and its chance of being deactivated would be greater the higher the pressure. In this way the results of the gas analysis could be qualitatively explained.

If this suggestion is correct then a correction is needed in our calculation of the rate constant K from dp/dt, for it is seen that the constant of proportionality would be different at different pressures. This effect, however, would not be sufficient to affect the general character of our results, nor the conclusions which one can draw from them.

Preliminary Results on Divinyl Ether

A series of experiments over a range of pressures from 0.5 to 150 mm. has been made with divinyl ether. The log K–log p curves are very similar to those of diethyl ether, with even more pronounced upward curvature.

Acknowledgment.—We are grateful to the Milton Fund of Harvard University for a grant which made it possible to complete the experimental work reported in this paper.

Summary

The rate of decomposition of diethyl ether vapor has been studied at temperatures of 525, 478 and 462° and over pressures ranging from one- or two-tenths of a millimeter to several hundred millimeters. These results have been presented both in tables and in graphs, and have been compared with the results of other experimenters. It is found that when one plots the logarithm of the rate constant as ordinate against the logarithm of the pressure, the curve which one obtains is in this case concave upward, contrary to the usual situation with unimolecular reactions.

A detailed account is given of two possible theories, which can explain this behavior. According to Hypothesis A, in addition to the unimolecular reaction whose rate constant is beginning to fall off at moderate pressures, there is a second, distinct unimolecular reaction by way of which diethyl ether can decompose, and which becomes of importance at low pressures because of the fact that, while its rate constant is relatively small, it does not fall below its limiting high pressure value even at the lowest pressures used. According to Hypothesis B, the molecule may be divided into an active part which can transmit energy rapidly to the bond which breaks or changes in the reaction, and an inactive part. The shape of the curves is then explained on the assumption that there is a slow transfer of energy from the inactive to the active part of the molecule. Various variants and generalizations of these theories are discussed, and their application to several other reactions is considered.

Some analyses of the reaction products, as they exist toward the beginning of a run in the decomposition of the diethyl ether, are reported. These are discussed in the light of the above theories, and a tentative suggestion is made concerning the mechanism of the reaction.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Photochemical Gas Phase Reaction between Chlorine and Bromotrichloromethane

BY HAROLD G. VESPER AND G. K. ROLLEFSON

The photochemical reaction between chlorine and bromotrichloromethane in solution was first studied by Noddack,[1] who reported a quantum yield of one at high concentrations decreasing to about 0.2 in dilute solutions. A later study by Grüss[2] reported a quantum yield of 0.88 ± 0.25 independent of the concentration of bromotrichloromethane. The variations found by Noddack were attributed to impurities in the reagents used by him. In both these researches it was assumed that the products formed were carbon tetrachloride and bromine and the extent to which the reaction had proceeded was determined by measuring the light absorbed by the bromine. As recent investigations in this Laboratory and elsewhere[3] have shown that bromine and chlorine react to form bromine chloride, which has a markedly different absorption coefficient from bromine, it seemed probable that this reaction was not as simple as had been supposed, but involved a chain process. The results to be presented in this paper confirmed this view and a

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[1] Noddack, *Z. Elektrochem.*, **27**, 359 (1921).

[2] Grüss, *ibid.*, **29**, 144 (1923).

[3] (a) Vesper and Rollefson, THIS JOURNAL, **56**, 620 (1934); (b) Blair and Yost, *ibid.*, **55**, 4489 (1933).

mechanism which will account for the observed facts has been set up.

Apparatus and Experimental Procedure

The apparatus used has been described previously.[3a] After several preliminary experiments with other light sources, the mercury arc with the filter for the 0.366 μ lines described there was used. For the first group of experiments, in which the dependence of reaction rate on the concentrations of reactants was studied, the filter was placed 12 cm. from the reaction vessel, so that the greater part of the vessel was illuminated, and as much illumination as possible with the available filter was obtained. In determining the quantum yield, and the effect of temperature and pressure, the filter was placed only 3 mm. from the front of the vessel, and provided with a screen having an opening 1.5 cm. high by 7.5 cm. long (the width of the filter), the whole placed so that the beam passed through the center portion of the vessel only. These arrangements are referred to in the discussion as A and B, respectively. The latter arrangement made it possible to determine quantum yields with only a small uncertainty arising from the curvature of the reaction vessel.

The group of lines at 0.366 μ was selected in order to avoid the decomposition of bromotrichloromethane itself, which occurs[2] in the region below 0.335μ according to the equation

$$2CBrCl_3 = C_2Cl_6 + Br_2$$

and because approximately monochromatic light of considerable intensity could thus be obtained with the arc and filter used.

Bromotrichloromethane was prepared by treating carbon tetrachloride with aluminum bromide, which in turn was prepared from the elements and purified by sublimation before using; 260 g. of aluminum bromide and 350 cc. of carbon tetrachloride were allowed to stand at room temperature for three days. The solid matter was then filtered out and the solution washed with dilute potassium carbonate solution and with water; the water was then separated and the solution of organic halides dried over calcium chloride. The bromotrichloromethane was then purified by repeated fractional distillation; 45 cc. of colorless product boiling between 104.2 and 104.35° at 758.5 mm., with a density of 2.012 at 23.5°, was finally obtained. These values agree closely with those obtained by Paterno.[4]

It was necessary to introduce the gaseous bromotrichloromethane into the reaction vessel first, since the total pressure upon adding the chlorine was greater than the vapor pressure of the acceptor. After adding the chlorine the mercury arc was started and brought to a steady state before exposing the reaction mixture.

The amount of reaction was measured by means of a König-Martens spectrophotometer, using the green lines of the helium discharge.

Experimental Results

A. Reaction Products.—It became evident in preliminary experiments that the free halogen produced by the reaction is largely bromine chloride, instead of bromine as assumed by the earlier workers. This was shown by the fact that after the reaction rate had dropped to zero, the extinction of the mixture in the green ($\lambda = 0.502\ \mu$) was only about 30% of the amount to be expected if all the bromotrichloromethane originally present had reacted to form bromine, and from the fact, which was to be expected, that gaseous bromine and carbon tetrachloride could be illuminated without evidence of reaction. (Thus the possibility of a photostationary state was ruled out.)

Examination of mixtures of bromine and chlorine as described previously established the value of the extinction coefficient at $\lambda = 0.502\ \mu$ and the value of the dissociation constant of gaseous bromine chloride. It then became possible to calculate the concentrations of chlorine, bromine chloride and bromine present at any time, from the total extinction and the initial chlorine concentration. The calculations showed that the formation of carbon tetrachloride from bromotrichloromethane was complete (within the limits of accuracy of the constants) after the reaction rate had dropped to zero. That the organic product of the reaction was solely carbon tetrachloride, no hexachloroethane being formed, was evident from the constancy of pressure of the reaction mixture throughout the course of the reaction.

The reaction, in presence of excess chlorine, may be expressed by the equations

$$Cl_2 + CBrCl_3 = BrCl + CCl_4, \text{ and}$$
$$Cl_2 + 2CBrCl_3 = Br_2 + 2CCl_4$$

the latter being almost negligible in extent. It should be noted that since 1 cm. of bromine chloride caused a change in the angle θ on the spectrophotometer of only 0.5°, it was necessary to read, *i. e.*, to set for equal brightness of the fields, with the greatest care, and to use at least sixteen observations in a set, in order to obtain the desired accuracy. Deviations of the experimental data from the mean values are to be attributed to this source above all others, especially since the slightest irregularity in the surface of the bearing parts would favor certain readings above others.

B. Dependence of the Rate upon Concentrations.—In these experiments the incident light intensity was kept fixed by controlling the voltage and current of the mercury arc; the initial concentration of one of the reactants was

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(4) Paterno, *Jahresb. Forts. Chemie*, **24**, 259 (1871).

then varied, using constant initial concentration of the other. The rate of reaction was found to decrease markedly as the reaction proceeded, in fact almost inversely as the concentration of bromine chloride after a slight amount had been formed. For this reason, extrapolation of the slopes of the reaction curves to obtain the value of the initial rate was rather uncertain, and recourse was had to a comparison of rates at given values of bromine chloride formed, for various concentrations of chlorine and of bromotrichloromethane.

As shown in Table I, the rate varies directly with the chlorine concentration, raised to a power greater than one, and less than 3/2. As shown in Table II, the rate varies with bromotrichloromethane concentration, raised to a power somewhat greater than 1/2.

The marked retarding effect of bromine chloride is shown, not only by Tables I and II, but also in a special series of experiments in which chlorine and bromine and bromotrichloromethane were allowed to stand together in the dark (about three hours) until nearly complete equilibrium between chlorine, bromine, and bromine chloride was attained; the mixture was then illuminated for about one minute to complete the attainment of halogen equilibrium, and then the extinction measured as usual and illumination over periods sufficient to produce new bromine chloride from the bromotrichloromethane was carried out. Representative rates thus obtained are shown in Table III, compared with rates obtained without initial bromine chloride. These are not comparable with the rates given in Tables I and II, as a different illumination arrangement was used.

TABLE I

RATES AT 2 CM. BrCl FORMED

Illum. arr. A; 28°C.; pressures in cm. of H_2SO_4 at 0°

No. of check runs..............	3	2	2	3
Initial Cl_2, cm.	70.8	35.2	23.1	16.9
Initial $CBrCl_3$, cm.	16.3	16.2	16.1	16.5
Rate, cm./min.	0.238	0.095	0.063	0.034
Rate/$(Cl_2) \times 10^3$	3.46	2.75	2.98	2.28
Rate/$(Cl_2)^{3/2} \times 10^4$	4.17	4.95	6.20	5.90

TABLE II

RATES AT 2 CM. BrCl FORMED

Illum. arr. A; 28°C.; pressures in cm. of H_2SO_4 at 0°

No. of check runs..............	3	3	2	2
Initial Cl_2, cm.	70.8	70.1	61.3	77.0
Initial $CBrCl_3$, cm.	16.3	8.43	5.62	2.84
Rate, cm./min.	0.238	0.157	0.093	0.0404
Rate/$(CBrCl_3)^{1/2} \times 10^2$	6.3	6.2	4.9	4.4
Rate/$(CBrCl_3) \times 10^2$	1.66	2.44	2.58	4.8

C. Dependence of the Rate upon Light Intensity.—No measurable reaction occurred in the absence of light, either at 28°, or at 50°. In the latter case, less than 0.1 cm. of bromine chloride appeared in ten hours; this change is within the limit of experimental error in the reading of the spectrophotometer.

The intensity of light incident upon the reaction vessel was varied by the use of a fine-mesh screen placed over the filter. This screen had been calibrated previously and found to have a transmission of 29.0%. A check of this figure was obtained by determining the relative intensity with and without the screen, after passing through the empty reaction vessel, by means of the photocell and illumination arrangement B previously described. This gave 30.3% as the transmission of the screen.

The galvanometer deflection using the photocell could then be taken as a measure of the relative light intensity for experiments made at different times, with and without the screen; slight changes in the condition of the arc were thus allowed for. Some of the results are given in Table IV; the galvanometer deflections for the empty vessel just after the runs are designated (g).

It is evident from Table IV that incident light intensity enters the rate law to a power slightly greater than one-half. It was thus possible to separate the effect of light absorption from the specific effect of concentration of chlorine, upon the reaction rate.

The extinction coefficients, at λ = 0.366μ, for chlorine and bromine chloride were determined experimentally, using illumination arrangement

TABLE III

Illum. arr. B; 28°C.; pressures in cm. of H_2SO_4 at 0°

Initial pressures, cm.				At CCl_4 formed:			At CCl_4 formed:		
Cl_2	BrCl	Br_2	$CBrCl_3$	cm.	BrCl cm.	Rate cm./min.	cm.	BrCl, cm.	Rate cm./min.
71.6	0	0	16.4	1.0	1.0	0.198	2.0	2.0	0.134
60.2	10.4	0.2	16.4	1.0	11.4	0.039−	2.0	12.4	0.032

Since chlorine pressure affects the rate, a small correction should be made to allow for the somewhat smaller chlorine pressure in the runs with added bromine chloride, but this is a second order effect compared to the retardation due to BrCl.

TABLE IV

Illum. arr. B; 28°C.; pressures in cm. of H_2SO_4 at 0°

No. of check runs		3	2
(G.), cm.		50.8	17.7
Initial Cl_2, cm.		71.6	71.6
Initial $CBrCl_3$, cm.		16.4	16.5
At 2 cm. BrCl formed	Rate cm./min.	0.134	0.076
	Rate/g.$^{1/2}$ × 10^2	1.88	1.80
	Rate/g. × 10^3	2.60	4.30
At 3 cm. BrCl formed	Rate cm./min.	0.100	0.054
	Rate/g.$^{1/2}$ × 10^2	1.40	1.28
	Rate/g. × 10^3	2.00	3.10

B and the photocell previously mentioned. This was a Weston Photronic cell, with a cardboard screen fitted over its face to cover all but an oblong area 6 mm. high and 27 mm. long just below the inactive button in the center. The cell was mounted just behind the reaction vessel, in line with the center of the beam from the 15 × 75 mm. slit in the metal covering of the glass filter. Table V shows the fraction of the incident intensity absorbed by chlorine and by bromine chloride in the presence of each other, for various initial concentrations of chlorine, as the concentration of bromine chloride is increased during the course of the reaction. The figures are computed on the basis of 38 mm. average distance traversed by the beam (illumination arrangement B), but may also be used for illumination arrangement A without serious error, as the average distance traversed is slightly less, but the relative effect is about the same.

TABLE V

LIGHT ABSORPTION BY MIXTURES OF CHLORINE AND BROMINE CHLORIDE

I_0 = incident intensity; $\lambda = 0.366\,\mu$; $I_a = AI_0$ = total intensity absorbed, where $A = 1 - e^{-(i'c' + i''c'')d}$ = fraction of incident intensity absorbed by both: i' = coefficient for Cl_2 = 0.00787; i'' = coefficient for BrCl = 0.0282; c' = cm. of H_2SO_4 (0°C.) Cl_2; d = 3.8 (cm.); c'' = same for BrCl; $A = A' + A''$ where $A' = i'c'A/(i'c' + i''c'')$ = fraction of I_0 absorbed by Cl_2 and similarly for A''.

Initial Cl_2, cm.	Bromine chloride formed: 0 cm. $A = A'$- ($A'' = 0$)	2 cm. A	2 cm. A'	2 cm. A''	4 cm. A	4 cm. A'	4 cm. A''
71.0	0.724	0.749	0.678	0.071	0.771	0.635	0.136
52.0	.610	.645	.564	.081	.677	.521	.156
32.2	.442	.492	.398	.094	.538	.356	.182
23.9	.352	.408	.307	.101	.462	.268	.194
13.1	.211	.282	.177	.105	.346	.134	.212

It is apparent from Table V that the relative absorption of light by the bromine chloride formed as the reaction proceeds is considerable. "Internal filter" action may thus be partly responsible for the marked decrease in rate produced by bromine chloride, although it fails to account for more than a part of the total effect. Furthermore, as will be shown later, the reaction has a quantum yield several times unity; in such a reaction the formation of atoms effective in continuing chains is more important than the source of the atoms. If the chains are initiated by chlorine atoms and continued through bromine atoms, absorption of light by bromine chloride should be as effective, or nearly so, as absorption of light by chlorine. For the present, the total absorption by the mixture will be used in separating the effect of light absorption from a specific effect of chlorine concentration. Since incident intensity enters the rate law to a power slightly over one-half, the rates divided by the square root of Å, the total fraction of light absorbed, will be used. Table VI shows the result; chlorine concentration enters the rate law specifically to a power between one-half and one.

The data used are the same as given in Table I; the mean values of reaction rate at each bromine chloride concentration are carried over to Table VI.

TABLE VI

Initial Cl_2, cm.	70.8	35.2	23.1	16.9
Initial $CBrCl_3$, cm.	16.3	16.2	16.1	16.5
At 2 cm. BrCl:				
Rate, cm./min.	0.238	0.095	0.063	0.034
A	.748	.519	.400	.330
Rate/$A^{1/2}(Cl_2)^{1/2}$	.0332	.0229	.0216	.0153
Rate/$A^{1/2}(Cl_2)$	.00400	.00375	.00472	.00397

D. Dependence of the Rate upon Total Pressure.—As shown in Table VII, the addition of the inert gases, nitrogen and carbon dioxide, produced practically no effect upon the reaction rate (except for a slight inhibiting effect in some cases at the beginning of the reaction), although the total pressure was thus increased up to five-fold.

TABLE VII

Illumination arrangement B; 28°C.

Initial Cl_2, cm.	Initial $CBrCl_3$, cm.	Added gas, cm.		Total pressure, cm.	Rate at BrCl formed = 1 cm.	2 cm.	3 cm.	4 cm.
70.9	8.20	N_2	323	402	0.138	0.078	0.050	0.036
70.8	8.21	CO_2	331	410	.129	.073	.047	.035
70.7	8.20	CO_2	206	285	.111	.061	.044	.035
70.7	8.17	CO_2	102	181	.130	.072	.040	.033
70.7	8.17		...	79	.134	.079	.051	.037
71.0	8.13		...	79	.120	.074	.052	.043

E. Temperature Coefficient.—In order to determine the effect of temperature on this reaction, three experiments were performed at 50°. Columns two to four of Table VIII show the values for the ratio $\text{rate}_{50°}/\text{rate}_{28°}$ for various initial chlorine concentrations and for various concentrations of bromine chloride formed. Since this ratio increases only slightly with increasing bromine chloride concentration, the effect of a change in the extinction coefficient of bromine chloride with temperature upon the temperature coefficient of the reaction may be assumed to be small. No appreciable amount of the temperature coefficient can be attributed to change in the absorption by the chlorine as Gibson and Bayliss[5] have shown that the extinction coefficient of chlorine at $\lambda = 0.364\ \mu$ increases only 3% upon raising the temperature from 18 to 168°. Therefore the effect we have observed is to be attributed entirely to the effect of temperature upon the processes following the light absorption.

The effect of temperature is definitely greater at the lower chlorine concentrations. Aside from a possible change in the extinction of bromine chloride, which would be more noticeable at lower chlorine concentration, the effect would indicate that temperature enters in more than one way into the rate law. The effect is, however, small, and may be neglected in comparison to the over-all coefficient. The effect of temperature upon a given rate constant may be expressed by the Arrhenius equation

$$k = se^{-E/RT}$$

where the factor s includes collision number, which varies as $T^{1/2}$, and steric and probability factors, assumed independent of temperature.

Values of E, the heat of activation, obtained from the experimental rate ratios by use of this equation, are given in the last column of Table VIII.

TABLE VIII

Initial Cl_2, cm.	Rate at 50°/Rate at 28° at BrCl formed =				E, cal./mole
	1 cm.	2 cm.	3 cm.	Av.	
54	1.71	1.77	1.98	1.82	5100
35.5	2.04	1.87	2.05	1.95	5700
23.5	2.38	2.75		2.59	8300

F. Quantum Yield.—It is evident that the quantum yield of this reaction is actually several times the value given by Noddack[1] or by Grüss,[2] even from their own experimental results, since if the reaction product were mainly bromine chloride instead of bromine as they supposed, the extinction obtained would represent about ten times the number of chlorine molecules decomposed, even allowing for an equilibrium mixture containing some bromine. The quantum yield, defined as molecules of Cl_2 which reacted per quantum of light absorbed, thus appears to be the order of magnitude ten instead of one in their experiments.

To determine the quantum yield in the gaseous reaction, the photocell described in Section C was calibrated at $\lambda = 0.366\ \mu$ against a surface thermopile, which in turn was calibrated by means of a carbon filament lamp standardized by the U. S. Bureau of Standards; the photocell was used as described on page 1458.

Values of the quantum yield so obtained are given in the last two columns of Table IX, calculated on the basis of total absorption, and of absorption by chlorine only, respectively. It is evident that "internal filter" action is not alone responsible for the retarding action of bromine chloride.

TABLE IX

Illum. arr. B; 28°

(G)	Cl_2, cm.	Br_2, cm.	BrCl, cm.	$CBrCl_3$, cm.	Rate, cm./min.	A (total)	A' (Cl_2)	γ_A	$\gamma_{A'}$
46.2	70.0	0	1.0	15.4	0.188	0.736	0.700	28.6	30.0
	69.0	.01	2.0	14.4	.134	.749	.678	20.0	22.1
	68.0	.02	3.0	13.4	.100	.760	.656	14.7	17.0
45.3	34.2	.01	1.0	15.4	.086	.496	.449	19.8	21.9
	33.2	.02	2.0	14.4	.063	.519	.426	13.8	16.8
	32.2	.03	3.0	13.4	.042	.541	.405	8.8	11.8

Discussion of Results

It is evident from the values of quantum yield that the reaction involves chains of over 30 links at the start, and that the chain length is affected adversely by the products of the reaction. Addition of carbon tetrachloride in certain experiments produced no marked effect upon the reaction rate, while addition of bromine chloride did (see Table III). Therefore bromine chloride must use up the active intermediates or render them less effective.

Although the rate varied approximately as the square root of incident intensity, no pressure effect could be observed. Therefore recombination of the active intermediates to inactive substances is homogeneous, but does not require triple collisions.

The absence of any pressure change during the reaction leads to the conclusion that radicals such as CCl_3 probably do not occur in the mechanism as they might be expected to form C_2Cl_6 which would condense out and cause a pressure change. This actually occurs when CCl_3Br is

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[5] Gibson and Bayliss, *Phys. Rev.*, [2] **44**, 188 (1933).

illuminated with light which dissociates it into CCl_3 and atomic bromine.

From the marked specific effect of chlorine, it is evident either that the reaction of chlorine atoms with bromotrichloromethane is enhanced by the presence of molecular chlorine, or that the retarding effect of bromine chloride is decreased by chlorine, or that chlorine is necessary to the continuance of the chains, or more than one of the possibilities taken together.

A chain mechanism satisfying the above requirements is as follows

$$
\begin{array}{llll}
(1) & Cl_2 + h\nu & = Cl + Cl & \\
(2) & Cl + Cl_2 & = Cl_3 & \\
(3) & Cl + CBrCl_3 & = CCl_4 + Br & \\
(3') & Cl_3 + CBrCl_3 & = CCl_4 + Cl_2 + Br & \\
(4) & Br + Cl_2 & = BrCl + Cl & \text{Chain-continuing step} \\
(5) & Cl + BrCl & = Cl_2 + Br & \left.\right\} \text{Retarding effect of} \\
(5') & Cl_3 + BrCl & = 2Cl_2 + Br & \left.\right\} \text{BrCl} \\
(6) & BrCl + h\nu & = Br + Cl & \\
(7) & Br + Cl_3 & = BrCl + Cl_2 & \text{Principal chain-terminating reaction}
\end{array}
$$

No other single chain-terminating reaction gives a rate law in as good agreement with the experimental results as does the one written, although it is not unlikely that other such reactions may occur to some extent.

Applying the usual methods of calculation and making no approximations other than neglecting terms due to chain terminating steps which appear in sums with terms due to the chain continuing reactions, we obtain

$$
\frac{d(CBrCl_3)}{dt} = \frac{k_3'(Cl_2)(CBrCl_3)\sqrt{(k_2k_4/k_7)}\,AI_0}{qq'} + k_3(CBrCl_3)\sqrt{\frac{k_4}{k_2k_7}\,AI_0\,\frac{q'}{q}} \qquad (J)
$$

in which

$$
\begin{aligned}
q &= k_2(Cl_2) + k_3(CBrCl_3) + k_5(BrCl) \\
q' &= k_3'(CBrCl_3) + k_5'(BrCl)
\end{aligned}
$$

The first term of this rate law is in accord with the experimental facts but the second is not, therefore we may assume that 3′ is the principal reaction yielding carbon tetrachloride and 3 may be neglected. The equation then becomes

$$
-\frac{d(CBrCl_3)}{dt} = \frac{k_0\sqrt{A(Cl_2)(CBrCl_3)}}{\sqrt{\left(1 + k'\frac{(BrCl)}{(Cl_2)}\right)\left(1 + k''\frac{(BrCl)}{(CBrCl_3)}\right)}} \qquad (K)
$$

in which

$$
k_0 = \sqrt{\frac{k_3'k_4}{k_7}}\,I_0 \qquad k' = \frac{k_5}{k_2} \qquad k'' = \frac{k_5'}{k_3'}
$$

If Cl_3 is not introduced into the mechanism of the reaction, recombination would involve atoms only. Since the rate depends on the square root of light intensity, recombination is second order, with respect to the active intermediates. Such recombination, if involving two free atoms, should require a "triple collision," the third body being necessary to remove part of the heat of reaction and thus stabilize the newly-formed molecule. The higher the total pressure, the faster the recombinations and the less the rate of the main reaction should be; such effects have been observed in the recombination of hydrogen atoms by Smallwood[6] and by Senftleben and Riechemeier.[7] Since increase of pressure has no effect upon the rate of the present reaction, some doubt is cast upon the possibility of recombination through free atoms. Nevertheless, we have calculated the rate laws corresponding to the chain terminating steps $Br + Cl = BrCl$, $Br + Br = Br_2$ and $Cl + Cl = Cl_2$. In no case did the calculated law agree with experiment. We have also calculated the theoretical laws corresponding to $Cl + Cl_3 = 2Cl_2$ and $Cl_3 + Cl_3 = 3Cl_2$ and found them to be incompatible with the experimental results. The only chain-terminating step which gives a law in agreement with the experiments is our reaction (7) $Br + Cl_3 = BrCl + Cl_2$.

The resulting rate law, equation (L) may be rewritten

$$
(\text{rate})^2 = \frac{k_0^2(Cl_2)A(CBrCl_3)}{\left(1 + k'\frac{(BrCl)}{(Cl_2)}\right)\left(1 + k''\frac{(BrCl)}{(CBrCl_3)}\right)}
$$

$$
\text{or } \frac{(Cl_2)A(CBrCl_3)}{(\text{rate})^2\left(1 + k''\frac{(BrCl)}{(CBrCl_3)}\right)} = \frac{1}{k_0^2} + \frac{k''\,(BrCl)}{k_0^2\,(Cl_2)} \qquad (M)
$$

$$
\text{or } \frac{(Cl_2)A(CBrCl_3)}{(\text{rate})^2\,(1 + k'\,(BrCl)/(Cl_2))} = \frac{1}{k_0^2} + \frac{k''\,(BrCl)}{k_0^2\,(CBrCl_3)} \qquad (N)
$$

By arbitrarily choosing one constant, as k'' in equation (M), the left side of the equation may be evaluated and plotted as a function of the variable ratio on the right side of the equation, as $(BrCl)/(Cl_2)$ in equation (M). The intercept on the axis of ordinates will then be $1/k_0^2$, and the slope of the straight line will be (for equation (M)) k'/k_0^2. Thus k' is determined. This has been done for $k'' = 0$ and for $k'' = 0.7$ (Fig. 1). While the two-constant equation ($k'' = 0$) is in moderately good agreement with experiment, the introduction of $k'' = 0.7$ gives excellent agreement. This is shown conversely by choosing

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[6] Smallwood, THIS JOURNAL, **51**, 1985 (1929).

[7] Senftleben and Riechemeier, *Physik. Z.*, **31**, 360 (1930); *Ann. Physik*, [5] **6**, 105 (1930).

$k' = 200$ from the slope in Fig. 1 and evaluating the left side of equation (N). This plotted as a function of $(BrCl)/(CBrCl_3)$—(Fig. 2)—has a slope corresponding to $k'' = 0.7$; the intercept is, as before, 0.18×10^4. These results are with illumination arrangement, A.

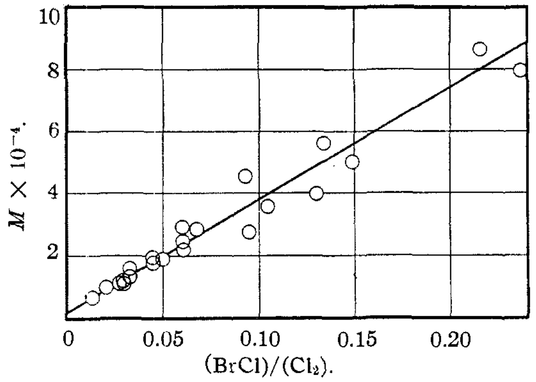

Fig. 1.—Linear representation of results.

$$M = \frac{(Cl_2)A(CBrCl_3)}{(\text{rate})^2 1 + k''((BrCl)/(CBrCl_3))}$$

(Equation (M): $k'' = 0.7$)

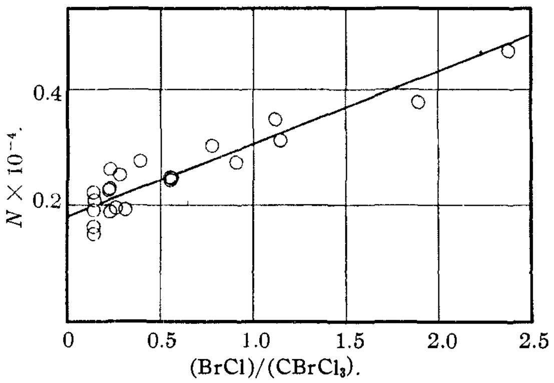

Fig. 2.—Linear representation of results.

$$N = \frac{(Cl_2)A(CBrCl_3)}{(\text{rate})^2 1 + k'((BrCl)/(Cl_2))}$$

(Equation (N): $k' = 200$)

The heat of activation calculated from the temperature coefficient is the net effect produced by the several heats of activation (all of which are small) for the reactions taking place. The trend of the experimental value, from 5 to 8 kg. cal. as the chlorine concentration is reduced to one-third of the highest value, may be due to relative change in the magnitudes of k_2 and k_5, or to the appearance, to a small extent, of other reactions at the higher temperature—other types of recombination perhaps, or the second term of equation (J), representing reaction of free chlorine atoms with bromotrichloromethane. In the latter case, the actual heat of activation for that reaction is probably higher than that for reaction (3′).

Summary

The photochemical reaction between chlorine and bromotrichloromethane in the gaseous state has been investigated kinetically, using the wave length 0.366 μ. The reaction may be expressed by the equations:

$$Cl_2 + CBrCl_3 = BrCl + CCl_4 \quad (1)$$

$$Cl_2 + 2CBrCl_3 = Br_2 + CCl_4 \quad (2)$$

reaction (2) being almost negligible.

The photochemical reaction goes to completion; the rate is proportional to absorbed intensity raised to a power slightly over one-half. No reaction occurs in the dark, at temperatures up to 50°.

The reaction rate is markedly retarded by bromine chloride. The rate is not affected by increase of total pressure, but is doubled by inincrease of temperature from 28 to 50°.

The quantum yield of the reaction is at least 30 at the beginning of the reaction, and decreases to less than 10 as the concentration of bromine chloride becomes large. Decrease in chlorine concentration or in bromotrichloromethane concentration decreases the quantum yield.

A mechanism for the reaction has been proposed, and a rate law derived therefrom, which fits the experimental data.

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