pounds involved in this reaction and of other unstable molecules under sound radiation of various frequencies will at once be undertaken. In this field, as well as in several others which we can only suggest in so cursory a survey of the chemical phenomena produced by high frequency sound waves, we hope to obtain further information in the near future.

Summary

It has been demonstrated that intense high frequency compressional waves produce certain chemical effects, especially discharging metastable systems of great sensibility. They furthermore expel gases from liquids, cause ebullition in pure liquids at temperatures considerably below their boiling points at atmospheric pressure, and accelerate certain chemical reactions. The conditions of intensity and frequency affecting these phenomena have been considered. The reasons for this action are discussed, tentative explanations for various anomalous effects being advanced.

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[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO]

PHOTOCHEMICAL STUDIES. VI. THE PHOTOCHEMICAL REACTION BETWEEN OXYGEN AND MERCURY VAPOR AT RELATIVELY LOW PRESSURES

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The fundamental researches of Cario and Franck,[1] which showed that active hydrogen is produced by the illumination of a mixture of hydrogen and mercury vapor with the resonance radiation of mercury, have led to many interesting results in photochemical work. Nearly all of the reactions studied have involved hydrogen or molecules containing hydrogen atoms.

Dickinson and Sherrill[2] have shown that ozone is formed when a mixture of oxygen and mercury vapor is exposed to the resonance radiation of mercury in a dynamic system. They also observed the formation of a brown deposit which they assumed to be mercuric oxide. It is difficult to make determinations of the quantum efficiencies of reactions involving the resonance radiation of mercury due to the exceedingly small width of the absorption line of mercury vapor at 253.7mμ, but Dickinson and Sherrill showed that at least seven molecules of ozone were produced per mercury atom passing through the reaction vessel.

The present work was started with the object of ascertaining whether

[1] Cario and Franck, *Z. Physik*, **11**, 161 (1922).

[2] Dickinson and Sherrill, *Proc. Nat. Acad. Sci.*, **12**, 175 (1926).

mercuric oxide is formed as a primary process in the reaction between oxygen molecules and excited mercury. The results to be reported conflict in no way with the findings of Dickinson and Sherrill and will, it is hoped, throw some light on the mechanism of the pressure decrease accompanying the photochemical reaction of oxygen with mercury vapor.

I. Experimental Procedure and Results

The oxygen used in these experiments was prepared by heating solid potassium permanganate. It was dried by standing over phosphorus pentoxide.

No stopcocks were used in the main apparatus. The only source of impurity of this sort would be the wax used to attach the window to the reaction vessel. In most of the experiments a special vacuum wax was used. The edge of the vessel was well ground and the windows were plane so that relatively little surface of wax was exposed. In order to obtain evidence as to the possible effect of the wax, sealing wax was used in part of the experiments with no noticeable change in results.

Previous to making a run the vacuum system was always evacuated for several hours with continual flaming of all parts except the reaction vessel proper. Due to the wax the reaction vessel could not be heated.

The window was of plane, transparent, crystalline quartz. To eliminate the short wave lengths two different varieties of special glass were used. The first of these showed no transmission below 245 mμ when photographed with a quartz spectrograph, even with a relatively long exposure. The transmission of this glass was obtained with the use of the quartz spectrograph and rotating sector. It showed approximately 50% transmission at 253 mμ. The second glass showed faint transmission as far as 230 mμ and a somewhat greater transmission than the other variety at 253 mμ. In addition it showed only extremely faint transmission in the visible spectrum for wave lengths longer than 440 mμ. Both of these glasses eliminated those wave lengths which cause direct, unsensitized ozone formation and in addition the second of the two absorbed most of those radiations in the visible spectrum which cause ozone decomposition.[3]

The quartz mercury arc lamp was made in the laboratory. The arc played in a tube about 5 mm. in diameter. In most of the experiments the arc was operated under water. One series of experiments was made with the warm arc. However, the reversal of the 253.7 mμ line is not complete in an arc of this type and, moreover, the general characteristics of the spectrum changed when the arc was allowed to warm up, so that in the final runs partial reversal of the resonance radiation was obtained in two different manners: (1) by interposing a cylinder open to the air at both ends, but containing a ring of liquid mercury at the lower end; (2) the apparatus shown in Fig. 1 was adopted in most of the runs. The reaction vessel is represented by D. A is a quartz window about 3.5 cm. in diameter while B is a second quartz window about 3.0 cm. in diameter. C is connected to the McLeod gage and to the vacuum pumps. E is connected to the vacuum pumps through the trap F. The trap could be isolated from the main apparatus by means of a mercury cut-off. The quartz mercury arc lamp was placed below A and the level of water is shown by the dotted line.

It is difficult to make an exact estimate of the extent to which the intensity of the 253.7 mμ is reduced by the method used. Wood[4] has stated that mercury vapor at room temperature (which he gives as 22°) reduces the intensity of the resonance radiation of mercury by 50% in a distance of 5 mm. He states that a simple exponential

[3] Griffith and Shutt, *J. Chem. Soc.*, **119**, 1948 (1922).

[4] Wood, *Phil. Mag.*, **23**, 689 (1912); *Physik. Z.*, **13**, 353 (1912). The recent work of Hughes and Thomas [*Phys. Rev.*, **30**, 466 (1927)] agrees approximately with this work.

law is not exactly followed, but that it may be used approximately for thicknesses of mercury vapor up to one or two centimeters. This absorption line of mercury vapor should be broadened by the presence of foreign gases. However, the oxygen used in these experiments was at sufficiently low pressure so that little effect of this sort would be noticed. Nevertheless a few runs were made in which nitrogen at a pressure of six or seven centimeters was admitted to the absorption cell E. Theoretically this addition of nitrogen should produce a slight effect, but this seemed to be less than the experimental error. The thickness of mercury vapor traversed by the radiation was about 2.1 cm. The temperatures used in these experiments were slightly higher than 22°, but if calculations based on the above figures are made the intensity of the resonance radiation of mercury should be reduced by 90 to 95% by the arrangement described. When reversal of the resonance radiation was not desired the trap F was immersed in liquid air.

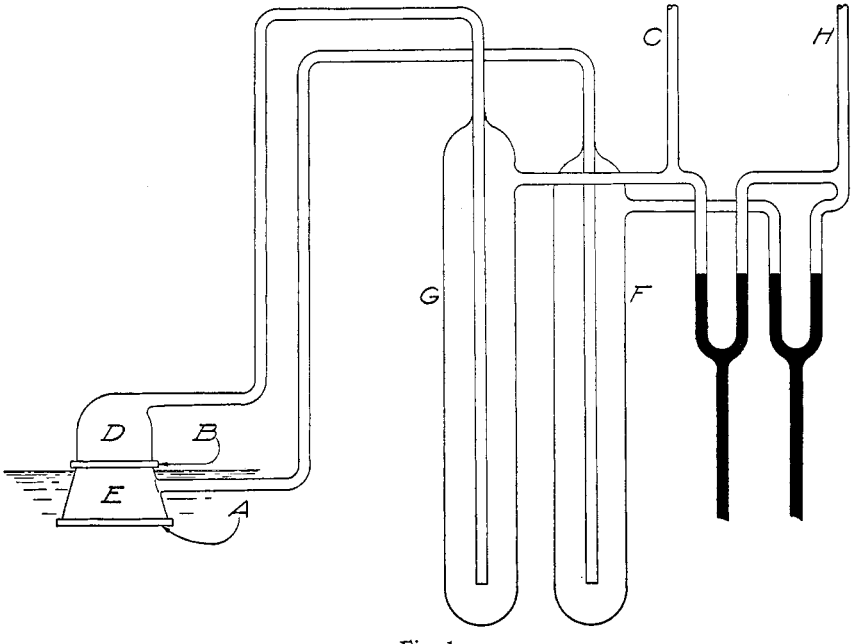

Fig. 1.

Liquid mercury in the reaction system was about a meter distant from the reaction vessel. The vapor pressure of the mercury was that at room temperature in most of the experiments. In a few of the experiments it was lowered by immersing the trap G in an ice-water mixture.

Exact calculations based on pressure change are impossible due to the fact that the quartz window became covered with a film. This film when dissolved in nitric acid showed characteristic tests for mercury with hydrogen sulfide and with a copper wire. Since the mercuric oxide was deposited on the window and on the walls for a distance of 1.0 to 1.5 cm. from the window, this is evidence that the resonance radiation of mercury is important.

With the experimental devices described, it was possible to carry out the following series of experiments.

A. The reaction between mercury vapor and oxygen in the presence of radiation from the cooled mercury arc, that is, with radiation which causes direct ozone formation and the resonance radiation of mercury both present.

B. In the presence of radiation from the cooled mercury arc with the exception of radiation which causes direct (unsensitized) ozone formation.

C. In the presence of radiation from the cooled mercury arc with the exception of the resonance radiation which was partially reversed.

D. In the presence of radiation from the cooled mercury arc with the exception of the resonance radiation of mercury which was partially reversed and the radiation which causes direct ozone formation.

The following tables show various examples of the data obtained. Due to the fact that the mercuric oxide film caused a gradual decrease in the intensity of the radiation, only those values listed together should be compared.

TABLE I

EFFECT OF MERCURIC OXIDE FILM ON REACTION RATE

Time, min.	Pressure of oxygen, mm.	dp/dt, mm./min. $\times 10^4$	Experimental conditions
0–100	0.1986–0.1834	1.52	Full radiation from cooled mercury arc
150–200	.1768– .1703	1.30	
300–350	.1602– .1562	0.80	
500–550	.1468– .1438	.60	
1000–1100	.1248– .1230	.18	

TABLE II

EFFECT OF ELIMINATING SHORT WAVE LENGTHS AND OF PARTIAL REVERSAL OF THE RESONANCE RADIATION

Time interval, min.	Pressure of oxygen, mm.	dp/dt, mm./min. $\times 10^4$	Experimental conditions
136	0.2226–0.2196	0.221	Full radiation
685	.2196– .2192	.006	Without wave lengths shorter than 245 mμ
205	.2192– .2161	.151	Full radiation
365	.2161– .2159	.005	Without wave lengths shorter than 230 mμ and visible radiation
60	.2159– .2146	.217	Full radiation
645	.2146– .2119	.0419	Full radiation except with partial reversal of 253.7 mμ
650	.2119– .2049	.108	Full radiation
800	.2049– .2025	.030	Full radiation except with partial reversal of 253.7 mμ
120	.2105– .2105	.00	Full radiation from warm arc without wave lengths shorter than 245 mμ

The data given in the tables are examples chosen from a large number of runs. The effect of eliminating the short wave lengths is practically to stop the reaction, in many cases the change in pressure being less than the experimental error. As the average of a large number of determinations, it is found that the reaction rate with the short wave lengths absent is about 3% of the reaction rate with the full mercury arc. The results with partial reversal of the resonance line are somewhat less constant, but the average of a large number of determinations shows that the reversal of the resonance radiation reduces the reaction rate to approximately 25% of the rate obtained with the full mercury arc.

II. Discussion of Results and Conclusions

We may summarize the results obtained in the following table if the reaction rate with radiation from the full cooled mercury arc is taken as 100 and the intensity of each part of the spectrum is expressed in per cent. of radiation from the cooled mercury arc.

TABLE III

SUMMARY OF RESULTS

Approximate intensity of resonance radiation, %	Approximate intensity of short wave lengths, %	Relative reaction rates
100	100	100
50	0	3
10	100	25
10	0	0

The ionization potential of mercury vapor is 10.4 volts, while the resonance potential is 4.9 volts. The ionization potential of excited mercury vapor should be 5.5 volts. If the formation of mercuric oxide involves the transfer of electrons from the mercury to the oxygen, the reaction between excited mercury and normal oxygen should take place if molecular oxygen has an electron affinity of the proper magnitude. The work of Gibson and Noyes[5] indicates that molecular oxygen does not have a pronounced tendency to pick up electrons. That the reaction between excited mercury and normal oxygen to form mercuric oxide is not appreciable is indicated by the above results.

The results described indicate fairly definitely that the reduction in pressure in the system is to be ascribed to a reaction between mercury vapor and ozone. Ozone may be formed in the system by two methods, viz., by the direct unsensitized reaction and by the action of excited mercury and oxygen as indicated by Dickinson and Sherrill.[2] However, the quantity of ozone present in a static system when a mixture of mercury vapor and oxygen is illuminated with the resonance radiation of mercury must be exceedingly small since the reaction rate is practically zero under these conditions.

[5] Gibson and Noyes, THIS JOURNAL, **43**, 1255 (1921).

At a first glance it might seem that the reaction is largely between excited mercury and ozone. A simple calculation based on kinetic theory shows that the average time between collisions of a mercury atom with oxygen is of the order of 10^{-6} second. Since the duration of mercury in the excited state is of the order of 10^{-7} second[6] and the pressure of ozone in the system is certainly small compared to the pressure of the oxygen, it would appear that collisions between excited mercury and ozone would be exceedingly rare. It might be possible to avoid this difficulty by postulating an intermediate complex of some sort with relatively long life, or by ascribing a large diameter to excited mercury atoms. The latter assumption would necessitate the additional assumption of low efficiency of collision between excited mercury and oxygen.

It is possible to show that, if the short wave lengths and the 253.7 mμ line act independently and the effects of the two types of radiation are additive, the reaction rate due to resonance radiation must be proportional to about the fourth power of its intensity. This is an unreasonable value. It seems necessary to conclude, therefore, that there is some interaction between the products formed by the radiation of short wave length and the products formed by the action of the resonance radiation. It can be shown that the reaction between excited mercury and ozone to produce mercuric oxide and two atoms of monatomic oxygen is thermodynamically possible. The result of this reaction would be to increase the rate of formation of ozone in the system.

Dickinson and Sherrill[2] consider that activated oxygen molecules (or perhaps monatomic oxygen) may be formed by the interaction of excited mercury with oxygen. It is probable that the action of the short wave lengths is to produce activated oxygen molecules which may dissociate upon collision.[7] It does not seem possible at the present time to ascertain whether these two types of activated molecules would be at all similar. Since the heat of dissociation of oxygen is now considered to be approximately 160,000 calories per mole, active mercury atoms would only be able to dissociate oxygen under exceptional circumstances due to a deficiency of some 45,000 calories per mole in energy content. However, it may not be unreasonable to expect a temporary combination of the nature of a mercury peroxide, for oxygen is paramagnetic, a fact which has led Lewis to conclude that the structure of the oxygen molecule may be represented by the formula $:\dot{\underset{\cdot\cdot}{O}}:\dot{\underset{\cdot\cdot}{O}}:$.[8] This sort of compound would in all probability

[6] See Tolman, "Statistical Mechanics with Applications to Physics and Chemistry," The Chemical Catalog Company, New York, **1927**, p. 176–177.

[7] See Franck, *Trans. Faraday Soc.*, **21**, 536 (1926); Birge and Sponer, *Phys. Rev.*, **28**, 259 (1926). This applies, of course, to those wave lengths longer than the region of continuous absorption (below 175 mμ).

[8] Lewis, *Chemical Reviews*, **1**, 231 (1924); THIS JOURNAL, **46**, 2027 (1924).

be analogous to such unstable compounds as Hg_2 and Na_2, which Franck[7] considers to be formed only when one of the atoms entering into combination is in the excited state. If the formation of such a complex is postulated, ozone may result upon collision of the complex with oxygen, or perhaps a larger amount of ozone upon collision of the complex with an activated oxygen or an ozone molecule. This would offer an explanation of the results herein reported. It is not possible, however, to draw such conclusions with entire certainty, as other conclusions may appear more plausible to various workers in this field. Lind and his co-workers[9] have, however, used the ionic cluster in the explanation of reactions produced by alpha particles.

The possible effect of the mercury line at 184.9 mμ has been neglected in this discussion. The intensity of this line should be negligible in the apparatus described.

The results reported in the present article do not conflict in any way with the findings of Dickinson and Sherrill,[2] but offer a possible explanation of the relatively large amount of ozone found by them. Unless it is assumed that each mercury atom passed through several complete cycles resulting in ozone formation while traversing their reaction vessel, it is necessary to find some means to explain the formation of at least seven molecules of ozone per mercury atom in their experiments. The above explanation, while somewhat artificial, would indicate that several molecules of ozone might be formed by the action of the unstable complex with excited oxygen or ozone.

Summary

1. The photochemical reaction between oxygen and mercury vapor is found to be due largely to the reaction between ozone and mercury vapor.

2. It is not possible to explain the phenomena observed by assuming that ozone is formed by both the sensitized and unsensitized reactions and that the effects are additive. It is suggested, therefore, that a complex (relatively unstable) may be formed between excited mercury and oxygen and that this complex may give ozone through collision with oxygen molecules, or perhaps a larger amount of ozone through collision with activated oxygen or ozone molecules.

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[9] See, for example, Lind and Bardwell, THIS JOURNAL, **48**, 2335 (1926).