

CCCXVIII.—*The Mean Life of the Catalyst postulated in the Photochemical Union of Chlorine and Hydrogen.*

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IN a recent communication by the authors (J., 1928, 3233), experiments were described which showed that when a mixture of equal volumes of chlorine and hydrogen is exposed to white light of constant intensity, combination of the constituent gases occurs more slowly in a narrow capillary tube than in one of wider diameter. To explain the effect we postulated that the union of chlorine and hydrogen is due to an unstable catalyst, and that this is destroyed when it comes into contact with glass or a film of water. In order that the surface inhibition may be measurable, the normal mean life of the catalyst must be of the same order of magnitude as the average time taken by the catalyst molecules produced within the reaction chamber to reach the surface, and the effect will be more pronounced when the ratio of the mean life to the diffusion time is large.

It may be stated immediately that the results obtained in this investigation do not, so far as we can see, give any indication of the nature of the catalyst, and it may therefore, for the present purpose, be looked upon as a chain of alternately formed chlorine and hydrogen atoms, as Nernst and Bodenstein assume, or as unstable nuclei of unknown structure. It is, however, to be regarded as the carrier of energy derived initially from a quantum, and the dissipation of the energy and the destruction of the catalyst are to be considered as being necessarily the same event.

The following assumptions and approximations are made : (1) The rate of formation of the catalyst is for light of the same quality proportional to the energy absorbed. (2) The catalyst is everywhere removed at a rate proportional to its concentration. (3) The rate of reaction is proportional to the concentration of the catalyst. (4) The diffusion of the catalyst follows the same laws as that of a single substance. (5) The intensity of the light, and therefore the rate of formation of the catalyst, is uniform throughout the illuminated gas. (6) Every catalyst molecule which comes into contact with the walls of the vessel is destroyed.

The assumptions (1), (2), and (3) have been previously made, and are supported by the fact that the rate of reaction is proportional to the intensity of the light; (4) and (5) are approximations, (4) being probably true provided that the proportion of chlorine to hydrogen in the mixture remains the same. The error due to (5) cannot be estimated, but it is probably small. Assumption (6) is a working

hypothesis, for which the results of this survey of the phenomenon of surface inhibition furnish some justification. It will be obvious that the establishment of its complete truth could only be given by precision experiments, which in the present state of our knowledge would be difficult to perform.

The symbols used in the analysis of the theory are the following :

- $a$  = the radius of the tube ;
- $C$  = diffusion coefficient of the catalyst through the gas ;
- $A$  = light absorbed per unit volume in unit time ;
- $\rho$  = concentration of the catalyst ;
- $\omega$  = concentration of the inhibitor ;
- $k_1$  = coefficient of rate of formation of catalyst ;
- $k_2$  = coefficient of rate of destruction of catalyst by inhibitor.

Using Cartesian co-ordinates, consider the action in an element of volume  $dx \cdot dy \cdot dz$ . When the steady state has been reached, the concentration of the catalyst is maintained constant from three causes :

- (1) Gain by formation, viz.,  $k_1 A \cdot dx \cdot dy \cdot dz$  per sec.
- (2) Loss by destruction by inhibitor, viz.,  $k_2 \omega \rho \cdot dx \cdot dy \cdot dz$  per sec.
- (3) Gain by diffusion, viz.,  $C \cdot \nabla^2 \rho \cdot dx \cdot dy \cdot dz$  per sec.

Therefore in the steady state

$$C \cdot \nabla^2 \rho + k_1 A - k_2 \omega \rho = 0 \quad \dots \quad (1)$$

If the action is taking place in a circular cylindrical tube of infinite length, the above equation, after application of the conditions for the symmetry imposed, is transformed into

$$C \left( \frac{\partial^2 \rho}{\partial r^2} + \frac{1}{r} \frac{\partial \rho}{\partial r} \right) + k_1 A - k_2 \omega \rho = 0 \quad \dots \quad (2)$$

in which  $r$  is the distance from the axis of the tube.

This differential equation can be solved as a series in the form

$$\rho = S \left( 1 + \frac{Br^2}{2^2} + \frac{B^2 r^4}{2^2 \cdot 4^2} + \frac{B^3 r^6}{2^2 \cdot 4^2 \cdot 6^2} + \dots \right) + \frac{k_1 A}{k_2 \omega} \quad \dots \quad (3)$$

where  $B = k_2 \omega / C$  and  $S$  is a constant.

By the working hypothesis (6),  $\rho = 0$  when  $r = a$ , therefore

$$\rho = \left( 1 - \frac{1 + \frac{Br^2}{2^2} + \frac{B^2 r^4}{2^2 \cdot 4^2} + \dots}{1 + \frac{Ba^2}{2^2} + \frac{B^2 a^4}{2^2 \cdot 4^2} + \dots} \right) \frac{k_1 A}{k_2 \omega} \quad \dots \quad (4)$$

If  $\bar{\rho}$  is the average concentration of the catalyst throughout the tube,

$$\bar{\rho} = \frac{2\pi \int_0^a \rho r \cdot dr}{\pi a^2} \quad \dots \quad (5)$$

whence, after insertion of the value of  $\rho$  given by equation (4),

$$\bar{\rho} = \left( 1 - \frac{1 + \frac{1}{2} \frac{Ba^2}{2^2} + \frac{1}{3} \frac{B^2a^4}{2^2 \cdot 4^2} + \dots}{1 + \frac{Ba^2}{2^2} + \frac{B^2a^4}{2^2 \cdot 4^2} + \dots} \right) \frac{k_1 A}{k_2 \omega} \quad (6)$$

which may be expressed in terms of Bessel functions with an imaginary argument

$$\bar{\rho} = \left( 1 - \frac{2I_1(x)}{xI_0(x)} \right) = F(x) \quad (7)$$

where  $x = a\sqrt{B}$ .

By hypothesis, the rate of reaction varies as  $\bar{\rho}$ , therefore,

$$\frac{\text{Rate in a tube of radius } a_1}{\text{Rate in a tube of radius } a_2} = \frac{F(x_1)}{F(x_2)} \quad (8)$$

If the experimental conditions (*e.g.*, intensity of light, composition, etc.) are the same for both tubes

$$x_1/x_2 = a_1/a_2 \quad (9)$$

Now, by plotting  $F(x)$  against  $x$ , values of  $x_1$  and  $x_2$  can be found to satisfy equations (8) and (9), and thus the value of  $B$  for a given mixture can be determined.

In an infinitely wide tube (except very near to the surface),  $\rho$  has a constant value, *viz.*, that given by the quotient  $k_1 A/k_2 \omega$ . Furthermore, in such a tube the mean life of the catalyst is the quotient of its concentration by the rate of its formation or the rate of its destruction, the two last magnitudes being for this case equal to one another. Therefore for an infinitely wide tube the mean life of the catalyst

$$= \rho/k_2 \omega \rho = 1/BC.$$

In a narrow tube the removal of the catalyst is almost entirely effected by collisions with the walls, and inhibitors such as oxygen have only a small effect. This is shown by equation (6), which reduces to

$$\bar{\rho} = k_1 A a^2 / 8C \quad (10)$$

when  $a$  is small. Thus, for a sufficiently narrow tube the rate of formation of hydrogen chloride per unit volume ought to be independent of the concentration of an inhibitor such as oxygen, and proportional to the square of the radius of the tube.

#### EXPERIMENTAL.

The determinations were conducted with the simple apparatus previously described (*loc. cit.*). It consisted of a hermetically sealed U-tube, one limb of which was a wide tube (2.0—2.5 cm.

internal diameter) and the other a narrow tube of the same length whose internal diameter varied in the different experiments from 0.05 to 0.50 cm. About 2 c.c. of water were introduced into the apparatus to dissolve the hydrogen chloride formed, and to serve as an index.

The following is a brief account of the procedure finally adopted. The actinometers were filled with equimolecular mixtures of chlorine and hydrogen, the usual precautions being taken. Immediately after being filled, the actinometer was sealed and detached from the rest of the apparatus. In doing this on the capillary-tube side of the actinometer, the glass was not pulled away in the usual manner, but after being sealed, was pushed back into position and carefully melted in with a very small flame. By cutting the tube about 1 cm. above the seal, the actinometer was left with a short glass extension, to which a rod could later be sealed to serve as a handle.

The actinometer was next placed in a small electric heater and maintained at 130° for 10 hours, in order to destroy all traces of destructible impurities. After cooling, all liquid was expelled from the capillary tube by passing steam over it. The actinometer was then immersed in a thermostat and kept at 25° for several hours. During this time it was repeatedly shaken, in order completely to saturate the water it contained with chlorine. After the removal of the actinometer from the thermostat, a little water, which was to serve as an index, was allowed to enter the capillary tube. The glass rod already mentioned was then sealed to the extension of the capillary tube, and by means of this the actinometer was firmly held in a bath containing a mixture of bromobenzene and xylene having the same refractive index as the glass of the actinometer. The actinometer was held in the bath in such a manner that either limb could be exposed to light at will. The whole was placed in a thermostat kept at 25°. The object of immersing the apparatus in the iso-refractive liquid was to ensure that the conditions of illumination should be the same for the two tubes. In conducting the experiments, the tubes were illuminated with a 40-watt gas-filled lamp placed at a distance of 30 cm. The current used to heat the filament of the lamp was maintained constant by a rheostat and sensitive ammeter. The movement of the meniscus in the capillary tube was observed with a small cathetometer. By operating in this way, the combination in the wide tube is measured as a change in pressure at almost constant volume, and that in the capillary tube as a change in volume at almost constant pressure. Before an exposure to light, the reading of the meniscus in the capillary tube was not taken until we were satisfied that the index was stationary and that equilibrium had been established, and after an exposure the final

reading was not taken until 12 hours had elapsed. The rate of combination during an exposure to light was calculated on the assumption that the rate is proportional to the pressure (compare M. C. C. Chapman, J., 1923, **123**, 3062), but owing to the very small range of pressure over which the determinations were made, any deviations from this law would introduce only very small errors in the final results.

A filled actinometer was generally used to make a series of observations during the course of which the pressure fell in some cases as low as 0.25 atm. The pressure during any one determination could be estimated from either the initial or the final pressure and the recorded movements of the index during the intermediate determinations. The measurement of the final pressure was made in two ways: (1) by opening the wide tube and observing the contraction of the gas in the capillary tube, and (2) by analysing the contents of the actinometer.

#### *Results.*

The theory [see equation (10)] requires that in a sufficiently narrow tube the rate of reaction shall be independent of the concentration of oxygen. The results of two experiments quoted below are in agreement with this requirement. In a narrow tube filled with electrolytic gas the rate of decrease of volume of the enclosed gas ought to be nearly proportional to the volume of uncombined gas, *i. e.*, to the light absorbed, whereas in a wider tube, in which the oxygen can exert its usual inhibitive effect, the rate of decrease in volume ought to be proportional to the square of the volume of uncombined gas, since during the combination the concentration of the oxygen and the volume of uncombined gas are in inverse ratio. The results of the two experiments are tabulated below. In the table  $k_3 = (\log l_1 - \log l_2)/(t_2 - t_1)$ , and  $k_4 = (1/l_2 - 1/l_1)/(t_2 - t_1)$ , where  $l_1$  and  $l_2$  are the initial and final lengths of the tube filled with gas, and  $t_1$  and  $t_2$  are the initial and final time (in minutes). With the narrow tube,  $k_3$  is more nearly constant than  $k_4$ , whilst with the wide tube the reverse is the case.

The best test which we can give at present of the approximate accuracy of the theory is the fact that the quotient of the mean life of the catalyst by the sensitivity of the electrolytic gas is at the same pressure a constant, *i. e.*, that  $L/R \times$  (a function of the pressure) is constant, where  $L$  is the mean life and  $R$  the sensitivity. That this is true for wide ranges of the magnitudes  $L$  and  $R$  is shown by the final results recorded in Table II. It must here be pointed out that the function of the pressure  $P$ , *viz.*,  $P^{2.5}$ , which agrees with the experimental results, is not entirely in accord with expectation. In an infinitely wide tube  $L \propto P/A$ ; but for electrolytic gas  $A$  is nearly

TABLE I.

Narrow capillary tube ( $a = 0.035$ cm.).				Wide capillary tube ( $a = 0.282$ cm.).			
$t$ , mins.	$l$ , cm.	$k_2 \times 10^4$ .	$k_4 \times 10^4$ .	$t$ , mins.	$l$ , cm.	$k_2 \times 10^4$ .	$k_4 \times 10^4$ .
10	11.81	—	—	0	5.86	—	—
12	11.63	33	6.6	1	5.38	371	152
14	11.45	34	6.8	2	5.01	309	137
16	11.28	33	6.6	3	4.67	305	145
20	10.94	33	6.9	4	4.38	278	142
23	10.74	27	5.7	5	4.13	255	138
25	10.59	31	6.6	6	3.91	238	136
28	10.39	28	6.1	7	3.73	205	123
30	10.25	29	6.6	8	3.54	227	144
33	10.01	34	7.8	9	3.38	201	134
35	9.86	33	7.6	11	3.11	181	128
37	9.72	31	7.3				
40	9.50	33	8.0				
43	9.30	31	7.6				
45	9.16	33	8.2				

proportional to  $P$ , and therefore  $L \propto \rho/P$ . Now, according to the most approved theories of the mechanism of the change,  $R$  should be proportional to the concentration of the catalyst and to the concentration of the electrolytic gas, or  $R \propto \rho P$ . Therefore we should have  $L/R \propto P^{-2}$ , whereas our experiments indicate that  $L/R \propto P^{-2.5}$ . It is hoped that when the technique has been revised and rendered more accurate an explanation of this difficulty will be found.

TABLE II.

Radius of capillary, $a$ , cm.	Pressure, $P$ , cm. Hg.	Rate in wide tube, $R = -dP/dt \times 10^2$ ,*	Rate in capillary, $r = -dp/dt \times 10^2$ ,*	Mean life, $L$ , sec.	$L/R \times P^{2.5}$ .	$R/R_{\infty}$ .
0.085†	73.5	18.5	9.93	0.00186	466	0.958
0.041	78.0	81.9	4.57	0.014	918	0.885
0.038	76.0 ?	88.2	3.98	0.015	856	0.892
0.043†	76.0	3.95	1.95	0.0065	829	0.978
0.073	65.0	363	14.5	0.062	582	0.750
	52.6	265	7.21	0.081	613	0.686
	48.5	228	5.47	0.089	639	0.665
0.197	62.2	62.8	35.2	0.0096	467	0.894
	56.3	51.6	26.5	0.011	507	0.882
0.041	55 ?	110	2.70	0.024	489	0.826
0.071	64.7	123	9.83	0.024	672	0.847
	59.1	88.7	6.44	0.025	757	0.839
	41.3	54.5	1.81	0.044	885	0.747
	36.7	45.1	1.58	0.038	888	0.749
0.102	61.5	53.5	13.0	0.012	665	0.882
	53.0	47.7	9.5	0.014	600	0.864
	44.9	34.6	6.73	0.012	590	0.863

\* The rates are given as changes of pressure per minute on the assumption that the volume is kept constant. The unit of pressure is taken as that exerted by a column of mercury 1 cm. high.

† Oxygen added.

In order to calculate the mean life of the catalyst, a value had to be assumed for its diffusion coefficient through a mixture of equal volumes of chlorine and hydrogen at atmospheric pressure. The value of this constant probably lies between 0.1 and 0.5. We have throughout assumed it to be 0.3.

It will be seen that at the same pressure  $L/R$  was approximately constant, although  $R$  was varied from 3.9 to 360.

In the last column of the preceding table the calculated degree to which the reaction is inhibited by the glass surface of a tube of 2 cm. internal diameter is recorded, the figures given being the ratio of the rate of reaction in such a tube to that in a tube of infinite diameter, it being of course assumed in the calculation that the intensity of illumination is uniform and the same for both tubes. This ratio is smaller the lower the pressure and the greater the sensitivity of the gas. For the most sensitive mixture the value of the ratio at atmospheric pressure is about 80%.

An examination of the table discloses the fact that the mean life always increases with decreasing pressure. This appears to show that one or both of the interacting gases have an inhibitive effect, a conclusion which is supported by the observation of M. C. C. Chapman (*loc. cit.*) that hydrogen can act as a weak inhibitor.

The results obtained by us are consistent with those of Weigert and Kellermann (*Z. physikal. Chem.*, 1923, **107**, 1), who made the first attempt to estimate the life of the catalyst which is formed when electrolytic gas is exposed to light.

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