the removal of the copper, as well as the negative results obtained in the hydriodic acid reduction prove that the prosthetic group is neither a porphyrin nor a closely related substance such as a bile pigment.

The stability of the black copper complex and its tendency to form soluble, highly colored complexes with amines (and also denatured albumen) indicates that the compound we have in hand is involved in the union of the copper to the protein in hemocyanin. The function of the prosthetic group thus appears to be the same as that of protoporphyrin in hemoglobin, namely, to provide a basis for a very stable metallic complex. Beyond this analogy, however, there seems to be little or no chemical relationship between the prosthetic groups in limulus hemocyanin and hemoglobin. It should be noted that since limulus hemocyanin differs markedly in its copper content from the hemocyanin of other species,[2] the conclusions we have drawn do not necessarily apply to the nature of the prosthetic group in the other hemocyanins.

We are greatly indebted to Mr. I. S. Danielson for his assistance in procuring the initial material and for carrying through a number of the experiments.

[1] E. Philippi, *Zeit. Physiol. Chemie*, **104**, 88 (1919).
[2] Redfield, Coolidge and Shatts, *J. Biol. Chem.* **76**, 185 (1928).

THE PHOTOCHEMICAL DISSOCIATION OF NITROGEN PEROXIDE

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When the substance, nitrogen peroxide, consisting of a mixture of two gases, nitrogen peroxide, NO_2, and nitrogen tetraoxide, N_2O_4, is illuminated with approximately monochromatic light from a quartz mercury arc, an increase in pressure occurs which is greater than that to be expected from the heating effect of the radiation on the gas. The abnormal rise in pressure has been attributed to photochemical decomposition. Norrish[1] almost exclusively studied the equilibrium involved, and in later work[2] investigated the quantum yield so far as to determine the number of oxygen molecules formed in the reaction system per quantum of light absorbed. One molecule of oxygen was produced for every quantum absorbed in the spectral regions 2700–3160 Å and 3660 Å, while at longer wave lengths of 4050 Å and 4360 Å, 0.37 and 0.0 molecules of oxygen, respec-

tively, were produced for each quantum absorbed. Dickinson and Baxter[3] effectively showed the products of the photochemical decomposition to be nitric oxide and oxygen. The variation of the quantum yield with wave lengths of light used in illumination leads to the belief in a photochemical threshold which must exist between 4050 Å, the region in which dissociation began to take place, and 3660 Å, the region where full photochemical equivalent was observed. The quantum yield at intermediate wave lengths has not been investigated.

Since nitrogen peroxide contains two kinds of molecules, the analysis and formulation of the reaction becomes increasingly difficult. For instance, it was equally as possible to begin upon the assumption that the photoactive species was either the NO_2 molecule or the N_2O_4 molecule. On the other hand, it was not inconceivable that both molecules may be involved. The question can at least be partially solved by a study and
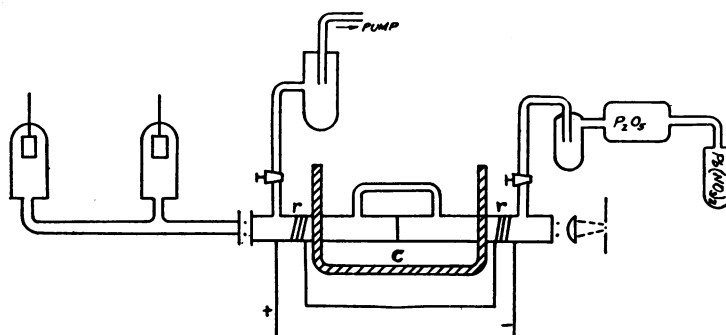

FIGURE 1

review of the existing absorption spectrum data concerning these two gases.

Harris[4] reported the absorption spectrum of nitrogen peroxide to consist of two separate and distinct types of absorption. The first, which was attributed to NO_2, extends from the visible region of the spectrum into the ultra-violet as far as 2250 Å, and exhibits a complex banded structure. The second, which is attributed to N_2O_4, begins within the limit of experimental error, at about 4000 Å, and exhibits a *continuous* absorption spectrum which increases in intensity to a maximum at about 3500 Å. These results were confirmed in hitherto unpublished work of the writer. While photographing the absorption spectrum of nitrogen pentoxide, the writer found it necessary to photograph both the absorption spectrum of nitrogen peroxide and nitrogen tetraoxide, since the latter two gases were ultimately produced in the decomposition of the pentoxide, and the presence of either in appreciable amounts would have masked the true absorption spectrum of the pentoxide. Photographs of NO_2 at the temperature of 140° C. and solid N_2O_4 at the temperature of liquid air were taken, the following precautions being observed:

Pure nitrogen peroxide was made from heated lead nitrate, passed over phosphorus pentoxide, and condensed into a trap surrounded by carbon dioxide–ether mush. The trap, the 30-cm. length quartz absorption cell, the drying tube and the lead nitrate bulb were pumped free of air, and the inlet and outlet stopcocks to the absorption cell were closed. By taking the freezing mixture away from the trap, and manipulating the inlet stopcock, any desired quantity of the brown gas could be admitted to the absorption cell. The absorption cell was constructed with two compartments such that light traversing the cell had to pass through three quartz windows. The gas was free to flow from one compartment to the other by way of the by-pass around the inner window. Figure 1 illustrates the apparatus used. The source of continuous ultra-violet light was afforded by a hydrogen discharge tube. The light rays from the discharge tube, after passing the length of the absorption cells, were focused on the slit of the spectrograph. A Hilger E-37 quartz spectrograph was used in addition to a larger E-3 instrument.

A number of successive exposures were taken with NO_2 gas in the absorption cell, at varying pressures less than atmospheric. The temperature was kept at $140°$ by means of electrical heating elements which were wrapped the whole length of the absorption cell, and this temperature was measured by means of a thermometer enclosed within the asbestos casing about the cell. These exposures are shown upon plate 1. The complex banded absorption attributed to NO_2 by Harris begins in the visible region of the spectrum, rises to a maximum at approximately 3900 Å, and then decreases to a minimum intensity at approximately 3200 Å. Apparently, NO_2 absorbs radiation very weakly in the region 3200 to 2495 Å. A second series of bands begin at 2490 Å, the wave lengths of which have been previously determined by Harris, for the reason that they possess a very much simplified appearance in comparison to those bands due to NO_2 in the visible spectrum.

Plate 1 also shows a photograph made with solid N_2O_4. The following method was used to obtain this photograph. Referring again to figure 1 the gaseous contents of the absorption cell, after photographing the mixture of the two oxides at room temperature, were condensed out upon the inner window, by pouring liquid air into the plaster-of-paris container C, which was moulded about the absorption cell. The brown gas, which turned into white crystalline N_2O_4 upon the inside window, therefore, formed a semi-transparent layer on both sides of the quartz disk. This was ascertained by viewing the absorption cell, end on, with the eye while the hydrogen discharge tube was turned on. The ends of the absorption cell which protruded from the cold container C were kept free from condensed moisture, by means of the electrical heating elements, r. This photograph, therefore, shows the region of the spectrum absorbed by
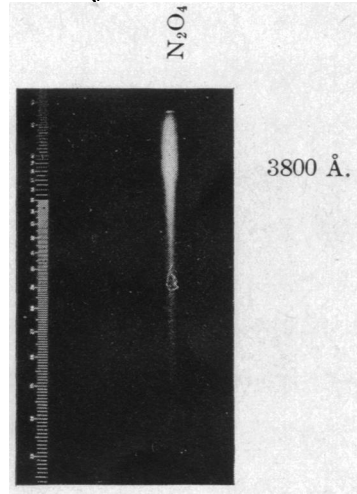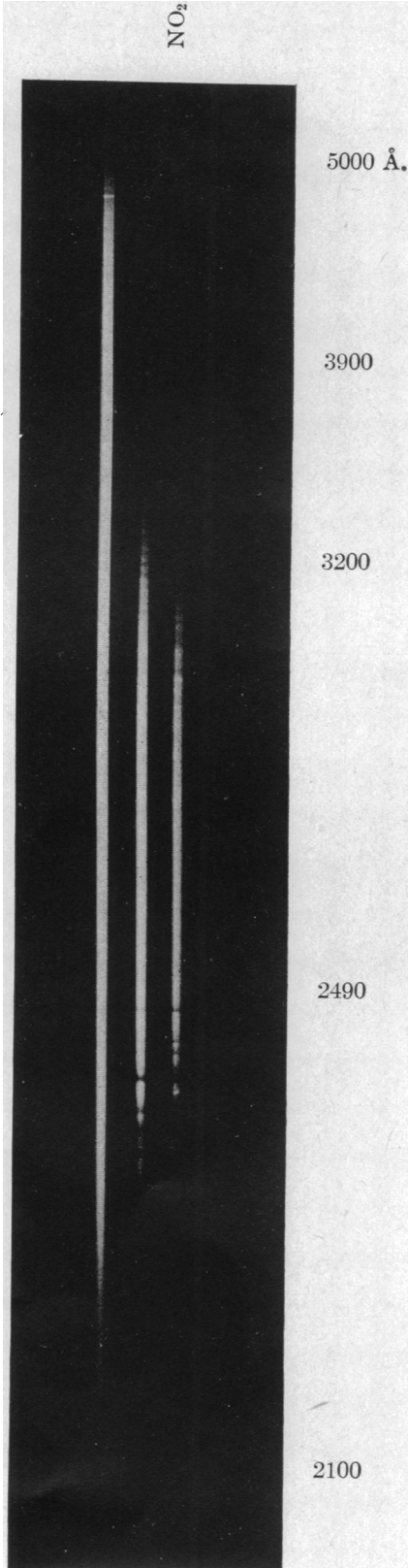
NO₂

5000 Å.

3900

3200

2490

2100

N₂O₄

3800 Å.

PLATE 1.

crystalline N_2O_4 at the temperature of liquid air, $-182°C$. Absorption begins, within the limit of experimental error, at about 3820 Å, increasing in intensity toward the shorter wave lengths. Some diffuse light was transmitted below 3820 Å, but this was to be expected, and may be accounted for in reflection of light from crystal face to crystal face in the thin layer. This photograph is doubtless of no other value except that it enables the long wave length limit of absorption to be determined for N_2O_4 while in the crystalline state.

In general, within the limit of experimental error, the light energy of activation should not vary to a great extent, regardless of the state, solid, liquid, or gas, which the molecules might be in. This is not, however, exactly correct. The heat of activation in the gaseous state, according to conventional thermochemical calculations, differs from the heat of activation in the solid state, by an amount of the order of the difference in thermal energy possessed by the substance at two temperatures. The difference in thermal energy in this case may be divided in five separate parts, $\Delta E_1 = \int_{T_1}^{T_2} C_p dT$, the energy necessary to raise a mol of N_2O_4 from the temperature of liquid air to its melting point, $-10°C$., plus the heat of fusion, ΔE_2, plus $\Delta E_3 = \int_{T_2}^{T_3} C_p dT$, the energy necessary to raise the substance from its melting point to its boiling af $18°C$., plus the heat of vaporization, ΔE_4, plus $\Delta E_5 = \int_{T_3}^{T_4} C_p dT$, the energy necessary to raise the gas from its boiling point to room temperature. The specific heat of nitrogen tetraoxide is not known, and for that reason, assumed values must be used. Making use of Kopp's Law, C_p for solid N_2O_4 is about 22 calories per mol. The first quantity above then becomes $\Delta E_1 = 3.984$ kilo-calories. ΔE_2 is 0.034 kilo-calories (I. C. T. value). ΔE_3 becomes 0.670 kilo-calories, assuming the rough value of 24 calories per mol for the heat capacity of liquid N_2O_4. ΔE_4 is probably very small. The specific heat of gaseous N_2O_4 is doubtlessly less than for two mols of NO_2 and is not greater than about 18 calories per mol. ΔE_5 then becomes 0.126 kilo-calories, and the total change in thermal energy between the temperature of liquid air and the room temperature of $25°C$., is of the order of 4–5 kilo-calories. The long wave length limit observed for N_2O_4 at liquid air temperature is 3820 Å corresponding to 74.6 kilo-calories for the least heat of optical activation to which the molecule is susceptible. Subtracting this value of about 4.5 kilo-calories energy, which must be present in the gas at $25°C$. from the heat of activation at $-182°C$., 70.2 kilo-calories is obtained which must correspond to the least energy of optical activation at the higher temperature. This latter

figure for N_2O_4 at room temperature corresponds to wave lengths of light at 4060 Å.

This method of treatment may account for the shifting of the absorption spectrum of N_2O_4 toward the longer wave lengths with increasing temperature. Harris shows the absorption spectrum of liquid N_2O_4 to begin at about 4000 Å.

The majority of photochemical reactions are very complicated, involving transfers of energy so rapid as to obscure the original primary process. Only those changes which find themselves within the boundary of Einstein Photochemical Equivalence Law are capable of analysis, and even then these become difficult for the study of complex molecules. The problem involving the correlation between the thermal energy required to decompose a substance, and the optical energy necessary to bring about the same transformation has been partially understood in the study of the simpler types of molecules during the last few years. Franck[5] was able to conclude that Cl_2, I_2 and Br_2 dissociated into atoms beyond a certain region in their absorption spectra. This region was the convergence limit of the band series, beyond which continuous absorption and complete primary dissociation occurred. The energy of dissociation for the thermal change was somewhat less than the energy involved in the photochemical dissociation, but the difference was accounted for in assuming that one of the atoms on dissociation was left in the 2^2P_1 excited state. For simple diatomic molecules (H_2, I_2, HI, HCl, O_2, etc.) the linkages or bonds holding the atoms together were classed as polar or non-polar. Franck, Kuhn, and Rollefson[6] showed the energy calculated from the long wave limit of the continuous absorption for polar molecules to be equal to the thermal energy of dissociation. This is the case for the alkali halides. The non-polar molecules gave an energy of dissociation corresponding to the long wave-length limit of continuous absorption greater than the thermal energy of dissociation, which was equivalent to the thermal energy of dissociation plus an amount of energy necessary to excite one of the atoms. The halogen molecules were examples of this latter type.[7]

These observations have been limited to diatomic molecules. With more complex molecules, in the special case where a region of continuous absorption indicated an electronic activation of some linkage in the molecule, the dissociation process was considered analogous to the cases of photochemical dissociation in diatomic molecules, and since the study was not confined to band structure with quantized states of molecules, but only to continuous spectra, it became difficult to draw a distinction between the primary processes taking place in the two instances (diatomic molecules and polyatomic molecules). Iredale and Wallace[8] measured the long wave-length limit of the continuous absorption due to the com-

plex organic molecules, methyl iodide, ethyl iodide, iodo-benzene, etc., and obtained an unmistakable agreement between the thermal energy of dissociation and the optical energy of dissociation. Urey, Dawsey, and Rice[9] considered the continuous absorption spectrum of nitrogen pentoxide to indicate a primary dissociation of the molecule.

If the continuous character of the nitrogen tetraoxide spectrum may be interpreted to indicate a primary photochemical dissociation for that molecule, the difficulty which prevents a clear understanding of the photo-chemical decomposition in nitrogen peroxide–tetraoxide mixtures and the quantum yield obtained therein is considerably altered. Measurable quantum yields were obtained only over the spectral range covered by the continuous absorption spectrum of N_2O_4. The photochemical decomposition may be complicated by secondary reactions in the presence of nitrogen peroxide molecules, the tendency being to obscure, rather than assist, the principal photochemical change while on the other hand NO_2 may act as a photo-catalyst, i.e., an energy carrier, whereby some such mechanism as, first, absorption of light by NO_2, and second, a collision between the activated NO_2 molecule and an N_2O_4 molecule, resulting in the disruption of the N_2O_4, may occur. Aside from this possibility, the absorption spectra of these two gases indicate that only one main, primary photochemical process is likely to take place in a mixture of the two. The products of the decomposition are known to be nitric oxide and oxygen, the absorption spectra point to N_2O_4 as being the photoactive constituent, and the thermal data offers a source from which to check energy relations involved in the photochemical change. The primary photochemical reaction is therefore thought to be

$$N_2O_4 \xrightarrow{hv} 2NO + O_2(^1S) \tag{1}$$
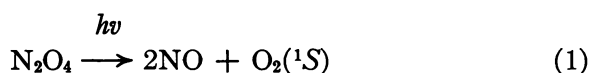
where $hv = \dfrac{74.6}{N}$ kilo-calories corresponding to the wave length 3820 Å.

The corresponding energy for the thermal change is 39.6 kilo-calories. It is assumed that the oxygen molecule is left in the ^1S excited state on dissociation of the nitrogen tetraoxide molecule. The energy necessary to excite an oxygen molecule in the normal ^3S to the ^1S excited state is 1.62 volts,[10] and is equivalent to 35 kilo-calories. Thus, the sum of the energy for the thermal change plus the energy of excitation of the oxygen molecule is 74.6 kilo-calories, and agrees very well with the energy value obtained from the short wave-length limit of the continuous absorption spectrum.

Summary.—1. The absorption spectrum of nitrogen dioxide and nitrogen tetraoxide have been photographed at room temperature and the temperature of liquid air, respectively, and compared with previous work.

2. Consideration of the absorption spectra of these two gases leads to the conclusion that the primary photochemical decomposition in nitrogen peroxide, which consists of nitrogen peroxide and nitrogen tetraoxide, is due to the tetraoxide constituent.

3. The threshold for complete photochemical equivalence is calculated to be at about 3800 Å.

4. The mechanism, $N_2O_4 \xrightarrow{h\nu} 2NO + O_2(^1S)$, is proposed to account for the primary photochemical dissociation, and the continuous absorption spectrum of N_2O_4. The energy changes involved agree closely with thermal data.

[1] Norrish, *J. Chem. Soc.*, Part 1, 761 (1927).

[2] *Ibid.*, Part 2, 1158 (1929).

[3] Dickinson and Baxter, *J. Am. Chem. Soc.*, **50**, 774 (1928).

[4] Harris, *Proc. Nat. Acad. Sci.*, **14**, 690 (1928).

[5] Franck, *Trans. Farad. Soc.*, **21**, 536 (1926).

[6] Franck, Kuhn and Rollefson, *Zeit. Phys.*, **43**, 155 (1927).

[7] Franck and Kuhn, *Zeit. Phys.*, **43**, 164 (1927).

[8] Iredale and Wallace, *Phil. Mag.*, **8**, 1093 (1929).

[9] Urey, Dawsey and Rice, *J. Am. Chem. Soc.*, **51**, 3190 (1929).

[10] Mulliken, *Phys. Rev.*, **32**, 880 (1928).

THE STUDY OF ABSORPTION SPECTRA OF ORGANIC COMPOUNDS AT LIQUID AIR TEMPERATURES

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It is well known that certain broad bands in the ultra-violet absorption spectrum of benzene are broken into finer lines at liquid air temperatures. At the suggestion of Professor Linus Pauling we have examined the visible absorption spectra at low temperatures of solutions of porphyrins and certain other colored organic compounds to see if the same phenomenon could be noted. As Professor Pauling has suggested, the characteristic spectrum of a porphyrin, which consists of a number of relatively very narrow bands, is probably due to the fact that the chromophoric groups are protected from thermal disturbances by the large cyclic system; the porphyrins might thus be considered analogous to the rare earths. It might be expected, therefore, that the visible spectrum of a porphyrin would be resolved into narrower bands at low temperatures. The sub-