CLIII.—*The Influence of the Intensity of Illumination on the Velocity of the Photochemical Union of Bromine and Hydrogen.*

By MAX BODENSTEIN, WILHELM JOST, and GERHARD JUNG.

BRIERS and CHAPMAN (J., 1928, 1802) recently investigated the influence of light intensity on the photochemical combination of bromine and hydrogen, and concluded that the reaction velocity is proportional to a power of the light intensity which varies between $\frac{1}{2}$ and 1 and is always greater the weaker the light. From their experiments they found that the velocity of disappearance of "the catalyst, excited bromine molecules or bromine atoms," which causes the reaction is given by the sum of a uni- and a bi-molecular reaction

$$-dA/dt = C_1A^2 + C_2A \quad . \quad . \quad . \quad . \quad (1)$$

(A is the concentration of the catalyst) and that its mean life is about 0·063 sec.

The first observation is apparently in contradiction to the measurements of Bodenstein and Lütkemeyer (*Z. physikal. Chem.*, 1925, **114**, 208), who found an exact proportionality between the reaction rate and the square root of the light intensity, and to their theory, that the catalyst, if we are to use this term, is actually bromine atoms. We have carried out a series of further experiments * which undoubtedly clear up these really only apparent discrepancies. According to these experiments, the velocity with which the catalyst disappears can, under certain conditions, be proportional to even the first power of the concentration, and, moreover, the mean life is of the same order of magnitude as in the work of Briers and Chapman.

Bodenstein and Lütkemeyer explained their results by assuming that the velocity of formation of bromine atoms is proportional to the light absorbed and that they are removed by recombination in

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* They will appear shortly as the work of Jost and Jung in the *Zeitschrift für physikalische Chemie.*

the gas phase, the rate of this recombination being assumed to be proportional to the concentration of the atoms.

However, according to the theory (Jeans, "The Dynamical Theory of Gases," 2nd. edtn., 1916, p. 211; Herzfeld, *Z. Physik*, 1921, **8**, 132; Born and Franck, *ibid.*, 1925, **31**, 411) which has been developed in the meanwhile, the recombination of atoms is possible only in three-body collisions; a quasi-molecule, formed by the collision of two atoms, is not stable, but decomposes immediately if it cannot transfer its reaction energy by collision within its life period of *ca.* 10^{-13} sec. This means that the recombination of two atoms to form a diatomic molecule is a *termolecular* reaction. The velocity is dependent, not only on the concentration of the atoms, but also on the total pressure (the concentration of all the gases present). This leads to the following reaction mechanism for the formation of hydrogen bromide in light :

(1) $Br_2 + h\nu = 2Br$, velocity $= 2I_{abs.}$;
(2) $Br + H_2 = HBr + H$, vel. coeff. k_2;
(3) $H + Br_2 = HBr + Br$, vel. coeff. k_3;
(4) $H + HBr = H_2 + Br$, vel. coeff. k_4;
(6) $Br + Br = Br_2'$, vel. coeff. k_6;
(8) $Br_2' = Br + Br$, vel. coeff. k_8;
(9) $Br_2' + N = Br_2 + N'$, vel. coeff. k_9;

where Br_2' is the quasi-molecule and N any molecule at all. Instead of equations (6)—(9), Bodenstein and Lütkemeyer have simply (6) $Br + Br = Br_2$, which is not admissible according to our present ideas of molecule formation. The concentration of the molecules N which occurs in equation (9) is proportional to the total pressure at constant temperature—we may avoid considering the specific factors of individual gases in this case—and therefore we introduce this pressure in the following equations for the sake of convenience.

From the foregoing mechanism the following velocity equation is obtained (by a small approximation which is permissible if the pressure is not too high):

$$\frac{d\,[\mathrm{HBr}]}{dt} = \frac{2k_2[\mathrm{H}_2]\cdot\sqrt{I_{\mathrm{abs}}\cdot\dfrac{k_8}{k_6k_9p}}}{1+\dfrac{k_4[\mathrm{HBr}]}{k_3[\mathrm{Br}_2]}} \quad . \quad . \quad . \quad (2)$$

This equation differs from that obtained experimentally by Bodenstein and Lütkemeyer only by the factor $\sqrt{k_8/k_9p}$ which indicates a dependence upon the total pressure; and this dependence has been studied in our work.

At first a very large flask was used, from which samples of gas could be taken for analysis. In order to obtain intensive illumination the vessel was made in the shape of a ring (cross section

10 × 30 cm.; capacity 20 litres), and a lamp of 1-kw. capacity with a perpendicular spiral filament was placed within the ring. The apparatus was placed in an aluminium thermostat at 195°, and the reaction was measured over a pressure range of 4—400 mm. of mercury.

The factor $\sqrt{k_8/k_9p}$ thus underwent a ten-fold increase between the highest and the lowest pressure, the velocity rising in the same manner. However, it was impossible to measure the intensity of the absorbed light in these experiments; furthermore, there arose considerations against the use of white light, because in the meantime the analysis of the absorption spectra of the halogens (Franck, *Trans. Faraday Soc.*, 1925, **21**, 3; Franck, Kuhn, and Roleffson, *Z. Physik*, 1922, **43**, 155) had shown that in the case of bromine a direct decomposition into atoms occurs at $\lambda > 5107$ Å.; and at lower wave-lengths, on the other hand, excited bromine molecules are formed, which decompose only on collision with other molecules, when this collision follows soon enough afterwards. Hence it became necessary to work with monochromatic light, of which the absorbed intensity could be measured. In this way in preliminary experiments it was shown that the wave-length has no influence: at the pressures employed, all excited bromine molecules decompose into atoms (Jost, *Z. physikal. Chem.*, 1928, **134**, 92).

For the main experiments the following method was used. The reaction vessel of quartz (2 × 4 × 40 cm.) was illuminated through its 4 × 40 cm. surface, and the concentration of bromine, and hence the progress of the reaction, was followed by measuring with a spectrophotometer a beam of light passing down its long axis. Heating, as before, was by means of an aluminium thermostat. In this arrangement the light intensity and the thickness of the reaction vessel were appreciably smaller than in the preliminary work—this is of importance for what follows.

The results now showed a large fall in reaction velocity with decreasing pressure, quite different from the results described above and from what was to be expected from equation (2).

The explanation of this phenomenon is that at low pressures and in a narrow vessel the bromine atoms, especially at low concentrations, *e.g.*, with weak illumination, are eliminated not so much by recombination in the gas phase, but rather by diffusion to the walls, where they are adsorbed and recombine. In the same way the completely analogous observation in our work on the photochemical formation of carbonyl chloride has been explained (Bodenstein, Lenher, and Wagner, *Z. physikal. Chem.*, in course of publication). It can be shown that the reaction velocity " constants," which are calculated from equation (2) and are of course no longer constant if the wall plays a part, are only a function of a magnitude

$$\pi = \text{const.}\ \sqrt{I_{\text{abs.}}}\ p/D \quad . \quad . \quad . \quad . \quad . \quad (3)$$

(D is the diffusion constant of bromine atoms). The course of this function can be calculated, partly exactly and partly by approximation, and the observed values agree very well. It follows at once that in the case of the large reaction vessel the wall must be of no importance, because of the large light intensity and the dimensions of the vessel.

Accordingly, we can see that bromine atoms in illuminated bromine are used up in two processes :

(1) Recombination by three-body collisions in the gas phase, the velocity of which is derived from equations (6), (8), and (9) :

$$- d[\text{Br}]/dt = [\text{Br}]^2 k_6 k_9 p/k_8\,{}^{*} \quad . \quad . \quad . \quad . \quad (4)$$

$= C_1[\text{Br}]^2$ at constant total pressure.

The constants can be calculated by combining the measurements of the light reaction with those of the dark reaction (see Bodenstein and Lütkemeyer, *loc. cit.*; Jung and Jost, *loc. cit.*).

(2) Recombination through diffusion to the walls, where they are absorbed until they combine, which process can be shown to be unimolecular at constant total pressure :

$$- d[\text{Br}]/dt = C_2[\text{Br}] \quad . \quad . \quad . \quad . \quad . \quad (5)$$

By superimposing both processes, one obtains the equation for the decrease in bromine atom concentration

$$- d[\text{Br}]/dt = C_1[\text{Br}]^2 + C_2[\text{Br}] \quad . \quad . \quad . \quad . \quad (6)$$

which is identical with the one found by Briers and Chapman. It can readily be seen that C_1 and C_2 are dependent on the pressure, C_1 being directly proportional and C_2 inversely proportional to it. If Briers and Chapman had varied the ratio of their gases and the total pressure, they would certainly have found this influence of pressure.

Finally, we will calculate the actual value of the velocity coefficients and the mean life of the atoms from our measurements as found by Briers and Chapman. An uncertainty affects these calculations from the fact that these authors did not measure the light intensity and gave no data on the observed degree of combination. We may, however, assume that this amounted to 10—30% of the bromine present and so, by comparison with Lütkemeyer's measurements, we can obtain the missing values.

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* Again we neglect a second-order term.

For $k_6 k_9 p / k_8 = C_1$ we get from our own measurements at those pressures at which Briers and Chapman worked :

$$C_1 = 1{\cdot}55 \times 10^{11}.$$

In order to obtain good values for the mean life, τ_1, if the recombination occurs solely in the gas phase, we must know the concentration of the atoms, and we obtain an approximate value as follows : Lütkemeyer found a combination of the bromine present of 10—30% in about 10—20 minutes. The amount which Chapman observed and which ought to have been of the same order of magnitude was reached in *ca.* 100 minutes of uninterrupted illumination. Therefore their velocity was approximately 5—10 times smaller than Lütkemeyer's. Chapman and Briers worked at 191° (the b. p. of dimethylaniline) and Lütkemeyer at 218°. This difference of temperature gives rise to a factor 3. The ratio thus corrected is due to the difference in concentration of the bromine atoms. Thus this amounts, in the case of Chapman to about $\frac{3}{5}$—$\frac{3}{10}$ of that of Bodenstein and Lütkemeyer, where it is equal to $5{\cdot}5 \times 10^{-11}$ mole of bromine atoms per c.c. So in Chapman's work this is from $3{\cdot}3 \times 10^{-11}$ to $1{\cdot}65 \times 10^{-11}$ mole/c.c. A quite similar value is obtained also if the data of Chapman and Briers on the lamp and optical arrangement, and so the energy absorbed, be taken into account, and the concentration of atoms calculated. Thus the mean life will be

$$\tau_1 = \frac{1}{C_1 A} = \frac{1}{C_1[\mathrm{Br}]} \sim \frac{1}{1{\cdot}55 \times 10^{11} \times (1{\cdot}65 \text{ to } 3{\cdot}3) \times 10^{-11}}$$

or

$$\tau_1 \sim 0{\cdot}4 \text{ to } 0{\cdot}2 \text{ sec.}$$

If now τ_2 corresponds approximately to the time which is necessary for a bromine atom to diffuse from within the flask to the walls, then the average distance from the walls being about 1 cm., and the diffusion constant of bromine atoms being of the order of magnitude of 1 cm.^{2} sec.$^{-1}$, we have

$$\tau_1 \sim \frac{(\Delta x)^2}{2D} \sim 0{\cdot}5 \text{ sec.}$$

τ_2 would be still smaller if convection were taken into account. Thus for $A = 1$ *

$$C_1 : C_2 = 1/\tau_1 : 1/\tau_2 \sim (2{\cdot}5 \text{ to } 5) : 2$$

while Briers and Chapman (using the notation k_1 and k_2, which we have used in another sense) found

$$C_1 : C_2 = 0{\cdot}63 : 0{\cdot}37 \sim 3{\cdot}4 : 2$$

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* The mean life is defined according to Briers and Chapman by $A = 1$ (in their units).

Thus we obtain a good agreement. For the mean life, from $1/\tau = 1/\tau_1 + 1/\tau_2$, we have $\tau = 0{\cdot}14$—$0{\cdot}22$ sec., which, in view of the uncertainty of some of the underlying data, is in satisfactory agreement with the value found by Briers and Chapman, *viz.*, $\tau = 0{\cdot}063$ sec.

Our work agrees, then, with that of Briers and Chapman as well as the accuracy of the underlying data will permit. Furthermore, it leads distinctly to the fact that all measurements and theory must be based on bromine atoms and not on the excited molecules. That the thermal reaction between hydrogen and bromine to form hydrogen bromide goes through bromine atoms was shown independently by Christiansen (*Dansk. Vid. Math. Phys. Medd.*, 1919, **1**, 14), Herzfeld (*Z. Elektrochem.*, 1919, **25**, 301; *Ann. Physik*, 1919, **59**, 635), and Pólányi (*Z. Elektrochem.*, 1920, **26**, 50), who arrived at these conclusions from the measurements of Bodenstein and Lind (*Z. physikal. Chem.*, 1906, **57**, 168) on the dark reaction. The investigation of Bodenstein and Lütkemeyer showed, then, the same result for the light reaction, and that is through this work fully verified and extended in the manner described.

A quite analogous theory explains, of course, the work of Chapman and Grigg (J., 1928, 3233) on the influence of the wall on the combination of hydrogen and chlorine in light, though here the lack of numerical data makes the work only of a qualitative nature.

BERLIN, PHYSIKALISCH-CHEMISCHES INSTITUT DER UNIVERSITÄT.
HANNOVER, ELECTROCHEMISCHES INSTITUT DER TECHNISCHEN HOCHSCHULE.
GREIFSWALD, CHEMISCHES UNIVERSITÄTS-LABORATORIUM.

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