LXXVII.—*The Influence of the Intensity of Illumination on the Velocity of Photochemical Changes. The Determination of the Mean Life of a Hypothetical Catalyst.*

By FRANK BRIERS, DAVID LEONARD CHAPMAN, and
ERNEST WALTERS.

ONLY a few researches have been conducted on the variation of the rates of photochemical changes with the intensity of the light, and at present there is some degree of discordance in the conclusions drawn by different experimenters from the results of their experiments.

Draper (*Phil. Mag.*, 1843, **23**, 401) announced that the rate at which chlorine and hydrogen combine in light is proportional to the intensity of the illumination. Baly and Barker (J., 1921, **119**, 653) maintained that the ratio of the rate of union of the two gases to the intensity of the light increases as the intensity of the light is increased. M. C. C. Chapman (J., 1924, **125**, 1521) obtained a result in substantial agreement with that of Draper. She found, however, that as the intensity of the radiation is increased the rate of formation of hydrochloric acid increases in a slightly smaller ratio. Berthoud (*Helv. Chim. Acta*, 1924, **7**, 324) considered that the rate of union of chlorine and hydrogen in the absence of inhibitors would be proportional to the square root of the intensity of illumination, and he saw in some of Mrs. Chapman's results evidence that such is the case. Kornfeld and Müller (private communication from Professor Bodenstein) have confirmed Mrs. Chapman's results. They find that the rate of formation of hydrochloric acid is proportional to the intensity of the light when the intensity is varied in the ratio of 1 : 64.

Draper, Baly and Barker, and Mrs. Chapman used electrolytic gas, which always contains a small amount of oxygen. Kornfeld and Müller removed oxygen from the hydrogen; but the chlorine they used may have contained a little oxygen.

It is possible that Berthoud's contention is right. The electrolytic gas used by Mrs. Chapman undoubtedly contained a little oxygen, and the small deviations from proportionality observed by her were in the direction required by Berthoud's view.

In a recent paper by Bodenstein and Lütkemeyer (*Z. physikal. Chem.*, 1924, **114**, 208) on the photochemical synthesis of hydrobromic acid it is concluded that the rate of formation of this compound from its elements is directly proportional to the square root of the intensity of the light. The striking difference, in this particular, of the influence of light on mixtures of bromine with hydrogen and of chlorine with hydrogen may possibly be due to the effect of small quantities of oxygen on the photochemical union of the latter gases. The question needs to be submitted to further investigation.

In connexion with the subject of this communication, the reaction between iodine and potassium oxalate is of especial interest. This reaction is represented by the equation :

$$C_2O_4K_2 + I_2 = 2CO_2 + 2KI.$$

It has been studied by Dhar (*Proc. K. Akad. Wetensch. Amsterdam*, 1916, **16**, 1097; *Ann. Chim.*, 1919, **11**, 130; J., 1923, **123**, 1856) and by Berthoud and Bellenot (*Helv. Chim. Acta*, 1924, **7**, 307). In his first paper, Dhar maintained that the velocity of the action is proportional to the intensity of the light. On the other hand, Berthoud and Bellenot asserted that it is proportional to the square root of the intensity of the light, both for red and for blue light. In order to vary the intensity of the light the latter investigators inserted between the source of illumination and the solution a large disc of black cardboard which could be set in rapid rotation, and from which two equal sectors had been removed for the first series of measurements; four for a second series, and eight for a third series, so as to make the intensity vary in the ratios 1 : 2 : 4. They realised that this method of varying the intensity of the light would not be legitimate unless the duration of the secondary reactions considerably exceeded the intervals between successive illuminations, and they deduced that if this condition were fulfilled the velocity of reaction ought to diminish as the rate of rotation of the disc is reduced. They observed the anticipated falling off in the velocity of the reaction, but they were unable to obtain the theoretical result when the disc was rotating very slowly.

We have repeated the experiments of Dhar and of Berthoud and Bellenot, and our results agree with those of the latter researchers. We have also examined more closely the theory of the effect of intermittent illumination on photochemical reactions of the same class, and have drawn conclusions from the theory and from our experimental results which will be given below.

The reaction between potassium oxalate and iodine, according to Berthoud and Bellenot, is of the same class as that between chlorine and hydrogen. One quantum of absorbed light is sufficient to cause the interaction of a large number of molecules of the reacting substances. For the explanation of such reactions several special hypotheses have been proposed. These hypotheses have one feature in common in that they postulate the formation of an unstable catalyst (or chain of catalysts) by the direct action of the light. We shall make no special assumption concerning the nature of the catalyst, but we shall assume that:

(I) the rate of formation of the catalyst is proportional to the intensity of illumination;

(II) the rate of reaction is proportional to the concentration of the catalyst; and

(III) the rate of destruction of the catalyst is proportional to a power of its concentration.

If [A] represents the concentration of the catalyst and I the intensity of the light, we have from assumptions I and III

$$\begin{aligned} d[\mathrm{A}]/dt &= cI - k[\mathrm{A}]^n \\ &= 0 \text{ in the steady state,} \end{aligned}$$

and therefore in the steady state

$$I^{1/n} \propto [\mathrm{A}] \propto \text{the rate of reaction (from assumption II).}$$

Therefore in the case of the formation of hydrochloric acid from electrolytic gas $n = 1$ if the experiments of Mrs. Chapman and of G. Kornfeld and H. Müller are trustworthy, whereas in the case of the interaction of iodine and potassium oxalate $n = 2$ if the observations of Berthoud and Bellenot and of the authors are not subject to some unsuspected source of error.

We have spent 6 months in attempts to discover some explanation of Berthoud and Bellenot's results other than that given by the authors, namely, that in this reaction the velocity of change is not proportional to the intensity of illumination but to its square root, and we have satisfied ourselves that none of the following causes could furnish such an explanation :

(1) The presence of an inhibitor.

(2) The varying rates of escape of the carbon dioxide produced in the reaction.

(3) The more rapid removal of the iodine from that portion of the solution which is nearest to the light.

(4) The method employed for varying the intensity of the light.*

When the method of varying the intensity of the light was that of a rotating disc, consistent and reproducible results in agreement with those of Berthoud and Bellenot were obtained. The results were independent of the rate of rotation of the disc when this rate exceeded one thousand revolutions per minute. It must therefore be concluded that when the solution has been exposed to light the chemical action continues for some time after the light has been shut off: for otherwise the rate of chemical change would be

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* That inhibitors were not present was proved by the fact that the velocity of the reaction was not affected by the purification of the materials used (*i.e.*, by the fractional crystallisation of the potassium oxalate or by the sublimation of the iodine), the results being reproducible and, within reasonable limits, independent of the degree of purity of the reagents. Variation of the hydrogen-ion concentration had very little effect.

That the dissolved carbon dioxide had no effect was proved by the fact that the total amount of change in a given time, employing a constant intensity of light, was the same when the exposure was continuous and when it was intermittent, provided that the intervals of exposure were not too short.

Another method employed for varying the intensity of the light was the following. Two one thousand-watt lamps, A and B, were placed side by side so as to be symmetrically situated with respect to the reaction tube, which was contained in a thermostat. The currents passed through the lamps were separately adjusted so that each lamp emitted light of the same intensity. The reaction vessel was exposed for 4 hours to the light emitted by A alone, and then for 4 hours to the light emitted by B alone. The change was measured, and compared with that effected in half the time by an exposure of the reaction vessel, filled with a solution of the same composition, to the light emitted simultaneously by both lamps. The mean ratio of the change effected by the light from one lamp in 8 hours to that effected by the light from two lamps in 4 hours was 1·32 : 1, the theoretical result calculated on the assumption that the rate of change is proportional to the square root of the intensity of the light being 1·41 : 1. The fact that the theoretical ratio was greater than that found experimentally can be explained by the circumstance that the large size of the bulbs of the two lamps made it impossible to place their filaments close together. That the effect of this source of error would be in the direction stated can be seen immediately by considering the effect of placing the lamps on opposite sides of the comparatively strongly absorptive solution.

proportional to the number of sectors left open in the disc, and not to the square root of this number. In other words, the catalyst assumed above has a life of appreciable duration.

Determination of the Life of the Catalyst or Chain.—The rate of disappearance of the catalyst is given by $k[\mathrm{A}]^2$ and therefore in the steady state the mean life of the catalyst is

$$[\mathrm{A}]/k[\mathrm{A}]^2 = 1/k[\mathrm{A}].$$

The problem is therefore to determine the value of $k[\mathrm{A}]$ when the solution is exposed to light of a given intensity and has reached the steady state.

In the light

$$d[\mathrm{A}]/dt = cI - k[\mathrm{A}]^2.$$

Multiply both sides of the equation by k and put $ckI = a^2$ and $k[\mathrm{A}] = x$.

The equation becomes

$$dx/dt = a^2 - x^2.$$

Or putting τ for at, and y for x/a,

$$dy/d\tau = 1 - y^2$$

the solution of which is

$$\left.\left[\log_e \frac{1+y}{1-y}\right]\right|_{y_1}^{y_2} = 2\tau_2 - 2\tau_1 \quad . \quad . \quad . \quad . \quad (1)$$

y is the ratio of $k[\mathrm{A}]$ at the moment under consideration to its value in the steady state when the intensity of the light is I, and τ is the ratio of the time, t, to the duration of a mean life.

The differential equation which holds in the dark is

$$d[\mathrm{A}]/dt = -k[\mathrm{A}],^2$$

and its solution in terms of the variable y and τ is

$$\frac{1}{y_3} - \frac{1}{y_2} = \tau_3 - \tau_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

in which y_3 and y_2 are the final and initial values of y, and τ_3 and τ_2 the corresponding values of τ.

In our experiments, the disc has eight sectors, each of angle $\pi/8$, symmetrically situated. Accordingly, when the disc was rotating uniformly, the duration of illumination was equal to the time during which the light was shut off, *i.e.*, $\tau_2 - \tau_1 = \tau_3 - \tau_2$. Also under the same conditions y_1 must attain a steady value which must be equal to y_3. Therefore from (1) and (2)

$$\log_e \frac{1+y_2}{1-y_2} + \frac{2}{y_2} = \log_e \frac{1+y_1}{1-y_1} + \frac{2}{y_1}.$$

For each value of y_1 the corresponding value of y_2 can be obtained from the above equation.

Moreover, if the value of τ is selected such that when $y = 0$ $\tau = 0$, equation (1) becomes

$$\log_e \frac{1+y}{1-y} = 2\tau \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (3)$$

and for each value of y there is a corresponding value of τ.

We shall now find the mean value of y for a given rate of rotation of the disc. From (3) the value of y during illumination is given by

$$y = \tanh \tau$$

and from (2) the value of y during the period of non-illumination is given by

$$y = 1/\left(\tau + \frac{1}{y_2}\right)$$

in which τ is the time (taking the mean life as the unit) during which the solution is in the dark and y_2 is the value of y when the light is shut off.

The mean value of y during uniform rotation of the disc is manifestly given by

$$y = \frac{\log_e \cosh \tau_2 - \log_e \cosh \tau_1 + \log\left[(\tau_2 - \tau_1)y_2 + 1\right]}{2(\tau_2 - \tau_1)}$$

But the mean value of y when the disc is rotating very rapidly is $1/\sqrt{2}$. Consequently, since the mean value of y is proportional to the rate of chemical change,

$$\frac{\log_e \cosh \tau_2 - \log_e \cosh \tau_1 + \log\left[(\tau_2 - \tau_1)y_2 + 1\right]}{\sqrt{2}(\tau_2 - \tau_1)} = \frac{\text{rate of change when the disc rotates at the given rate}}{\text{rate of change when the disc rotates very rapidly}}.$$

By trial a value of τ_1 is found which satisfies this equation. This can be done, since for every value of τ_1 there are corresponding values of τ_2 and y_2. Furthermore, as $\tau_2 - \tau_1$ is the duration of the exposure to light in mean lives, the value of the mean life can be calculated from the known rate of rotation of the disc.

EXPERIMENTAL.

The composition of the solution was potassium oxalate $N/2$, iodine 0·00625N, and potassium iodide 0·00931N. The reaction vessel was a glass cylinder of 4 cm. diameter, and it contained 80 c.c. of the above solution. The cylinder was closed with a ground glass stopper in order to prevent loss of iodine by evaporation, and during an experiment it was maintained at a temperature of 20°

in a thermostat filled with water and having sides of plane glass. A black screen was placed behind the reaction tube and the thermostat was covered so that no light could enter it except that which had passed through a sector of the disc and a window of the same shape as the sector in one of the glass sides of the thermostat. The reaction tube was placed near to the window in such a position that the whole of the solution it contained was equally illuminated. The source of light was a thousand-watt incandescent lamp placed at a horizontal distance of 38 cm. from the reaction vessel. The light from the lamp passed through an aperture of an appropriate shape in a large piece of cardboard which was placed immediately in front of the lamp, the aperture being of such a size that its penumbra was outside the window of the thermostat. The rotating disc was as near as possible to the thermostat and the reaction vessel. The shadow cast by the edge of the 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, of course, 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 solution. 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 rates of chemical change were determined by finding the times required to bring about the same amount of chemical change as estimated by titration of the iodine with a standard solution of sodium thiosulphate. The mean life of the catalyst was in the first place determined when the solution was illuminated with white light. The results are recorded below:

A.	B.	C.	D.
20	71·75		
20	71·44	0·0303	0·000688
Very fast	62·21		
,,	62·20		
24	71·12		
24	70·68	0·0299	0·000678
Very fast	62·21		

In column A is recorded the number of revolutions per minute of the disc; in column B the time of exposure in minutes needed to effect the same amount of chemical change; in column C the calculated mean life, in seconds; and in column D the quotient of the mean life and the time required to effect the given amount of chemical change when the solution was exposed without interruption to the light. This quotient should be a constant.

In a third determination light which had been filtered through a solution of iodine was used. The light passed through 5·5 cm. of an aqueous solution of iodine and potassium iodide of such a strength that the concentration of each of the dissolved substances was twice as great as the corresponding concentration in the solution contained in the reaction vessel. The effect of using such filtered light would, of course, be to render the velocity of chemical change much more uniform throughout the solution. The results are recorded below :

A.	B.	C.	D.
21	293·2		
5	327·8		
5	324·7	0·1212	0·000605
Very fast	282·8		

From any of the above results the mean life of the catalyst in the dark at the temperature of the experiment can be calculated, provided that the rate of the chemical change in the dark is known, and similar assumptions are made concerning the mechanism of the change. The time required to effect the specified amount of change in the dark was found by experiment to be 10,430 minutes. Using the constant determined in the last experiment, we have

the mean life of the catalyst in the dark = 10430 × 0·000605 = 6·31 seconds.

Although we are unable without conducting further research to estimate the errors of the methods described for determining the constant, we believe that the accuracy of the determination is sufficient for present needs, namely, for the purpose of testing a hypothesis.

THE LABORATORY,
JESUS COLLEGE, OXFORD.

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