CCXXXI.—*The Influence of the Intensity of Illumination on the Velocity of the Photochemical Union of Bromine and Hydrogen, and the Determination of the Mean Life of a Postulated Catalyst.*

By Frank Briers and David Leonard Chapman.

In a previous communication (Briers, Chapman, and Walters, J., 1926, 562) experimental evidence was submitted in support of the contention of Berthoud and Bellenot (*Helv. Chim. Acta*, 1924, **7**, 307) that the rate of photochemical interaction of iodine and potassium oxalate in aqueous solution is proportional to the square root of the intensity of illumination. Formerly, it seemed to be not improbable that all photochemical changes would be found to be strictly proportional to the intensity of the light (*vide* Draper, *Phil. Mag.*, 1843, **23**, 401; M. C. C. Chapman, J., 1923, **123**, 3062; 1924, **125**, 1521; Kornfeld and Müller, *Z. physikal. Chem.*, 1925, **117**, 242), and clearly this must always be the case when the " quantum efficiency " is a true constant. However, Bodenstein and Lütkemeyer (*Z. physikal. Chem.*, 1924, **114**, 208) have recently announced that the rate of union of hydrogen and bromine in the light is proportional to the square root of the energy absorbed when the intensity of the light is kept constant. It is therefore not improbable that the rate of this gaseous reaction is also proportional to the square root of the intensity of the light. We shall show that this assertion of Bodenstein and Lütkemeyer is true without considerable error under suitable conditions. In addition to investigating the dependence of the rate of the change on the intensity of illumination, we have, as in the action of iodine on potassium oxalate, determined the mean life of the postulated catalyst on the concentration of which the rate of the change depends, and the principle of the method employed for this purpose has been the same as that adopted in the case of the other reaction.

EXPERIMENTAL.

The mean life of the catalyst was estimated by determining the hydrogen bromide formed when a mixture of bromine and hydrogen, of constant composition and enclosed in an appropriate actinometer, was exposed to intermittent light of constant intensity in such a manner that the period during which the mixture was in light bore a constant ratio to the period during which it was in darkness. In these circumstances, the amount of chemical change per unit of radiant energy supplied is dependent on the length of the equal short periods of illumination. From the quantitative relation between the frequency of illumination and the chemical change per unit of energy supplied, the mean life of the catalyst can be determined.

FIG. 1.

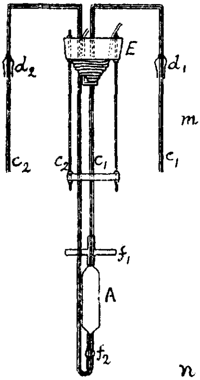
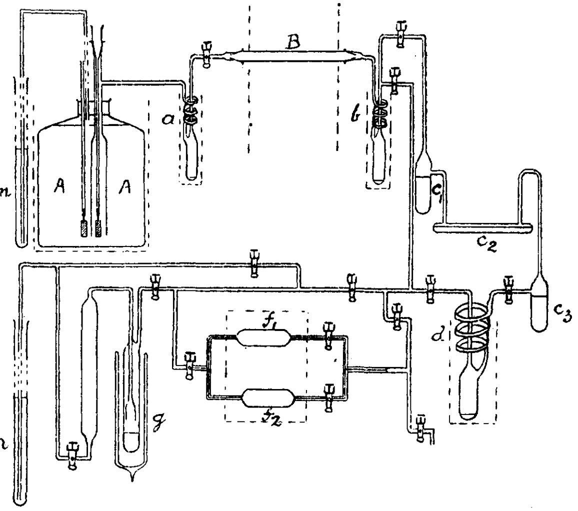


FIG. 2.



The actinometer (Fig. 1) was made from a wide glass tube, A, of 2·20 cm. internal diameter and 8 cm. long. The mixed gases entered the actinometer through the capillary tube, c_1, and escaped through the capillary tube c_2. The ground glass joints at d_1 and d_2 served to connect the actinometer with the apparatus employed to analyse its contents at the end of an experiment. During an exposure of the actinometer to light it was immersed in the vapour of boiling dimethylaniline contained in a wide tube of pyrex glass (not shown in the figure) which was kept in position by the stopper E. The ends of the glass crosses at f_1 and f_2 touched the sides of the pyrex tube and served to keep the actinometer centrally in the same fixed position.

After the actinometer had been filled, its exposure to intermittent light was accomplished in the following manner. The insolation tube was screened by blackened asbestos board so that no light could enter it except that which had passed through sectors cut out of a rotating disc of stout cardboard and through a plate-glass window of the same shape as each of the sectors. The disc was provided with eight equal sectors, each being 8 cm. long and situated at a mean distance of 21 cm. from the centre. The sectors were at equal distances from one another, but the angle subtended by each sector at the centre was changed whenever it was desired to alter the ratio of the periods of darkness and illumination. The pyrex jacket was placed as near as possible to the plate-glass window in such a position that the whole of the mixture in the actinometer was equally illuminated. The source of illumination was a 1000-watt incandescent-filament lamp, placed at a horizontal distance of 30 cm. from the reaction vessel. The light from the lamp passed through an aperture of appropriate shape in a large piece of stout sheet-iron which was placed immediately in front of the lamp, the aperture being of such a size that its penumbra was outside the plate-glass window. The current supplied to the lamp was maintained constant with a rheostat worked by hand, and was recorded by a mirror galvanometer. The rotating disc was placed as near as possible to the plate-glass window. The shadow cast by the edge of a sector was quite sharp, but there was some error, which could neither be avoided nor estimated, occasioned by reflexion from the inner wall of the glass bulb of the lamp. The lamp itself was placed in such a position that its incandescent wire subtended in a plane at right angles to the top edge of the window the minimum angle at a point in the actinometer. The disc was kept in rotation by means of a geared motor, and in some of the experiments in which the rotation was slow, by a clock.

The filling of the actinometer with the mixture of hydrogen and bromine was accomplished with the apparatus shown in Fig. 2. The hydrogen was prepared by the electrolysis of an aqueous solution of baryta contained in the large electrolytic cell, *A*, and was freed from excess of water vapour by passage through a glass worm, *a*, surrounded by water at a temperature 2° below that of the laboratory. The oxygen was removed by passing the gas through a quartz tube, *B*, filled with palladised asbestos and heated to redness, and the water formed was condensed in the worm, *b*, which was kept at the same temperature as *a*. The moist hydrogen then passed slowly over a large surface of pure liquid bromine contained in glass vessels, three of which are shown diagrammatically at c_1, c_2, and c_3. The hydrogen thus saturated with bromine and almost saturated with water vapour then passed through a long glass worm *d* immersed in a thermostat kept at 12°. The issuing hydrogen, which thus contained a constant proportion of water vapour and bromine, streamed through two almost identical actinometers (shown diagrammatically at f_1 and f_2) which, during the filling, were kept at a constant temperature of 25°. The bromine in the escaping hydrogen was recovered by condensation in a freezing mixture contained in the thermos flask *g*. While the actinometers were being filled, the pressure in the apparatus was kept constant by adjusting the height of the columns of water in *m* and *n*. At the end of a filling, the pressure in the actinometers was reduced to 50 cm. of mercury and the actinometers were then sealed off at the points c_1 and c_2 (Fig. 1). The two almost identical actinometers, thus filled under exactly the same conditions, were subsequently used to compare the rates of formation of hydrogen bromide per unit of radiant energy absorbed under different conditions of illumination.

The analysis of the contents of the actinometers at first presented a difficulty, since the ordinary procedure was found not to be sufficiently accurate. The bromine and hydrogen bromide had to be separated before their amounts were estimated. In principle, the method adopted was to admit into the actinometer a limited amount of pure water and to distil the bromine from the solution of hydrogen bromide and thence into a cooled solution of potassium iodide, the distillation being conducted in such a manner that the hydrobromic acid was retained in the actinometer and in a trap inserted between it and the bulbs containing the potassium iodide solution. The liberated iodine was titrated with standard sodium thiosulphate, and the hydrobromic acid with standard baryta in an atmosphere of hydrogen.

All the bromine used was purified from chlorine and iodine as well as from organic matter by the method recommended by Scott (J., 1913, **103**, 847), and the water used in the electrolytic cell and in the analyses was purified by the following method. Ordinary distilled water was saturated with chlorine and boiled for several hours in a large flask provided with a fused-on reflux condenser. At the end of this operation sufficient potassium bromide was added to interact with the small amount of chlorine still present, and the liberated bromine was removed by boiling under reduced pressure. A few drops of pure potash solution were then added, and after it had been heated, the water was distilled in dust-free air, and the distillate collected in carefully cleaned glass-stoppered bottles.

Discussion.

The experimental results show clearly that if, with a constant intensity of illumination, the disc is made to rotate at different rates, the amount of chemical change in a given time is greater when the rate of rotation of the disc is greater, the increase in the amount of change being such that it tends to a limit as the rate of rotation is made more rapid. When the disc rotates very slowly, the amount of hydrogen bromide formed in a given time is, of course, independent of the rate of rotation, and becomes the same as that produced by continuous illumination for the same total length of time. The mean life of the postulated catalyst is calculated from the result of a determination of the rate of rotation of the disc for which the mean velocity of chemical change is mid-way between the mean velocities of chemical change previously found for a very rapid and for a very slow rate of rotation of the disc.

That the photochemical union of hydrogen with chlorine and bromine is attributable to ephemeral catalysts (either atoms or active molecules) is now commonly assumed, and the assumption is supported by the fact, now established for the interaction of hydrogen and bromine, that the total amount of chemical change is not solely dependent on the total time of illumination by light of a constant intensity, but alters when the supply of the light is rendered intermittent. In adopting this theory we shall make the following assumptions concerning the catalyst :

(1) For light of a given quality, the rate of formation of the catalyst is proportional to the energy absorbed.

(2) The rate of destruction of the catalyst is the sum of two terms, one being proportional to the first power and the other to the second power of its concentration.

(3) The rate of formation of hydrogen bromide is directly proportional to the concentration of the catalyst.

Taking for granted (1) and (3), we can show that if the rate of destruction of the catalyst is proportional to its concentration, the rate of union of hydrogen and bromine is proportional to the intensity of the light, whereas, if the rate of destruction of the catalyst is proportional to the square of its concentration, the rate of union is proportional to the square-root of the intensity of the light. Thus, on the one hand, if A represents the concentration of the catalyst, I the intensity of the light, t the time, and k and k_2 are constants, the differential equation for the variation of A is

$$dA/dt = kI - k_2A (= 0 \text{ in the steady state}).$$

Wherefore, in the steady state A is proportional to I. Such would be the case if the destruction of the catalyst were caused principally by the impacts of its molecules with molecules of an inhibitor. On the other hand, if

$$dA/dt = kI - k_1A^2 \ (= 0 \text{ in the steady state}),$$

A would be proportional to the square-root of the intensity of the light, and such would be the case if the destruction of the catalyst were caused principally by the impact of two of its molecules.

Our results indicate that the rate of interaction of hydrogen and bromine, for very high intensities of the light, approximates to values which are proportional to the square-root of the intensity, but for low intensities the rate becomes more nearly equal to values proportional to the intensity. Accordingly, we must conclude that the destruction of the catalyst is at the same time both a first- and a second-order reaction, and that the differential equation which gives the time variation of its concentration is

$$dA/dt = kI - k_1A^2 - k_2A \text{ } (= 0 \text{ in the steady state}) \quad . \quad . \quad (1)$$

Let the units of time, energy, and concentration be so chosen that $k = 1$, $I = 1$, and $A = 1$ in the steady state when the actinometer is fully exposed to light; the values of the constants k_1 and k_2 can then be determined experimentally in the following manner. The actinometer is, in the first place, exposed to the light with the disc rotating very slowly, and the time, t_1, needed for the production of a given amount of hydrogen bromide is determined. Then with the twin actinometer a similar experiment is performed with the disc rotating very rapidly. Let us suppose that the time required for the production of the specified amount of hydrogen bromide is t_2. If α is the ratio to 2π of the sum of the angles subtended at the centre of the disc by all the sectors, then in the first experiment the actinometer was exposed to light of unit intensity for the time αt_1, whilst the result of the second experiment ought obviously to be the same as that of an exposure of the actinometer for a time t_2 to light of intensity α. But since the amount of chemical change is proportional to the product of the concentration of the catalyst and the time of exposure, we must have

$$\alpha t_1 = A_2t_2 \text{ or } A_2 = \alpha t_1/t_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (1.1)$$

in which A_2 is the approximately constant concentration of the catalyst in the second experiment.

With the new units, equation (1) becomes

$$dA/dt = I - k_1A^2 - k_2A \text{ } (= 0 \text{ in the steady state}) \quad . \quad . \quad (1.2)$$

In the first experiment, I and A both have by definition the value 1, and in the second experiment I has the value α, and A the value $\alpha t_1/t_2$. On substituting these values in (1.2), we obtain the following two equations from which the values of k_1 and k_2 can be deduced:

$$1 = k_1 + k_2$$

and

$$\alpha = k_1(\alpha t_1/t_2)^2 + k_2(\alpha t_1/t_2)$$

An actual experiment gave for $\alpha t_1/t_2$ the value 0·2391 when α was $\frac{1}{8}$, from which it follows that k_1 and k_2 are respectively 0·6272 and 0·3728. These were the values of the two constants adopted for the determination of the mean life of the catalyst.

The Determination of the Mean Life of the Catalyst.

In the system of units proposed above, the rate of increase of A becomes $I - k_1A^2 - k_2A_1$, and in this expression I is equal to the rate of production of the catalyst, and $k_1A^2 + k_2A$ to its rate of destruction, per unit volume. The mean life of the catalyst in the steady state is the quotient of A by the rate of production of A, *i.e.*, it is equal to A/I. But under continuous illumination the intensity has been taken as unity, and, under the same conditions, A in the steady state has also been taken as unity. Therefore in the conventional units adopted, the mean life of the catalyst is the unit of time.

Under all conditions the rate of chemical change is proportional to the mean value of A, and therefore, since A is unity when the actinometer is continuously illuminated, its mean value for a given moderate rate of rotation of the disc is the ratio of the rate of chemical change during that moderate rotation to the rate of chemical change under continuous illumination. Experiment therefore supplies us with the information that A has a certain known value when the disc is made to rotate at a known rate measured in seconds, or, in other words, when the equal intervals of illumination have a known value in seconds. It is also possible to calculate what rate of rotation of the disc measured in terms of the new unit of time (*i.e.*, the mean life of a molecule of the catalyst) would result in the same mean value of A. Accordingly, experiment furnishes the value of a rate in seconds, and calculation gives the value of the same rate in mean lives. The numerical ratio of the two values is clearly the value of a mean life in seconds.

The calculation of the rate of rotation of the disc (in mean-life units) which would result in a specified mean value of A is performed in the following way. For the purpose of the calculation it is more convenient to write the differential equation (1.2), which gives the rate of increase of A in the light, in the form $dA/d\tau = I - c_1{}^2A^2 - c_2A$, in which τ is written for t to indicate that the measurements of time are to be made with a unit equal to the mean life of the catalyst when the intensity of the light is unity, and c_1 and c_2 are constants. When I is taken as unity the solution of the equation is

$$\log_e \frac{\{1 + (c_2/2c_1)^2\}^{\frac{1}{2}} + \{x + c_2/2c_1\}}{\{1 + (c_2/2c_1)^2\}^{\frac{1}{2}} - \{x + c_2/2c_1\}} = 2c_1\{1 + (c_2/2c_1)^2\}^{\frac{1}{2}}\tau + C_1 \quad . \qquad (2)$$

where x is substituted for c_1A, and C_1 is the integration constant.

The same symbols being used, the differential equation for the decrease of A in the dark is $dA/d\tau = -c_1{}^2A^2 - c_2A$, of which the solution is

$$\log_e\left\{\frac{x + c_2/c_1}{x}\right\} = c_2\tau + C_2 \quad . \quad . \quad . \quad . \quad (3)$$

where C_2 is the integration constant.

For brevity, (2) is written as $f(x) = \tau$, and (3) as $F(x) = \tau$. If x_1 and x_2 are the values of x at the beginning and end of a period of illumination, and x_2 and x_3 the values of x at the beginning and end of a period of darkness, and τ_1, τ_2, τ_3, and τ_4 the corresponding values of τ

$$\frac{f(x_1) - f(x_2)}{F(x_2) - F(x_3)} = \frac{\tau_2 - \tau_1}{\tau_4 - \tau_3} = \beta$$ (a known constant when the rate of rotation is uniform).

But in the steady state, which is very rapidly approached, x_3 must be equal to x_1 since the increase in x during a period of illumination must then equal its decrease during a period of darkness, and therefore the above equation reduces to

$$f(x_1) + \beta F(x_1) = f(x_2) + \beta F(x_2) \quad . \quad . \quad . \quad . \quad (4)$$

It is easy to show that if any one of the infinite number of possible values of x_2 is introduced into this equation, the resulting equation for x_1 is satisfied by two real values, one of which is, of course, x_2. In other words, for every value of x_2 there is a corresponding value of x_1. Moreover, when x_1 and x_2 are known, the corresponding mean value of x, and also the length of a period of illumination in terms of a mean life of a molecule of the catalyst, can be computed with the aid of equations (2) and (3). By trial, a value of x_2 must be found which gives a mean value of x equal to the experimentally determined value of that constant. Then by a comparison of the calculated period of illumination in mean-life units with the period of illumination expressed in seconds, and deduced from the known rate of rotation of the disc, the mean life in seconds can be calculated.

It is obvious that the required result can also be obtained by graphical methods.

The actual experimental results are tabulated below. In column A the number of the determination is recorded; in B the rates of rotation of the disc in two comparative experiments; in C the ratio of the time of illumination to the sum of the periods of illumination and darkness; in D the times (in minutes) required to effect the same amount of chemical change in two comparative experiments; in E the ratio of these times; and in F and H the respective values of the constants k_1 and k_2.

A.	B.	C.	D.	E.	F.	H.
I	slow fast	$\frac{1}{2}$ $\frac{1}{2}$	225 174	1·29	0·6034	0·3966
			220 176	1·25		
			343 265·5	1·29		
			332 262	1·27		
			329 265·5	1·24		
			353 265·5	1·33		
II	fast fast	$\frac{1}{4}$ $\frac{1}{2}$	372 267	1·40	0·6701	0·3299
			275 174	1·58		
			273 174	1·57		
			287 174	1·65		
III	fast fast	$\frac{1}{8}$ $\frac{1}{2}$	415 174	2·38	0·6961	0·3039
			430 174	2·47		
			447 174	2·57		
IV	slow fast	$\frac{1}{32}$ $\frac{1}{32}$	910 435	2·09	0·5585	0·4415
V	slow fast	$\frac{1}{8}$ $\frac{1}{8}$	424 217·5	1·9494	0·6272	0·3728
			416 217·5	1·9126		
			409 217·5	1·8804		
			415 217·5	1·9080		
			mean =	1·9126		
VI	1 rev. in 4 secs. fast	$\frac{1}{8}$ $\frac{1}{8}$	246 217·5	1·13		
			238 217·5	1·09		
VII	1 rev. in 12·6 secs. fast	$\frac{1}{8}$ $\frac{1}{8}$	369 217·5	1·69		
VIII	1 rev. in 11·6 secs. fast	$\frac{1}{8}$ $\frac{1}{8}$	328 217·5	1·508		
			314 217·5	1·444		
			mean =	1·476		

For the calculation of the mean life of the catalyst the results of the determinations V and VIII were employed, the necessary figures being the mean ratios in column E, namely 1·9126 and 1·476 respectively. The mean life of the catalyst was estimated to be

0·063 second.

Under less intense illumination the mean life would be longer.

It will have been observed that certain approximations, which will affect to some extent the accuracy of the result, have been made.

Conclusion.

If the photochemical interaction of hydrogen and bromine is due to the presence of a catalyst (atoms or activated molecules), the catalyst is capable of existing for an appreciable fraction of a second.

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