combustion of hydrogen and oxygen from commercial cylinders show: (1) that the proportions in which the gases are brought together for reaction results in no significant change in the isotopic composition of either hydrogen or oxygen if the combustion occurs in a flame.

(2) That changes of isotopic composition sufficient to affect the density of the resulting water by several parts per million may occur if the combination takes place on a platinum catalyst. With oxygen in excess the density of the resulting water may be low and appears to be accounted for by lower reaction velocities of oxygen molecules containing the heavier isotopes. With hydrogen in excess the resulting water was found, under certain conditions, to be high in density. This appears to be the consequence of an incomplete exchange reaction between steam and the excess hydrogen.

An exchange reaction between steam and molecular oxygen does not appear to be significantly catalyzed by platinum at 300°.

Previous data[1] corrected for the hydrogen exchange are in quantitative agreement with Dole's discovery[10] that water produced from hydrogen and atmospheric oxygen is denser by about 6 parts per million than water produced by combination of the same hydrogen with oxygen obtained from normal water.

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[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF STANFORD UNIVERSITY]

Kinetics of the Vapor Phase Reaction of Mercury and Halogens

BY RICHARD A. OGG, JR., HENRY C. MARTIN AND PHILIP A. LEIGHTON

There appears to have been but little study of the familiar combination of mercury with halogens. In particular, no evidence has as yet been adduced to show that such a reaction can take place other than at the surface of liquid mercury. It is desired to report the preliminary results demonstrating the occurrence of a rapid vapor phase combination of mercury and bromine and to discuss the kinetics of this process.

The method previously described[1] for demonstrating visually the evaporation of mercury was extended to observe qualitatively the reaction of mercury vapor with halogens. A dish of warm liquid mercury was interposed between a mercury "resonance" lamp and a fluorescent screen. The ascending vapor was manifested as a dark shadow on the screen. Introduction of a small dish containing liquid bromine or warm iodine crystals into the space above the liquid mercury caused the shadows to vanish, only to reappear after removal of the halogen.

Estimates of the rate of the mercury–bromine reaction were made by an adaptation of the "diffusion flame" method employed by Frommer and Polanyi[2] in their studies of sodium vapor reactions. Mercury vapor (at a known partial pressure of some 0.01 to 0.1 mm.) carried in dry air at atmospheric pressure was allowed to flow through a nozzle into a reaction cell filled with air at atmospheric pressure and bromine vapor at a partial pressure of some 10 to 40 mm. The reaction zone was maintained at approximately 110°.

Quartz windows allowed a beam of light from a mercury "resonance" lamp to traverse the reaction zone and by means of quartz lenses an image of the nozzle and surrounding region was cast upon a fluorescent screen. With suitable rates of flow (a linear nozzle velocity of about 1 cc./sec.) the reaction "flame" was observed as a circular shadow projecting from the nozzle image. Visual estimation was made of the light absorption in various parts of the "flame," and compared with that in blank experiments in which air containing mercury vapor at various known concentrations was allowed to flow into the bromine-free cell. In this manner a rough estimate could be made of the total number of mercury atoms present in the mercury–bromine "flame." The reciprocal of the mean life of the mercury atoms in the "flame" divided by the bromine concentration yields the bimolecular velocity constant.

The mercury–bromine reaction appeared to be one of the first order with respect to each reactant. Upper and lower limits for the velocity constant under the above conditions were estimated as

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[1] P. A. Leighton and W. G. Leighton, *J. Chem. Education*, **12**, 139 (1935).

[2] L. Frommer and M. Polanyi, *Trans. Faraday Soc.*, **30**, 519 (1934).

10^7(mole/cc.)$^{-1}$ sec.$^{-1}$ and 10^5 (mole/cc.)$^{-1}$sec.$^{-1}$, respectively. Experiments were also made on the temperature coefficient. The temperature of the reaction cell was rapidly lowered from 120 to 50°, other conditions (rate of flow, concentrations of reactants) being maintained constant. No appreciable change could be observed in the size of the "flame" shadow. This result allows a conservative estimate of some 5 kcal. as the upper limit of the activation energy, and it may well be zero. A few experiments with mercury–iodine "flames" indicated the rate to be essentially the same as that of the mercury–bromine reaction. The reaction products were mercuric bromide and iodide, respectively.

These preliminary results allow decision between the only two plausible mechanisms for the mercury–bromine reaction. The first mechanism embodies two consecutive metatheses, of which the first would be rate determining.

$$Hg + Br_2 \longrightarrow HgBr + Br \qquad (1)$$
$$HgBr + Br_2 \longrightarrow HgBr_2 + Br \qquad (2)$$

The second mechanism involves only an association.

$$Hg + Br_2 \longrightarrow HgBr_2 \qquad (3)$$

The heat of dissociation of HgBr is given by Sponer[3] as 25.4 kcal. per mole. Using the accepted value of 45.2 kcal. per mole for the heat of dissociation of bromine, reaction (1) is seen to be endothermic by 19.8 kcal. Hence the corresponding activation energy would be at least this great. Experimentally the observed activation energy is nearly zero. Further, a bimolecular reaction having a normal collision rate [10^{14} (mole/cc.)$^{-1}$sec.$^{-1}$] and an activation energy of 19.8 kcal. would have at 110° a rate constant of only some 10^3(mole/cc.)$^{-1}$sec.$^{-1}$—a value much smaller than the lower limit estimated for the experimental value. Hence it may be concluded that the mechanism involving reactions (1) and (2) plays no appreciable role, and that the observed mercury–bromine reaction is due to the association reaction (3). Exactly similar considerations obtain for the mercury–iodine reaction.

An association reaction such as (3) may be slower than the collision rate for three reasons: (a) activation energy may be required; (b) there may be "steric hindrance"; (c) triple collision with a third body (in this case an oxygen or nitrogen molecule) may be necessary. Were the slowness of the observed mercury–bromine reaction due only to factor (a), the activation energy would be from 12 to 15 kcal., corresponding, respectively, to the upper and lower limits of the velocity constants. The extreme smallness of the observed activation energy leads to the conclusion that the second and third factors are more important.

As an approximate estimate of the rate of triple collision the rate constant for the recombination of bromine atoms in the presence of a third body may be chosen. For a considerable number of different molecules this constant has a value[4] of approximately 10^{15}(mole/cc.)$^{-2}$sec.$^{-1}$. At 110° and atmospheric pressure the concentration of air molecules is some 4×10^{-5}(mole/cc.). Hence if reaction (3) occurred at every triple collision the apparent bimolecular velocity constant would be some 4×10^{10}(mole/cc.)$^{-1}$sec.$^{-1}$. Since this value is over a thousand-fold greater than the estimated upper limit of the velocity constant for the mercury–bromine reaction, it is entirely consistent to assume that the association reaction (3) occurs only on collision with a third body. Theoretical considerations[5] indicate that association reactions which form a triatomic molecule should require triple collisions. The design of the apparatus was not such as to allow experimental test of the above conclusion by studying the dependence of the mercury–bromine reaction upon the concentration of inert gas. In future study of the reaction it is planned to make this test.

Assuming the mercury–bromine reaction to be a three-body process, it is seen that the efficiency of triple collisions is relatively small. The experimental results do not allow decision as to whether this is due to activation energy or "steric hindrance." Were the activation energy 5 kcal., the calculated rate at 110° would be reduced by a factor of some seven hundred.

It is interesting to compare the above results on the mercury–bromine and mercury–iodine association reactions with the studies of Polanyi[6] on the initiation of hydrogen–chlorine reaction chains by atoms of zinc, cadmium and mercury. At 300° zinc and cadmium atoms were found to initiate chains, presumably by processes analogous to reaction (1) above. The respective velocity constants were estimated as some 10^{10} and

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(3) H. Sponer, *Z. physik. Chem.*, **B11**, 425 (1931).

(4) K. Hilferding and W. Steiner, *ibid.*, **B30**, 399 (1935).

(5) L. S. Kassel, "Kinetics of Homogeneous Gas Reactions," Chemical Catalog Co., New York, 1932.

(6) M. Polanyi, *Trans. Faraday Soc.*, **24**, 606 (1928).

10^9(mole/cc.)$^{-1}$sec.$^{-1}$, respectively. This is not inconsistent with the assumption that zinc and cadmium atoms can combine with chlorine by association processes analogous to reaction (3). Presumably these reactions would also require triple collisions and have rate constants of the same order as those found for mercury–bromine and mercury–iodine association. Hence under the experimental conditions employed by Polanyi (total gas pressures of a few mm.), the bimolecular velocity constants for the zinc–chlorine and cadmium–chlorine association reactions may be estimated as at most some $10^5 - 10^6$(mole/cc.)$^{-1}$-sec.$^{-1}$. This is very much smaller than the experimentally observed velocity constants for the metathetic reactions, and hence the association plays a negligible role. With mercury atoms and chlorine it appears that the reverse situation obtains, since it can be shown that the process analogous to reaction (1) is about equally endothermic for all halogens. This conclusion is in agreement with the observation of Polanyi that mercury atoms do not initiate chains in hydrogen–chlorine mixtures.

Summary

1. It has been shown that mercury atoms enter into a rapid vapor phase reaction with halogens.

2. At 110° and in the presence of air at atmospheric pressure the mercury–bromine reaction appears to be of the first order with respect to each reactant, and the velocity constant lies between 10^7 and 10^5(mole/cc.)$^{-1}$sec.$^{-1}$.

3. The temperature coefficient is very small, an upper limit of 5 kcal. being estimated for the activation energy.

4. It appears that the mercury–bromine reaction must take place as an association process, most probably in triple collisions with molecules of inert gas. The efficiency of triple collisions appears to be relatively small.

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[CONTRIBUTION FROM THE DEPARTMENT OF PHYSICS, ALABAMA POLYTECHNIC INSTITUTE]

Photography of Minima in the Magneto-Optic Apparatus

BY GORDON HUGHES

The work of Allison[1] and others on the magneto-optic apparatus has been called into criticism by several investigators[2–4] due to their inability to operate the magneto-optic apparatus successfully. In the face of the many admitted complexities and difficulties encountered in its use the failure of some might be readily expected. The purpose of this investigation has been to develop a completely objective method for the study of the minima of light intensity in the apparatus and thus demonstrate, beyond doubt if possible, the reality of the minima and the validity of the visual results previously obtained with the apparatus. During the course of this study several photographic methods have been employed with only partial success. Their failure has been due entirely to mechanical difficulties. The method described here is free of these inherent defects and with it consistent positive results have been obtained. This method has been made as completely automatic as possible in an effort to reduce the personal factor to a minimum. Since the results obtained by this photographic method may be interpreted into fairly accurate quantitative measurements, this work has had the added purpose of determining the quality of the minima under varying conditions in an effort to improve them for visual work.

Experimental Technique

Methods have been devised[2–4] for testing the presence of minima by comparing the light through the apparatus with a sample of light brought to one side of the coils and then joined with the main beam. In these methods one is never sure that both beams suffer the same optical conditions at all times. The Wollaston prism was employed in this study since with it there is no doubt that the treatment of both beams is optically identical. That is to say, the intensity ratio of the two beams is independent of variations in the intensity of the incident light. It has the further advantage that its use doubles the absolute intensity change for the effect, on the hypothesis that the effect is a rotation of the plane of polarization of the incident light.

The apparatus was essentially identical with the conventional one used for visual work except for the substitu-

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(1) Allison and Murphy, THIS JOURNAL, **52**, 3796 (1930).

(2) Slack, *J. Franklin Inst.*, **218**, 445 (1934).

(3) McPherson, *Phys. Rev.*, **47**, 310 (1935).

(4) Farwell and Hawkes, *ibid.*, **47**, 78 (1935).