CCCXXX.—*On the Photobromination of* cyclo*Hexane.*

By Basil John Wood and Eric Keightley Rideal.

The photochemical bromination of *cyclo*hexane vapour has been studied by Pusch (*Z. Elektrochem.*, 1918, **24**, 336) and Noddack (*ibid.*, 1921, **27**, 359), who showed that approximately one molecule of bromine was removed for each quantum of light absorbed. The reaction appeared to be the simplest case of photobromination, for there was no evidence of chain formation as in the bromination of toluene, stilbene, cinnamic and tartaric acids, and possibly hydrogen.

The majority of these photobrominations possess marked temperature coefficients, a general interpretation for which has been given by Pratolongo (*Gazzetta*, 1918, **48**, i, 121) and Tolman (*J. Amer. Chem. Soc.*, 1923, **45**, 2285). The existence of a temperature coefficient is believed to be an indication that only those bromine molecules already excited, presumably thermally, to a definite sub-level are capable of becoming excited to a reacting level on absorption of a quantum of the monochromatic radiation employed. The existence of a temperature coefficient for this reaction would clearly be incompatible with the conclusions of Pusch and of Noddack, and the reaction is now shown, in fact, to possess no temperature coefficient for the mercury green line.

In the bromination of hydrogen (Bodenstein and Lütkemeyer, *Z. physikal. Chem.*, 1924, **114**, 208) and of stilbene, cinnamic acid, and potassium oxalate (Berthoud, *Trans. Faraday Soc.*, 1925, **21**, 557; *Helv. Chim. Acta*, 1924, **7**, 318; see also Ghosh and Purkayestha, *J. Indian Chem. Soc.*, 1926, 261), the rate of reaction is claimed to be proportional to the square root of the light intensity and thus to indicate that the reaction involves the formation of bromine atoms according to the reaction

$$\mathrm{Br_2} + h\nu \longrightarrow \mathrm{2Br} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Berthoud (*loc. cit.*) suggests the following mechanism

$$\mathrm{A + Br \longrightarrow ABr} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$$\mathrm{ABr + Br_2 \longrightarrow ABr_2 + Br} \quad . \quad . \quad . \quad . \quad (3)$$

$$\mathrm{2ABr \longrightarrow 2A + Br_2 \text{ or } ABr_2 + A} \quad . \quad . \quad . \quad . \quad (4)$$

and deduces the relationships $d[\mathrm{ABr_2}]/dt = kI^{\frac{1}{2}}[\mathrm{Br_2}]$ or $kI^{\frac{1}{2}}[\mathrm{Br_2}]^{\frac{3}{2}}$, respectively, for total or weak absorption of the active radiation, both rates being independent of the concentration of the acceptor. It is difficult to understand how the rate of a photochemical reaction involving bromine atoms with a high primary photochemical efficiency can vary with the square root of the light intensity. If we equate the rate of formation of bromine atoms by (1) and (3) to their rate of removal by (2) and by the following reactions

$$\mathrm{ABr} + \mathrm{Br} \longrightarrow \mathrm{ABr_2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

$$2\mathrm{Br} \longrightarrow \mathrm{Br_2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

we obtain

$$2kI_0[\mathrm{Br_2}] + k_3[\mathrm{ABr}][\mathrm{Br_2}] = k_2[\mathrm{A}][\mathrm{Br}] + k_5[\mathrm{ABr}][\mathrm{Br}] + k_6[\mathrm{Br}]^2.$$

The reaction rate is then

$$d[\mathrm{ABr_2}]/dt = k_5[\mathrm{ABr}][\mathrm{Br}] + k_4[\mathrm{ABr}]^2 + k_3[\mathrm{ABr}][\mathrm{Br_2}].$$

It is clear that this rate is not proportional to the square root of the light intensity unless the rates of the various methods by which $\mathrm{ABr_2}$ is formed can be considered as negligibly small in comparison with the reaction rate $2\mathrm{Br} \longrightarrow \mathrm{Br_2}$, *i.e.*, with a reaction of low photochemical efficiency.

If the reaction is not a chain mechanism, we can, following Berthoud, represent it on the atomic view as the sequence of reactions (1), (2), (5), and (6). As the concentration of the bromine atoms is small, we can equate their rate of formation at any instant to their rate of removal, thus, $d[\mathrm{Br}]/dt = 2kI_0[\mathrm{Br_2}] - k_2[\mathrm{A}][\mathrm{Br}] - k_5[\mathrm{ABr}][\mathrm{Br}] - k_6[\mathrm{Br}]^2 = 0$. Similarly, since [ABr] is small, $k_2[\mathrm{A}][\mathrm{Br}] = k_5[\mathrm{ABr}][\mathrm{Br}]$; moreover, $d[\mathrm{ABr_2}]/dt = k_5[\mathrm{ABr}][\mathrm{Br}]$. For weak absorption of active radiation we thus obtain

$$d[\mathrm{ABr_2}]/dt = kI_0[\mathrm{Br_2}] - k_6[\mathrm{Br}]^2/2 = kI_0[\mathrm{Br_2}],$$

since [Br] is assumed to be small.

On this view, the reaction velocity will again be proportional to the light intensity unless but a small fraction of the bromine atoms is removed by the acceptor, in which case the photochemical efficiency is small, and the reaction velocity will be dependent on the concentration of the acceptor.

If the reaction takes place between the acceptor and excited bromine molecules rather than atoms, we obtain for the rate of production of these molecules

$$d[\mathrm{Br_2}']/dt = kI_0(1 - e^{a[\mathrm{Br_2}]d}),$$

where a is the extinction coefficient and d the thickness of the absorption layer. If τ be the life of an excited bromine molecule and T the time between successive collisions of the excited molecule and the acceptor, the rate of production of the reaction product is (compare Turner, *Physical Rev.*, 1924, **23**, 464)

$$\begin{aligned} d[\mathrm{ABr_2}]/dt &= kI_0(1 - e^{-a[\mathrm{Br_2}]d})\tau/(T + \tau) \\ &= kI_0[\mathrm{Br_2}]\tau/(T + \tau) \end{aligned}$$

for weak absorption. It is clear that this will be independent of the concentration of the acceptor if τ be large compared with T. Since τ is of the order of 10^{-8} second (possibly larger according to Eggert, *Physikal. Z.*, 1923, **24**, 504), we should anticipate that the reaction velocity will not be affected by the concentration of the acceptor until this has fallen to a pressure such that T becomes comparable with τ; this pressure can be calculated from the kinetic gas theory to be only some 0·3 mm. Hg in the case of *cyclo*hexane. Thus, if the primary photochemical action be either the formation of an excited bromine molecule or a dissociation into atoms, the reaction rate would be independent of the concentration of the acceptor except at very low pressures. We would also conclude that for weak light absorption the reaction velocity for the bromination of *cyclo*hexane would be strictly proportional to the light intensity, a view confirmed by experiment.

Finally, it is well known that bromination of many substances in solution is greatly affected by oxygen, which acts as an inhibitor. It was decided to investigate this effect in the case of *cyclo*hexane, because such a quantitative study would give information on the mechanism of the bromination process. The most probable hypothesis is that the reaction proceeds through an excited molecule in the following steps :

$$Br_2 + h\nu \longrightarrow Br_2' \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1A)$$

$$C_6H_{12} + Br_2' \longrightarrow C_6H_{12}Br_2' \quad . \quad . \quad . \quad . \quad . \quad (7)$$

$$C_6H_{12}Br_2' \longrightarrow C_6H_{11}Br' + HBr \quad . \quad . \quad . \quad . \quad (8)$$

or

$$C_6H_{12}Br_2' + O_2 \longrightarrow C_6H_{12} + Br_2 + O_2 + \varepsilon \quad . \quad (9)$$

$$C_6H_{11}Br' + Br_2 \longrightarrow C_6H_{10}Br_2 + HBr \quad . \quad . \quad (10)$$

The excited complex $C_6H_{12}Br_2'$ formed in (7) can either decompose spontaneously (8), or be deactivated by collision with oxygen (9).

The rate of formation of excited bromine molecules, for weak absorption, is equal to $kI_0[Br_2]$; the formation rate of the complex $= kI_0[Br_2]\tau/(T + \tau)$. Since its concentration is small, its formation rate can be equated to its rate of disappearance by reactions (8) and (9) with respective velocity coefficients k_8 and k_9. The reaction rate is determined by the probability of reaction (8), which is equal to $k_8/(k_8 + k_9[O_2])$. Hence the rate of bromination is given by

$$d[C_6H_{11}Br]/dt = kI_0[Br_2]\tau k_8/(\tau + T)(k_8 + k_9[O_2])$$

There are two alternative ways in which the inhibiting effect of oxygen might operate : (*a*) In the sequence of reactions $Br_2 + h\nu \longrightarrow 2Br$; $C_6H_{12} + Br \longrightarrow C_6H_{12}Br$; $C_6H_{12}Br + Br \longrightarrow C_6H_{11}Br + HBr$, the bromine atoms, in addition to combining with themselves, might be rendered inactive by the reactions $Br + O_2 \longrightarrow BrO_2$; $BrO_2 + Br \longrightarrow Br_2 + O_2$. (*b*) In the series $Br_2 + h\nu \longrightarrow Br_2'$; $C_6H_{12} + Br_2' \longrightarrow C_6H_{11}Br + HBr$, the activated bromine molecules may be deactivated by the reaction $Br_2' + O_2 \longrightarrow Br_2 + O_2$, as well as by $Br_2' \longrightarrow Br_2$. In either case, it can readily be shown that the inhibition must be dependent on the concentration of the acceptor, but since it has actually been found to be independent (see Experimental), it follows that these two hypothetical modes of operation are eliminated, and that the inhibiting mechanism is expressed by equation (9).

EXPERIMENTAL.

Pusch and Noddack in their examination of the reaction under consideration estimated the rate of removal of bromine by spectrophotometric and titration methods, but here the reaction was followed throughout its course by measuring the pressure change. Monochromatic light was employed, the green line $\lambda = 5460$ Å. from a mercury-vapour lamp and light filter being sufficiently intense to give easily measurable velocities.

The apparatus used is shown in Fig. 1. The reaction vessel used at first was a glass cylinder with flattened ends, but in the form subsequently employed the ends were of plane parallel glass fused on. It is connected by capillary tubes through two taps to reservoirs containing bromine and *cyclo*hexane. Two other connexions are made—one to the pumps, and the other to the gauge.

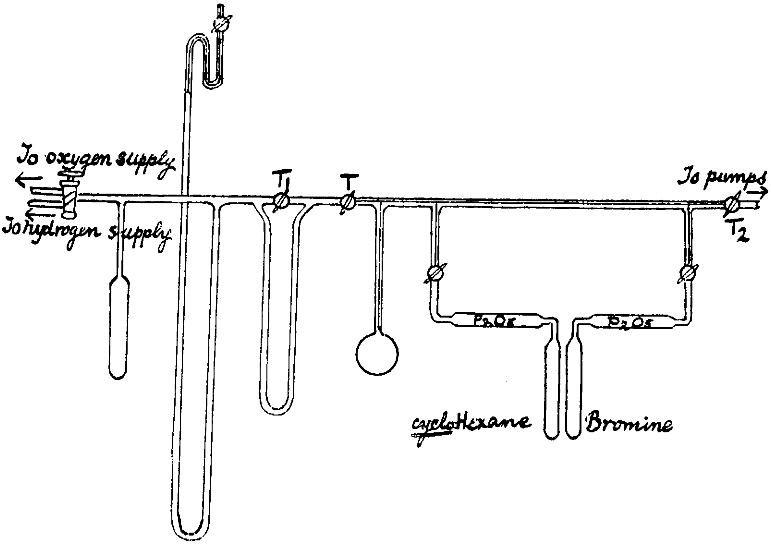
The pressure gauge consists of a sulphuric acid differential manometer of fine-bore tubing, connected to a mercury manometer and a large bulb kept in ice which serves to maintain a constant pressure. A two-way tap is connected to the gauge through which hydrogen and oxygen can be admitted. Exhaustion can be effected through a soda–lime tube and liquid-air trap by mercury diffusion pumps backed by an oil pump. This is necessary, as a high vacuum is required to remove oxygen and the reaction products. Connexion can also be made with a water pump when required.

The reaction vessel is contained in a metal box, with plane parallel glass faces, through which circulates water from a thermostat constant to within ± 0·1°.

Light from the mercury lamp reaches the reaction vessel after passing through (1) a vessel with plane parallel glass faces in which cold water removes the infra-red; (2) a filter of saturated potassium dichromate solution, to which neodymium magnesium nitrate has been added until the yellow line disappears, thus isolating the mercury green line (R. W. Wood, "Physical Optics," p. 15); and (3) an adjustable diaphragm. At first, a small glass mercury lamp was used, which was run in series with a resistance of 220 ohms from a constant 220 volts supply and took 0·65 amp. This was later replaced by a quartz mercury-vapour lamp taking 4 amps. with a *P.D.* of 150 volts, giving much more intense illumination.

Materials.—The purest obtainable bromine was further purified by distilling it twice over potassium bromide and zinc oxide, and finally over phosphorus pentoxide in an all-glass system; it was stored over phosphorus pentoxide. The *cyclo*hexane was purified by repeated shaking with sulphuric acid, and finally by distillation. The hydrogen used in the gauge was passed over hot palladinised copper and through drying tubes. Oxygen was obtained by electrolysis of hot baryta solution and was dried before entering the apparatus.

FIG. 1.



The tap leading to the bromine reservoir was lubricated with a mixture of nujol and paraffin wax, which sufficed for some weeks without renewal. The most satisfactory lubricant for the tap to the *cyclo*hexane reservoir was a mixture of chlorinated bees' wax and aniline.

Method of Operation.—Connexion was first made between the water pump and the *cyclo*hexane and bromine reservoirs in turn, and a quantity of the vapours was drawn over to remove air present in the reservoirs. This operation was only repeated after the taps on these reservoirs had been cleaned out.

The whole system was evacuated by the diffusion pumps for some hours. *cyclo*Hexane and bromine vapours were then admitted to the reaction vessel to known pressures, as follows : Pure hydrogen was let into the gauge up to the tap T to a measured pressure; by regulating the temperature of the *cyclo*hexane, it was then let into the system to a slight excess pressure, the tap T_1 was shut, T opened, and the excess drawn out by turning T_2 until the level on the sulphuric acid manometer was the same on both sides. T was now shut, more hydrogen was let into the gauge, and bromine vapour let into the reaction cell until the pressure was just below that in the gauge. T was then opened, T_1 shut, and bromine let in until the pressures on each side were the same.

The progress of the reaction was followed by observing the pressure decrease on the sulphuric acid manometer, T_1 being turned off when measurements were taken.

As the thermal reaction between bromine and *cyclo*hexane is appreciable at the temperatures used, it was necessary to measure this in order to ascertain the amount due to the photochemical reaction alone. This was usually done by screening off the light for a time and measuring pressure decreases due to the dark reaction only. Measurements were also made in which the thermal reaction was allowed to proceed to completion.

Before each run the system was evacuated for at least 2 hours. The reaction vessel was heated with a Bunsen burner while under a high vacuum to remove the reaction products which condensed on the cell and cut down the light entering the system.

The pressures employed (in terms of Hg, to which all measurements are reduced) were about 5 cm. of *cyclo*hexane and 4 cm. of bromine, an excess of the former being invariably present. The pressure changes finally recorded did not, in general, correspond to any definite stage in the bromine substitution, but were somewhat variable. It was therefore necessary to run the reaction to completion in each case, the final value being taken as proportional to the amount of bromine present, and bromine concentrations at any one time being deduced from the pressure changes at that time.

The following are the results of two typical runs at 30° for the dark reaction, which required about 4 hours for completion; $k = 1/t. \log_{10} a/(a - x)$. Cell A (with flattened ends) was used.

	(I.)	(II.)
Press. of bromine vapour (cm.)	3·89	3·86
,, *cyclo*hexane vapour (cm.)	5·51	5·55
Press. change for complete reaction, t_∞ (cm.)	1·620	1·470

	(I.)			(II.)		
t, mins.	Press. fall, cm.	$a - x$.	$k \times 10^4$.	Press. fall, cm.	$a - x$.	$k \times 10^4$.
0	0·606	1·014	—	0·108	1·362	—
25	0·907	0·713	64	0·509	0·961	60
50	1·088	0·532	63	0·801	0·669	62
75	1·217	0·403	57	0·961	0·509	58
100	1·320	0·300	56	1·100	0·370	55
125	1·418	0·202	55	1·198	0·272	55
150	1·480	0·140	57	1·277	0·193	57
175				1·326	0·144	59
		Mean	59		Mean	58

The thermal reaction is thus seen to conform to the unimolecular law. As the photochemical reaction also conforms to the same law, it was thought that this reaction might be due to diffuse daylight, but blackening of the lead tubes only reduced the coefficient to 0·0049, which must be due to a true dark reaction.

Temperature Coefficient of the Photochemical Reaction.—In these experiments, the first lamp mentioned on p. 2470 was used with a filter transmitting the green line. The reaction cell was filled as before, and removal of a stop let the light into the system. Readings were taken every minute, the light was shut off, and the thermal reaction velocity measured. As before, the reaction was taken to completion.

Experiments were conducted at 30° and at 40°, one of the latter being recorded as an example :

Br_2 pressure = 4·41 cm. C_6H_{12} pressure = 5·17 cm. $\propto$ value = 2·090 cm.

Green filter.

t.	$a - x$.	$k \times 10^4$.	t.	$a - x$.	$k \times 10^4$.	t.	$a - x$.	$k \times 10^4$.
0	1·937		8	1·598	103	12	1·451	101
5	1·718	102	9	1·556	105	13	1·417	104
6	1·682	101	10	1·522	104	14	1·385	103
7	1·635	104	11	1·484	104		Mean	103

k for thermal velocity = 70

	Press. of				
Temp.	C_6H_{12}.	Br_2.	k for green filter.	k (thermal).	k (green alone).
40°	4·41	5·17	0·0103	0·0071	0·0032
	4·03	5·27	0·0106	0·0070	0·0036
30	3·91	5·07	0·0099	0·0066	0·0033
	4·01	5·06	0·0099	0·0065	0·0034

The temperature coefficient of the photochemical reaction is thus unity within the limits of accuracy of the experiment. By the use of the mercury lamp with no filter, unimolecular coefficients were also obtained. Two experiments gave a temperature coefficient of 1·05 :

Temp.	k (total).	k (thermal).	k (photochemical alone).
40°	0·027	0·007	0·020
30	0·025	0·006	0·019

The thermal reaction appears to have only a slight temperature coefficient. In these experiments, the capillary connexions were not blackened.

The measurement of the thermal velocity coefficient at 100° gave a value of $k = 0{\cdot}011$.

The small temperature coefficient of the dark reaction would appear to point to this being a surface action rather than a true bulk reaction (compare Norrish, J., 1923, **123**, 306). Experiments with two different reaction cells at 30° gave identical velocity coefficients, and the ratio of surface area to volume was the same in each case, thus lending support to this view.

Effect of Intensity of Light.—In this series of experiments, the glass mercury lamp was replaced by a quartz lamp giving much more intense light. The reaction-cell used had plane parallel glass windows. The light intensities were compared by means of a thermopile and galvanometer. In making measurements, the thermostat cell was removed and the thermopile brought up to the same position behind the cell in each case. The intensity was varied by altering the distance of the lamp from the system, and is given in terms of the galvanometer deflexion.

Light intensity, cm.	Pressure of		$k \times 10^4$.	
	Br_2.	C_6H_{12}.		
9·55	3·73	5·33	645	Mean 654
	4·01	5·09	663	
6·00	4·06	5·02	450	Mean 441
	4·02	5·07	440	
	3·91	5·17	435	

Separate determination of the thermal velocity coefficient gave $k = 0{\cdot}0060$.

Ratio of reaction velocities $= (654 - 60)/(441 - 60) = 1{\cdot}56$.

Ratio of light intensities $= 9{\cdot}55/6{\cdot}00 = 1{\cdot}59$.

The agreement shows proportionality between velocity and light intensity.

Influence of Concentration of cyclo*Hexane.*—In all the foregoing experiments, the original *cyclo*hexane pressure was within 10% of 5 cm. No general falling off of the unimolecular coefficient was observed as the *cyclo*hexane concentration was reduced during the progress of the reaction, and it would thus appear that the rate is independent of the *cyclo*hexane pressure. An attempt was made to test this point by using *cyclo*hexane pressures of from 5 to 2 cm. with 4 cm. of bromine. With 5 and 4 cm. of *cyclo*hexane, the total pressure changes for complete reaction were approximately the same, and the unimolecular coefficients were identical, corresponding to the substitution of 2—3 atoms of bromine; with 3·2 cm. the total pressure changes were less, corresponding either to incomplete substitution or to incomplete removal of bromine. The reaction was therefore followed by direct measurement of the bromine concentration, which, together with pressure measurements, should give an indication of the extent of the substitution by bromine. This was effected by measurements of the intensity of the emergent light with a potassium photoelectric cell. The light from the mercury lamp passed through a condensing lens on to a stop placed at the focal distance from a second lens, the approximately parallel beam being passed through the reaction vessel on to the cell. The photoelectric cell was in series with a galvanometer, a high resistance, and a constant voltage of 159 volts. For calibration, galvanometer readings were taken corresponding to bromine pressures measured on the sulphuric acid manometer. The reaction could be followed by plotting galvanometer deflexions against time. Simultaneous galvanometer and pressure readings were made for experiments with various *cyclo*hexane concentrations. It was found that the bromine pressure plotted against pressure changes gave a straight line—the gradient in all cases corresponding to the substitution of two bromine atoms in the molecule—thus confirming the assumption that the bromine concentration could be taken as proportional to the difference in pressure from the infinity value. With low *cyclo*hexane concentrations, the pressure change ceased before complete removal of bromine, although, for the initial stages of the reaction, bromine pressures plotted against pressure changes gave a straight line of the same gradient as with higher *cyclo*hexane concentrations.

The table shows values of the unimolecular coefficient ($k' = 1/t . \log_{10} [Br_2]_0/[Br_2]_t$) for the removal of bromine calculated from bromine concentrations measured with the photoelectric cell for various *cyclo*hexane concentrations.

C_6H_{12} press., cm.	Br_2 press., cm.	$k' \times 10^4$.	C_6H_{12} press., cm.	Br_2 press., cm.	$k' \times 10^4$.
7·13	2·10	198	3·93	1·79	187
6·10	2·01	186	3·12	1·53	178
5·24	2·25	182	2·11	1·96	161

It will be seen that the rate is independent of the *cyclo*hexane concentration within the limits of experimental error.

Influence of Oxygen.—Preliminary experiments showed that the reaction was inhibited by oxygen. The velocity in the presence of pressures of oxygen from 0·01 to 1 cm. Hg was measured. Oxygen was let into the gauge up to the tap T to a known pressure, diluted with hydrogen, and pumped out to a measured pressure (about 2 cm. Hg); the reaction vessel was evacuated, and the oxygen–

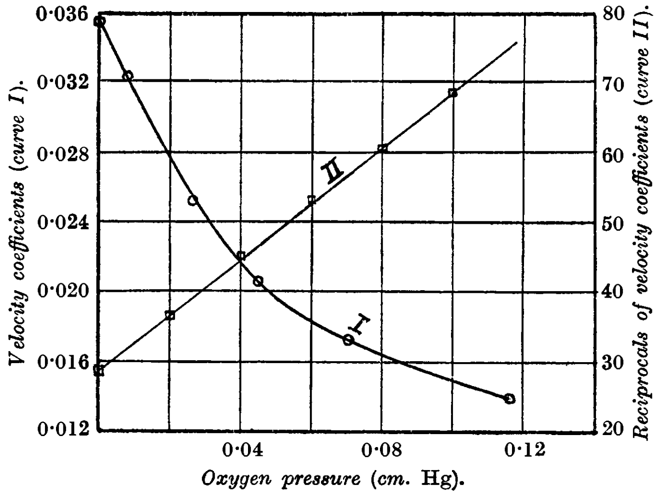
hydrogen mixture let in to the system; 5 cm. of *cyclo*hexane and 4 cm. of bromine were let into the reaction vessel as before, and the velocities measured.

In this series of experiments the capillary connexions were blackened; the thermal velocity was measured in the absence of oxygen and gave $k = 0{\cdot}0048$. The light intensity was kept constant throughout.

The table shows the velocity coefficients for various oxygen pressures. It is to be noted that the reaction still obeys the unimolecular law.

Pressures (cm. Hg) of					
O_2.	C_6H_{12}.	Br_2.	k.	k (thermal).	k (photochem.).
0·000	5·13	4·14	0·0403	0·0048	0·0355
0·0083	5·44	3·94	0·0380	,,	0·0322
0·0261	5·57	3·87	0·0300	,,	0·0252
0·045	5·05	3·96	0·0255	,,	0·0207
0·070	5·24	3·93	0·0221	,,	0·0173
0·116	5·19	3·95	0·0187	,,	0·0139
0·49	5·13	3·76	0·0094	0·0050	0·0044
1·05	4·87	4·00	0·0066	0·0045	0·0021

FIG. 2.



The thermal velocity coefficient does not diminish for oxygen pressures up to 0·49 cm., but for 1 cm. it appears to fall slightly. These results are plotted in Fig. 2 (Curve I). Curve II shows the values of oxygen pressure plotted against the reciprocals of the corresponding velocity coefficients; it will be seen that a straight line is obtained.

The inhibition by oxygen can thus be represented by the equation (compare p. 2468)

$$k_{O_2} = Kk_8/(k_8 + k_9[O_2]),$$

where K is the velocity coefficient in absence of oxygen, k_{O_2} is that for a pressure of oxygen $[O_2]$, and k_9 is a constant. From the gradient of the curve the value of k_9/k_8 is found to be 14·8, and the values deduced from the velocity coefficients with oxygen equal to 0·49 and 1·05 cm. Hg were 14·4 and 15·0, respectively, *i.e.*, agreement with this equation extends up to the highest oxygen pressures used. Experiments were not attempted at higher pressures because k_{O_2} becomes too small.

From the value of k_9/k_8, it is possible to deduce a value for the mean life of the excited complex $C_6H_{12}Br_2'$; when the oxygen pressure is expressed in mm. Hg (instead of cm.), $k_9/k_8 = 1·48$. Now, $k_9/k_8 = (1/T)/(1/\tau)$, where τ is the mean life of the complex, and T, the time between successive collisions of oxygen and the complex (each of which is assumed to be effective in causing deactivation) for unit oxygen pressure, is given by $T = 1/A\sigma^2$, where

$$A = 2667\sqrt{2\pi N(m_1 + m_2)/R\theta m_1 m_2} \text{ (Turner, \textit{loc. cit.})}.$$

Taking a value of σ as 10^{-7} cm. for the mean of the diameters of the oxygen molecule and the complex, we obtain $T = 2·1 \times 10^{-8}$ sec., whence $\tau = 3 \times 10^{-8}$ sec., a value comparable with those obtained for excited molecules by other methods.

Summary and Interpretation of Results.

In the photobromination of *cyclo*hexane under conditions where the light absorption is proportional to the concentration of bromine, it is found that the photoreaction has no temperature coefficient for light of wave-length $\lambda = 5460$ Å. in the range 30—40°. The reaction rate is directly proportional to the light intensity and independent of the concentration of the *cyclo*hexane.

This form of unimolecular law is shown to be compatible, when, as in this case, no chain formation occurs, with two hypotheses : (1) the reaction may proceed through the formation of bromine atoms, or (2) the primary action may be the formation of an excited bromine molecule, the life of which is long compared with the time between collisions with a molecule of the acceptor.

The reaction velocity is reduced by the presence of oxygen. The inhibition is found to be independent of the pressure of the *cyclo*hexane. The quantitative data lead to the conclusion that not atoms but excited bromine molecules are the primary photoactive constituent; further, that it is not these excited molecules but the excited $C_6H_{12}Br_2'$ molecules which are deactivated on collision with oxygen. The mean life of this complex is *ca.* 3×10^{-8} sec. The mechanism of the photobromination and inhibition by oxygen can accordingly be described by the reactions (1A), (7), (8), (9), and (10) (see p. 2468). The thermal bromination of *cyclo*hexane proceeds slowly on the surface of glass at 30°.

If the following values be taken for the heats (in Cals.) of linking in the various reactions employed: C–Br = 62; C–H = 87; $Br_2 \longrightarrow 2Br = 46{\cdot}2$; $H + Br = HBr + 77{\cdot}7$; energy in the radiation $Nh\nu = 53{\cdot}2$, it is clear that the excited bromine molecule of energy content 53·2 Cals. cannot break a C–H union by impact and subsequent transference of its energy alone, but only by forming an association complex, which then undergoes rearrangement. From the above data we obtain

$$C_6H_{12} + Br_2 \longrightarrow C_6H_{11}Br + HBr + 6{\cdot}5$$
$$C_6H_{12} + Br_2' \longrightarrow C_6H_{11}Br + HBr + 59{\cdot}7$$

The products of reaction thus contain 59·7 Cals. If, as is imagined by some (Marshall, *J. Physical Chem.*, 1925, **29**, 842), the hydrogen bromide carries away this energy, there seems no reason why there should not be reaction chains in this reaction as in the bromination of toluene where similar conditions obtain. If, on the other hand, the energy is retained by the bromo-derivative, the difference in structure between bromo*cyclo*hexane and benzoyl bromide may account for the difference in reaction; in one, the transfer of energy to another bromine–hydrogen complex in the same ring is possible, forming dibromo*cyclo*hexane; in the other, the energy is localised on a side chain and can apparently only be transmitted to another molecule on collision. It is hoped to examine the chain formation in the photobromination of toluene in the near future.

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