1} \times 10^{-11}$ (kJ$^{1/2}$ mol$^{-1/2}$ m^{-1})	$r_e \times 10^{11}$ (m)	$(r^{\#}/r_e)_0$	$-\Delta H_{e,\min}$ (kJ mol^{-1})
		$Y^{\bullet} + CH_2{=}CHX \rightarrow YCH_2C^{\bullet}HX$			
$H^{\bullet}$	101.6	2.21	4.56	0.41	211.9
$D^{\bullet}$	99.6	2.19	4.56	0.41	204.9
$Cl^{\bullet}$	50.5	1.86	3.82	0.39	82.9
$Br^{\bullet}$	31.2	1.69	3.30	0.35	37.9
$C^{\bullet}H_3$	82.6	2.45	3.71	0.45	194.4
$C_6H_5^{\bullet}$	105.3	2.45	4.19	0.45	252.0
$N^{\bullet}H_2$	61.0	2.24	3.49	0.41	226.0
$RO^{\bullet}$	65.2	2.23	3.62	0.41	119.0
$RO_2^{\bullet}$	90.5	1.97	4.83	0.36	150.4
$R_3Si^{\bullet}$	76.6	1.78	4.92	0.33	117.5
$PhS^{\bullet}$	31.4	1.64	3.42	0.30	34.7
		$Y^{\bullet} + HC{\equiv}CX \rightarrow YCH{=}C^{\bullet}X$			
$H^{\bullet}$	125.1	2.43	4.60	0.35	229.3
$C^{\bullet}H_3$	97.7	2.72	3.63	0.39	184.7
		$Y^{\bullet} + O{=}CR^1R^2 \rightarrow YC(O^{\bullet})R^1R^2$ or $YOC^{\bullet}R^1R^2$			
$H^{\bullet}$	102.9	2.30	4.41	0.38	149.7
$C^{\bullet}H_3$	72.9	2.33	3.66	0.39	112.2
$R_3Si^{\bullet}$	114.5	1.70	6.29	0.28	176.8

[a] See Refs. 44–49.

The IPM models gives Eq. (19.8) for ΔE_H as a function of ΔH_e, α, and br_e:

$$(\alpha^2 - 1)\Delta E_H = 2\alpha(br_e)^2\{[(\alpha^2 - 1)^{-2}(br_e)^{-2}\Delta H_e - 1]^{1/2} - 1\} + \alpha^2\Delta H_e \tag{19.8}$$

When the range of variation of ΔH_e is narrow, this dependence is close to linear.

$$\Delta E_H = \frac{\alpha}{1+\alpha}\Delta H_e + \frac{\alpha}{(2br_e)^2}\Delta H_e^2 \tag{19.9}$$

The E_{e0} values calculated from experimental br_e parameters made it possible to evaluate correctly the contribution for the enthalpy of addition to its activation energy. As an example, Table 19.6 presents the results of this comparison for two groups of addition reactions.

TABLE 19.6 Contribution ΔE_H of the Reaction Enthalpy ΔH to the Activation Energy E (Eq. 19.8)

R	Y	$-\Delta H$ (kJ mol^{-1})	E_e (kJ mol^{-1})	$-\Delta E_H$ (kJ mol^{-1})
		$H^\bullet + CH_2{=}CRY \rightarrow CH_3C^\bullet RY$		
H	H	162.1	22.5	79.1
H	Me	165.3	21.0	80.6
Me	Me	173.3	18.0	83.6
H	Cl	179.5	19.8	81.8
H	Ph	204.1	19.2	93.0
Ph	Ph	213.3	19.0	98.7
		$C^\bullet H_3 + CH_2{=}CRY \rightarrow CH_3CH_2C^\bullet RY$		
H	H	98.5	39.0	43.6
H	Me	96.1	36.9	45.7
Me	Me	98.3	35.7	46.9
H	Cl	104.3	33.6	49.0
H	Ph	143.3	26.6	63.4
Ph	Ph	154.0	24.5	69.3

It can be seen that these reactions are highly exothermic and the contribution of enthalpy to the activation energy is fairly high; it varies from −44 to −99 kJ mol^{-1}, that is, it amounts to 40–50% of ΔH.

19.6 FORCE CONSTANTS OF REACTING BONDS

The activation energy of a thermally neutral reaction is determined by two parameters: the distance r_e and the force constants of the reacting bonds α and b. In some classes of radical abstraction reactions, namely,

$$R^\bullet + R^1X \rightarrow RX + R^{1\bullet}$$

$$H^\bullet + R^1X \rightarrow HX + R^{1\bullet}$$

only the force constants change on passing from one class to another; thus, only the parameters α and b determine the activation energy of a thermally neutral reaction (see Chapter 17). There are no such examples among addition reactions;[39] therefore, it is expedient to compare different classes of reactions assuming (conditionally) that $r_e = \text{const}$. The parameter r_e for each reaction was taken to be 3.713×10^{-11} m for the addition of the methyl radical to $CH_2{=}CRY$, while the parameters b_i and b_f were varied in conformity with the structure of the reaction center. The calculations were carried out using Eq. (9.6).

Reaction	E_{e0} (calculated r_e = const) (kJ mol^{-1})	$b^2(1+\alpha)^{-2} \times 10^{-11}$ (kJ mol^{-1} m^{-2})	E_{e0} (experimental) (kJ mol^{-1})
$H^{\bullet} + C{=}C$	67.3	4.88	101.6
$H^{\bullet} + O{=}C$	73.2	5.29	102.9
$H^{\bullet} + C{\equiv}C$	81.3	5.90	125.2
$C^{\bullet}H_3 + C{\equiv}C$	64.0	7.40	97.7
$C^{\bullet}H_3 + C{=}C$	82.6	6.00	82.6
$C^{\bullet}H_3 + O{=}C$	74.9	5.43	68.1

Comparison of the calculated and experimental E_{e0} values shows a substantial influence of, on the one hand, the force constants (the range of variation of E_{e0} is 64–83 kJ mol^{-1}) and, on the other hand, the parameter r_e that varies for different reactions [cf. E_{e0} (experimental) and E_{e0} (calculated) for one reaction].

19.7 TRIPLET REPULSION IN THE TRANSITION STATE OF ADDITION REACTIONS

The activation energy of radical abstraction is influenced by the so-called triplet repulsion in the transition state. This influence is manifested in the fact that the stronger the X–R bond toward which the hydrogen atom moves in the thermally neutral reaction $X^{\bullet} + RH$, the higher the activation energy for this reaction (see Chapter 17). The triplet repulsion is due to the fact that three electrons cannot be accommodated in the bonding orbital of X–C; therefore, one electron occupies the nonbonding X–C orbital. Meanwhile, the stronger the X–C bond, the higher the energy of the nonbonding orbital and the higher the activation energy of abstraction.

How do matters stand with radical addition? Comparison of E_{e0} and r_e with the energy of dissociation of the resulting bond D_e has shown that this influence certainly does exist.[39–46] The parameters E_{e0} and r_e are juxtaposed with the dissociation energy of the bond formed D_e(X–C) in Table 19.7. For reactions of one class, namely, $X^{\bullet} + CH_2{=}CHY$, the following linear correlation holds:

$$E_{e0}(\text{kJ mol}^{-1}) = [5.95 \times 10^{-4}(\text{kJ}^{-2}\,\text{mol}^2)][D_e(\text{X–C})(\text{kJ mol}^{-1})]^2 \qquad (19.10)$$

And the following correlation was found to be fulfilled for reactions of all the 13 classes considered:

$$r_e(\text{m}) = (0.98 \times 10^{-13}(\text{kJ}^{-1}\,\text{mol m}) \times D_e(\text{X–C})(\text{kJ mol}^{-1}) \qquad (19.11)$$

This correlation should be regarded as empirical proof of the fact that the nonbonding orbital of the bond being formed actually does participate in the generation of the activation energy for addition. The stronger this bond, the higher the energy of the nonbonding orbital and the higher the activation energy of thermoneutral reaction. Empirical correlation (19.10) can be used to estimate the activation energies of diverse addition reactions roughly.

TABLE 19.7 Parameters of Various Classes of Radical Addition (E_{e0}, r_e) and Strength of the Bonds Formed[a]

Reaction	E_{e0} (kJ mol^{-1})	$r_e \times 10^{11}$ (m)	D_e(X−C) (kJ mol^{-1})	$(r_e/D_e(X-C)) \times 10^{13}$ (mmol kJ^{-1})
$H^{\bullet} + CH_2{=}CHR$	101.6	4.563	439	1.04
$D^{\bullet} + CH_2{=}CHR$	99.6	4.557	439	1.04
$Cl^{\bullet} + CH_2{=}CHR$	50.5	3.427	357	0.96
$Br^{\bullet} + CH_2{=}CHR$	31.2	2.949	299	0.99
$H^{\bullet} + HC{\equiv}CR$	125.2	4.608	462	1.00
$H^{\bullet} + O{=}CR^1R^2$	102.9	4.402	459	0.96
$C^{\bullet}H_3 + CH_2{=}CHR$	82.6	3.713	378	0.98
$Me_2C^{\bullet}H + CH_2{=}CHR$	78.3	3.617	372	0.97
$Me_3C^{\bullet} + CH_2{=}CHR$	68.3	3.377	360	0.94
$C_6H_5^{\bullet} + CH_2{=}CHR$	105.3	4.194	436	0.96
$N^{\bullet}H_2 + CH_2{=}CHR$	62.1	3.530	360	0.98
$RO^{\bullet} + CH_2{=}CHR$	65.2	3.617	359	1.01
$R^{\bullet} + O{=}CR^1R^2$	68.1	3.540	365	0.97

[a] See Refs. 39–42 and 46.

19.8 INFLUENCE OF NEIGHBORING π-BONDS ON THE ACTIVATION ENERGY OF RADICAL ADDITION

Radical abstraction reactions that involve molecules with π-bonds in the vicinity of the reaction center are characterized by higher E_{e0} values than the corresponding reactions involving similar hydrocarbons without these bonds (see Chapter 17).[44–48] This is due to triplet repulsion. In these reactions, the three electrons of the reaction center interact with the neighboring π-electrons; as a consequence, the energy of the nonbonding orbital in the transition state increases and, hence, the activation energy also increases. It was seen that neighboring π bonds influence the E_{e0} values of radical addition (Table 19.8). The difference between $E_{e0}(\pi)$ and the $E_{e0}(CH_2{=}CHY)$ can be used to evaluate the contribution of this factor to the activation barrier.[40,46,47]

$$\Delta E(\pi) = E_{e0}(\pi) - E_{e0}(CH_2{=}CHY) \tag{19.12}$$

Triplet repulsion also manifests itself in the reactions in question; for example, in the reaction

$$R^{\bullet} + CH_2{=}CHCH{=}CH_2 \rightarrow RCH_2C^{\bullet}HCH{=}CH_2$$

a multicenter multielectron $R \cdots C \cdots C \cdots C \cdots C$ bond arises in the transition state; this increases the strength of the bond, and, hence, enhances the triplet repulsion and its contribution to the activation energy. It can be seen from the data of Table 19.8 that this contribution can reach 40 kJ mol^{-1}. The increase in the dissociation energy D_e(X−C) caused by this electron delocalization can be estimated using Eq. (19.12).

TABLE 19.8 Influence of a π-Bond Adjacent to the Reaction Center on the Activation Energy of the Radical Addition to Alkenes[a]

Reaction	br_e, $(\mathrm{kJ\,mol^{-1}})^{1/2}$	E_{e0}, $(\mathrm{kJ\,mol^{-1}})$	ΔE_{π} $(\mathrm{kJ\,mol^{-1}})$	$\Delta D_e(\pi)$ $(\mathrm{kJ\,mol^{-1}})$
$H^{\bullet} + CH_2{=}CHR$	24.59	101.6	0	0
$H^{\bullet} + CH_2{=}CHPh$	25.85	112.2	10.6	24.1
$H^{\bullet} + CH_2{=}CPh_2$	26.47	117.7	16.1	36.0
$H^{\bullet}$ + 1,3-*cyclo*-C_6H_8	26.47	117.7	16.1	36.0
$H^{\bullet} + CH_2{=}CHCN$	25.45	108.8	7.2	16.4
$C^{\bullet}H_3 + CH_2{=}CHR$	20.01	82.6	0	0
$C^{\bullet}H_3 + CH_2{=}CHPh$	20.82	89.4	6.8	15.5
$C^{\bullet}H_3 + CH_2{=}CMePh$	20.67	88.7	6.1	12.6
$C^{\bullet}H_3 + CH_2{=}CPh_2$	21.33	94.4	11.8	25.2
$C^{\bullet}H_3 + CH_2{=}CHCH{=}CH_2$	20.88	89.9	7.3	16.6
$C^{\bullet}H_3 + MeCH{=}CHCH{=}CHMe$	21.15	92.2	9.6	21.8
$C^{\bullet}H_3 + CH_2{=}CMeCMe{=}CH_2$	21.03	91.2	8.6	19.5
$C^{\bullet}H_3$ + 1,3-*cyclo*-C_6H_8	22.27	102.3	19.7	43.2
$C^{\bullet}H_3$ + 1,4-*cyclo*-C_6H_8	22.23	101.9	19.3	42.5
$N^{\bullet}H_2 + CH_2{=}CHR$	18.82	61.0	0	0
$N^{\bullet}H_2$ + (*E*)-$CH_2{=}CHCH{=}CH_2$	20.52	72.5	10.4	23.7
$RO^{\bullet} + CH_2{=}CHR$	19.49	61.8	0	0
$RO^{\bullet} + CH_2{=}CHPh$	21.09	76.4	14.6	30.6
$RO_2^{\bullet} + CH_2{=}CHR$	26.04	90.5	0	0
$RO_2^{\bullet} + CH_2{=}CHPh$	27.23	99.0	8.5	22.8
$RO_2^{\bullet} + CH_2{=}CPh_2$	28.04	105.0	14.5	38.3
$R_3Si^{\bullet} + CH_2{=}CHR$	26.46	76.6	0	0
$R_3Si^{\bullet} + CH_2{=}CHPh$	28.52	89.0	12.4	27.9
$R_3Si^{\bullet} + O{=}CR^1R^2$	37.62	114.5	0	0
$R_3Si^{\bullet} + O{=}CMePh$	39.74	127.6	13.1	22.5
$R_3Si^{\bullet} + O{=}CPh_2$	40.02	129.3	14.8	25.5

[a] See Refs. 40 and 44–46.

The same trend is observed for the addition of the benzyl radical to the monomers $CH_2{=}CRY$.[40]

R	Y	br_e $(\mathrm{kJ\,mol^{-1}})^{1/2}$	E_{e0} $(\mathrm{kJ\,mol^{-1}})$	ΔE_{π} $(\mathrm{kJ\,mol^{-1}})$
Me	OMe	24.98	128.7	46.1
H	OEt	24.85	127.8	45.2
H	Ph	24.88	127.7	45.1
Me	Ph	24.93	128.2	45.6

The average E_{e0} value for these reactions is 128.0 $\mathrm{kJ\,mol^{-1}}$, respectively; the value for the addition of a methyl radical is 82.6 $\mathrm{kJ\,mol^{-1}}$. The greater E_{e0} value found in the case of the addition of benzyl radicals points to stronger triplet repulsion caused by electron delocalization.

The substantial influence of the π bonds located near the reaction center of the activation energy can also be followed for the addition of methyl radicals to the C=O group in *p*-benzoquinone.[48] This can be clearly seen when comparing the corresponding parameters for the addition of a methyl radical to acetone and to *p*-benzoquinone.

$R^1C(O)R^2$	br_e $(kJ\,mol^{-1})^{1/2}$	E_{e0} $(kJ\,mol^{-1})$	$r_e \times 10^{11}$ (m)
MeC(O)Me	21.95	68.1	3.54
OC_6H_4O	23.15	81.1	3.86

The observed difference in the parameters is due most likely to the electron delocalization in the aromatic ring and, hence, to the increase in the triplet repulsion. The difference between the E_{e0} values for the reactions considered amounts to 13 $kJ\,mol^{-1}$. For the addition of the polystyrene radical to *p*-benzoquinone, $br_e = 25.03\ (kJ/mol)^{1/2}$ and $E_{e0} = 94.8\ kJ\,mol^{-1}$. In this case, the E_{e0} value is 26.7 $kJ\,mol^{-1}$ greater than that for the reaction of the methyl radical with acetone. The very large $\Delta E(\pi)$ value can be accounted for by the interaction of the π electrons of the two neighboring benzene rings with the reaction center. With allowance for the examples considered above, correlation (19.11) can be extended and written in the following form:

$$r_e(\mathrm{m}) = [0.98 \times 10^{-13}(\mathrm{kJ^{-1}mol\,m})] \times [D_e(\mathrm{X{-}C}) + \Delta E(\pi)] \qquad (19.13)$$

19.9 ROLE OF THE RADIUS OF THE ATOM BEARING THE FREE VALENCE

The greater the radius of the atom carrying the free valence, the higher the E_{e0} for radical abstraction (see Chapter 17). Does the radius of the atom that attacks the double bond influence the activation energy of addition reactions? This question was answered as a result of the analysis of experimental data on the addition of triethylsilyl and phenylthiyl radicals to alkenes.[49]

Since the strength of the C−X (D_e) bond being formed influences the parameter r_e [see Eq. (19.11)], the characteristic to be compared for the addition of various radicals to alkenes is the r_e/D_e ratio (Table 19.9). The lengths *r*(C−X) of the bonds formed upon the addition of radicals such as $C^{\bullet}H_3$, $N^{\bullet}H_2$, and $RO^{\bullet}$ to the C=C bond and upon the addition of $C^{\bullet}H_3$ to the C=O bond are close; therefore, the ratio r_e/D_e = const. However, in the case of addition of $PhS^{\bullet}$ and

TABLE 19.9 Strengths (D_e/kJ mol^{-1}) and Lengths [r(C−X) or r(O−X)/m] of the Bonds Formed Upon the Addition of X$^\bullet$ Radicals to C=C or C=O Double Bonds[a]

X	D_e (kJ mol^{-1})	r(C−X) [or r(O−X)] × 10^{10} (m)	r_e × 10^{11} (m)	(r_e/D_e) × 10^{11} (mmol kJ^{-1})
		$X^\bullet + CH_2{=}CHY \rightarrow XCH_2C^\bullet HY$		
$C^\bullet H_3$	378	1.52	3.71	0.98
$N^\bullet H_2$	360	1.47	3.53	0.98
$RO^\bullet$	359	1.43	3.62	1.01
$RS^\bullet$	284	1.79	3.41	1.20
$R_3Si^\bullet$	378	1.89	4.91	1.30
		$X^\bullet + O{=}CR^1R^2 \rightarrow XOC^\bullet R^1R^2$		
$C^\bullet H_3$	365	1.43	3.54	0.97
$R_3Si^\bullet$	487	1.64	6.28	1.20

[a] See Refs. 40–42 and 49.

$R_3Si^\bullet$ to the C=C bond, the r_e/D_e ratio is much greater and a linear correlation is observed between r_e/D_e and r(C−X). The empirical correlation has the following form:

$$r_e(\mathrm{m}) = [8.81 \times 10^{-4}(\mathrm{mol\,kJ^{-1}})] \times [r(\mathrm{X{-}C})(\mathrm{m}) - 0.42 \times 10^{-10}][D_e(\mathrm{kJ\,mol^{-1}})] \qquad (19.14)$$

Thus, the radius of the atom carrying the free valence has a substantial influence on the activation barrier to the addition reaction: The greater the radius of this atom, the higher the activation energy. Apparently, this effect is due to repulsion in the transition state, the repulsion being due to the interaction between the electron shells of the double bond being attacked and the atom that attacks this bond.

19.10 INTERACTION OF TWO POLAR GROUPS

The polar effect involved in radical addition has been repeatedly discussed in the scientific literature.[19–25] The parabolic model opens up new prospects for the correct estimation of the polar effect. It permits one to determine the contribution of this effect to the activation energy using experimental data. This contribution (ΔE_μ) is estimated by choosing a reference reaction that involves the same reaction center but in which one or both reactants are nonpolar. The reference reaction is characterized by the parameter br_e and the reaction with two polar reactants is characterized by the parameter $(br_e)_\mu$. The component of the activation energy caused by polar interaction (ΔE_μ) is calculated from Eq. (19.15).

$$\Delta E_\mu = [(br_e)_\mu^2 - (br_e)^2](1+\alpha)^{-2} \qquad (19.15)$$

TABLE 19.10 Contribution of the Polar Effect ΔE_{μ} to the Activation Energy for the Addition of Polar Radicals to Polar Monomers $CH_2{=}CRY$ (Calculated from the Data of Several Studies)[a]

	ΔE_{μ}(kJ mol^{-1})					
X, Y	$Me_2(HO)C^{\bullet}$	$Me_2(CN)C^{\bullet}$	$Me_3COC(O)C^{\bullet}H_2$	*sec*-$RO_2^{\bullet}$	*tert*-$RO_2^{\bullet}$	$HO_2^{\bullet}$
H, EtO	−1.9	−4.9	13.2			
Me, MeO	−6.5	−9.4	10.1			
H, AcO	−15.1	−11.2	17.5	9.5	7.3	11.5
Me, AcO	−16.4	−4.3	19.5			
Me, Cl	−8.2	−4.4	10.8			
Cl, Cl	−10.2	−3.8	13.4			
H, C(O)OMe	−20.1	−1.4	13.1	−0.3	−2.0	
Me, C(O)OMe		−3.4		−5.2	−6.4	−4.7
H, CN	−23.2	−0.9	13.8	−9.0	−10.8	−7.9

[a] See Refs. 44 and 52–54.

Table 19.10 presents the results of the calculation of ΔE_{μ} for the reactions of six polar radicals with a number of polar monomers. It can be seen that the polar interaction in the transition states for the addition can either decrease ($\Delta E_{\mu} < 0$) or, in other cases, increase ($\Delta E_{\mu} > 0$) the activation energy. The ΔE_{μ} values vary from +19.5 to −23 kJ mol^{-1}, that is, they can be rather large.

The following semi-empirical description of polar effect in radical addition reactions was proposed recently by Fischer and Radom.[55] In accord with the quantum chemical treatment of addition reactions, the four lowest doublet configurations of the three-center–three-electron system influence the energy of the transition state. These are the reactant ground-state configuration with a singlet electron pair on the alkene ($R^{\bullet} + C{=}C$), the excited reactant configuration with triplet electron pair ($R^{\bullet} + C{=}C^3$), and two polar charge-transfer configurations ($R^+ + C{=}C$ and $R^- + C{=}C$). The polar effects are expected to increase with decreasing energy of either of the charge-transfer configurations; namely, $E_I(R) - E_{EA}(C{=}C)$ and/or $E_I(C{=}C) - E_{EA}(R)$ of the reactants, where E_I is potential of ionization and E_{EA} is electron affinity. The following equation was proposed for the calculation of the activation energy of radical addition reactions:

$$E = 50 + 0.22 F_n F_e \tag{19.16}$$

where factor F_n depends on $E_I(R) - E_{EA}(C{=}C)$ and factor F_e depends on $E_I(C{=}C) - E_{EA}(R)$. The results of this calculation are in good agreement with experimental measurements.[55]

19.11 MULTIDIPOLE INTERACTION IN ADDITION REACTIONS

The multidipole interaction in a bimolecular reaction arises if one or both reactants contain several (more than two) polar groups.[56] The multidipole effect

TABLE 19.11 Multidipole Effect $\Delta\Delta E_\mu$ in the Addition of Cumylperoxyl Radicals to Unsaturated Polyatomic Esters (n is the Number of Reacting Double Bonds in the Ester Molecule)[a]

Ester	k(323 K) (L mol^{-1} s^{-1})	k(323 K)/n (L mol^{-1} s^{-1})	$\Delta\Delta E_\mu$ (kJ mol^{-1})
$CH_2=CHC(O)OMe$	0.50	0.50	0
$[CH_2=CHC(O)OCH_2]_2CMe_2$	0.76	0.38	0.8
$[CH_2=CHC(O)OCH_2]_2CHOC(O)CH=CH_2$	1.05	0.35	1.0
$(CH_2=CHC(O)OCH_2)_4C$	1.28	0.32	1.2
$CH_2=CMeC(O)OMe$	1.79	1.79	0
$[CH_2=CMeC(O)OCH_2]_2CHOC(O)MeC=CH_2$	3.93	1.31	0.9
$[CH_2=CMeC(O)OCH_2]_4C$	3.08	0.77	2.3

[a] See Ref. 57.

shows itself as a deviation of the rate constant for the addition of a polar radical to a polyfunctional compound (calculated in relation to one reaction center) from the rate constant for addition to a monofunctional compound. The multidipole effect was discovered for radical abstraction of a hydrogen atom from polyfunctional esters induced by peroxyl radicals. Later, this effect was found in the addition of peroxyl radicals to the double bonds of polyatomic unsaturated esters. Table 19.11 summarizes the results of the calculations of the contribution of the multidipole effect to the activation energy performed using relation (9.15). A monofunctional ester for the corresponding structure served as the reference compound. It can be seen that the role of the multidipole interaction in these reactions is fairly low: The contribution of the interaction of several polar groups $\Delta\Delta E_\mu$ varies from 0.8 to 2.3 kJ mol^{-1}.

The multidipole effect is also manifested in the addition of chlorine atoms to chloroalkenes. The scope of influence of this factor on the activation energy of these reactions can be judged from the data given in Table 19.12. The interaction of a polar reaction center with one polar C—Cl group increases the activation energy by 17 kJ mol^{-1}, whereas the interaction with several polar C—Cl groups, conversely, results in a lower activation energy.

TABLE 19.12 Parameters br_e, ΔE_μ, and $\Delta\Delta E_\mu$ for the Addition of Chlorine Atom to Chloroalkenes[a]

Alkene	br_e (kJ mol^{-1})$^{1/2}$	ΔE_μ (kJ mol^{-1})	$-\Delta\Delta E_\mu$ (kJ mol^{-1})
$CH_2=CHCl$	21.23	17.0	0.0
(Z)-$CHCl=CHCl$	20.43	11.4	5.6
$CH_2=CCl_2$	19.64	6.6	10.4
$CCl_2=CHCl$	20.50	11.8	5.2
$CCl_2=CCl_2$	19.46	5.6	11.4

[a] See Ref. 45.

19.12 STERIC HINDRANCE

The addition of trialkylsilyl radicals to 1,2-disubstituted ethylene derivatives is subject to a steric effect.[40,49] This shows itself in the E_{e0} value for the $Et_3Si^•$ addition to RCH=CHR, which is greater than that for the addition of the same radical to CH_2=CHR. The contribution of steric repulsion to the activation energy can be characterized by the increment ΔE_S.

Alkene	br_e (kJ mol^{-1})$^{1/2}$	E_{e0} (kJ mol^{-1})	ΔE_S (kJ mol^{-1})
CH_2=CHR	26.46	76.6	0.0
RCH=CHR	27.54	83.0	6.4

No effect of this type is manifested for the addition of alkyl radicals to the same alkenes. Evidently, the steric effect involved in the addition of trialkylsilyl radicals to 1,2-disubstituted ethylene derivatives is due to the repulsion between the carbon and silicon atoms, caused by the large size of the silicon atom, in the reaction center of the transition state.

The addition of the tris-2,4,6-(*tert*-butyl)phenoxyl radical to styrene can serve as an example of a reaction subject to the steric effect. This reaction is characterized by br_e(kJ mol^{-1})$^{1/2}$ = 23.89, whereas the addition of the *tert*-butoxyl radical to styrene (a reaction with a similar structure of the reaction center) has the parameter br_e(kJ mol^{-1})$^{1/2}$ = 21.09. The difference between these values is matched by the difference between the activation energies of the corresponding thermally neutral reactions, $E_{e0} = 21.6$ kJ mol^{-1}; this can be regarded as a rough estimate of the energy of additional repulsion in the transition state of the reacting system. This repulsion in the transition state is brought about by two *tert*-butyl groups of the phenoxyl radical.

The rate constants for radical addition reactions are collected in handbooks and databases.[20,58–66] The values of enthalpies, activation energies, and rate constants of• addition reactions calculated by the IPM method (see parameters in Tables 19.1–19.2 and the equations in Chapter 9) are presented in Tables 19.13–19.23.

19.13 ADDITION OF ALKYL RADICALS TO DIOXYGEN

Alkyl radicals produced from the initiator or formed from the oxidized organic compound RH react with dioxygen, and then, when they are already peroxyl radicals, they attack RH. Being attacked by these radicals, RH gives rise to alkyl radicals.

The reaction of dioxygen addition to an alkyl radical,

$$R^• + O_2 \rightarrow RO_2^•$$

is exothermic. The change in the enthalpy of this reaction depends on the structure of alkyl radical.

$R^{\bullet}$	$C^{\bullet}H_3$	$MeC^{\bullet}H_2$	$Me_2C^{\bullet}H$	$Me_3C^{\bullet}$	$PhMe_2C^{\bullet}$
$-\Delta H (\mathrm{kJ\,mol^{-1}})$	137.0	148.4	155.4	152.8	47.3
$R^{\bullet}$	$C^{\bullet}H_2Cl$	$C^{\bullet}HCl_2$	$C^{\bullet}Cl_3$	$MeC^{\bullet}HCl$	$MeC^{\bullet}Cl_2$
$-\Delta H (\mathrm{kJ\,mol^{-1}})$	122.4	108.2	92.0	131.2	112.2

In solution, these reactions proceed very rapidly with diffusion controlled rate constants (see Table 19.24).

TABLE 19.13 Enthalpies (ΔH_e), Activation Energies (E), Preexponential Factors (A), and Rate Constants (k) of Methyl Radical Addition to Olefins (Calculated by the IPM Method)[a]

$CH_2{=}CHY$	$-\Delta H_e$ ($\mathrm{kJ\,mol^{-1}}$)	E ($\mathrm{kJ\,mol^{-1}}$)	A ($\mathrm{L\,mol^{-1}\,s^{-1}}$)	k(300 K) ($\mathrm{L\,mol^{-1}\,s^{-1}}$)
$CH_2{=}CH_2$	98.5	27.8	1.0×10^9	1.43×10^4
$CH_2{=}CHMe$	96.1	28.8	5.0×10^8	4.94×10^3
$CH_2{=}CHEt$	96.6	28.6	5.0×10^8	5.34×10^3
$CH_2{=}CMe_2$	98.3	27.9	5.0×10^8	6.95×10^3
(E)-$MeCH{=}CHMe$	95.6	28.9	1.0×10^9	9.14×10^3
(Z)-$MeCH{=}CHMe$	99.0	27.6	1.0×10^9	1.55×10^4
$CH_2{=}CHCl$	104.3	25.6	5.0×10^8	1.73×10^4
$CH_2{=}CMeCl$	94.3	29.5	5.0×10^8	3.73×10^3
$CH_2{=}CCl_2$	117.3	20.9	5.0×10^8	1.15×10^5
$CH_2{=}CHF$	100.3	27.1	5.0×10^8	9.45×10^3
$CH_2{=}CHOAc$	104.8	25.4	5.0×10^8	1.87×10^4
$CH_2{=}CHOEt$	96.5	28.6	5.0×10^8	5.26×10^3
$CH_2{=}CMeOMe$	109.0	23.9	5.0×10^8	3.48×10^4
$CH_2{=}CMeOAc$	117.0	21.0	5.0×10^8	1.10×10^5
$CH_2{=}CHC(O)OMe$	102.0	26.5	5.0×10^8	1.22×10^4
$CH_2{=}CMeC(O)OMe$	128.3	17.2	5.0×10^8	5.14×10^5
(E)-$MeCH{=}CHC(O)OH$	127.6	17.4	5.0×10^8	4.68×10^5
(Z)-$MeCH{=}CHC(O)OH$	131.8	16.0	5.0×10^8	8.12×10^5
$CH_2{=}CHCH_2OAc$	102.3	26.4	5.0×10^8	1.28×10^4
$CH_2{=}CHC(O)OCH_2Ph$	104.8	25.4	5.0×10^8	1.87×10^4
$CH_2{=}CHCN$	129.7	16.7	5.0×10^8	6.17×10^5
$CH_2{=}CMeCN$	127.0	17.6	5.0×10^8	4.32×10^5
$CH_2{=}CHCH{=}CH_2$	145.2	18.9	1.0×10^9	5.18×10^5
$MeCH{=}CHCH{=}CHMe$	136.7	21.7	1.0×10^9	1.67×10^5
$CH_2{=}CMeCMe{=}CH_2$	149.2	17.6	1.0×10^9	8.67×10^5
$CH_2{=}CHPh$	143.0	18.0	5.0×10^8	3.73×10^5

TABLE 19.13 (*continued*)

$CH_2=CHY$	$-\Delta H_e$ ($kJ\,mol^{-1}$)	E ($kJ\,mol^{-1}$)	A ($L\,mol^{-1}\,s^{-1}$)	k(300 K) ($L\,mol^{-1}\,s^{-1}$)
$CH_2=CMePh$	139.0	19.3	5.0×10^8	2.21×10^5
$HC\equiv CH$	104.4	31.2	2.0×10^9	7.39×10^3
$MeC\equiv CH$	105.3	30.8	1.0×10^9	4.34×10^3
$MeC\equiv CMe$	94.0	36.0	2.0×10^9	1.08×10^3

[a] See Chapter 9 and Table 19.4.

TABLE 19.14 Enthalpies (ΔH_e), Activation Energies (E), Preexponential Factors (A), and Rate Constants (k) of Methylethyl Radical Addition to Olefins (Calculated by the IPM Method)[a]

$CH_2=CHY$	$-\Delta H_e$ ($kJ\,mol^{-1}$)	E ($kJ\,mol^{-1}$)	A ($L\,mol^{-1}\,s^{-1}$)	k(300 K) ($L\,mol^{-1}\,s^{-1}$)
$CH_2=CH_2$	90.5	30.0	1.0×10^9	5.98×10^3
$CH_2=CHMe$	88.1	30.9	5.0×10^8	2.06×10^3
$CH_2=CHEt$	88.6	30.7	5.0×10^8	2.23×10^3
$CH_2=CMe_2$	90.3	30.0	5.0×10^8	2.93×10^3
(E)-$MeCH=CHMe$	87.6	31.1	1.0×10^9	3.80×10^3
(Z)-$MeCH=CHMe$	91.0	29.8	1.0×10^9	6.54×10^3
$CH_2=CHCl$	96.3	27.7	5.0×10^8	7.51×10^3
$CH_2=CMeCl$	86.3	31.6	5.0×10^8	1.54×10^3
$CH_2=CCl_2$	109.3	22.8	5.0×10^8	5.29×10^4
$CH_2=CHF$	92.3	29.3	5.0×10^8	4.02×10^3
$CH_2=CHOAc$	96.8	27.5	5.0×10^8	8.11×10^3
$CH_2=CHOEt$	88.5	30.8	5.0×10^8	2.20×10^3
$CH_2=CMeOMe$	101.0	25.9	5.0×10^8	1.54×10^4
$CH_2=CMeOAc$	109.0	22.9	5.0×10^8	5.06×10^4
$CH_2=CHC(O)OMe$	94.0	28.6	5.0×10^8	5.25×10^3
$CH_2=CMeC(O)OMe$	120.3	19.0	5.0×10^8	2.50×10^5
(E)-$MeCH=CHC(O)OH$	119.6	19.2	5.0×10^8	2.27×10^5
(Z)-$MeCH=CHC(O)OH$	123.8	17.8	5.0×10^8	4.02×10^5
$CH_2=CHCH_2OAc$	94.3	28.5	5.0×10^8	5.50×10^3
$CH_2=CHC(O)OCH_2Ph$	96.8	27.5	5.0×10^8	8.11×10^3
$CH_2=CHCN$	121.7	18.5	5.0×10^8	3.03×10^5
$CH_2=CMeCN$	119.0	19.4	5.0×10^8	2.09×10^5
$CH_2=CHCH=CH_2$	137.2	20.6	1.0×10^9	2.61×10^5
$MeCH=CHCH=CHMe$	128.7	23.5	1.0×10^9	8.13×10^4
$CH_2=CMeCMe=CH_2$	141.2	19.3	1.0×10^9	4.45×10^5
$CH_2=CHPh$	135.0	19.7	5.0×10^8	1.83×10^5
$CH_2=CMePh$	131.0	21.1	5.0×10^8	1.06×10^5
$HC\equiv CH$	96.4	33.9	2.0×10^9	2.50×10^3
$MeC\equiv CH$	97.3	33.5	1.0×10^9	1.46×10^3
$MeC\equiv CMe$	86.0	38.8	2.0×10^9	3.51×10^2

[a] See Chapter 9 and Table 19.4.

TABLE 19.15 Enthalpies (ΔH_e), Activation Energies (E), Preexponential Factors (A), and Rate Constants (k) of Dimethylethyl Radical Addition to Olefins (Calculated by the IPM Method)[a]

$CH_2=CHY$	$-\Delta H_e$ (kJ mol^{-1})	E (kJ mol^{-1})	A (L mol^{-1} s^{-1})	k(300 K) (L mol^{-1} s^{-1})
$CH_2=CH_2$	80.5	32.7	1.0×10^9	2.06×10^3
$CH_2=CHMe$	78.1	33.7	5.0×10^8	6.91×10^2
$CH_2=CHEt$	78.6	33.5	5.0×10^8	7.51×10^2
$CH_2=CMe_2$	80.3	32.7	5.0×10^8	9.96×10^2
(E)-$MeCH=CHMe$	77.6	33.9	1.0×10^9	1.27×10^3
(Z)-$MeCH=CHMe$	81.0	32.5	1.0×10^9	2.24×10^3
$CH_2=CHCl$	86.3	30.3	5.0×10^8	2.65×10^3
$CH_2=CMeCl$	76.3	34.4	5.0×10^8	5.11×10^2
$CH_2=CCl_2$	99.3	25.2	5.0×10^8	2.02×10^4
$CH_2=CHF$	82.3	31.9	5.0×10^8	1.38×10^3
$CH_2=CHOAc$	86.8	30.1	5.0×10^8	2.87×10^3
$CH_2=CHOEt$	78.5	33.5	5.0×10^8	7.39×10^2
$CH_2=CMeOMe$	91.0	28.4	5.0×10^8	5.60×10^3
$CH_2=CMeOAc$	99.0	25.4	5.0×10^8	1.93×10^4
$CH_2=CHC(O)OMe$	84.0	31.2	5.0×10^8	1.83×10^3
$CH_2=CMeC(O)OMe$	110.3	21.2	5.0×10^8	1.02×10^5
(E)-$MeCH=CHC(O)OH$	109.6	21.5	5.0×10^8	9.22×10^4
(Z)-$MeCH=CHC(O)OH$	113.8	20.0	5.0×10^8	1.67×10^5
$CH_2=CHCH_2OAc$	84.3	31.1	5.0×10^8	1.92×10^3
$CH_2=CHC(O)OCH_2Ph$	86.8	30.1	5.0×10^8	2.87×10^3
$CH_2=CHCN$	111.7	20.7	5.0×10^8	1.25×10^5
$CH_2=CMeCN$	109.0	21.7	5.0×10^8	8.46×10^4
$CH_2=CHCH=CH_2$	127.2	22.7	1.0×10^9	1.12×10^5
$MeCH=CHCH=CHMe$	118.7	25.7	1.0×10^9	3.33×10^4
$CH_2=CMeCMe=CH_2$	131.2	21.3	1.0×10^9	1.95×10^5
$CH_2=CHPh$	125.0	21.7	5.0×10^8	8.27×10^4
$CH_2=CMePh$	121.0	23.1	5.0×10^8	4.72×10^4
$HC\equiv CH$	86.4	37.2	2.0×10^9	6.67×10^2
$MeC\equiv CH$	87.3	36.8	1.0×10^9	3.91×10^2
$MeC\equiv CMe$	76.0	42.3	2.0×10^9	86.3

[a] See Chapter 9 and Table 19.4.

TABLE 19.16 Enthalpies (ΔH_e), Activation Energies (E), Preexponential Factors (A), and Rate Constants (k) of Phenyl Radical Addition to Olefins (Calculated by the IPM Method)[a]

$CH_2=CHY$	$-\Delta H_e$ (kJ mol^{-1})	E (kJ mol^{-1})	A (L mol^{-1} s^{-1})	k(300 K) (L mol^{-1} s^{-1})
$CH_2=CH_2$	164.1	12.7	1.0×10^9	6.10×10^6
$CH_2=CHMe$	161.7	13.4	5.0×10^8	2.30×10^6

TABLE 19.16 (*continued*)

CH_2=CHY	$-\Delta H_e$ (kJ mol^{-1})	E (kJ mol^{-1})	A (L mol^{-1} s^{-1})	k(300 K) (L mol^{-1} s^{-1})
CH_2=CHEt	162.2	13.3	5.0×10^8	2.44×10^6
CH_2=CMe_2	163.9	12.8	5.0×10^8	2.98×10^6
(*E*)-MeCH=CHMe	161.2	13.6	1.0×10^9	4.34×10^6
(*Z*)-MeCH=CHMe	164.6	12.6	1.0×10^9	6.46×10^6
CH_2=CHCl	169.9	11.1	5.0×10^8	5.91×10^6
CH_2=CMeCl	159.9	14.0	5.0×10^8	1.86×10^6
CH_2=CCl_2	182.9	7.6	5.0×10^8	2.39×10^7
CH_2=CHF	165.9	12.2	5.0×10^8	3.76×10^6
CH_2=CHOAc	170.4	10.9	5.0×10^8	6.25×10^6
CH_2=CHOEt	162.1	13.3	5.0×10^8	2.41×10^6
CH_2=CMeOMe	174.6	97.7	5.0×10^8	9.94×10^6
CH_2=CMeOAc	182.6	76.6	5.0×10^8	2.31×10^7
CH_2=CHC(O)OMe	167.6	11.7	5.0×10^8	4.56×10^6
CH_2=CMeC(O)OMe	193.9	4.9	5.0×10^8	7.05×10^7
(*E*)-MeCH=CHC(O)OH	193.2	5.0	5.0×10^8	6.60×10^7
(*Z*)-MeCH=CHC(O)OH	197.4	4.1	5.0×10^8	9.76×10^7
CH_2=$CHCH_2OAc$	167.9	11.6	5.0×10^8	4.72×10^6
CH_2=$CHC(O)OCH_2Ph$	170.4	10.9	5.0×10^8	6.25×10^6
CH_2=CHCN	195.3	4.6	5.0×10^8	8.04×10^7
CH_2=CMeCN	192.6	5.2	5.0×10^8	6.23×10^7
CH_2=CHCH=CH_2	210.8	6.9	1.0×10^9	6.22×10^7
MeCH=CHCH=CHMe	202.3	9.0	1.0×10^9	2.68×10^7
CH_2=CMeCMe=CH_2	214.8	6.0	1.0×10^9	9.10×10^7
CH_2=CHPh	208.6	6.0	5.0×10^8	4.47×10^7
CH_2=CMePh	204.6	7.0	5.0×10^8	3.04×10^7
HC ≡CH	170.0	11.5	2.0×10^9	1.99×10^7
MeC ≡CH	170.9	11.2	1.0×10^9	1.12×10^7
MeC ≡CMe	159.6	15.2	2.0×10^9	4.51×10^6

[a] See Chapter 9 and Table 19.4.

TABLE 19.17 Enthalpies (ΔH_e), Activation Energies (E), Preexponential Factors (A), and Rate Constants (k) of Hydroxyl Radical Addition to Olefins (Calculated by the IPM Method)[a]

CH_2=CHY	$-\Delta H_e$ (kJ mol^{-1})	E (kJ mol^{-1})	A (L mol^{-1} s^{-1})	k(300 K) (L mol^{-1} s^{-1})
CH_2=CH_2	121.7	5.8	8.75×10^{10}	8.56×10^9
CH_2=CHMe	119.3	6.6	8.75×10^{10}	6.23×10^9
CH_2=CHEt	119.8	6.4	8.75×10^{10}	6.66×10^9
CH_2=CMe_2	121.5	5.9	8.75×10^{10}	8.34×10^9
(*E*)-MeCH=CHMe	118.8	6.8	8.75×10^{10}	5.83×10^9

(*continued overleaf*)

TABLE 19.17 (*continued*)

CH$_2$=CHY	$-\Delta H_e$ (kJ mol^{-1})	E (kJ mol^{-1})	A (L mol^{-1} s^{-1})	k(300 K) (L mol^{-1} s^{-1})
(*Z*)-MeCH=CHMe	122.2	5.6	8.75×10^{10}	9.13×10^{9}
CH$_2$=CHCl	127.5	4.0	8.75×10^{10}	1.79×10^{10}
CH$_2$=CMeCl	117.5	7.2	8.75×10^{10}	4.89×10^{9}
CH$_2$=CCl$_2$	140.5	1.4	8.75×10^{10}	5.0×10^{10}
CH$_2$=CHF	123.5	5.2	8.75×10^{10}	1.08×10^{10}
CH$_2$=CHOAc	128.0	3.8	8.75×10^{10}	1.90×10^{10}
CH$_2$=CHOEt	119.7	6.5	8.75×10^{10}	6.58×10^{9}
CH$_2$=CMeOMe	132.2	2.5	8.75×10^{10}	3.15×10^{10}
CH$_2$=CMeOAc	140.2	1.5	8.75×10^{10}	4.80×10^{10}
CH$_2$=CHC(O)OMe	125.2	4.7	8.75×10^{10}	1.34×10^{10}
CH$_2$=CMeC(O)OMe	151.5	1.2	8.75×10^{10}	5.41×10^{10}
(*E*)-MeCH=CHC(O)OH	150.8	1.2	8.75×10^{10}	5.41×10^{10}
(*Z*)-MeCH=CHC(O)OH	155.0	1.2	8.75×10^{10}	5.41×10^{10}
CH$_2$=CHCH$_2$OAc	125.5	4.6	8.75×10^{10}	1.39×10^{10}
CH$_2$=CHC(O)OCH$_2$Ph	128.0	3.8	8.75×10^{10}	1.90×10^{10}
CH$_2$=CHCN	152.9	1.2	8.75×10^{10}	5.41×10^{10}
CH$_2$=CMeCN	150.2	1.2	8.75×10^{10}	5.41×10^{10}
CH$_2$=CHCH=CH$_2$	168.4	1.3	8.75×10^{10}	5.30×10^{10}
MeCH=CHCH=CHMe	159.9	3.6	8.75×10^{10}	2.10×10^{10}
CH$_2$=CMeCMe=CH$_2$	172.4	2.4	8.75×10^{10}	7.95×10^{10}
CH$_2$=CHPh	166.2	1.3	8.75×10^{10}	5.30×10^{10}
CH$_2$=CMePh	162.2	1.4	8.75×10^{10}	4.95×10^{10}
HC≡CH	127.6	35.4	8.75×10^{10}	6.01×10^{4}
MeC≡CH	128.5	35.0	8.75×10^{10}	7.19×10^{4}
MeC≡CMe	117.2	40.6	8.75×10^{10}	7.34×10^{3}

[a] See Chapter 9 and Table 19.4.

TABLE 19.18 Enthalpies (ΔH_e), Activation Energies (E), Preexponential Factors (A), and Rate Constants (k) of Dimethylethoxyl Radical Addition to Olefins (Calculated by the IPM Method)[a]

CH$_2$=CHY	$-\Delta H_e$ (kJ mol^{-1})	E (kJ mol^{-1})	A (L mol^{-1} s^{-1})	k(300 K) (L mol^{-1} s^{-1})
CH$_2$=CH$_2$	85.8	13.7	1.0×10^{9}	4.17×10^{6}
CH$_2$=CHMe	83.4	14.6	5.0×10^{8}	1.44×10^{6}
CH$_2$=CHEt	83.9	14.4	5.0×10^{8}	1.55×10^{6}
CH$_2$=CMe$_2$	85.6	13.8	5.0×10^{8}	2.02×10^{6}
(*E*)-MeCH=CHMe	82.9	14.8	1.0×10^{9}	2.65×10^{6}
(*Z*)-MeCH=CHMe	86.3	13.5	1.0×10^{9}	4.50×10^{6}
CH$_2$=CHCl	91.6	11.5	5.0×10^{8}	5.00×10^{6}
CH$_2$=CMeCl	81.6	15.3	5.0×10^{8}	1.08×10^{6}

TABLE 19.18 (*continued*)

$CH_2{=}CHY$	$-\Delta H_e$ (kJ mol^{-1})	E (kJ mol^{-1})	A (L mol^{-1} s^{-1})	k(300 K) (L mol^{-1} s^{-1})
$CH_2{=}CCl_2$	104.6	6.9	5.0×10^8	3.10×10^7
$CH_2{=}CHF$	87.6	13.0	5.0×10^8	2.75×10^6
$CH_2{=}CHOAc$	92.1	11.3	5.0×10^8	5.39×10^6
$CH_2{=}CHOEt$	83.8	14.4	5.0×10^8	1.53×10^6
$CH_2{=}CMeOMe$	96.3	9.8	5.0×10^8	9.90×10^6
$CH_2{=}CMeOAc$	104.3	7.0	5.0×10^8	2.98×10^7
$CH_2{=}CHC(O)OMe$	89.3	12.3	5.0×10^8	3.55×10^6
$CH_2{=}CMeC(O)OMe$	115.6	3.5	5.0×10^8	1.24×10^8
(E)-$MeCH{=}CHC(O)OH$	114.9	3.7	5.0×10^8	1.14×10^8
(Z)-$MeCH{=}CHC(O)OH$	119.1	2.4	5.0×10^8	1.87×10^8
$CH_2{=}CHCH_2OAc$	89.6	12.2	5.0×10^8	3.71×10^6
$CH_2{=}CHC(O)OCH_2Ph$	92.1	11.3	5.0×10^8	5.39×10^6
$CH_2{=}CHCN$	117.0	3.1	5.0×10^8	1.47×10^8
$CH_2{=}CMeCN$	114.3	3.9	5.0×10^8	1.06×10^8
$CH_2{=}CHCH{=}CH_2$	132.5	8.5	1.0×10^9	3.38×10^7
$MeCH{=}CHCH{=}CHMe$	124.0	11.2	1.0×10^9	1.10×10^7
$CH_2{=}CMeCMe{=}CH_2$	136.5	7.2	1.0×10^9	5.57×10^7
$CH_2{=}CHPh$	130.3	7.3	5.0×10^8	2.67×10^7
$CH_2{=}CMePh$	126.3	8.6	5.0×10^8	1.61×10^7
$HC{\equiv}CH$	91.7	26.9	2.0×10^9	4.09×10^4
$MeC{\equiv}CH$	92.6	26.5	1.0×10^9	2.44×10^4
$MeC{\equiv}CMe$	81.3	32.1	2.0×10^9	5.08×10^3

[a] See Chapter 9 and Table 19.4.

TABLE 19.19 Enthalpies (ΔH_e), Activation Energies (E), Preexponential Factors (A), and Rate Constants (k) of Benzoyloxyl Radical Addition to Olefins (Calculated by the IPM Method)[a]

$CH_2{=}CHY$	$-\Delta H_e$ (kJ mol^{-1})	E (kJ mol^{-1})	A (L mol^{-1} s^{-1})	k(300 K) (L mol^{-1} s^{-1})
$CH_2{=}CH_2$	96.9	9.6	2.0×10^9	4.31×10^7
$CH_2{=}CHMe$	94.5	10.4	1.0×10^9	1.53×10^7
$CH_2{=}CHEt$	95.0	10.3	1.0×10^9	1.64×10^7
$CH_2{=}CMe_2$	96.7	9.6	1.0×10^9	2.10×10^7
(E)-$MeCH{=}CHMe$	94.0	10.6	2.0×10^9	2.84×10^7
(Z)-$MeCH{=}CHMe$	97.4	9.40	2.0×10^9	4.63×10^7
$CH_2{=}CHCl$	102.7	7.6	1.0×10^9	4.81×10^7
$CH_2{=}CMeCl$	92.7	11.1	1.0×10^9	1.18×10^7
$CH_2{=}CCl_2$	115.7	3.4	1.0×10^9	2.52×10^8
$CH_2{=}CHF$	98.7	8.9	1.0×10^9	2.78×10^7

(*continued overleaf*)

TABLE 19.19 (*continued*)

CH_2=CHY	$-\Delta H_e$ (kJ mol^{-1})	E (kJ mol^{-1})	A (L mol^{-1} s^{-1})	k(300 K) (L mol^{-1} s^{-1})
CH_2=CHOAc	103.2	7.4	1.0×10^9	5.15×10^7
CH_2=CHOEt	94.9	10.3	1.0×10^9	1.62×10^7
CH_2=CMeOMe	107.4	6.0	1.0×10^9	8.96×10^7
CH_2=CMeOAc	115.4	3.5	1.0×10^9	2.43×10^8
CH_2=CHC(O)OMe	100.4	8.4	1.0×10^9	3.52×10^7
CH_2=CMeC(O)OMe	126.7	1.6	1.0×10^9	5.26×10^8
(*E*)-MeCH=CHC(O)OH	126.0	1.8	1.0×10^9	4.90×10^8
(*Z*)-MeCH=CHC(O)OH	130.2	1.2	1.0×10^9	6.18×10^8
CH_2=$CHCH_2OAc$	100.7	8.2	1.0×10^9	3.66×10^7
CH_2=$CHC(O)OCH_2Ph$	103.2	7.4	1.0×10^9	5.15×10^7
CH_2=CHCN	128.1	1.2	1.0×10^9	6.18×10^8
CH_2=CMeCN	125.4	1.9	1.0×10^9	4.67×10^8
CH_2=CHCH=CH_2	143.6	5.1	2.0×10^9	2.61×10^8
MeCH=CHCH=CHMe	135.1	7.6	2.0×10^9	9.37×10^7
CH_2=CMeCMe=CH_2	147.6	3.9	2.0×10^9	4.11×10^8
CH_2=CHPh	141.4	4.0	1.0×10^9	2.01×10^8
CH_2=CMePh	137.4	5.1	1.0×10^9	1.27×10^8
HC≡CH	102.8	21.6	4.0×10^9	6.84×10^5
MeC≡CH	103.7	21.2	2.0×10^9	4.04×10^5
MeC≡CMe	92.4	26.6	4.0×10^9	9.37×10^4

[a] See Chapter 9 and Table 19.4.

TABLE 19.20 Enthalpies (ΔH_e), Activation Energies (E), Preexponential Factors (A), and Rate Constants (k) of Methylethylperoxyl Radical Addition to Olefins (Calculated by the IPM Method)[a]

CH_2=CHY	$-\Delta H_e$ (kJ mol^{-1})	E (kJ mol^{-1})	A (L mol^{-1} s^{-1})	k(300 K) (L mol^{-1} s^{-1})
CH_2=CH_2	37.1	59.2	2.0×10^9	9.83×10^{-2}
CH_2=CHMe	34.7	60.6	1.0×10^9	2.80×10^{-2}
CH_2=CHEt	35.2	60.3	1.0×10^9	3.15×10^{-2}
CH_2=CMe_2	36.9	59.3	1.0×10^9	4.70×10^{-2}
(*E*)-MeCH=CHMe	34.2	60.9	2.0×10^9	5.00×10^{-2}
(*Z*)-MeCH=CHMe	37.6	58.9	2.0×10^9	0.11
CH_2=CHCl	42.9	55.8	1.0×10^9	0.19
CH_2=CMeCl	32.9	61.7	1.0×10^9	1.83×10^{-2}
CH_2=CCl_2	55.9	48.5	1.0×10^9	3.55
CH_2=CHF	38.9	58.2	1.0×10^9	7.47×10^{-2}
CH_2=CHOAc	43.4	55.6	1.0×10^9	0.21
CH_2=CHOEt	35.1	60.4	1.0×10^9	3.08×10^{-2}
CH_2=CMeOMe	47.6	53.2	1.0×10^9	0.55

TABLE 19.20 (*continued*)

CH_2=CHY	$-\Delta H_e$ (kJ mol^{-1})	E (kJ mol^{-1})	A (L mol^{-1} s^{-1})	k(300 K) (L mol^{-1} s^{-1})
CH_2=CMeOAc	55.6	48.7	1.0×10^9	3.32
CH_2=CHC(O)OMe	40.6	57.2	1.0×10^9	0.11
CH_2=CMeC(O)OMe	66.9	42.6	1.0×10^9	39.0
(*E*)-MeCH=CHC(O)OH	66.2	42.9	1.0×10^9	33.6
(*Z*)-MeCH=CHC(O)OH	70.4	40.7	1.0×10^9	82.1
CH_2=$CHCH_2OAc$	40.9	57.0	1.0×10^9	0.12
CH_2=$CHC(O)OCH_2Ph$	43.4	55.6	1.0×10^9	0.21
CH_2=CHCN	68.3	41.8	1.0×10^9	52.6
CH_2=CMeCN	65.6	43.3	1.0×10^9	29.5
CH_2=CHCH=CH_2	83.8	44.1	2.0×10^9	42.9
MeCH=CHCH=CHMe	75.3	48.5	2.0×10^9	7.13
CH_2=CMeCMe=CH_2	87.8	42.0	2.0×10^9	98.0
CH_2=CHPh	81.6	42.9	1.0×10^9	34.0
CH_2=CMePh	77.6	45.0	1.0×10^9	14.7
HC≡CH	43.0	78.0	4.0×10^9	1.04×10^{-4}
MeC≡CH	43.9	77.5	2.0×10^9	6.54×10^{-5}
MeC≡CMe	32.6	84.8	4.0×10^9	6.82×10^{-6}

[a] See Chapter 9 and Table 19.4.

TABLE 19.21 Enthalpies (ΔH_e), Activation Energies (E), Preexponential Factors (A), and Rate Constants (k) of Aminyl Radical ($N^{\bullet}H_2$) Addition to Olefins (Calculated by the IPM Method)[a]

CH_2=CHY	$-\Delta H_e$ (kJ mol^{-1})	E (kJ mol^{-1})	A (L mol^{-1} s^{-1})	k(300 K) (L mol^{-1} s^{-1})
CH_2=CH_2	88.5	9.4	1.6×10^8	3.63×10^6
CH_2=CHMe	86.1	10.3	8.0×10^7	1.27×10^6
CH_2=CHEt	86.6	10.2	8.0×10^7	1.37×10^6
CH_2=CMe_2	86.6	9.5	8.0×10^7	1.76×10^6
(*E*)-MeCH=CHMe	85.6	10.5	1.6×10^8	2.36×10^6
(*Z*)-MeCH=CHMe	89.0	9.3	1.6×10^8	3.91×10^6
CH_2=CHCl	94.3	7.4	8.0×10^7	4.18×10^6
CH_2=CMeCl	84.3	11.0	8.0×10^7	9.67×10^5
CH_2=CCl_2	107.3	3.1	8.0×10^7	2.32×10^7
CH_2=CHF	90.3	8.8	8.0×10^7	2.36×10^6
CH_2=CHOAc	94.8	7.2	8.0×10^7	4.49×10^6
CH_2=CHOEt	86.5	10.2	8.0×10^7	1.35×10^6
CH_2=CMeOMe	99.0	5.8	8.0×10^7	7.97×10^6
CH_2=CMeOAc	107.0	3.2	8.0×10^7	2.24×10^7

(*continued overleaf*)

TABLE 19.21 (*continued*)

$CH_2{=}CHY$	$-\Delta H_e$ (kJ mol^{-1})	E (kJ mol^{-1})	A (L mol^{-1} s^{-1})	k(300 K) (L mol^{-1} s^{-1})
$CH_2{=}CHC(O)OMe$	92.0	8.2	8.0×10^7	3.02×10^6
$CH_2{=}CMeC(O)OMe$	118.3	1.2	8.0×10^7	4.94×10^7
(*E*)-$MeCH{=}CHC(O)OH$	117.6	0.105	8.0×10^7	7.67×10^7
(*Z*)-$MeCH{=}CHC(O)OH$	121.8	1.2	8.0×10^7	4.94×10^7
$CH_2{=}CHCH_2OAc$	92.3	8.1	8.0×10^7	3.15×10^6
$CH_2{=}CHC(O)OCH_2Ph$	94.8	7.2	8.0×10^7	4.49×10^6
$CH_2{=}CHCN$	119.7	1.2	8.0×10^7	4.94×10^7
$CH_2{=}CMeCN$	117.0	1.5	8.0×10^7	4.38×10^7
$CH_2{=}CHCH{=}CH_2$	135.2	3.0	1.6×10^8	4.71×10^7
$MeCH{=}CHCH{=}CHMe$	126.7	5.6	1.6×10^8	1.71×10^7
$CH_2{=}CMeCMe{=}CH_2$	139.2	1.9	1.6×10^8	7.37×10^7
$CH_2{=}CHPh$	133.0	1.3	8.0×10^7	4.69×10^7
$CH_2{=}CMePh$	129.0	2.4	8.0×10^7	3.00×10^7
$HC{\equiv}CH$	94.4	41.4	3.2×10^8	19.6
$MeC{\equiv}CH$	95.3	41.0	1.6×10^8	11.8
$MeC{\equiv}CMe$	84.0	46.9	3.2×10^8	2.2

[a] See Chapter 9 and Table 19.4.

TABLE 19.22 Enthalpies (ΔH_e), Activation Energies (E), Preexponential Factors (A), and Rate Constants (k) of Triethylsilyl Radical Addition to Olefins (Calculated by the IPM Method)[a]

$CH_2{=}CHY$	$-\Delta H_e$ (kJ mol^{-1})	E (kJ mol^{-1})	A (L mol^{-1} s^{-1})	k(300 K) (L mol^{-1} s^{-1})
$CH_2{=}CH_2$	97.1	11.8	1.6×10^9	1.41×10^7
$CH_2{=}CHMe$	94.7	12.9	8.0×10^8	4.54×10^6
$CH_2{=}CHEt$	95.2	12.7	8.0×10^8	4.92×10^6
$CH_2{=}CMe_2$	96.9	11.9	8.0×10^8	6.78×10^6
(*E*)-$MeCH{=}CHMe$	94.2	13.1	1.6×10^9	8.38×10^6
(*Z*)-$MeCH{=}CHMe$	97.6	11.5	1.6×10^9	3.18×10^7
$CH_2{=}CHCl$	102.9	9.2	8.0×10^8	2.00×10^7
$CH_2{=}CMeCl$	92.9	13.7	8.0×10^8	3.29×10^6
$CH_2{=}CCl_2$	115.9	3.8	8.0×10^8	1.74×10^8
$CH_2{=}CHF$	98.9	10.9	8.0×10^8	1.01×10^7
$CH_2{=}CHOAc$	103.4	8.9	8.0×10^8	2.26×10^7
$CH_2{=}CHOEt$	95.1	12.7	8.0×10^8	4.92×10^6
$CH_2{=}CMeOMe$	107.6	7.2	8.0×10^8	4.46×10^7
$CH_2{=}CMeOAc$	115.6	3.9	8.0×10^8	1.67×10^8
$CH_2{=}CHC(O)OMe$	100.6	10.2	8.0×10^8	1.34×10^7
$CH_2{=}CMeC(O)OMe$	126.9	1.2	8.0×10^8	4.94×10^8
(*E*)-$MeCH{=}CHC(O)OH$	126.2	1.3	8.0×10^8	4.75×10^8

TABLE 19.22 (*continued*)

$CH_2{=}CHY$	$-\Delta H_e$ (kJ mol^{-1})	E (kJ mol^{-1})	A (L mol^{-1} s^{-1})	k(300 K) (L mol^{-1} s^{-1})
(Z)-$MeCH{=}CHC(O)OH$	130.4	1.2	8.0×10^8	4.94×10^8
$CH_2{=}CHCH_2OAc$	100.9	10.1	8.0×10^8	1.39×10^7
$CH_2{=}CHC(O)OCH_2Ph$	103.4	9.0	8.0×10^8	2.17×10^7
$CH_2{=}CHCN$	128.3	1.2	8.0×10^8	4.94×10^8
$CH_2{=}CMeCN$	125.6	1.5	8.0×10^8	4.38×10^8
$CH_2{=}CHCH{=}CH_2$	143.8	3.5	1.6×10^9	3.93×10^8
$MeCH{=}CHCH{=}CHMe$	135.3	6.7	1.6×10^9	4.37×10^7
$CH_2{=}CMeCMe{=}CH_2$	147.8	2.0	1.6×10^9	7.18×10^8
$CH_2{=}CHPh$	141.6	3.2	8.0×10^8	2.22×10^8
$CH_2{=}CMePh$	137.6	4.7	8.0×10^8	1.21×10^8
$HC{\equiv}CH$	103.0	9.6	3.2×10^9	6.82×10^7
$MeC{\equiv}CH$	103.9	9.1	1.6×10^9	4.17×10^7
$MeC{\equiv}CMe$	92.6	15.0	3.2×10^9	7.82×10^6

[a] See Chapter 9 and Table 19.4.

TABLE 19.23 Enthalpies (ΔH_e), Activation Energies (E), Preexponential Factors (A), and Rate Constants (k) of Ethylthiyl Radical Addition to Olefins (Calculated by the IPM Method)[a]

$CH_2{=}CHY$	$-\Delta H_e$ (kJ mol^{-1})	E (kJ mol^{-1})	A (L mol^{-1} s^{-1})	k(300 K) (L mol^{-1} s^{-1})
$CH_2{=}CH_2$	31.5	14.9	1.40×10^9	3.55×10^6
$CH_2{=}CHMe$	29.1	16.4	7.00×10^8	9.92×10^5
$CH_2{=}CHEt$	29.6	16.0	7.00×10^8	1.12×10^6
$CH_2{=}CMe_2$	31.3	15.0	7.00×10^8	1.69×10^6
(E)-$MeCH{=}CHMe$	28.6	16.7	1.40×10^9	1.76×10^6
(Z)-$MeCH{=}CHMe$	32.0	14.6	1.40×10^9	4.00×10^6
$CH_2{=}CHCl$	37.3	11.5	7.00×10^8	6.95×10^6
$CH_2{=}CMeCl$	27.3	17.5	7.00×10^8	6.38×10^5
$CH_2{=}CCl_2$	50.3	4.4	7.00×10^8	1.18×10^8
$CH_2{=}CHF$	33.3	13.8	7.00×10^8	2.73×10^6
$CH_2{=}CHOAc$	37.8	11.2	7.00×10^8	7.79×10^6
$CH_2{=}CHOEt$	29.5	16.1	7.00×10^8	1.09×10^6
$CH_2{=}CMeOMe$	42.0	8.9	7.00×10^8	2.01×10^7
$CH_2{=}CMeOAc$	50.0	4.6	7.00×10^8	1.11×10^8
$CH_2{=}CHC(O)OMe$	35.0	12.8	7.00×10^8	4.07×10^6
$CH_2{=}CMeC(O)OMe$	61.3	1.2	7.00×10^8	4.33×10^8
(E)-$MeCH{=}CHC(O)OH$	60.6	1.2	7.00×10^8	4.33×10^8
(Z)-$MeCH{=}CHC(O)OH$	64.8	1.2	7.00×10^8	4.33×10^9
$CH_2{=}CHCH_2OAc$	35.3	12.7	7.00×10^8	4.37×10^6

(*continued overleaf*)

TABLE 19.23 (*continued*)

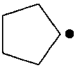
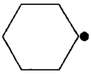
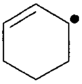
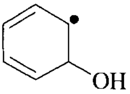
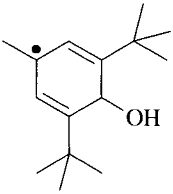
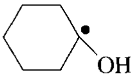
$CH_2{=}CHY$	$-\Delta H_e$ (kJ mol^{-1})	E (kJ mol^{-1})	A (L mol^{-1} s^{-1})	k(300 K) (L mol^{-1} s^{-1})
$CH_2{=}CHC(O)OCH_2Ph$	37.8	11.2	7.00×10^8	7.79×10^6
$CH_2{=}CHCN$	62.7	1.2	7.00×10^8	4.33×10^9
$CH_2{=}CMeCN$	60.0	1.2	7.00×10^8	4.33×10^8
$CH_2{=}CHCH{=}CH_2$	78.2	1.2	1.40×10^9	4.33×10^{10}
$MeCH{=}CHCH{=}CHMe$	69.7	1.2	1.40×10^9	4.33×10^9
$CH_2{=}CMeCMe{=}CH_2$	82.2	1.2	1.40×10^9	4.33×10^{10}
$CH_2{=}CHPh$	76.0	1.2	7.00×10^8	4.33×10^9
$CH_2{=}CMePh$	72.0	1.2	7.00×10^8	4.33×10^9
$HC{\equiv}CH$	37.4	9.6	2.80×10^9	5.87×10^7
$MeC{\equiv}CH$	38.3	9.1	1.40×10^9	3.69×10^7
$MeC{\equiv}CMe$	27.0	16.5	2.80×10^9	3.78×10^6

[a] See Chapter 9 and Table 19.4.

TABLE 19.24 Rate Constants of Dioxygen Addition to Alkyl Radicals

$R^{\bullet}$	Solvent	T (K)	k (L mol^{-1} s^{-1})	Reference
$C^{\bullet}H_3$	Water	296	4.7×10^9	67
$C^{\bullet}H_3$	Water, pH 1.0	298	4.1×10^9	68
$C^{\bullet}H_3$	Water, pH 3.0	298	3.7×10^9	69
$MeC^{\bullet}H_2$	Water, pH 0.0	298	2.1×10^9	68
$MeC^{\bullet}H_2$	Water	298	2.9×10^9	70
$EtC^{\bullet}H_2$	Water, pH 8.5	298	1.9×10^9	71
$Me_2C^{\bullet}H$	Water, pH 1.0	298	3.8×10^9	68
$PrC^{\bullet}H_2$	Water, pH 0.0	298	1.8×10^9	68
$PrC^{\bullet}H_2$	Water, pH 8.5	298	1.3×10^9	71
$EtMeC^{\bullet}H$	Water, pH 1.0	298	3.2×10^9	68
$Me_2CHC^{\bullet}H_2$	Water, pH 1.0	298	3.2×10^9	68
$Me_3C^{\bullet}$	Cyclohexane	300	4.9×10^9	72
$Me(CH_2)_3C^{\bullet}H_2$	Water, pH 0.0	298	3.8×10^9	68
$Me(CH_2)_4C^{\bullet}H_2$	Water, pH 0.0	298	3.9×10^9	68
$Me_3CC^{\bullet}H_2$	Water, pH 1.0	298	2.7×10^9	68
$Me(CH_2)_6C^{\bullet}H_2$	Water, pH 1.0	298	2.4×10^9	68
$Me(CH_2)_5C^{\bullet}$ HMe	Water, pH 1.0	298	2.4×10^9	68
$Me(CH_2)_7C^{\bullet}HMe$	Decane	298	4.8×10^9	73
$Me(CH_2)_{13}C^{\bullet}HMe$	Hexadecane	298	1.5×10^9	74
$Me(CH_2)_{14}C^{\bullet}HMe$	Heptadecane	298	1.5×10^9	74
$Me(CH_2)_4CH{=}CHC^{\bullet}HCH{=}CH(CH_2)_7COOH$	Linoleic acid	295	3.0×10^8	75
$Et(CH{=}CHCH_2)_2CH{=}CHC^{\bullet}H(CH_2)_6COOH$	Linolenic acid	295	3.0×10^8	75

TABLE 19.24 (*continued*)

$R^{\bullet}$	Solvent	T (K)	k ($L\,mol^{-1}\,s^{-1}$)	Reference
	Water, pH 1.0	298	3.5×10^9	68
	Cyclohexane	298	2.0×10^9	76
	Benzene	300	1.6×10^9	72
	Water	*RT*	1.5×10^8	77
	Toluene, 3,5-bis-1,1-dimethylethyl-	298	9.0×10^7	74
$C^{\bullet}H_2Cl$	Water, pH 1.0	298	1.9×10^9	68
$C^{\bullet}H_2Br$	Water, pH 0.0	298	2.0×10^9	68
$MeC^{\bullet}HCl$	Water	298	9.0×10^8	78
$CH_3C^{\bullet}Cl_2$	Water	298	1.5×10^9	78
$CF_3C^{\bullet}HCl$	Water/*tert*-butanol	298	1.3×10^9	79
$CH_2ClC^{\bullet}HCl$	Water	298	9.7×10^8	78
$N{\equiv}CC^{\bullet}H_2$	Water/acetonitrile	298	1.3×10^9	80
$Me_2NC^{\bullet}H_2$	Trimethylamine	298	3.5×10^9	81
$C^{\bullet}H_2OH$	Water, pH 10.7	298	4.2×10^9	82
$C^{\bullet}H_2CH_2OH$	Water, pH 1.0	298	6.6×10^9	83
$MeC^{\bullet}HOH$	Water, pH 7.0	298	4.6×10^9	84
$EtC^{\bullet}HOH$	Water, pH 7.0	298	4.7×10^9	84
$Me_2C^{\bullet}OH$	2-Propanol	300	3.9×10^9	72
$Me_2C^{\bullet}OH$	Acetonitrile	297	6.6×10^9	85
$Me_2CHC^{\bullet}HOH$	Water, pH 7.0	298	3.4×10^9	84
$EtMeC^{\bullet}OH$	Water, pH 7.0	298	4.0×10^9	84
$HOCH{=}C^{\bullet}H$	Ethanol	295	1.0×10^9	86
$C^{\bullet}\ H(OH)CH_2OH$	Water, pH 7.0	298	3.2×10^9	84
	Acetonitrile	297	5.4×10^9	85
$C^{\bullet}H_2CO_2^-$	Water, pH 8.0	298	1.7×10^9	87
$(CO_2^-)_2C^{\bullet}OH$	Water	293	1.6×10^9	88

(*continued overleaf*)

TABLE 19.24 (*continued*)

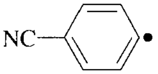
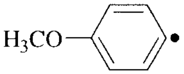
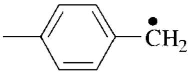
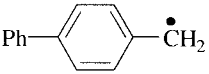
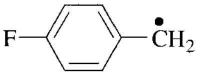
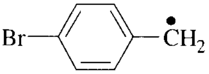
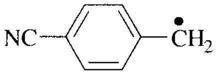
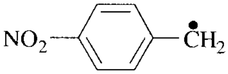
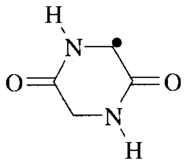
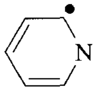
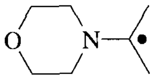
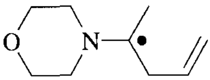
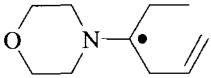
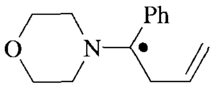
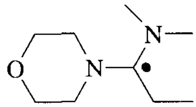
$R^{\bullet}$	Solvent	*T* (K)	*k* ($L\,mol^{-1}\,s^{-1}$)	Reference
$MeC(O)C^{\bullet}H_2$	Water	298	3.1×10^{9}	89
$MeC(O)OC^{\bullet}H_2$	Water	298	1.4×10^{10}	90
$C^{\bullet}H_2C(O)OCH_3$	Water	*RT*	1.8×10^{9}	90
$C_6H_5^{\bullet}$	Water	293	3.3×10^{9}	91
	Water	288	2.7×10^{9}	91
	Water	293	3.2×10^{9}	91
$PhC^{\bullet}H_2$	Water, pH 1.0	298	2.8×10^{9}	68
$PhC^{\bullet}H_2$	Benzene	300	2.9×10^{9}	72
$PhC^{\bullet}H_2$	Hexane	300	2.8×10^{9}	72
$PhC^{\bullet}H_2$	Cyclohexane	300	2.4×10^{9}	72
$PhC^{\bullet}H_2$	Hexadecane	300	1.0×10^{9}	72
$PhC^{\bullet}H_2$	Acetonitrile	300	3.4×10^{9}	72
$PhC^{\bullet}H_2$	2-Propanol	300	2.5×10^{9}	72
$PhC^{\bullet}H_2$	Toluene	294	2.0×10^{9}	92
$PhC^{\bullet}H_2$	Hexane	298	2.6×10^{9}	93
	Hexane	298	3.4×10^{9}	93
	Hexane	298	1.7×10^{9}	93
	Hexane	298	2.9×10^{9}	93
	Hexane	298	1.3×10^{9}	93
	Hexane	298	5.8×10^{8}	93
	4-Nitrotoluene	294	9.0×10^{8}	92
$PhC^{\bullet}HMe$	Ethylbenzene	323	8.8×10^{8}	94
$PhC^{\bullet}HOMe$	Water	293	3.2×10^{9}	95
$PhMe_2C^{\bullet}$	Cumene	323	9.0×10^{8}	72
$Ph_2C^{\bullet}H$	Diphenylmethane	294	7.5×10^{8}	92
$Ph_3C^{\bullet}$	Triphenylmethane	293	1.2×10^{9}	96
$EtCH_2C^{\bullet}HPh$	1-Phenylpropane	323	8.0×10^{7}	94
$Ph_2NC^{\bullet}HMe$	Ethyldiphenylamine	300	4.9×10^{9}	72

TABLE 19.24 (*continued*)

$R^\bullet$	Solvent	T (K)	k ($\mathrm{L\,mol^{-1}\,s^{-1}}$)	Reference
	Water	298	2.0×10^9	97
	Water/methanol	293	2.2×10^9	98
	Acetonitrile	297	6.3×10^9	85
	Acetonitrile	297	4.5×10^9	85
	Acetonitrile	297	3.9×10^9	85
	Acetonitrile	297	2.3×10^9	85
	Acetonitrile	297	4.3×10^9	85

REFERENCES

1. N. C. Billingham and A. D. Jenkins, in *Comprehensive Chemical Kinetics*, C. H. Bamford and C. F. H. Tipper (Eds.), Elsevier, Amsterdam, The Netherlands, 1976, Vol. 14A, p. 419.
2. C. H. Bamford, W. G. Barb, A. D. Jenkins, and P. F. Onyon. *The Kinetics of Vinyl Polymerisation by Radical Mechanisms*, Butterworths Scientific Publishers, London, U.K., 1958.
3. Kh. S. Bagdasaryan, *Theory of Free Radical Polymerization* (Russian), Izdatelstvo AN SSSR, Moscow, 1966.
4. S. S. Ivanchev, *Free Radical Polymerization* (Russian), Khimiya, Leningrad, Russia, 1985.
5. G. P. Gladyshev, *Vinyl Polymerization* (Russian), Izdatelstvo AN KazSSR, Alma-Ata, USSR, 1964.

6. C. Walling, *Free Radicals in Solution*, Chapman and Hall, New York, 1957.
7. K. J. Laidler and L. F. Loucks, in *Comprehensive Chemical Kinetics*, C. H. Bamford and C. F. H. Tipper (Eds.), Elsevier, Amsterdam, The Netherlands, 1972, Vol. 5, p. 1.
8. E. T. Denisov and V. V. Azatyan, *Inhibition of Chain Reactions*, Gordon and Breach, London, 1999.
9. T. Mill and D. G. Hendry, in *Comprehensive Chemical Kinetics*, C. H. Bamford and C. F. H. Tipper (Eds.), Elsevier, Amsterdam, The Netherlands, 1980, Vol. 16, p. 1.
10. M. M. Mogilevich and E. M. Pliss, *Oxidation and Oxidative Polymerization of Nonsaturated Compounds* (Russian), Khimiya, Moscow, 1990.
11. C. Chatgilialoglu and P. Renaud, in *General Aspects of the Chemistry of Radicals*, Z. B. Alfassi (Ed.), John Wiley & Sons, Inc., Chichester, U.K., 1999, p. 501.
12. B. Giese, *Radicals in Organic Synthesis: Formation of Carbon Bonds*, Pergamon Press, Oxford, U.K., 1986.
13. W. B. Motherwell and D. Crich, in *Organic Synthesis*, Academic Press, London, 1992, p. 245.
14. D. P. Curran, N. A. Porter, and B. Giese, *Stereochemistry of Radical Reactions*, VCH, Weinheim, Germany, 1995.
15. D. P. Curran, in *Comprehensive Organic Synthesis*, B. M. Ttrost and I. Fleming (Eds.), Pergamon Press, Oxford, U.K., 1991, Vol. 4, p. 715.
16. N. N. Semenov, *Some Problems of Chemical Kinetics and Reactivity*, Pergamon Press, London, 1958, Vol. 1; 1959, Vol. 2.
17. V. N. Kondratiev and E. E. Nikitin, *Gas-Phase Reactions*, Springer-Valley, Berlin, 1981.
18. P. I. Abell, in *Free Radicals*, J. K. Kochi (Ed.), John Wiley & Sons, Inc., New York, 1973, Vol. 2, p. 63.
19. K. U. Ingold, in *Free Radicals*, J. K. Kochi (Ed.), John Wiley & Sons, Inc., New York, 1973, Vol. 1, p. 37.
20. P. I. Abell, in *Comprehensive Chemical Kinetics*, C. H. Bamford and C. F. H. Tipper, Elsevier, Amsterdam, The Netherlands, 1976, Vol. 18, p. 111.
21. J. M. Tedder and J. C. Walton, *Adv. Free Radical Chem.* **6**, 155 (1980).
22. B. Giese, *Angew. Chem., Int. Ed. Engl.* **22**, 753 (1983).
23. J. M. Tedder, *Angew. Chem., Int. Ed. Engl.* **21**, 401 (1982).
24. H. Fischer and H. Paul, *Acc. Chem. Res.* **20**, 200 (1987).
25. K. Heberger, M. Walbiner, and H. Fischer, *Angew. Chem., Int. Ed. Engl.* **31**, 365 (1992).
26. M. G. Evans, J. Gergly, and E. C. Seaman, *J. Polym. Sci.* **3**, 866 (1948).
27. T. Zytowski and H. Fischer, *J. Am. Chem. Soc.* **118**, 437 (1996).
28. T. Alfrey and C. C. Price, *J. Polym. Sci.* **101**, 2 (1947).
29. C. H. Bamford and A. D. Jenkins, *Trans. Faraday Soc.* **59**, 530 (1963).
30. A. D. Jenkins, *Adv. Free Radical Chem.* **3**, 1329 (1967).
31. O. Ito and M. Matsuda, *Prog. Polym. Sci.* **17**, 827 (1992).
32. O. Ito, *Trends Phys. Chem.* **3**, 245 (1992).
33. O. Ito, *Res. Chem. Intermed.* **21**, 69 (1995).

34. O. Ito, in *General Aspects of the Chemistry of Radicals*, Z. B. Alfassi (Ed.), John Wiley & Sons, Inc., Chichester, 1999, p. 209.
35. M. W. Wong, A. Pross, and L. Radom, *Isr. J. Chem.* **33**, 415 (1993).
36. M. W. Wong, A. Pross, and L. Radom, *J. Am. Chem. Soc.* **115**, 11050 (1993).
37. M. W. Wong, A. Pross, and L. Radom, *J. Am. Chem. Soc.* **116**, 6284 (1994).
38. M. W. Wong, A. Pross, and L. Radom, *J. Am. Chem. Soc.* **116**, 11938 (1994).
39. E. T. Denisov, in *General Aspects of the Chemistry of Radicals*, Z. B. Alfassi (Ed.), John Wiley & Sons, Inc., New York, 1999, p. 79.
40. E. T. Denisov, *Russ. Chem. Rev.* **69**, 153 (2000).
41. E. T. Denisov, in *Book of Abstracts of International Conference on Chemical Kinetics*, Gaithersburg, 1997, p. 9.
42. E. T. Denisov, in *Proceedings of 5th Arab International Conference on Polymer Science and Technology*, Part 1, Luxor-Aswan, Egypt, 1999, p. 241.
43. E. T. Denisov, *Kinet. Catal.* **33**, 50 (1992).
44. T. G. Denisova and E. T. Denisov, *Petroleum Chemistry* **38**, 12 (1998).
45. E. T. Denisov and T. G. Denisova, *Chem. Phys. Reports* **17**, 2105 (1998).
46. E. T. Denisov, *Russ. Chem. Bull.* **48**, 442 (1999).
47. E. T. Denisov, *Kinet. Catal.* **40**, 756 (1999).
48. E. T. Denisov, *Kinet. Catal.* **41**, 293 (2000).
49. E. T. Denisov, *Kinet. Katal.* **42**, 30 (2001).
50. I. M. Borisov and E. T. Denisov, *Neftekhimiya* **41**, 24 (2001).
51. E. T. Denisov and T. G. Denisova, *Russ. Chem. Rev.* **71**, 417 (2002).
52. K. Heberger and H. Fischer, *Int. J. Chem. Kinet.* **25**, 249 (1993).
53. K. Heberger and H. Fischer, *Int. J. Chem. Kinet.* **25**, 913 (1993).
54. J. Q. Wu, I. Beranek, and H. Fischer, *Helv. Chim. Acta* **78**, 194 (1995).
55. H. Fisher and L. Radom, *Angew. Chem. Intern. Ed.* **40**, 1340 (2001).
56. E. T. Denisov, *Izv. AN SSSR, Ser Khim.* 1746 (1978).
57. V. A. Machtin, E. M. Pliss, and E. T. Denisov, *Izv. AN SSSR, Ser Khim.* 746 (1981).
58. J. A. Kerr and M. J. Parsonage, *Evaluated Kinetic Data on Gas Phase Addition Reactions: Reactions of Atoms and Radicals with Alkenes, Alkynes, and Aromatic Compounds*, Butterworths Scientific Publishers, London, 1972.
59. J. Warnatz, in *Rate Coefficients in the C/H/O System Combustion Chemistry*, W. C. Gardiner (Ed.), Springer-Verlag, New York, 1984, p. 197.
60. W. Tsang and R. F. Hampson, *J. Phys. Chem. Ref. Data* **15**, 1087 (1986).
61. G. V. Buxton, C. L. Greenstock, W. P. Helman, and A. B. Ross. *J. Phys. Chem. Ref. Data* **17**, 513 (1988).
62. W. G. Mallard, F. Westley, J. T. Herron, and R. F. Hampson, *NIST Chemical Kinetics Database*, Version 6.0, NIST Standard Reference Data, Gaithersburg, MD, 1994.
63. *Radical Reaction Rates in Liquids*, Landolt-Bornstein New series, Group 2 (Atomic and Molecular Physics), H. Fischer (Ed.), Springer-Verlag, Berlin, 1984–1985, Vol. 13, subvolumes (a)–(e).
64. *Radical Reaction Rates in Liquids*, Landolt-Bornstein New series, Group 2 (Atomic and Molecular Physics), H. Fischer (Ed.), Springer-Verlag, Berlin, Suppl., 1997, Vol. 13, subvolumes (a)–(e).

65. G. V. Buxton, C. L. Greenstock, W. P. Helman, and A. B. Ross. *J. Phys. Chem. Ref. Data* **17**, 513 (1988).
66. W. G. Mallard, A. B. Ross, and W. P. Helman, *NDRL/NIST Solution Kinetics Database*, Version 2, NIST Standard Reference Data, Gaithersburg, MD, 1994.
67. J. K. Thomas, *J. Phys. Chem.* **71**, 1919 (1967).
68. A. Marchaj, D. G. Kelly, A. Bakach, and J. H. Esperson, *J. Phys. Chem.* **95**, 4440 (1991).
69. A. Sauer, H. Cohen, and D. Meyerstein, *Inorg. Chem.* **27**, 4578 (1988).
70. B. Hickel, *J. Phys. Chem.* **79**, 1054 (1975).
71. N. Getoff, *Radiat. Phys. Chem.* **37**, 673 (1991).
72. B. Mailard, K. U. Ingold, and J. C. Scaiano, *J. Am. Chem. Soc.* **105**, 5095 (1983).
73. R. W. Fessenden, P. M. Carton, and H. Shimamori, *J. Phys. Chem.* **86**, 3803 (1982).
74. O. Brede, R. Herman, and R. Mehnert, *J. Chem. Soc., Faraday Trans. 1*, **83**, 2365 (1987).
75. K. Hasegawa and L. K. Patterson, *Photochem. Photobiol.* **28**, 817 (1978).
76. O. Brede and L. Wojnarovits, *Radiat. Phys. Chem.* **37**, 573 (1991).
77. X.-M. Pan, M. N. Schuchmann, and C. von Sonntag, *J. Chem. Soc., Perkin Trans. 2*, 289 (1993).
78. M. Lal, C. Schoeneich, J. Moenig, and K.-D. Asmus, *Int. J. Radiat. Biol.* **54**, 773 (1988).
79. J. Moenig, K.-D. Asmus, M. Schaeffer, T. F. Slater, and R. L. Willson, *J. Chem. Soc., Perkin Trans. 2*, 1133 (1983).
80. S. Mossery, P. Neta, and D. Meisel, *Radiat. Phys. Chem.* **36**, 683 (1990).
81. S. Das, M. N. Schuchmann, and C. von Sonntag, *Ber. Bunsenges. Phys. Chem.* **120**, 319 (1987).
82. J. Rabani, D. Klug-Roth, and A. Henglein, *J. Phys. Chem.* **78**, 2089 (1974).
83. C. F. Cullis, J. M. Francis, Y. Raef, and A. J. Swallow, *Proc. R. Soc. London, Ser. A*, 300, 443 (1967).
84. G. E. Adams and R. L. Willson, *Trans. Faraday Soc.* **65**, 2981 (1969).
85. S. Jockusch and N. J. Turro, *J. Am. Chem. Soc.* **121**, 3921 (1999).
86. D. Schulte-Frohlinde, R. Anker, and E. Bothe, in *Oxygen and oxy-radicals in chemistry and biology*, M. A. J. Rogers, and E. L. Powers (Eds.), Academic Press, New York, 1981, p. 61.
87. M. N. Schuchmann, H. Zegota, and C. von Sonntag, *Z. Naturforsch B. Anorg. Chem., Org. Chem. B*, **40**, 215 (1985).
88. M. N. Schuchmann, H. P. Schuchmann, and C. von Sonntag, *J. Phys. Chem.* **99**, 9122 (1995).
89. H. Zegota, M. N. Schuchmann, D. Schulz, and C. von Sonntag, *Z. Naturforsch. B, Chem. Sci.* 1015 (1986).
90. M. T. Nenadovic and O. I. Micic, *Radiat. Phys. Chem.* **12**, 85 (1978).
91. X. Fang, R. Mertens, and C. von Sonntag, *J. Chem. Soc., Perkin Trans. 2*, 1033 (1995).
92. P. Neta, R. E. Huie, S. Mosseri, L. V. Shastry, J. P. Mettal, P. Maruthamuthu, and S. Steenken, *J. Phys. Chem.* **93**, 4099 (1989).

93. K. Tokumara, H. Nosaka, and T. Ozaki, *Chem. Phys. Lett.* **169**, 321 (1990).
94. A. L. Aleksandrov, E. M. Pliss, and V. F. Shuvalov, *Izv. AN SSSR, Ser. Khim.* 2446 (1979).
95. J. L. Faria and S. Steenken, *J. Chem. Soc., Perkin Trans. 2*, 1153 (1997).
96. E. Zador, J. Warman, and A. Hummel, *J. Chem. Soc., Faraday Trans. 1*, **75**, 914 (1979).
97. O. Mieden, M. N. Schuchmann, and C. von Sonntag, *J. Phys. Chem.* **97**, 3783 (1993).
98. Z. B. Alfassi, G. I. Khaikin, and P. Neta, *J. Phys. Chem.* **99**, 4544 (1995).

Handbook of Free Radical Initiators. E.T. Denisov, T.G. Denisova, T.S. Pokidova
Copyright © 2003 John Wiley & Sons, Inc.
ISBN: 0-471-20753-5

20

RECOMBINATION AND DISPROPORTIONATION OF FREE RADICALS

20.1 ALKYL RADICALS

The reaction of two alkyl radicals leads either to one molecule by combination, for example,

$$C^{\bullet}H_3 + C^{\bullet}H_3 \rightarrow C_2H_6$$

or to two molecules by the transfer of a hydrogen atom from one radical to the second one, for example,[1-4]

$$C^{\bullet}H_3 + CH_3C^{\bullet}H_2 \rightarrow CH_4 + CH_2{=}CH_2$$

The latter process is called disproportionation (the back reaction is called retrodisproportionation, see Chapter 10).

Disproportionation of organic radicals occurs only if at least one radical has a hydrogen atom in the position-β to the radical center.

$$H^{\bullet} + CH_3CH_2C^{\bullet}H_2 \rightarrow H_2 + CH_3CH{=}CH_2$$

$$HO^{\bullet} + HOC^{\bullet}H_2 \rightarrow H_2O + H_2C{=}O$$

$$R^{\bullet} + H_2NC^{\bullet}H_2 \rightarrow RH + CH_2{=}NH$$

Radicals containing fluorine atoms can disproportionate with abstraction of the hydrogen atom from the carbon atom with the free valence to form of carbene.[3,4]

$$C^{\bullet}HF_2 + C^{\bullet}HF_2 \rightarrow CH_2F_2 + CF_2$$

Recombination and disproportionation of alkyl radicals play an important role in many chain reactions, for example, pyrolysis, photolysis and radiolysis of organic compounds, free radical polymerization, chlorination of hydrocarbons, various organic free radical synthesis, polymer degradation, and so on.

Reactions of free radical recombination are very exothermic. Entropies of these reactions are negative due to the association of two species with free valence. For example, the reaction

$$C_2H_5^{\bullet} + C_2H_5^{\bullet} \rightarrow C_4H_{10}$$

occurs (in the gas phase) with $\Delta H^\circ = -366.5$ kJ mol^{-1} and $\Delta S^\circ = -192.4$ J mol^{-1} s^{-1}.

For the disproportionation of two ethyl radicals in the gas phase, ΔH°=-270 kJ mol^{-1} and $\Delta S^\circ = -36.3$ J mol^{-1} s^{-1} (see Table 20.1).

Recombination of atoms and radicals leads to the formation of energized molecules. Such an energized molecule (RR*) should be stabilized in the collision with another molecule. The mechanism of free radical recombination in the

TABLE 20.1 Enthalpies (ΔH) and Entropies (ΔS) for Recombination and Disproportionation ($R^{1\bullet} + R^{2\bullet} \rightarrow R^1H$ + Olefin) of Alkyl Radicals[a]

Radicals		Recombination		Disproportionation	
$R^{1\bullet}$	$R^{2\bullet}$	$-\Delta H$ (kJ mol^{-1})	$-\Delta S$ (J mol^{-1} K)	$-\Delta H$ (kJ mol^{-1})	$-\Delta S$ (J mol^{-1} K)
$C^{\bullet}H_3$	$MeC^{\bullet}H_2$	372.5	166.8	288.2	31.1
$C^{\bullet}H_3$	$EtC^{\bullet}H_2$	375.2	170.7	301.4	27.4
$C^{\bullet}H_3$	$Me_2C^{\bullet}H$	374.5	178.6	291.4	19.9
$C^{\bullet}H_3$	$Me_2CHC^{\bullet}H_2$	373.5	165.1	308.1	28.8
$C^{\bullet}H_3$	$Me_3C^{\bullet}$	362.5	189.4	328.2	15.9
$MeC^{\bullet}H_2$	$MeC^{\bullet}H_2$	366.5	192.4	269.8	36.3
$MeC^{\bullet}H_2$	$EtC^{\bullet}H_2$	367.5	180.3	283.0	32.6
$MeC^{\bullet}H_2$	$Me_2C^{\bullet}H$	364.5	178.2	273.0	25.1
$EtC^{\bullet}H_2$	$MeC^{\bullet}H_2$	367.5	180.3	271.3	39.8
$EtC^{\bullet}H_2$	$EtC^{\bullet}H_2$	367.5	184.8	303.5	36.1
$EtC^{\bullet}H_2$	$Me_2C^{\bullet}H$	364.5	185.2	393.5	28.6
$Me_2C^{\bullet}H$	$MeC^{\bullet}H_2$	364.5	178.2	261.3	32.3
$Me_2C^{\bullet}H$	$EtC^{\bullet}H_2$	364.5	185.2	314.7	28.6
$Me_2C^{\bullet}H$	$Me_2C^{\bullet}H$	363.5	192.4	264.5	21.1
$EtCH_2C^{\bullet}H_2$	$MeC^{\bullet}H_2$	367.5	181.3	303.1	40.2
$EtCH_2C^{\bullet}H_2$	$EtCH_2C^{\bullet}H_2$	367.5	187.3	282.4	34.4
$Me_2CHC^{\bullet}H_2$	$MeC^{\bullet}H_2$	367.5	176.8	270.9	44.1
$Me_2CHC^{\bullet}H_2$	$Me_2CHC^{\bullet}H_2$	367.5	190.2	290.8	41.8
$Me_3C^{\bullet}$	$MeC^{\bullet}H_2$	354.5	178.6	291.0	30.3
$Me_3C^{\bullet}$	$Me_3C^{\bullet}$	323.5	214.0	331.0	15.1

[a] See Ref. 5.

gas phase is referred as the energy-transfer mechanism. It includes the stages[1,6]

$$R^{\bullet} + R^{\bullet} \rightarrow RR^{*}$$

$$RR^{*} \rightarrow R^{\bullet} + R^{\bullet}$$

$$RR^{*} + M \rightarrow RR + M$$

The detailed kinetic schemes and equations of free radical recombination in the gas phase are published.[1,2,4,6]

The study of recombination (k_c) and disproportionation (k_{dis}) of ethyl radicals proved the dependence of the ratio k_{dis}/k_c on the solvent (see Table 20.2).[4,7,8]

Stefani found that $\log(k_{dis}/k_c)$ is a linear function of the solubility δ_s, which is equal to the square root of the cohesive energy density of the solvents (D_{ce}) :[7]

$$\log(k_{dis}k_c) = a \times \delta_s + b \qquad (20.1)$$

TABLE 20.2 The Values for the Rate Constant Ratio k_{dis}/k_c in Different Solvents in Comparison with ΔH_{vap} (298 k) and the Solubility Parameter δ_s[a]

Solvent	k_{dis}/k_c	ΔH_{vap} (298 K) (kJ mol^{-1})	δ_s (MPa)$^{1/2}$
	Ethyl Radical		
Gas phase	0.14		
Isooctane	0.145	35.1	15.6
Ethylbenzene	0.156	42.2	18.0
m-Xylene	0.165	42.6	18.0
Toluene	0.167	37.3	18.2
2-Butanol	0.168	49.7	22.1
2-Propanol	0.178	45.4	23.5
1-Propanol	0.181	47.4	24.3
Aniline	0.195	55.8	21.1
Acetonitrile	0.204	32.9	24.3
Ethyleneglycol	0.241		29.9
Water	0.350	44.0	47.9
	1,1-Dimethylethyl Radical		
Gas phase	2.30		
Octane	5.4	41.5	15.6
Decane	5.7	51.4	15.8
Dodecane	5.9	61.5	16.2
Tetradecane	6.4	71.3	16.4
Hexadecane	6.9	81.4	16.6
Acetonitrile	7.3	32.9	24.3

[a] See Eq. (20.1) and Refs. 4 and 7–9.

The latter depends on the energy of evaporation (U_{ev})

$$D_{ce} = \frac{U_{ev}}{V} = \frac{\Delta H_{ev} - RT}{M/\rho} \tag{20.2}$$

where V is the molecular volume, ΔH_{ev} is the enthalpy of solvent evaporation, M and ρ are the molecular weight and density of the solvent, respectively. The ratio values of k_{dis}/k_c for ethyl and 1,1-dimethylethyl radicals and the δ_s of solvents are listed in Table 20.2. This dependence of the k_{dis}/k_c ratio on the cohesive energy density of solvents proves that the transition state of radical recombination has a loose structure and that of the disproportionation reaction has a compact structure. The greater the pressure of the cage molecules on the pair of reacting radicals, the faster the reaction of disproportionation. Stefani[7] saw that the k_{dis}/k_c ratio increased with decreasing temperature. This phenomena can be explained because of an increase in the internal pressure of liquid with decreasing temperature.

Alkyl radicals react very rapidly in solution. The rate of their disappearance is limited by the frequency of their encounters. This situation is known as microscopic diffusion control or encounter control, when the measured rate is almost exactly equal to the rate of diffusion.[6] The rate of diffusionally controlled reaction of free radical disappearance is the following (2 is the stoichiometric coefficient of reaction):[6]

$$v = 2k_D[R^\bullet]^2 = 32\pi D_R r_R [R^\bullet]^2 \tag{20.3}$$

where D_R and r_R are the diffusion coefficient and radius of the radical, respectively. According to Stokes's law

$$D_R = kT/6\pi r_R \eta \tag{20.4}$$

and the rate constant of the diffusion controlled reaction is inversely proportional to viscosity.

$$k_D = 16kT/3\eta = \text{const} \times T/\eta \tag{20.5}$$

Schuh and Fischer[9] studied the kinetics of the 1,1-dimethylethyl radical disproportionation in different solvents and proved the validity of Eq. (20.5) for this reaction (see Table 20.3). The values for the rate constants of alkyl radical combination in solution are in Table 20.3 and these of the hydroxyl, alkoxyl, and $R_3E^\bullet$ radicals (E = Si, Ge, and Sn) are in Table 20.4.

20.2 MACRORADICALS

Chain termination in the free radical polymerization of monomers $CH_2{=}CHX$ occurs also by reactions of recombination (k_c) and disproportionation (k_{dis}) of

TABLE 20.3 Rate Constants ($2k_t$) of Alkyl Radical Combination in Solution ($k_t = k_c + k_{dis}$)

$R^{\bullet}$	Solvent	T (K)	E (kJ mol^{-1})	log (2A), A (L mol^{-1} s^{-1})	$2k_t$(298 K) (L mol^{-1} s^{-1})	Reference
$C^{\bullet}H_3$	Cyclohexane	298			8.9×10^9	10
$C^{\bullet}H_3$	Cyclohexane	218			1.4×10^9	11
$C^{\bullet}H_3$	*tert*-Butyl peroxide	255			1.1×10^{10}	12
$C^{\bullet}H_3$	Water, pH 5.5	298			2.48×10^9	13
$C^{\bullet}H_3$	Water	279–340	16.0	12.30	3.13×10^9	14
$C^{\bullet}H_3$	1,1,2-Trichloro trifluoroethane	297			1.6×10^{10}	15
$MeC^{\bullet}H_2$	Ethane	98–196	3.5	10.11	3.14×10^9	16
$MeC^{\bullet}H_2$	Water, pH 5.5	298			1.92×10^9	13
$MeC^{\bullet}H_2$	Water, pH 4.4	278–341	16.0	12.19	2.43×10^9	14
$MeC^{\bullet}H_2$	Water, pH 5.5	298			1.9×10^9	13
$EtC^{\bullet}H_2$	Benzene	298			4.2×10^8	17
$EtC^{\bullet}H_2$	Cyclohexane	298			3.4×10^9	17
$EtC^{\bullet}H_2$	Water	298			1.26×10^9	18
$BuC^{\bullet}H_2$	Benzene	298			2.0×10^9	17
$BuC^{\bullet}H_2$	Cyclohexane	298			4.2×10^8	19
$BuC^{\bullet}H_2$	Toluene	192–292	10.5	12.30	2.88×10^{10}	20
$Me_3CC^{\bullet}H_2$	*tert*-Butyl peroxide	297			4.0×10^9	12
$BuCH_2C^{\bullet}H_2$	Cyclohexane	298			2.2×10^9	10
$BuCH_2C^{\bullet}H_2$	Cyclopropane	190–232	8.8	11.6	1.14×10^{10}	21
$BuCH_2C^{\bullet}H_2$	Hexane	280–327	7.1	11.26	1.04×10^{10}	22
$BuCH_2C^{\bullet}H_2$	Hexane	298			3.83×10^9	23
$BuCH_2C^{\bullet}H_2$	Hexane	298			6.2×10^9	24
$BuCH_2C^{\bullet}H_2$	Water	298			2.4×10^9	24

(continued overleaf)

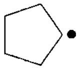
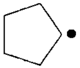
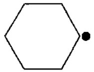
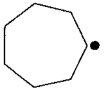
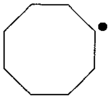
TABLE 20.3 (*continued*)

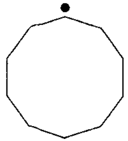
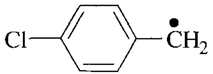
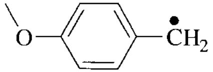
$R^\bullet$	Solvent	T (K)	E (kJ mol^{-1})	log (2A), A (L mol^{-1} s^{-1})	$2k_t$(298 K) (L mol^{-1} s^{-1})	Reference
$Me(CH_2)_5C^\bullet H_2$	Heptane	277–333	8.1	11.27	7.08×10^9	22
$Me(CH_2)_5C^\bullet H_2$	Heptane	298			2.92×10^9	23
$Me(CH_2)_6C^\bullet H_2$	Octane	279–349	6.8	10.94	5.60×10^9	22
$Me(CH_2)_6C^\bullet H_2$	Octane	298			2.30×10^9	23
$Me(CH_2)_7C^\bullet H_2$	Nonane	284–322	9.4	11.34	4.92×10^9	22
$Me(CH_2)_7C^\bullet H_2$	Nonane	298			2.45×10^9	23
$Me(CH_2)_8C^\bullet H_2$	Decane	283–333	10.9	11.62	5.12×10^9	22
$Me(CH_2)_8C^\bullet H_2$	Decane	298			1.89×10^9	23
$Me(CH_2)_9C^\bullet H_2$	Undecane	298			1.61×10^9	23
$Me(CH_2)_{10}C^\bullet H_2$	Dodecane	278–347	13.5	11.80	2.71×10^9	25
$Me(CH_2)_{10}C^\bullet H_2$	Dodecane	298			1.60×10^9	23
$Me(CH_2)_{10}C^\bullet H_2$	Cyclohexane	298			2.4×10^9	18
$Me(CH_2)_{11}C^\bullet H_2$	Tridecane	291–347	11.3	11.44	2.88×10^9	25
$Me(CH_2)_{11}C^\bullet H_2$	Tridecane	298			1.2×10^9	23
$Me(CH_2)_{12}C^\bullet H_2$	Tetradecane	298			1.14×10^9	23
$Me(CH_2)_{13}C^\bullet H_2$	Pentadecane	298			1.18×10^9	23
$Me(CH_2)_{14}C^\bullet H_2$	Hexadecane	293–358	13.0	11.74	2.89×10^9	25
$Me(CH_2)_{14}C^\bullet H_2$	Hexadecane	298			7.7×10^8	23
$Me(CH_2)_{15}C^\bullet H_2$	Heptadecane	298			6.3×10^8	23
$Me(CH_2)_{16}C^\bullet H_2$	Cyclohexane	298			6.2×10^9	19
$Me_2C^\bullet H$	Heptane	313–353	5.6	10.87	7.73×10^9	26
$Me_2C^\bullet H$	Hexadecane	312			3.5×10^9	27
$Me_2C^\bullet H$	Hexadecane	333			4.0×10^9	26
$Me_2C^\bullet H$	3-Methyl-3-pentanol	333			5.2×10^9	26
$Me_2C^\bullet H$	Tetraethyl siloxane	333			8.0×10^9	26

$Me_3CC^\bullet HCHMe_2$	Isooctane	298			3.0×10^9	28
$Me_3C^\bullet$	Acetonitrile	266–349	8.3	11.30	7.00×10^9	29
$Me_3C^\bullet$	Benzene	298			7.3×10^9	30
$Me_3C^\bullet$	Benzene	292			5.7×10^9	31
$Me_3C^\bullet$	Benzene	281–351	10.2	11.57	6.05×10^9	29
$Me_3C^\bullet$	Benzene	298			8.0×10^8	26
$Me_3C^\bullet$	Benzene	298			7.2×10^8	17
$Me_3C^\bullet$	Cyclohexane	298			2.5×10^9	32
$Me_3C^\bullet$	Cyclohexane	298			2.7×10^9	10
$Me_3C^\bullet$	Cyclohexane	283			5.0×10^9	33
$Me_3C^\bullet$	Cyclohexane	298			1.2×10^9	17
$Me_3C^\bullet$	Cyclohexane	298			4.0×10^9	24
$Me_3C^\bullet$	Cyclohexane	298			1.2×10^9	34
$Me_3C^\bullet$	Cyclohexane	295			2.4×10^9	35
$Me_3C^\bullet$	Cyclohexane	298			3.2×10^9	28
$Me_3C^\bullet$	Cyclopentane	223			8.0×10^8	33
$Me_3C^\bullet$	Decane	291–351	10.7	11.65	5.95×10^9	9
$Me_3C^\bullet$	1,1-Dimethyl ethanol/pinacol	267–378	6.2	11.58	3.11×10^{10}	9
$Me_3C^\bullet$	1,1-Dimethyl ethanol	287–356	3.3	11.16	3.82×10^{10}	9
$Me_3C^\bullet$	Dodecane	294–366	11.3	11.62	4.36×10^9	9
$Me_3C^\bullet$	Heptane	291–362	9.6	11.63	8.86×10^9	9
$Me_3C^\bullet$	Hexadecane	296–363	14.4	12.03	3.21×10^9	9
$Me_3C^\bullet$	Isobutane	170–330	4.3	10.78	1.1×10^9	36
$Me_3C^\bullet$	3-Methyl-3-pentanol	248–293	3.6	11.32	4.89×10^{10}	9
$Me_3C^\bullet$	2-Methylpropane	250			1.11×10^9	36
$Me_3C^\bullet$	2-Methylpropane	188–262	4.2	10.2	2.91×10^9	12
$Me_3C^\bullet$	Octane	294–364	9.9	11.58	6.99×10^9	9

(*continued overleaf*)

TABLE 20.3 (*continued*)

$R^\bullet$	Solvent	T (K)	E (kJ mol^{-1})	log (2A), A (L mol^{-1} s^{-1})	$2k_t$(298 K) (L mol^{-1} s^{-1})	Reference
$Me_3C^\bullet$	Pentane	298			5.4×10^9	10
$Me_3C^\bullet$	*tert*-Butyl peroxide	297			8.1×10^9	12
$Me_3C^\bullet$	Tetradecane	294–365	13.5	11.93	3.66×10^9	9
$Me_3C^\bullet$	Tridecane	298			1.8×10^9	10
$Me_3C^\bullet$	Toluene	218			9.8×10^9	36
$Me_3C^\bullet$	Water, pH 7	295			2.0×10^9	37
$Me_3C^\bullet$	Water	298			4.0×10^9	38
$Me_3C^\bullet$	Water	298			2.8×10^9	24
$Me_3C^\bullet$	Water, pH 10.5	298			2.4×10^9	39
	Cyclopentane	283–333	13.2	11.66	7.22×10^9	22
	Cyclopentane	298			2.52×10^9	23
	Cyclohexane	298			2.02×10^9	23
	Cycloheptane	298			1.48×10^9	23
	Cyclooctane	298			8.6×10^8	23

	Cyclodecane	298			5.0×10^8	23
$CH_2{=}CHC^{\bullet}H_2$	*tert*-Butyl peroxide/chlorobenzene	235–391	11.5	11.18	1.46×10^9	40
$PhC^{\bullet}H_2$	Benzene	298			8.2×10^9	41
$PhC^{\bullet}H_2$	Cyclohexane	298			4.0×10^9	42
$PhC^{\bullet}H_2$	Cyclohexane	298			4.0×10^9	41
$PhC^{\bullet}H_2$	Cyclohexane	283–332	8.1	10.70	1.91×10^9	26
$PhC^{\bullet}H_2$	Toluene	222–331	12.5	11.90	5.12×10^9	26
$PhC^{\bullet}H_2$	*tert*-Butylbenzene	269–318	13.7	11.90	3.15×10^9	43
$PhC^{\bullet}H_2$	Water	298			3.1×10^9	44
$PhC^{\bullet}H_2$	Water	299			8.2×10^9	45
$PhC^{\bullet}H_2$	Methanol	298			1.4×10^9	45
	*tert*-Butylbenzene	297–337	11.3	11.6	4.16×10^9	43
	*tert*-Butylbenzene	297–331	9.8	11.0	1.92×10^9	43
$PhC^{\bullet}HMe$	Water	298			4.7×10^9	46
$PhC^{\bullet}HMe$	*tert*-Butylbenzene	261–330	12.2	11.4	1.83×10^9	43
$PhC^{\bullet}HMe$	Isooctane	268–323	8.7	11.2	9.68×10^9	43

(continued overleaf)

TABLE 20.3 (*continued*)

$R^\bullet$	Solvent	*T* (K)	*E* (kJ mol^{-1})	log (2*A*), *A* (L mol^{-1} s^{-1})	$2k_t$(298 K) (L mol^{-1} s^{-1})	Reference
$PhC^\bullet(Me)_2$	*tert*-Butylbenzene	240–325	13.4	11.4	1.13×10^9	43
$PhC^\bullet(Me)_2$	Cyclohexane	298			3.6×10^8	47
$PhCH_2C^\bullet H_2$	Water, pH 7	298			4.5×10^9	48
$Ph_2C^\bullet H$	Benzene	294			1.4×10^9	49
$Ph_2C^\bullet H$	Hexane	296			5.1×10^9	50
$Ph_2C^\bullet H$	Acetonitrile	296			3.6×10^9	50
$C^\bullet H_2OH$	Methanol	216–288	11.0	11.70	5.91×10^9	51
$C^\bullet H_2OH$	Water	298			1.7×10^9	52
$C^\bullet H_2NH_2$	Water, pH 12.3	298			4.0×10^9	53
$C^\bullet H_2CN$	Chlorobenzene	223–283	11.3	11.20	1.66×10^9	54
$C^\bullet H_2COOH$	Acetic acid	298			1.8×10^9	55
$Me_2C^\bullet C(O)OMe$	Acetonitrile	258–338	7.9	11.1	5.19×10^9	43
$[HO(O)C]_2C^\bullet H$	Water, pH 10	296			4.0×10^8	56
$C^\bullet Cl_3$	Benzene	298			1.6×10^8	57
$C^\bullet Cl_3$	Cyclohexene	303			1.0×10^8	57
$C^\bullet Cl_3$	Cyclohexane	298			1.2×10^9	11

$C^{\bullet}Cl_3$	Water	298			7.4×10^8	58
$C^{\bullet}Cl_3$	Methanol	233			1.8×10^9	59
$Me_2C^{\bullet}OH$	Benzene	283–349	13.0	11.79	3.25×10^9	26
$Me_2C^{\bullet}OH$	Heptane	239–338	9.8	11.60	7.62×10^9	26
$Me_2C^{\bullet}OH$	2-Propanol	203–309	19.7	12.72	1.85×10^9	26
$Me_2C^{\bullet}OH$	2-Propanol	283–349	12.8	11.29	1.11×10^9	26
$Me_2C^{\bullet}OH$	Tetradecane	239–305	11.3	10.31	2.13×10^9	26
$Me_2C^{\bullet}OH$	Water, pH 6	298			1.4×10^9	60
$Me_2C^{\bullet}OH$	Water, pH 9.4	289			1.9×10^9	61
$Me_2C^{\bullet}OH$	Isopropyl alcohol	223–275	13.3	11.4	1.17×10^9	62
$Me_2C^{\bullet}NH_2$	Water, pH 12.2	298			1.6×10^9	53
$Me_2C^{\bullet}CN$	Benzene	298			4.4×10^9	63
$Me_2C^{\bullet}CN$	Chlorobenzene/*tert*-butyl peroxide	227–346	15.7	11.80	1.12×10^9	54

TABLE 20.4 Rate Constants ($2k_t$) for the Combination of HO$^\bullet$, RO$^\bullet$, PhSO$^\bullet$R$_3$Si$^\bullet$, R$_3$Ge$^\bullet$, R$_3$Sn$^\bullet$, and PhS$^\bullet$ Radicals in Solution ($k_t = k_c + k_{dis}$)

R$^\bullet$	Solvent	T (K)	E (kJ mol^{-1})	log (2A), A (L mol^{-1} s^{-1})	$2k_t$(298 K) (L mol^{-1} s^{-1})	Reference
HO$^\bullet$	Water, pH 7	293–353	7.7	11.21	7.25×10^9	64
HO$^\bullet$	Water	293–453	3.7	10.58	8.54×10^9	65
HO$^\bullet$	Water	298			1.10×10^{10}	66
HO$^\bullet$	Water, pH 7	298			1.04×10^{10}	67
HO$^\bullet$	Water, pH 7	298			1.24×10^{10}	68
HO$^\bullet$	Water, pH 3.7	298			1.04×10^{10}	69
O$^{-\bullet}$	Water, pH 13	298			1.68×10^{10}	70
O$^{-\bullet}$	Water, pH > 12	298			1.8×10^9	68
Me$_3$CO$^\bullet$	*tert*-Butyl peroxide	298			1.3×10^9	71
Me$_3$CO$^\bullet$	Carbon tetrachloride	313			2.8×10^9	71
Me$_3$CO$^\bullet$	*tert*-Butyl peroxide	295			2.6×10^9	72
PhSO$^\bullet$	Ethylether	298			1.3×10^{10}	73
PhSO$^\bullet$	Hexane	298			1.0×10^{10}	73
PhSO$^\bullet$	Acetonitrile	298			6.4×10^9	73
PhSO$^\bullet$	Cyclohexane	298			6.2×10^9	73
PhSO$^\bullet$	Water	298			4.0×10^9	73
PhSO$^\bullet$	Ethanol	298			3.5×10^9	73
PhSO$^\bullet$	Propanol	298			2.5×10^9	73
PhSO$^\bullet$	Isopropyl alcohol	298			3.1×10^9	73
PhSO$^\bullet$	2-Methyl-2-propanol	298			1.7×10^9	73
Me$_3$Si$^\bullet$	*tert*-Butyl peroxide	298			5.5×10^9	74
Me$_3$Ge$^\bullet$	*tert*-Butyl peroxide	233			3.6×10^9	74
Me$_3$Sn$^\bullet$	*tert*-Butyl peroxide	233			2.8×10^9	74
Me$_3$Sn$^\bullet$	Cyclohexane	298			3.1×10^9	10
Bu$_3$Sn$^\bullet$	Cyclohexane	298			1.4×10^9	10
Ph$_3$Sn$^\bullet$	Cyclohexane	298			2.8×10^9	10
PhS$^\bullet$	1,1-Dimethylethanol	298			1.8×10^9	73

macroradicals.[75,76]

$$\mathrm{RCH_2C^\bullet HX + RCH_2C^\bullet HX \rightarrow RCH_2CHXCHXCH_2R}$$

$$\mathrm{RCH_2C^\bullet HX + RCH_2C^\bullet HX \rightarrow RCH{=}CHX + RCH_2CH_2X}$$

Since one macromolecule is formed in the first reaction and two in the second, the mode of termination controls the molecular weight of the polymer.[75–80] For recombination termination, the number-average degree of polymerization P_n is twice as large as its kinetic chain length in the absence of chain-transfer reactions. For disproportionation termination the number-average degree of polymerization of the polymer P_n is equal to its kinetic chain length. Molecular weight distributions are also affected. The ratio of the weight-average P_w to number-average P_n degree of polymerization is equal to 1.5 for recombination and 2.0 for disproportionation.[75]

Reaction of Termination	P_n	P_w/P_n
Recombination	$\dfrac{(k_p[\text{Monomer}])^2}{k_c \times v_p}$	1.5
Disproportionation	$\dfrac{(k_p[\text{Monomer}])^2}{2k_{\text{dis}} \times v_p}$	2.0

Here the rate of polymerization is v_p and the rate constant of chain propagation is k_p.

Macroradicals are reactive species and the rate constants of chain termination $2k_t = 2(k_c + k_{\text{dis}})$ are high (10^6–10^7 L mol^{-1} s^{-1}).[26,76] However, they are not as high as low-molecular-weight radicals (see Table 20.4). This difference is the result of the complex diffusive processes of two macroradicals through a viscous media.

It was observed that the rate of polymerization increased rapidly after some critical conversion. This increase in the rate of polymerization is a consequence of a decrease in the rate constant for chain termination, and hence, an increase in the concentration of macroradicals. The latter is the result of the large increase in viscosity restriction for the diffusion of the macroradicals and their segments. The autoacceleration is a feature of the polymerization of many monomers and is known as the "gel-effect".[75–80] It was proved that k_t is reduced in the period of such acceleration of methyl methacrylate polymerization and the rate constant k_p remains unchanged.

The diffusion control of chain termination in free radical polymerization is not restricted to high conversions but exists in many monomers at zero conversion. The activation energies for termination are the same as for diffusion, which was proven in the studies of polymerization in solvents of different viscosities. The theoretical analysis of physical models for the reaction of two macroradicals showed that the segmental rearrangement diffusion of the reactive sites brought them into close proximity and is the controlling factor for the termination act. The values of $2k_t$ for several monomers are listed in Table 20.5.

20.3 PEROXYL RADICALS

Hydroperoxyl radicals are formed by reactions of free radicals with hydrogen peroxides, for example,

$$HO^{\bullet} + H_2O_2 \rightarrow H_2O + HO_2^{\bullet}$$

and in oxidation of alcohols and some olefins.[81] Chain termination occurs via the disproportionation of two hydroperoxyl radicals.

$$HO_2^{\bullet} + HO_2^{\bullet} \rightarrow H_2O_2 + O_2$$

TABLE 20.5 Rate Constants for the Chain Termination ($2k_t$) of Monomer Polymerization[a]

Monomer	Solvent	T (K)	E (kJ mol^{-1})	log(2A)A (L mol^{-1} s^{-1})	$2k_t$(298 K) (L mol^{-1} s^{-1})	Reference
CH_2=CHPh	Styrene	273–333	5.8	8.99	9.40×10^7	75
CH_2=CHC(O)OMe	Methyl acrylate	288–333	22.2	10.45	3.62×10^6	75
CH_2=CMeC(O)OMe	Methyl methacrylate	278–333	7.9	8.77	2.43×10^7	75
CH_2=CEtC(O)OMe	Methyl ethacrylate	333			4.2×10^7	77
CH_2=CMeC(O)Et	Benzene	298			7.35×10^6	76
CH_2=CMeC(O)OCHMe$_2$	Benzene	298			4.52×10^6	76
CH_2=CMeC(O)OBu	Benzene	298			1.02×10^7	75
CH_2=CMeC(O)OPr	Benzene	298			4.51×10^6	76
CH_2=CMeC(O)OPh	Benzene	298			1.19×10^7	76
CH_2=CMeC(O)CH_2Ph	Benzene	298			4.19×10^7	76
CH_2=CHOC(O)Me	Vinyl acetate	273–338	23.3	11.81	5.26×10^7	75
CH_2=CCH(O)OPh	Phenyl acrylate	333			6.40×10^7	78
CH_2=CHC(O)NH_2	Acrylamide	298			1.45×10^7	75
CH_2=CHCl	Tetrahydrofuran	298			1.06×10^9	76
$Me_3C[CH_2CMe(C(O)OMe)]n$ $CH_2C_6H_4CH=CH_2$	Benzene	253			1.08×10^2	79

[a] See Refs. 65, 66, 77–79.

Hydrogen bonds for the hydroperoxyl radical with polar molecules of solvent, for example, water, decrease the rate constant of disproportionation (see Table 20.6). Deuteroperoxyl radicals disproportionate more slowly than hydroperoxyl radicals (see Table 20.6).

Chain termination during oxidation of hydrocarbons is usually a result of the interaction of two peroxyl radicals by the multistep mechanism. The first step involves the reversible formation of unstable tetroxide:[82,83]

$$2RO_2^{\bullet} \Leftrightarrow ROOOOR$$

The equilibrium for this reaction is characterized by the following thermodynamic parameters:[82]

$RO_2^{\bullet}$	$Me_3CO_2^{\bullet}$	$Et_2MeCO_2^{\bullet}$	$PhMe_2CO_2^{\bullet}$
K (mol L^{-1}) (303 K)	0.083	0.12	0.45
ΔH (kJ mol^{-1})	−37	−31	−39
ΔS (J mol^{-1} K^{-1})	−141	−121	−134

When R is a tertiary alkyl radical, tetraoxide decomposes with the formation of $RO^{\bullet}$ and O_2:[82–84]

$$ROOOOR \rightarrow [RO^{\bullet} + O_2 + RO^{\bullet}]$$

$$[RO^{\bullet} + O_2 + RO^{\bullet}] \rightarrow ROOR + O_2$$

$$[RO^{\bullet} + O_2 + RO^{\bullet}] \rightarrow 2RO^{\bullet} + O_2$$

Chain termination is a result of only $RO^{\bullet}$ recombination in the solvent cage. In the case of primary and secondary peroxyl radicals, tetroxide decomposes by the coordinated Russel mechanism into alcohol, ketone, and dioxygen.[85]

$$R_1R_2HCOOOOCHR_1R_2 \rightarrow R_1R_2C{=}O + O_2 + HOCHR_1R_2$$

This reaction is very exothermic (e.g., $\Delta_r H = -405$ kJ mol^{-1} for cyclohexyltetraoxide). Rate constants for the primary and secondary peroxyl radical disproportionation $2k_t = 10^6$–10^8 L mol^{-1} s^{-1} are sufficiently lower, namely, 10^3–10^5 for tertiary $RO_2^{\bullet}$.[85]

The high exothermicity of peroxyl radicals disproportionation cause chemiluminescence, whose source is a tripley excited carbonyl compound.[86] The mechanism for this phenomenon was suggested to include tetroxide decomposition via an intermediate short-lived biradical.

$$HROOOORH \rightarrow [HRO^{\bullet} + {}^{\bullet}OOORH]$$

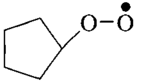
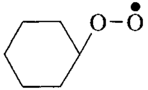
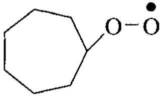
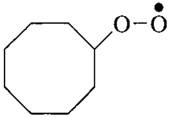
$$[HRO^{\bullet} + {}^{\bullet}OOORH] \rightarrow HROH + {}^{\bullet}OOOR^{\bullet}$$

$${}^{\bullet}ROOO^{\bullet} \rightarrow R{=}O^{*} + O_2$$

$$R{=}O^{*} \rightarrow R{=}O + h\nu$$

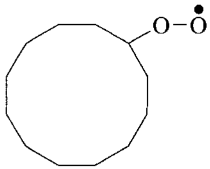
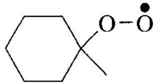
TABLE 20.6 Rate Constants for Peroxyl Radical Disproportionation

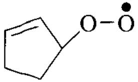
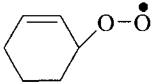
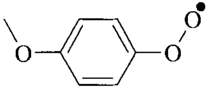
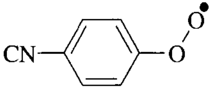
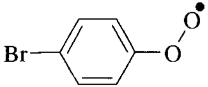
$RO_2^\bullet$	Solvent	T (K)	E ($kJ\,mol^{-1}$)	$\log(2A)A$ ($L\,mol^{-1}\,s^{-1}$)	$2k_t$(298 K) ($L\,mol^{-1}\,s^{-1}$)	Reference
$HO_2^\bullet$	Acetonitrile	303			8.6×10^6	91
$HO_2^\bullet$	Carbon tetrachloride	303			1.1×10^{10}	91
$HO_2^\bullet$	Chlorobenzene	303			1.26×10^{10}	91
$HO_2^\bullet$	Decane	303			1.34×10^9	91
$HO_2^\bullet$	Water	274–316	25.0	11.06	4.74×10^6	92
$HO_2^\bullet$	Water, pH 2	298			1.35×10^6	93
$HO_2^\bullet$	Water	298	24.2	10.09	7.05×10^5	94
$HO_2^\bullet$	Chlorobenzene	298	24.2	10.09	1.0×10^8	95
$DO_2^\bullet$	Water	298	30.5	10.35	1.01×10^5	94
$Me_3O_2^\bullet$	Carbon tetrachloride	295			7.7×10^8	96
$Me_3O_2^\bullet$	Water	295			7.9×10^8	96
$Me_2CHO_2^\bullet$	Cyclopentane	210–300	10.3	7.89	1.21×10^6	97
$Me_2CHO_2^\bullet$	1,1-Dichloro-difluoroethylene	210–300	8.1	7.33	8.13×10^5	97
$Me_2CHO_2^\bullet$	Pentane	210–300	9.2	7.68	1.17×10^6	97
$Me_2CHO_2^\bullet$	Cyclohexane	293–396	20.0	9.70	1.56×10^6	98
$Me_2CHO_2^\bullet$	Decane	293–396	20.0	9.70	1.56×10^6	98
$Me_2CHO_2^\bullet$	Dodecane	293–396	20.0	9.70	1.56×10^6	98
$Me(CH_2)_2CH_2O_2^\bullet$	Tetralin	303			4.0×10^7	99
$Me(CH_2)_3CH_2O_2^\bullet$	Pentane	253–303	9.1	9.70	1.27×10^8	100
$EtMeCHO_2^\bullet$	Cyclopentane	193–257	11.3	9.00	1.04×10^7	101
$EtMeCHO_2^\bullet$	Pentane	253–303	6.9	7.30	1.23×10^6	100
$Me_3CO_2^\bullet$	Benzene	295			4.0×10^3	102
$Me_3CO_2^\bullet$	Cyclopentane	225–249	35.1	12.11	9.07×10^5	102

$Me_3CO_2^{\bullet}$	Methanol	295			1.0×10^4	102
$Me_3CO_2^{\bullet}$	Water	295			2.5×10^4	102
$MePrCHO_2^{\bullet}$	Pentane	253–303	6.9	7.30	1.23×10^6	100
$PrC(O_2^{\bullet})Me_2$	2-Methylpentane	213–273	39.0	11.11	1.88×10^4	103
$Me_3CC(O_2^{\bullet})Me_2$	2,2,3-Trimethylpentane	243–293	31.4	9.20	1.6×10^9	103
$MeBuCHO_2^{\bullet}$	Hexane	283–320	8.4	7.46	9.72×10^5	104
$MeCH(O_2^{\bullet})(CH_2)_4Me$	Heptane	294–324	8.4	7.46	9.72×10^5	104
$MeCH(O_2^{\bullet})(CH_2)_5Me$	Octane	283–356	8.4	7.46	9.72×10^5	104
$MeCH(O_2^{\bullet})(CH_2)_6Me$	Nonane	283–324	8.4	7.46	9.72×10^5	104
$MeCH(O_2^{\bullet})(CH_2)_7Me$	Decane	283–355	8.4	7.46	9.72×10^5	104
$MeCH(O_2^{\bullet})(CH_2)_9Me$	Dodecane	284–355	8.4	7.46	9.72×10^5	104
$MeCH(O_2^{\bullet})(CH_2)_{10}Me$	Tridecane	293–358	8.4	7.46	9.72×10^5	104
$Me_2C(O_2^{\bullet})CH_2CHMeCH_2$ $CHMeCHMe_2$	2,4,6,7-Tetramethyloctane	243–293	46.0	13.41	2.25×10^5	105
	Cyclopentane	175–200	10.9	9.60	4.89×10^7	106
	Cyclohexane	285–333	5.4	7.28	2.15×10^6	107
	Cycloheptane	298			8.6×10^6	108
	Cyclooctane	298			1.4×10^7	108

(continued overleaf)

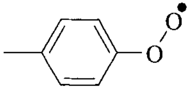
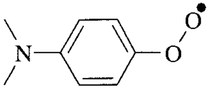
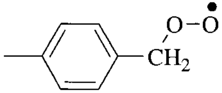
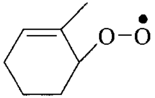
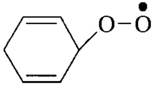
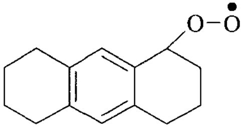
TABLE 20.6 (*continued*)

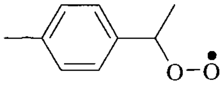
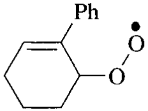
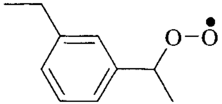
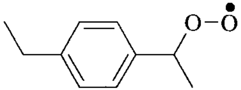
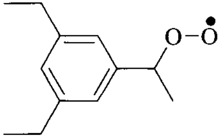
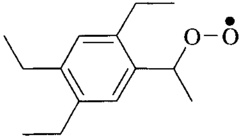
$RO_2^\bullet$	Solvent	T (K)	E (kJ mol^{-1})	log $(2A)A$ (L mol^{-1} s^{-1})	$2k_t$(298 K) (L mol^{-1} s^{-1})	Reference
	Cyclododecane	345–417	7.8	8.11	5.53×10^6	109
	Methylcyclohexane	187–263	25.2	8.87	2.83×10^4	110
$CH_2{=}CHCH(O_2^\bullet)CH{=}CH_2$	1,4-Pentadiene	303			1.1×10^9	109
$Me_2C{=}CHCH(O_2^\bullet)Me$	2-Methyl-2-pentene	313–333	5.0	7.40	3.32×10^6	111
$MeCH_2CH{=}CHCH(O_2^\bullet)Et$	3-Heptene	303			6.4×10^6	109
(Z)-$PrCH{=}CHCH(O_2^\bullet)Et$	(Z)-4-Octene	323			1.5×10^7	112
$PhCH{=}CHCH_2O_2^\bullet$	1-Phenyl-1-propene	303			4.4×10^8	113
$CH_2{=}CHCH(O_2^\bullet)(CH_2)_4Me$	1-Octene	298			1.0×10^7	114
$Me_2C{=}CHC(O_2^\bullet)MeCH_2CHMeCHMe_2$	2,4,6,7-Tetramethyl-2-octene	234–293	21.0	10.20	3.30×10^6	105
$EtCH{=}CHCH(O_2^\bullet)CH{=}CHCH_2CH{=}CHCH_2C(O)OMe$	α-Linolenic acid, methyl ester	353			1.8×10^7	107
$Me(CH_2)_4CH{=}CHCH(O_2^\bullet)CH{=}CH(CH_2)_7C(O)OMe$	Linolic acid, methyl ester	303			2.4×10^6	108
$Me(CH_2)_7CH{=}CHCH(O_2^\bullet)$	9-Octadecenoic acid,	303			1.1×10^6	115

$(CH_2)_6C(O)OMe$	methyl ester					
$Me(CH_2)_4CH{=}CHCH(O_2^\bullet)$ $CH{=}CH(CH_2)_7C(O)OEt$	Linolic acid, ethyl ester	298			3.0×10^7	116
	Cyclopentene	193–257	4.2	7.80	1.16×10^7	101
$PhO_2^\bullet$	Water, pH 7	293			1.1×10^9	117
$PhCH_2O_2^\bullet$	Toluene	303			3.0×10^8	115
$PhMe_2CO_2^\bullet$	Isooctane	323			2.5×10^5	118
$PhMe_2CO_2^\bullet$	Benzene	323			2.4×10^5	118
$PhMe_2CO_2^\bullet$	Acetonitrile	323			1.4×10^5	118
$PhMe_2CO_2^\bullet$	*tert*-Butanol	323			6.0×10^5	118
$PhMe_2CO_2^\bullet$	Pyridine	323			4.5×10^5	118
	Cyclohexene	282–319	8.3	8.75	1.97×10^7	119
	Water, pH 7	293			1.2×10^9	117
	Water, pH 7	293			8.6×10^8	117
	Water, pH 7	293			9.6×10^8	117

(*continued overleaf*)

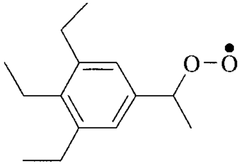
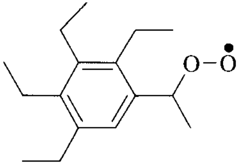
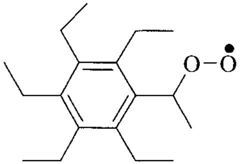
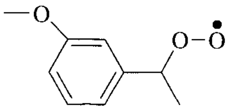
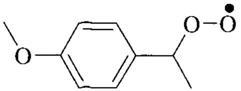
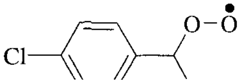
TABLE 20.6 (*continued*)

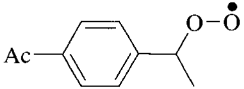
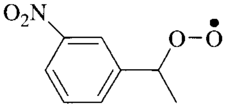
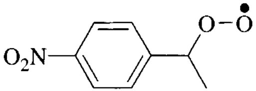
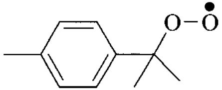
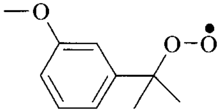
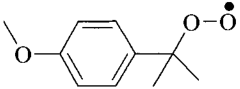
$RO_2^\bullet$	Solvent	T (K)	E (kJ mol^{-1})	log (2A)A (L mol^{-1} s^{-1})	2k_t(298 K) (L mol^{-1} s^{-1})	Reference
	Water, pH 7	293			8.8×10^8	117
	Water, pH 7	293			6.6×10^8	117
	4-Xylene	348			2.6×10^8	120
	1-Methylcyclohexane	313			8.6×10^5	121
	1,4-Cyclohexadiene	273			1.0×10^8	122
	1,2,3,4,5,6,7,8-Octahydroanthracene	348			2.5×10^7	123
$MePhCHO_2^\bullet$	Ethylbenzene	323–353	9.4	9.11	2.90×10^7	124

	1-Ethyl-4-methylbenzene	348	1.0×10^7	125
	1-Phenylcyclohexene	313–343	2.5×10^8	126
	1,3-Diethylbenzene	348	1.1×10^7	127
	1,4-Diethylbenzene	348	1.0×10^7	128
	1,3,5-Triethylbenzene	348	1.0×10^7	128
	1,2,4,5-Tetraethylbenzene	348	1.9×10^6	128

(*continued overleaf*)

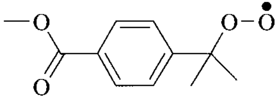
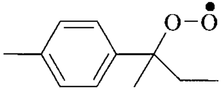
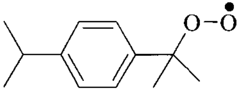
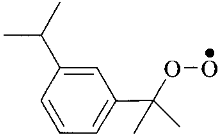
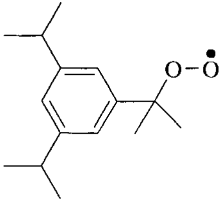
TABLE 20.6 (*continued*)

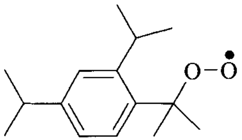
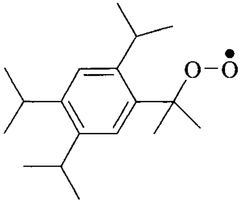
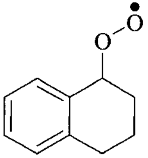
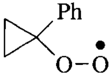
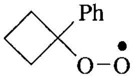
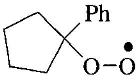
$RO_2^\bullet$	Solvent	T (K)	E (kJ mol^{-1})	log (2A)A (L mol^{-1} s^{-1})	2k_t(298 K) (L mol^{-1} s^{-1})	Reference
	1,3,4,5-Tetraethylbenzene	348			3.3×10^6	128
	Pentaethylbenzene	348			6.0×10^5	128
	Hexaethylbenzene	348			4.5×10^5	128
	1-Ethyl- 3-methoxybenzene	348			1.3×10^7	127
	1-Ethyl- 4-methoxybenzene	348			9.0×10^6	127
	1-Chloro-4-ethylbenzene	348			1.6×10^7	127

	1-Acetyl-4-ethylbenzene	348			1.5×10^7	127
	1-Ethyl-3-nitrobenzene	348			2.3×10^7	127
	1-Ethyl-4-nitrobenzene	348			2.4×10^7	127
$EtPhCHO_2^\bullet$	Propylbenzene	348			3.0×10^7	125
$PhCH(O_2^\bullet)NH_2$	Benzylamine	338			2.6×10^8	129
$Me_2PhCO_2^\bullet$	2-Phenylpropane	164–243	25.1	9.20	6.32×10^4	130
$EtMePhCO_2^\bullet$	2-Phenylbutane	303–329	37.7	9.30	4.92×10^2	131
	4-Methylcumene	308–338			2.0×10^5	132
	3-Methoxycumene	303			6.0×10^4	133
	4-Methoxycumene	303			4.0×10^4	133

(continued overleaf)

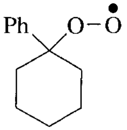
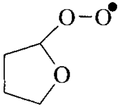
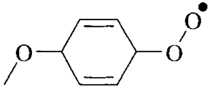
TABLE 20.6 (*continued*)

$RO_2^•$	Solvent	T (K)	E (kJ mol^{-1})	log (2A)A (L mol^{-1} s^{-1})	$2k_t$(298 K) (L mol^{-1} s^{-1})	Reference
	4-Methoxyoxocumene	303			3.0×10^4	133
	1-Methyl-4-(1-methyl)propylbenzene	348			6.6×10^6	125
	1,4-Diethylbenzene	348			1.1×10^5	134
	1,3-Diethylbenzene	348			1.0×10^5	134
	1,3,5-Triethylbenzene	348			1.0×10^5	134

	1,2,4-Triethylbenzene	348			3.2×10^5	134
	1,2,4,5-Tetraethylbenzene	348			8.0×10^6	135
$Ph_2CHO_2^{\bullet}$	Diphenylmethane	303			1.6×10^8	113
$Et_2PhCO_2^{\bullet}$	2-Phenylpentane	348			2.7×10^6	125
	Tetralin	286–323	18.0	9.94	6.09×10^6	113
	Phenylcyclopropane	348			1.9×10^6	125
	Phenylcyclobutane	348			8.0×10^3	125
	Phenylcyclopentane	348			8.1×10^5	125

(continued overleaf)

TABLE 20.6 (*continued*)

$RO_2^\bullet$	Solvent	T (K)	E (kJ mol^{-1})	log (2A)A (L mol^{-1} s^{-1})	2k_t(298 K) (L mol^{-1} s^{-1})	Reference
	Phenylcyclohexane	348			8.9×10^5	125
	Water	283–343	15.5	12.0	1.92×10^9	136
$Me_2C(O_2^\bullet)OCHMe_2$	Water	293–333	12.3	9.9	5.55×10^7	136
$MeC(O)CH_2O_2^\bullet$	Water	283–313	14.4	11.7	1.50×10^9	136
$MeC(O)CH_2CH_2O_2^\bullet$	Water	303–333	12.1	11.1	9.53×10^8	136
$MeS(O)_2CH_2O_2^\bullet$	Water	288–308	17.5	12.1	1.08×10^9	136
$MeS(O)_2CH_2CH_2O_2^\bullet$	Water	293–333	14.6	11.2	4.37×10^8	136
	Water, pH 6.5	298			8×10^8	137
$PhCH(O_2^\bullet)OH$	Benzyl alcohol	333–358	19.0	10.51	1.51×10^7	138
$PhCH(O_2^\bullet)Cl$	Benzyl chloride	348			8×10^7	138

Hydrogen peroxide was revealed among the products of disproportionation of ethylbenzene and toluene peroxy radicals. The mechanism of successive fragmentation seems to be very probable:[87]

$$R_1R_2CHOOOOCHR_1R_2 \rightarrow [R_1R_2HCO^{\bullet} + {}^{\bullet}OOOCHR_1R_2]$$
$$\rightarrow R_1R_2C{=}O + HOOOCHR_1R_2$$
$$R_1R_2HCOOOH \rightarrow [R_1R_2HCO^{\bullet} + HO_2^{\bullet}] \rightarrow R_1R_2C{=}O + H_2O_2$$

Based on the available literature data, one can propose the following putative diagram of the disproportionation of primary, secondary, and tertiary peroxyl radicals:[88,89]

$$RO_2^{\bullet} + RO_2^{\bullet} \rightarrow ROOOOR$$
$$ROOOOR \rightarrow [RO^{\bullet} + {}^{\bullet}OOOR]$$
$$[RO^{\bullet} + {}^{\bullet}OOOR] \rightarrow [RO^{\bullet} + RO^{\bullet}] + O_2$$
$$[RO^{\bullet} + RO^{\bullet}] \rightarrow ROOR$$
$$[RO^{\bullet} + RO^{\bullet}] \rightarrow 2RO^{\bullet}$$

The primary and secondary peroxyl radicals can be converted additionally according to the reactions:

$$HROOOORH \rightarrow [HRO^{\bullet} + {}^{\bullet}OOORH]$$
$$[HRO^{\bullet} + {}^{\bullet}OOORH] \rightarrow HROH + {}^{\bullet}OOOR^{\bullet}$$
$${}^{\bullet}OOOR^{\bullet} \rightarrow O_2 + R{=}O^{*}$$
$$[HRO^{\bullet} + {}^{\bullet}OOORH] \rightarrow R{=}O + HOOORH$$
$$[HRO^{\bullet} + {}^{\bullet}OOORH] \rightarrow [HRO^{\bullet} + HRO^{\bullet}] + O_2$$
$$[HRO^{\bullet} + HRO^{\bullet}] \rightarrow HROH + R{=}O$$
$$HROOOH \rightarrow [HRO^{\bullet} + HO_2^{\bullet}]$$
$$[HRO^{\bullet} + HO_2^{\bullet}] \rightarrow R{=}O + H_2O_2$$
$$[HRO^{\bullet} + HO_2^{\bullet}] \rightarrow HROH + O_2$$

It can be seen that primary and secondary $RO_2^{\bullet}$ radicals disproportionate in the cage with the participation of the α-C—H bond, which explains why the substitution of D in the α-position for H retards the recombination of $RO_2^{\bullet}$ ($k_H/k_D = 1.9$ for ethylbenzene and 3.9 styrene).[85] Because of this, the $RO_2^{\bullet}$ radicals of unsaturated compounds with a double bond in the α-position to the peroxyl free valence disproportionate more rapidly than structurally analogous aliphatic peroxyl radicals (at 300 K, $2k_t = 2 \times 10^7$ and 3.8×10^6 $L\,mol^{-1}\,s^{-1}$ for

$RO_2^{\bullet}$ radicals of cyclohexene and cyclohexane, respectively).[90] The peroxyl radicals of esters disproportionate at a very high rate (at 293 K, $2k_t = 7 \times 10^7 – 4 \times 10^8$ L mol^{-1} s^{-1}),[25] which is probably due to a polar ester group polarizing the neighboring bonds. Alkyl radicals recombine with peroxyl radicals at a rate of diffusion corresponding to the rate constant $2k_t = (2–6) \times 10^9$ L mol^{-1} s^{-1} in RH at 293 K.[25] For the rate constants of peroxyl radical disproportionation see Table 20.6.

REFERENCES

1. V. N. Kondratiev and E. E. Nikitin, *Gas-Phase Reactions*, Springer-Valley, Berlin, 1981.
2. J. A. Kerr, in *Free Radicals*, J. K. Kochi (Ed.), John Wiley & Sons, Inc., New York, 1973, Vol. 1, p. 1.
3. K. U. Ingold, in *Free Radicals*, J. K. Kochi (Ed.), John Wiley & Sons, Inc., New York, 1973, Vol. 1, p. 37.
4. Z. B. Alfassi, in *General Aspects of the Chemistry of Radicals*, Z. B. Alfassi (Ed.), John Wiley & Sons, Inc., Chichester, 1999, p. 139.
5. S. G. Lias, J. F. Liebman, R. D. Levin, and S. A. Kafafi, *NIST Positive Ion Energetics*, Version 2.0, NIST Standard Reference Data 19A, Gaithersburg, MD, 1993.
6. K. K. Laidler, *Chemical Kinetics*, Harper and Row, New York, 1987.
7. A. P. Stefani, *J. Am. Chem. Soc.* **90**, 1964 (1968).
8. A. Bazkac and J. H. Espenson, *J. Am. Chem. Soc.* **90**, 325 (1968).
9. H. Schuh and H. Fischer, *Helv. Chem. Acta* **61**, 2463 (1978).
10. D. J. Carlsson and K. U. Ingold, *J. Am. Chem. Soc.* **90**, 7047 (1968).
11. D. J. Carlsson, K. U. Ingold, and L. C. Bray, *Int. J. Chem. Kinet.* **1**, 315 (1969).
12. G. B. Watts and K. U. Ingold, *J. Am. Chem. Soc.* **94**, 491 (1972).
13. G. C. Stevens, R. M. Clarke, and E. J. Hart, *J. Phys. Chem.* **76**, 3863 (1972).
14. B. Hickol, *J. Phys. Chem.* **79**, 1054 (1975).
15. T. Zytovski and H. Fischer, *J. Am. Chem. Soc.* **118**, 437 (1996).
16. R. W. Fessenden, *J. Phys. Chem.* **68**, 1508 (1964).
17. R. D. Burkhart, *J. Phys. Chem.* **73**, 2703 (1969).
18. N. Getoff, *Radiat. Phys. Chem.* **37**, 673 (1991).
19. R. D. Burkhart, R. F. Boynton, and J. C. Merril, *J. Am. Chem. Soc.* **93**, 5613 (1971).
20. K. U. Ingold, B. Maillard, and J. C. Walten, *J. Chem. Soc., Perkin Trans 2*, 970 (1981).
21. P. Schmid, D. Griller, and K. U. Ingold, *Int. J. Chem. Kinet.* **11**, 333 (1979).
22. A. I. Nikolaev, R. L. Safiullin, and V. D. Komissarov, *Khim. Fizika* **3**, 257 (1984).
23. J. A. LaVerne and Wojnarovits, *J. Phys. Chem.* **98**, 12640 (1994).
24. M. C. Saner and I. Mani, *J. Phys. Chem.* **72**, 3856 (1968).
25. A. I. Nikolaev, *Kinetics of interaction of alkyl, alkylperoxyl and alkylsulphonyl radicals*, Ph.D. Dissertation (Russian), Institute of Chemical Physics, Chernogolovka, USSR, 1984.

26. *Radical Reaction Rates in Liquids*, Landolt-Bornstein New series, Group 2 (Atomic and Molecular Physics), H. Fischer (Ed.), Springer-Verlag, Berlin, Germany, 1984, Vol. 13, subvolume (a).
27. C. Huggenberger and H. Fischer, *Helv. Chim. Acta* **64**, 338 (1981).
28. G. M. Zimina and R. Cech, *Radiochem. Radioanal. Lett.* **38**, 119 (1979).
29. H.-H. Schuh and H. Fischer, *Helv. Chim. Acta* **61**, 2130 (1978).
30. S. A. Weiner and G. S. Hammond, *J. Am. Chem. Soc.* **91**, 986 (1969).
31. E. J. Hamilton and H. Fischer, *J. Phys. Chem.* **77**, 722 (1973).
32. M. Ebert, J. P. Keene, E. J. Land, and A. J. Swallow, *Proc. R. Soc. London, Ser A*, **287**, 1 (1965).
33. B. Smaller, J. R. Remko, and E. C. Avery, *J. Chem. Phys.* **48**, 5174 (1965).
34. T. Reitberger and K. Niblacus, *Chem. Scr.* **13**, 52 (1978–1979).
35. M. Simic and E. Hayon, *J. Phys. Chem.* **75**, 1677 (1971).
36. J. E. Bennett and R. Summers, *J. Chem. Soc., Perkin Trans. 2*, 1504 (1977).
37. J. Rabani, M. Pick, and M. Simic, *J. Phys. Chem.* **78**, 1049 (1974).
38. T. Soylemez and R. H. Schuler, *J. Phys. Chem.* **78**, 1052 (1974).
39. R. H. Schuler and L. K. Patterson, *Chem. Phys. Lett.* **27**, 369 (1974).
40. H.-G. Korth, H. Trill, and R. Sustmann, *J. Am. Chem. Soc.* **113**, 4483 (1981).
41. R. D. Burkhart and J. C. Merrili, *J. Phys. Chem.* **73**, 2699 (1969).
42. R. J. Hagemana and H. A. Schwarz, *J. Phys. Chem.* **71**, 2694 (1967).
43. J. Sobek, R. Martschke, and H. Fischer, *J. Am. Chem. Soc.* **123**, 2849 (2001).
44. H. C. Christensen, K. Schested, and E. J. Hart, *J. Phys. Chem.* **77**, 983 (1973).
45. T. O. Meiggs, L. I. Grossweiner, and S. I. Miller, *J. Am. Chem. Soc.* **94**, 7981 (1972).
46. O. von Brede, W. Helmstreit, and R. Mehnert, *J. Prakt. Chem.* **316**, 402 (1974).
47. T. Sumiyoshi, M. Kamachi, Y. Kuwal, and W. Schnabell, *Bull. Chem. Soc. Jpn.* **60**, 77 (1987).
48. N. A. McAskill and D. F. Sangster, *Aust. J. Chem.* **34**, 721 (1981).
49. I. W. C. E. Arends, P. Mulder, K. B. Clark, and D. D. M. Wayner, *J. Phys. Chem.* **99**, 8182 (1995).
50. Y. Guo, A. P. Darmanyan, and W. S. Jenks, *Tetrahedron Lett.* **38**, 8619 (1997).
51. H. Paul, *Chem. Phys.* **15**, 115, (1976).
52. W. F. Wang, M. N. Schuchmann, V. Bachler, H. P. Schuchmann, and C. von Sonntag, *J. Phys. Chem.* **100**, 15843 (1996).
53. M. Simic, P. Neta, and E. Havon, *Int. J. Radiat. Phys. Chem.* **3**, 309 (1971).
54. H. G. Korth, P. Lommes, W. Sicking, and R. Gustmann, *Int. J. Chem. Kinet.* **15**, 267 (1983).
55. P. Neta, M. Simic, and E. Hayon, *J. Phys. Chem.* **73**, 4207 (1969).
56. M. N. Schuchmann, R. Rao, M. Hauser, S. C. Muller, and C. von Sonntag, *J. Chem. Soc., Perkin Trans. 2*, 491 (2000).
57. H. W. Melville, J. C. Robb, and R. C. Tutton, *Disc. Faraday Soc.* **14**, 150 (1953).
58. B. Lesigne, L. Gifles, and R. J. Woods, *Can. J. Chem.* **52**, 1135 (1974).
59. H. Paul, *Int. J. Chem. Kinet.* **11**, 495 (1979).

60. M. Simic, P. Neta, and E. Hayon, *J. Phys. Chem.* **73**, 3794 (1969).
61. H. Paul, *J. Phys. Chem.* **82**, 2754 (1978).
62. D. Ruegge and H. Fischer, *J. Chem. Soc., Faraday Trans. 1*, **84**, 3187 (1988).
63. S. Weiner and G. S. Hammond, *J. Am. Chem. Soc.* **90**, 1659 (1968).
64. A. J. Elliot, *Radiat. Phys. Chem.* **34**, 753 (1989).
65. A. J. Elliot, D. R. McCracken, G. V. Buxton, and N. D. Wood, *J. Chem. Soc., Faraday Trans. 1*, **86**, 1539 (1990).
66. G. V. Buxton, C. L. Greenstock, W. P. Helman, and A. B. Ross, *J. Phys. Chem. Ref. Data* **17**, 513 (1988).
67. P. Paagsberg, H. Christensen, J. Rabani, G. Nilsson, and J. Fenger, *J. Phys. Chem.* **73**, 1029 (1969).
68. J. Rabani and M. S. Matheson, *J. Phys. Chem.* **70**, 761 (1966).
69. J. R. Thomas, *J. Am. Chem. Soc.* **87**, 3935 (1965).
70. G. E. Adams, J. W. Boag, and B. D. Michael, *Proc. R. Soc. London, Ser. A*, **289**, 321 (1966).
71. P. C. Wong and D. Griller, *J. Org. Chem.* **46**, 2327 (1981).
72. S. A. Weiner and G. S. Hammond, *J. Am. Chem. Soc.* **91**, 986 (1969).
73. A. P. Darmanyan, D. D. Gregory, Y. S. Guo, and W. S. Jenks, *J. Phys. Chem.* **101**, 6855 (1997).
74. G. B. Watts and K. U. Ingold, *J. Am. Chem. Soc.* **94**, 491 (1972).
75. N. C. Billingham and A. D. Jenkins, in *Comprehensive Chemical Kinetics*, C. H. Bamford and C. F. H. Tipper (Eds.), Elsevier, Amsterdam, The Netherlands, 1976, Vol. 14 A, p. 419.
76. R. Houwink and A. J. Staverman, *Chemie und Technologie der Kunststoffe*, Gest and Porfig, Leipzig, Germany, 1962, B. 1.
77. B. Yamada, in *Preprints 37 International Symposium on Macromolecules*, Cold Cost, Australia, 1998, p. 636.
78. M. Azukizawa, B. Yamada, P. J. Pometry, and D. J. T. Hill, in *Preprints 37 International Symposium on Macromolecules*, Cold Cost, Australia, 1998, p. 667.
79. K. Hatada, T. Kitayama, and E. Masuda, *Macromol. Chem. Rapid. Commun.* **11**, 101 (1990).
80. G. Moad and D. H. Solomon, *The Chemistry of Free Radical Polymerisation*, Pergamon Press, New York, 1995.
81. E. T. Denisov, in *Comprehensive Chemical Kinetics*, C. H. Bamford and C. F. H. Tipper (Eds.), Elsevier, Amsterdam, The Netherlands, 1980, Vol. 16, p. 125.
82. T. Mill and D. G. Hendry, in *Comprehensive Chemical Kinetics*, C. H. Bamford and C. F. H. Tipper (Eds.), Elsevier, Amsterdam, The Netherlands, 1980, Vol. 16, p. 1.
83. E. T. Denisov and T. G. Denisova, *Handbook of Antioxidants*, CRC Press, Boca Raton, FL, 2000.
84. J. A. Howard, in *Free Radicals*, J. K. Kochi (Ed.), John Wiley & Sons, Inc., New York, 1973, Vol. 2, p. 1.
85. G. A. Russel, *J. Am. Chem. Soc.* **79**, 3871 (1957).
86. V. Ya. Shlyapintokh, O. N. Karpukhin, L. M. Postnikov, V. F. Tsepalov, A. A. Vichutinskii, and I. V. Zakharov, *Chemiluminescence Techniques in Chemical Reactions*, Consultants Bureau, New York, 1968.

87. E. T. Denisov, *Neftekhimiya* **26**, 723 (1986).
88. S. L. Khursan, V. S. Martemyanov, and E. T. Denisov, *Kinet. Katal.* **31**, 1031 (1990).
89. E. T. Denisov, *Uspekhi Khimii* **39**, 62 (1970).
90. R. L. Vardanyan, R. L. Safiullin, and V. D. Komissarov, *Kinet. Katal.* **26**, 1327 (1985).
91. J. A. Howard and K. U. Ingold, *Can. J. Chem.* **45**, 785 (1967).
92. B. H. J. Bielski and E. J. Saito, *J. Phys. Chem.* **66**, 2266 (1962).
93. D. Behar and G. Czapski, *Isr. J. Chem.* **8**, 699 (1970).
94. B. H. J. Bielski and E. J. Saito, *J. Phys. Chem.* **75**, 2263 (1971).
95. R. E. Pliss, V. A. Machtin, and E. M. Pliss, in *Regulation of Biological Processes by Free Radicals: Role of Antioxidants*, Free Radical Scavengess, and Chelators, Moscow-Yaroslavl, 1998, p. 17.
96. A. I. Nikolaev, R. L. Safiullin, L. P. Enikeeva, and V. D. Komissarov, *Khim. Fizika* **11**, 69 (1992).
97. J. E. Bennett, G. Brunton, J. R. L. Smith, T. M. F. Salmon, and D. J. Waddington, *J. Chem. Soc., Faraday Trans. I*, **83**, 2421 (1987).
98. J. E. Bennett, *J. Chem. Soc., Faraday Trans. 1*, **83**, 1805 (1987).
99. J. A. Howard and K. U. Ingold, *J. Am. Chem. Soc.* **90**, 1058 (1968).
100. S. L. Khursan, R. L. Safiullin, and S. Yu. Serenko, *Khim. Fizika* **9**, 375 (1990).
101. J. A. Howard and J. E. Bennett, *Can. J. Chem.* **50**, 2374 (1972).
102. W. J. Maguire and R. C. Pink, *Trans. Faraday Soc.* **63**, 1097 (1967).
103. J. E. Bennett, D. M. Brown, and B. Mile, *Trans. Faraday Soc.* **66**, 386 (1970).
104. S. I. Maslennikov, A. I. Nikolaev, and V. D. Komissarov, *Kinet. Katal.* **20**, 326 (1979).
105. A. Faucitano, A. Buttafava, F. Martinotti, V. Comincoli, and P. Bortolus, *Polymer Photochem.* **7**, 491 (1986).
106. E. Furimsky, J. A. Howard, and J. Selwyn, *Can. J. Chem.* **58**, 677 (1980).
107. S. I. Maslennikov, L. G. Galimova, and V. D. Komissarov, *Izv. AN SSSR, Ser. Khim.* 631 (1979).
108. B. Smaller, J. R. Retko, and E. C. Avery, *J. Chem. Phys.* **48**, 5174 (1968).
109. B. Ya. Ladygin, G. M. Zimina, and A. V. Vannikov, *Khim. Vys. Energ.* **18**, 301 (1984).
110. L. A. Tavadyan, M. V. Musaelyan, and V. A. Mardoyan, *Khim. Fiz.* **10**, 511 (1991).
111. G. E. Zaikov, Z. K. Maizus, and N. M. Emanuel, *Izv. AN SSSR, Ser. Khim.* 2265 (1968).
112. V. A. Ickovich, V. M. Potekhin, W. Pritzkow, V. A. Proskuryakov, and D. Schnurpfeil, *Autoxidation von Kohlenwasserstoffen*, VEB Deutsch. Verlag Gerundstoffindustrie, Berlin, 1981, p. 183.
113. J. A. Howard and K. U. Ingold, *Can. J. Chem.* **44**, 1119 (1966).
114. R. L. McCarthy and A. MacLachlan, *Trans. Faraday Soc.* **57**, 1107 (1961).
115. J. A. Howard and K. U. Ingold, *Can. J. Chem.* **45**, 703 (1967).
116. L. Bateman, G. Gee, A. L. Morris, and W. F. Watson, *Disc. Faraday Soc.* 250 (1951).

117. X. Fang, R. Mertens, and C. von Sonntag, *J. Chem. Soc., Perkin Trans. 2*, 1033 (1995).
118. M. Lucarini, G. F. Pedulli, and L. Valgimigli, *J. Org. Chem.* **63**, 4497 (1998).
119. R. L. Vardanyan, R. L. Safiullin, and V. D. Komissarov, *Kinet. Katal.* **26**, 1140 (1985).
120. T. P. Kenisberg, N. G. Ariko, and N. I. Mitskevich, *Dokl. AN BSSR* **24**, 817 (1980).
121. J. C. Robb and M. Shanin, *Trans. Faraday Soc.* **55**, 1753 (1959).
122. G. E. Zaikov, J. A. Howard, and K. U. Ingold, *Can. J. Chem.* **47**, 3017 (1969).
123. S. A. Gerasimova, A. G. Matvienko, I. A. Opeida, and I. O. Kachurin, *Zh. Org. Khim.* **34**, 781 (1998).
124. A. N. Nikolayevskii, V. G. Koloyerova, and R. V. Kucher, *Neftekhimiya* **16**, 752 (1976).
125. V. A. Belyakov, G. Lauterbach, W. Pritzkow, and V. Voerckel, *J. Prakt. Chem. (Leipzig)* **340**, 475 (1992).
126. V. I. Rubailo, A. B. Gagarina, and N. M. Emanuel, *Dokl. AN SSSR* **224**, 883 (1975).
127. I. A. Opeida, A. G. Matvienko, I. V. Yefimova, and I. O. Kachurin, *Zh. Org. Khim.* **24**, 572 (1988).
128. I. A. Opeida, A. G. Matvienko, and I. V. Yefimova, *Kinet. Katal.* **28**, 1341 (1987).
129. G. A. Kovtun and A. L. Aleksandrov, *Izv. AN SSSR, Ser. Khim.* 38 (1977).
130. I. S. Gaponova, T. V. Fedotova, and V. F. Tsepalov, *Kinet. Katal.* **12**, 1137 (1971).
131. J. A. Howard and K. U. Ingold, *Can. J. Chem.* **46**, 2655 (1968).
132. J. A. Howard and J. C. Robb, *Trans. Faraday Soc.* **59**, 487 (1963).
133. J. A. Howard, K. U. Ingold, and M. Symonds, *Can. J. Chem.* **46**, 1017 (1968).
134. S. A. Gerasimova, I. O. Kachurin, A. G. Matvienko, and I. A. Opeida, *Neftekhimiya* **30**, 476 (1990).
135. I. A. Opeida, I. V. Yefimova, A. G. Matvienko, A. F. Dmitruk, and O. M. Zarechnaya, *Kinet. Katal.* **31**, 1342 (1990).
136. R. L. Safiullin, V. V. Zapol'skych, L. R. Yakupova, R. N. Zaripov, and A. N. Teregulova, *Khim. Fizika* **20**, 110 (2001).
137. X.-M. Pan, M. N. Schuchmann, and C. von Sonntag, *J. Chem. Soc., Perkin Trans. 2*, 289 (1993).
138. A. N. Shendrik, *Kinetic Models of the Liquid-Phase Oxidation with Participation of the Short-life Molecular Intermediates*, Ph.D. Thesis (Russian), NASU, Institute of Physical-Organic Coal Chemistry, Donetsk, Ukraine, 1996.

Handbook of Free Radical Initiators. E.T. Denisov, T.G. Denisova, T.S. Pokidova
Copyright © 2003 John Wiley & Sons, Inc.
ISBN: 0-471-20753-5

INDEX