FORMATION OF OZONE BY OPTICALLY EXCITED MERCURY VAPOR

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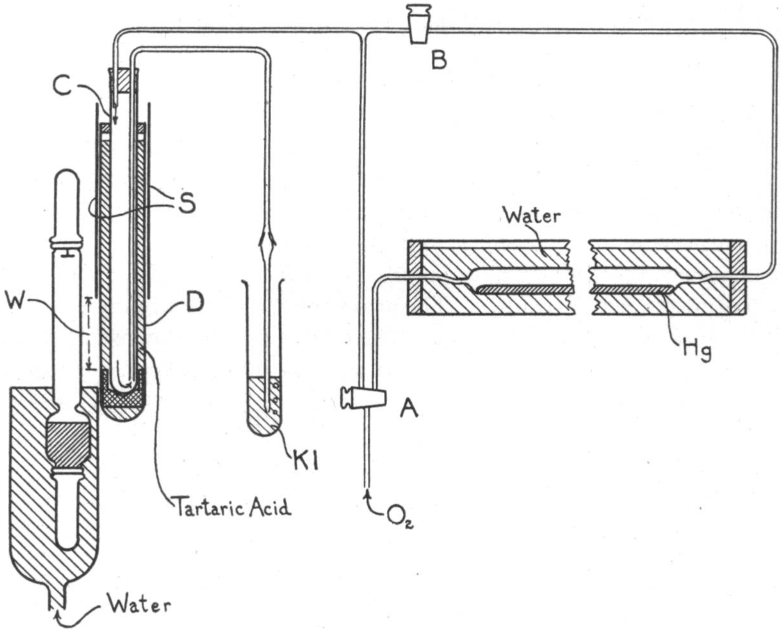
In the course of experiments[1] on the combination of hydrogen and oxygen in the presence of mercury vapor activated by absorption of the resonance radiation λ 2537 Å, it was found that the irradiation of oxygen alone in presence of mercury produced a small but still noticeable decrease of pressure. This effect might be due to ozone formation and subsequent oxidation of mercury, or to some other cause. The present experiments were accordingly undertaken to determine whether mercury vapor in the presence of its resonance radiation would cause formation of ozone.



It seemed desirable to employ a chemical method for the detection of any ozone formed. It was also important constantly to renew the traces of mercury vapor used for sensitization as fast as it became oxidized, without employing liquid mercury in the reaction tube. These conditions were met by the use of a flow method at atmospheric pressure. In order not to have the photo-sensitized reaction obscured by ordinary photo-chemical ozone formation, the radiation was filtered to remove the shortest wave-lengths from the quartz mercury-arc spectrum, since the region below 2000 Å produces ozone[2] strongly without sensitization. These considerations led to the adoption of the following procedure.

Tank oxygen was passed through a flow meter, and over heated platinized asbestos, soda-lime and phosphorus pentoxide. It was then passed through a three-way stopcock *A* (see figure) into the quartz reaction tube *C* either directly or over a water-jacketed pool of mercury 45 cm. long. In the former case the cock *B* was closed. The gas issuing from the reaction tube was bubbled through 5 cc. of 2% KI solution, and this was then titrated[3] with 0.0008 normal As_2O_3 from a 2-cc. buret, using starch as indicator. With the aid of a larger quartz tube *D* the reaction tube was jacketed with 3 mm. of a 1.7% solution of tartaric acid to filter out short wave-lengths.[4] Since tartaric acid undergoes a slow photochemical transformation,[5] the solution was frequently renewed. The commercial lamp used was placed one centimeter from the jacket *D;* the lamp was water-cooled and provided with a magnet to deflect the arc against the wall adjacent to the reaction tube.

With this arrangement, no formation of ozone was observed when the oxygen was passed directly into the reaction tube. Ozone was, however, formed in appreciable amount when the oxygen had been passed over mercury. It was formed in greater amount when an opaque shield *S* was so interposed as to cut off part of the reaction tube from illumination. After the apparatus had been in long-continued operation, a slight yellowish brown deposit, probably mercuric oxide, was frequently observed in the reaction tube. It was easily removed by heating.

A consecutive series of typical results is given in the table. The duration of each exposure was 5 minutes. The arc current was 2.0 amperes. The temperature of the mercury was 20 °C. The rate of oxygen flow was 147 cc. per minute, corresponding to an average linear velocity of 2.6 cm. per second.

EXTENT OF OZONE FORMATION UNDER VARIOUS CONDITIONS

NO.	WINDOW, W CMS.	CONDITIONS OF EXPERIMENT	CC. OF As_2O_3 REQUIRED	PARTIAL PRESSURE OZONE IN MM.
1	7.0	O_2 and Hg vapor	0.37	0.0037
2	4.0	O_2 and Hg vapor	0.92	0.0092
3	2.0	O_2 and Hg vapor	0.81	0.0081
4	1.0	O_2 and Hg vapor	0.57	0.0057
5	4.0	O_2 without Hg	0.00	0.0000
6	4.0	Duplicate of No. 2	0.85	0.0085
7	4.0	Duplicate of No. 5	0.00	0.0000
8	4.0	Duplicate of No. 2	0.90	0.0090
9	4.0	O_2 and Hg. No water or magnet on arc	0.04	0.0004
10	4.0	O_2 without Hg. No tartaric acid filter	15.30	0.1522

The results show that with the filtered radiation used, the presence of mercury vapor was essential to the ozone formation. The effect of the shield *S* in increasing the yield is readily explained: when a given portion of the gas is exposed long enough to the radiation, the ozone first formed oxidizes all the mercury vapor; the remaining ozone is then photochemically decomposed. Evidence of this effect was also found by decreasing the rate of flow, which caused the *concentration* of the ozone in the issuing gas to decrease.

Since the amount of ozone formation was strongly dependent on the extent of reversal in the arc (compare Expts. 2 and 9) and since the line λ 1849 Å was absent, the first step in the sensitized ozone formation must be the excitation of a mercury atom from the normal state to the $2p_2$ state by the absorption of λ 2537 Å.

The second step in the process can hardly be the reaction: $Hg(2p_2) + O_2 = HgO + O$; for at least seven molecules of ozone were obtained per atom of mercury used. This estimate is simply the ratio of the partial pressure of the ozone to the vapor pressure of mercury, 0.0013 mm. at 20°. If the oxygen was not saturated with mercury vapor, this estimate is too low; moreover, the computed ratio is too low because both photochemical decomposition of ozone, and oxidation of mercury by ozone were neglected.

The simplest hypothesis seems to be that the second step is a collision between a mercury atom in the $2p_2$ state and an oxygen molecule, resulting in reversion of the mercury atom to the normal state and either dissociation of the oxygen molecule or production of an excited oxygen molecule. Ozone is then produced by reaction of the dissociated or excited oxygen with normal oxygen. If the collision results in dissociated oxygen the heat of dissociation of oxygen must be less than about 112,300 calories per mol, since this corresponds to the energy of the quantum λ 2537 Å. But if an excited oxygen molecule O_2' is the intermediary and ozone is produced by the reactions $O_2' + O_2 = O_3 + O$ and $O_2 + O = O_3$, then taking the heat of formation of O_3 from $\frac{3}{2} O_2$ as 34,000 calories absorbed,[6] it readily follows that the heat of dissociation of oxygen must be less than about 156,600 calories. In these calculations the kinetic energies of the colliding molecules have been neglected. Either of these results is in disagreement with the calculated value of Eucken[7] (more than 400,000 calories), but not with that of Wulf[8] (between 56,400 and 137,400 calories). It is, however, difficult rigorously to exclude possible mechanisms involving either multiple absorptions of radiation or triple collisions.

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Summary.—It has been shown that the photochemical formation of ozone in oxygen at atmospheric pressure by radiation from a cooled quartz mercury arc is sensitized by mercury vapor. The experiments show that activated mercury atoms can give up energy of activation to oxygen molecules instead of simply reacting with them to form oxide.

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[1] Dickinson, *Proc. Nat. Acad. Sci.*, **10,** 409 (1924).

[2] Regener, *Ann. Physik.* [4], **20,** 1033 (1906).

[3] Wartenberg and Podjaski, *Zeit. anorg. allg. Chem.*, **148,** 392 (1925).

[4] Williamson (*Physic. Rev.*, **21,** 110, 1923), using a tartaric acid solution composed of 64 parts of water to 1 of saturated solution in an absorption cell 3.2 cm. in length, found no transmission below 2450 Å. Using a 3 mm. layer of 1.7% solution we found with a quartz spectrograph no transmission below 2340 Å. Moreover, through even a 0.17% solution, we obtained no unsensitized ozone formation.

[5] Kailan, *Monatshefte Chem.*, **34,** 1209 (1913).

[6] Lewis and Randall, *Thermodynamics*, McGraw-Hill Book Co., **1922,** p. 476.

[7] Eucken, *Ann. Chem.*, **440,** 111 (1924).

[8] Wulf, *J. Amer. Chem. Soc.*, **47,** 1944 (1925).

DIFFUSION OF ELECTRONS

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In order to calculate the efficiency of resonance it is necessary to know the average number of impacts Z that an electron makes in traversing a layer of gas when there is no field. The calculation of the quantity Z is given in this paper.

Method I.—Consider an element of area df in the xy plane located at the origin of a set of polar coördinates r, θ, ϕ. At a distance r from the origin there is a volume-element dV. In polar coördinates the element $dV = r^2 \sin \theta d\theta d\phi dr$. θ is the angle between the radius vector r and the z-axis. ϕ is the angle between the x, z plane and the plane containing r and z. If ρ is the number of electrons in unit-volume and N is the number of electrons that pass through a square centimeter per second, *more* in the positive than in the negative direction, then the number of such electrons that pass through the element of area df per second is [1,2]

$$Ndf = \int \frac{\rho v}{\lambda} e^{-\frac{s}{\lambda}} dVd\,\omega \qquad (1)$$

where v is the constant velocity of the electrons, λ is their mean free path and $d\omega$ is the solid angle subtended by df at dV. The integration is taken with respect to the total volume V. If no electric field acts then s is the radius vector r; otherwise it is the length of the parabolic path of the electrons between df and dV.

The solid angle $d\omega$ is the fraction of the surface $4\pi r^2$ which the element df subtends at dV.

$$d\omega = \frac{df \cos \theta}{4\pi r^2}.$$