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The Bromine Sensitized Photochemical Decomposition of Gaseous Dibromotetrachloroethane

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In an attack on the problem of addition of halogens to carbon double bonds under the influence of light the photochemical addition of chlorine to tetrachloroethylene has been studied[1,2] both in carbon tetrachloride solution and in the gaseous state. In each, the chlorination was found to proceed as a chain reaction with rates approximately represented by the equation $-d(Cl_2)/dt = k(I_{abs.})^{1/2}(Cl_2)$. With the object of examining other reactions of this type, we have made preliminary experiments on the bromination of gaseous tetrachloroethylene. These experiments involved the measurement of pressure changes when a gaseous mixture of bromine and tetrachloroethylene was illuminated. In one case, using substantially the same apparatus as previously described,[2] a mixture of 85 mm. of bromine and 26 mm. of tetrachloroethylene was illuminated at 50° in a liter flask. Although the pressure decreased with the formation of colorless crystals, the rate was very low; two 60-watt lighting bulbs placed near the reaction vessel without filters gave a pressure drop of only 3 mm. per hour. In an effort to obtain higher rates for convenient measurement, the apparatus was rebuilt to operate at higher temperatures. However, when a mixture was illuminated at 100° very little if any pressure decrease was observed. A mixture of 26.2 mm. of bromine and 15.2 mm. of tetrachloroethylene showed on prolonged illumination with a 500-watt projection lamp a drop in total pressure from 41.4 to 40.4 mm., an amount hardly outside the experimental error. Nevertheless, when this same mixture was illuminated at 30° a definite, although slow, pressure decrease occurred, and crystals formed.

These experiments suggested that a bromine-sensitized photochemical decomposition of dibromotetrachloroethane readily occurs. Further experiments have borne out this supposition; these experiments are described in the present paper together with measurements which show the decomposition to be a chain reaction and which give indication of its mechanism.

Materials

Bromine was prepared from potassium bromate and potassium bromide. Potassium bromate and then concentrated sulfuric acid was added to a saturated solution of potassium bromide (each salt had been twice recrystallized). Bromine was distilled off and allowed to stand over anhydrous calcium bromide (prepared by twice recrystallizing C. P. calcium bromide and dehydrating at 145°). The bromine was distilled off and the treatment with calcium bromide repeated.

Dibromotetrachloroethane was prepared by the direct union of bromine and tetrachloroethylene under the influence of white light.[3] Liquid tetrachloroethylene (prepared as previously described[2]) and a slight excess of bromine were sealed in a small tube and illuminated with an incandescent lamp. The excess bromine was pumped off and the solid sublimed *in vacuo*. From its mode of preparation, the symmetrical compound 1,1,2,2-tetrachloro-1,2-dibromoethane is presumed to result.

Apparatus

The reaction was followed by measuring pressure in an apparatus with the reacting substances in contact with glass only. The reaction cell was a cylindrical Pyrex vessel with flat end faces; it was 6.2 cm. in diameter and 4.0 cm. in length (internal dimensions). Attached to the cell were a small side tube to which liquid air could be applied, and a clicker type glass diaphragm gage[4] for use with a mercury manometer. There was also a connection to a diffusion pump and finally a connection to a side-tube containing a weighed sample of dibromotetrachloroethane (in a glass capsule sealed *in vacuo*), and a magnetically operated hammer. Similar provision was made for admitting bromine and tetrachloroethylene.

Before filling, the reaction cell was first surrounded by a gas furnace and evacuated and baked out. The reactants were admitted using a technique similar to that previously described.[2] Finally the solid dibromotetrachloroethane was sublimed onto the side walls of the cylindrical reaction vessel; the end windows were kept reasonably free of solid and the clicker diaphragm entirely so. The reaction volume remaining was 132 cc. and was kept substantially constant from one experiment to another.

After filling, the reaction cell, side-tube and clicker were surrounded by a light-tight air thermostat provided with a vigorous fan; a chimney around the cell ensured circulation. Illumination occurred through a window in the thermostat wall; the light beam was well collimated and defined by a diaphragm opening 4.00 cm. in diameter. The light source used for quantum yield determinations was a vertical type quartz mercury arc provided with filters for the blue line 4358 Å. as previously described.[2] The light intensity was measured frequently by moving

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[1] J. A. Leermakers and R. G. Dickinson, THIS JOURNAL, **54**, 4648 (1932).

[2] R. G. Dickinson and J. L. Carrico, *ibid.*, **56**, 1473 (1934).

[3] Beilstein, 4th ed., Vol. 1, p. 93.

[4] Smith and Taylor, THIS JOURNAL, **46**, 1393 (1924).

the light source unit away from the thermostat and placing a Moll small-surface thermopile at the center of the 4.00-cm. diaphragm. The thermopile and its galvanometer were calibrated bare against a Bureau of Standards lamp; in use, the thermopile was provided with a window which compensated the reflection loss at the thermostat window. After correction for (a) reflection loss at the entrance window of the reaction cell, (b) slight non-uniformity of the beam over the area of the diaphragm, and (c) non-linearity of galvanometer scale it was found that 1 cm. of corrected galvanometer deflection corresponded to a flux of 623 ergs per second or 2.28 × 10^{-10} einsteins per second of radiation 4358 Å. entering the reacting gas.

The fraction of the radiation absorbed was ordinarily calculated from the known partial pressure of bromine. The equation used was $I/I_0 = 10^{-\alpha c d}$ where c is the concentration of bromine in moles per liter, $d = 4.00$ cm., and $\alpha = 154$. This value of α was determined by Dr. P. G. Murdoch in this Laboratory. Gray and Style[5] found 160, and Ribaud[6] found 149.5. We have ignored the small change of α with the temperature. In some cases the fraction of radiation absorbed was measured directly by allowing the radiation which had traversed the reaction vessel to pass through a second thermostat window to a thermopile. The absorption was determined by making alternate galvanometer readings with and without liquid air applied to the freezing-out tube. In the calculation of quantum yields, account was taken of the absorption of radiation reflected from the back windows of the cell and thermostat.

In some experiments where higher light intensities were desired a 500-watt projection lamp was substituted for the mercury arc.

The Vapor Pressure of Dibromotetrachloroethane

Since solid dibromotetrachloroethane was present in many of the experiments, a knowledge of the vapor pressure was necessary. This was obtained by subliming dibromotetrachloroethane into the evacuated reaction vessel, pumping down, sealing off, and measuring the pressure at various temperatures with the clicker and manometer. Measurements made in a series of ascending temperatures up to 135° agreed with those made by progressively lowering the temperature, except in one case that gave evidence of a very slow thermal decomposition at 135°. The measurements were made on dibromotetrachloroethane from two different samples. The thermal decomposition at 150° was slow enough that the value at this temperature is nearly as reliable as the others.

TABLE I

VAPOR PRESSURE OF SOLID DIBROMOTETRACHLOROETHANE

Temp., °C.	Vapor press., mm.	Temp., °C.	Vapor press., mm.
50	0.4	110	9.8
75	1.3	125	19.6
90	3.5	135	29.4
100	6.0	150	50.9

The Nature of the Reaction.—When a gas containing dibromotetrachloroethane and not too high pressures of bromine and tetrachloroethylene was illuminated at temperatures of 100° or more, a steady increase of pressure occurred which continued until the dibromotetrachloroethane was substantially gone. This is illustrated by the data of Table II, which were obtained by illumination with 4358 Å. at 135° until no further pressure increase occurred. The final pressures calculated on the assumption of complete decomposition are in substantial agreement with the observed values.

TABLE II

EXTENT OF PHOTODECOMPOSITION AT 135°

Initial composition			Final total pressure	
$C_2Cl_4Br_2$, mg.	C_2Cl_4, mg.	Br_2, mg.	Obsd., mm.	Calcd., mm.
41.2	..	21.2	75.7	74.4
81.7	..	22.0	121.8	123.3
89.0	22.2	..	130.9	131.2

After a series of decomposition measurements had been made at a given elevated temperature, the reaction could be reversed by bringing the mixture to room temperature and illuminating it strongly. Enough recombination of bromine and tetrachloroethylene could be secured in this way to permit making a new series of dibromotetrachloroethane decomposition measurements in a pressure range comparable to that of the first.

A check on the supposition that these pressure increases and decreases corresponded to decomposition and formation of dibromotetrachloroethane was obtained by measuring, at various times, the transmission of the gas for 4358 Å. Values of the bromine partial pressure calculated from the light transmission ordinarily agreed to within about 1 mm. with those calculated from the initial composition and momentary total pressure of the reaction mixture.

When mixtures containing comparatively large amounts of tetrachloroethylene and bromine but initially no dibromotetrachloroethane were illuminated at 135°, a slow pressure decrease occurred which ceased before the total pressure drop had become large. Thus a mixture of 124.5 mm. of bromine and 155.1 mm. of tetrachloroethylene showed on fifty-six hours illumination a pressure decrease of 13.4 mm.; and one containing initially 203.5 mm. of bromine and 147.5 mm. of tetrachloroethylene showed a drop of 15.7 mm. A quantum yield determination made at the beginning of the first of these experiments gave only 0.3 mole of dibromotetrachloroethane produced per einstein absorbed.

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(5) L. M. T. Gray and D. W. G. Style, *Proc. Roy. Soc.* (London), **126**, 603 (1930).

(6) G. Ribaud, *Ann. Physik*, **12**, 107 (1919).

After the mixtures described in the preceding paragraph had reached a steady state at 135°, they were cooled to 100° in the dark. It was found that their pressures remained several mm. higher than would be calculated from the gas laws and the vapor pressure of dibromotetrachloroethane on the assumption that the pressure decrease at 135° was due solely to dibromotetrachloroethane formation. This discrepancy was shown not to be due to supersaturation and can hardly be due to perfect gas law failure. Since the gases had been given unusually long illuminations at 135°, the effect suggests that some slow secondary reaction, possibly an isomerization, occurred. When illumination of these mixtures was continued at 100°, a further pressure drop with the separation of solid took place; the steady total pressures at this temperature were 231.6 mm. and 227.0 mm., respectively.

In experiments on dibromotetrachloroethane decomposition much lower partial pressures of bromine and tetrachloroethylene than those in the above experiments have been used in order to make the rate of formation negligible. In the decomposition experiments alteration of the temperature of mixtures in which reaction had occurred gave pressure changes in satisfactory agreement with those expected from the gas laws and the vapor pressure of dibromotetrachloroethane.

Quantum Yield Measurements.—The results of some of the measurements of the quantum yield of dibromotetrachloroethane decomposition are summarized in Table III. The pressures listed are in all cases the means of the values prevailing at the beginning and end of intervals of illumination. In Nos. 1 to 27 and 32 to 61 a considerable excess (about 2 g.) of solid dibromotetrachloroethane was present in the reaction vessel; in experiments 28 to 31 a much smaller amount of solid was present. There is good assurance that the gas remained substantially saturated with this substance during illumination; for successive pressure measurements made in the dark but beginning immediately after the close of illumination, showed no pressure increase. Thermal reaction was found negligible up to temperatures including 135°. In computing quantum yields at 150° we have first subtracted the dark rate from the much larger total rate in the light; this procedure is, of course, somewhat arbitrary. Separate fillings of the reaction vessel

TABLE III

QUANTUM YIELD OF DECOMPOSITION OF DIBROMOTETRACHLOROETHANE 4358 Å.

(Quantum yield at 150° corrected for a thermal decomposition rate of 13.8×10^{-4} mm. total pressure increase per second.)

No.	Mean pressure of bromine, mm.	Δp_{total}, mm.	Corrected galv. defl., cm.	Fraction of light absorbed	Time of illum., sec.	Moles of $C_2Cl_4Br_2$ dec. per einstein
1	4.7	3.3	25.4	0.274	12,090	0.490
2	13.0	12.8	22.4	.579	24,600	.497
3	17.9	7.0	21.9	.693	10,920	.527
4	22.8	4.6	22.5	.776	7,500	.438
5	31.7	7.2	19.9	.869	14,760	.352
6	46.2	3.9	21.0	.946	9,000	.272
Nos. 1 to 6: T = 100°; $p_{C_2Cl_4Br_2}$ = 6.0 mm.; $p_{C_2Cl_4} = p_{Br_2} - 3.9$ mm.						
7	18.7	13.8	28.4	0.685	2160	3.83
8	24.4	9.1	6.9	.775	5400	3.68
9	29.0	9.4	26.7	.832	1410	3.50
10	33.3	7.8	26.7	.865	1200	3.29
11	37.3	8.0	26.7	.895	1200	3.26
12	42.8	14.4	26.7	.925	2400	2.84
Nos. 7 to 12: T = 125°; $p_{C_2Cl_4Br_2}$ = 19.6 mm.; $p_{C_2Cl_4} = p_{Br_2} - 4.0$ mm.						
13	18.1	10.0	20.5	0.665	1140	7.30
14	23.6	11.7	20.5	.756	1255	6.84
15	29.6	12.2	20.8	.827	1260	6.39
16	35.7	12.1	20.8	.877	1260	6.00
17	40.3	6.1	5.3	.905	2400	6.04
18	45.3	14.0	20.8	.930	1500	5.49
Nos. 13–18: T = 135°; $p_{C_2Cl_4Br_2}$ = 29.4 mm.; $p_{C_2Cl_4} = p_{Br_2} - 4.1$ mm.						
19	7.9	11.7	24.4	0.386	966	14.7
20	13.2	9.5	6.1	.554	1914	16.8
21	17.0	5.8	6.2	.645	960	17.3
Nos. 19 to 21: T = 135°; $p_{C_2Cl_4Br_2}$ = 29.4 mm.· $p_{C_2Cl_4} = p_{Br_2}$; p_{N_2} = 484 mm.						
22	6.3	7.6	19.1	0.323	300	46.7
23	10.35	8.6	19.1	.470	240	45.4
24	14.9	9.6	19.1	.594	240	40.2
25	21.1	15.2	19.1	.719	330	38.2
26	27.0	8.4	19.0	.800	180	34.9
27	32.55	13.8	18.9	.855	300	32.3
Nos. 22 to 27: T = 135°; $p_{C_2Cl_4Br_2}$ = 29.4 mm.; $p_{C_2Cl_4} = p_{Br_2}$						
28	6.3	6.7	14.9	0.323	600	26.4
29	10.05	8.2	14.5	.461	540	25.9
30	14.2	8.4	14.4	.580	480	23.85
31	18.3	8.0	14.6	.670	420	22.2
Nos. 28 to 31: T = 135°; $p_{C_2Cl_4Br_2}$ = 29.4 mm.; $p_{C_2Cl_4} = p_{Br_2} + 25.8$ mm.						
32	33.4	18.8	22.3	0.857	600	17.2
33	41.1	9.6	5.64	.902	1200	14.4
34	46.7	10.5	22.3	.932	600	15.2
Nos. 32 to 34: T = 150°; $p_{C_2Cl_4Br_2}$ = 50.9 mm.; $p_{C_2Cl_4} = p_{Br_2} - 4.3$ mm.						

gave rates which were sometimes discordant to the extent of 5-fold. In an effort to reduce this irreproducibility a number of series of measurements were made on a single filling by the device of reversing the reaction at room temperature after each series had been made. In Table III, Nos. 1 to 18 and 32 to 34 were made on the same filling; in these the quantum yield of decomposition is seen to increase considerably with the temperature and to reach values sufficiently high as to leave little doubt that the reaction has a chain mechanism.

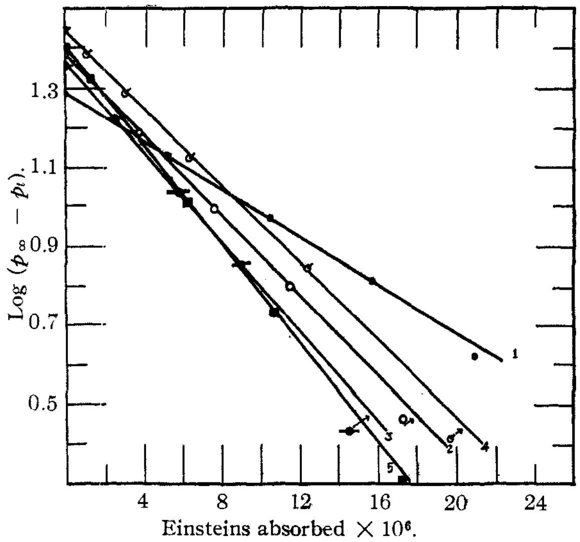

Fig. 1.—Runs at 135° showing linear dependence of rate of dibromotetrachloroethane photodecomposition on partial pressure of dibromotetrachloroethane. $\text{Log}_{10}(p_\infty - p_t)$ approximates $\log_{10} p_{C_2Cl_4Br_2}$, p_∞ being final total pressure and p_t being total pressure at the time t. Incident radiation intensity was kept essentially constant for each run.

	p_∞, mm.	Final p_{Br_2}, mm.	Final $p_{C_2Cl_4}$ mm.
1	75.7	50.7	25.0
2	121.7	73.2	46.8
3	120.8	72.3	45.9
4	130.9	52.4	78.1
5	129.6	51.1	76.8

Effect of Bromine and Tetrachloroethylene.—Consecutive measurements on a single filling showed only a minor dependence of the quantum yield of decomposition on the partial pressures of the products. Thus in 22 to 27 a five-fold increase in the partial pressures of the products produced a 30% decrease in quantum yield. In view of the small quantum yield of *formation* at much higher bromine and tetrachloroethylene pressures, this decrease is more probably ascribable to inhibition of the decomposition than to reversal of the reaction.

Effect of Dibromotetrachloroethane.—In order to investigate the effect of dibromotetrachloroethane pressure independently of that of temperature, quantum yield measurements were made at 135° in the absence of solid. The quantum yields were found to fall off with dibromotetrachloroethane pressure and to do so approximately linearly. The results of the measurements are shown in Fig. 1, where the abscissas are $I_{\text{abs.}}$, the total radiation absorbed in einsteins, and the ordinates are $\log_{10}(p_\infty - p_t)$; p_t is the momentary total pressure and p_∞ its final constant value. Since the partial pressure of dibromotetrachloroethane was very low at the steady state, its momentary value is given approximately by $(p_\infty - p_t)$; moreover, since the rate of dibromotetrachloroethane *formation* may be presumed to vary little during these runs compared with the rate of *decomposition*, linearity of the log $(p_\infty - p_t)$ *vs.* $I_{\text{abs.}}$ plot implies proportionality of rate to dibromotetrachloroethane pressure in the decomposition.

Dependence of Rate on Intensity of Incident Light.—The dependence of rate on intensity was examined at somewhat higher intensities at 135° by substituting for the mercury arc a 500-watt projection lamp used with the same filters. (The spectral region isolated was from about 4100 to 4800 Å.) Results of such experiments are Nos. 42 to 47 of Table IV. The relative intensities of the incident radiation were controlled by interposing in the incident beam neutral wire screens of known transmission. Since the lamp intensity was kept constant, the fractional transmission τ of the screen is a measure of the relative incident intensity. Measurements at lower and higher intensities were alternated on the same reaction mixture. The results are expressed as ratios of rates to incident relative intensities; values of these ratios $\Delta p/\tau\Delta t$ are seen to be larger at the lower intensities than in the adjacent higher intensity runs.

The effect was examined at much higher intensities by using the projection lamp with no filters except the cupric chloride solution. Since the rates became very large, it was necessary to use special precautions to ensure that a decrease in $\Delta p/\tau\Delta t$ did not result simply from depletion of dibromotetrachloroethane in the reaction zone. For this purpose a magnetically operated shutter timed by a pendulum was used. The reaction was carried on in one-second periods and after each second of illumination the reaction mixture was left in the dark for two minutes. Numbers 48 to 52 give results of such measurements; an 11-fold decrease in the light intensity produced a 1.66-fold increase in $\Delta p/\tau\,\Delta t$. Numbers 53 to 55 were made with the same radiation with screens of much lower transmission; in these experiments the rates are not far from proportional to the intensities.

In order to determine whether depletion of dibromotetrachloroethane in the reaction zone at high intensities had been sufficiently avoided, measurements (Nos. 56 to 61) were made in which a single four-second illumination at the highest intensity was followed by four one-second illuminations separated by two-minute dark intervals. The two modes of illumination gave indistinguishable values of $\Delta p/\tau\,\Delta t$.

The experiments then show that at the lower intensities of Table III the rates are essentially proportional to the first power of the intensity; but that at sufficiently high intensities, the rates increase less rapidly than with the first power.

TABLE IV

EFFECT OF LIGHT INTENSITY ON RATE OF DECOMPOSITION

Nos. 42 to 48: Projection lamp light filtered to give 4100–4800 Å. Nos. 48 to 62. Projection lamp light filtered to give 4100–6400 Å.

No.	Mean p_{Br_2}, mm.	Time Δt, sec.	Press. increase, Δp, mm.	$I_0 = \tau_{screen}$	$\Delta p/\tau\,\Delta t$
42	27.2	1200	10.3	0.090	0.096
43	31.7	90	8.0	1.000	.089
44	35.2	600	5.8	0.090	.107
45	38.5	90	7.7	1.000	.086
46	41.9	600	6.0	0.090	.111
47	47.1	90	8.0	1.000	.089
48	25.7	10	7.6	1.000	0.76
49	29.4	60	7.3	0.090	1.35
50	35.8	17	14.7	1.000	0.86
51	42.3	50	6.7	0.090	1.49
52	45.3	7	6.5	1.000	0.93
53	32.9	255	6.8	0.0132	2.02
54	36.7	1005	8.2	.0038	2.15
55	40.6	265	7.4	.0132	2.11
56	48.7	4[a]	3.3	1.000	0.83
57	50.4	4[b]	3.5	1.000	.88
58	52.2	4[a]	3.4	1.000	.85
59	53.8	4[b]	3.3	1.000	.83
60	55.5	4[a]	3.4	1.000	.85
61	57.2	4[b]	3.4	1.000	.85

$T = 135°$; $p_{C_2Cl_4Br_2} = 29.4$ mm.; $p_{C_2Cl_4} = p_{Br_2}$; $p_{N_2} = 484$ mm.

[a] Illumination in consecutive seconds. [b] Illumination in single seconds separated by two-minute dark intervals.

Mechanism of the Reaction.—The bromine-sensitized photodecomposition of gaseous dibromotetrachloroethane is similar, in a number of respects, to the iodine-sensitized decomposition of ethylene iodide in carbon tetrachloride solution. For the latter reaction the rate of decomposition according to Schumacher and Wiig[7] is given by the equation $d(I_2)/dt = k(I_{abs.})^{1/2}(C_2H_4I_2)$. Following the suggestions made by Polissar[8] concerning the mechanism of the sensitized thermal decomposition of ethylene iodide, Schumacher and Wiig have given a chain mechanism for the photochemical decomposition. In this mechanism, recombination of iodine atoms in collision with carbon tetrachloride molecules is the chain-breaking step, and leads to proportionality of the rate with the square root of the intensity. Essentially the same mechanism may be adapted to the dibromotetrachloroethane case if it be supposed that at the lower pressures and intensities recombination of the bromine atoms occurs (presumably as a wall reaction) in such a way that this recombination is of first order with respect to the bromine atom pressure. This supposition is not entirely arbitrary; the bromine atom recombination in the photochemical formation of hydrogen bromide has been interpreted[9] as a wall reaction at low pressures and a gaseous reaction at high pressures. Allowing also for the possibility of dibromotetrachloroethane formation, the mechanism becomes

$$Br_2 + h\nu \longrightarrow 2Br \qquad (1)$$
$$Br + C_2Cl_4Br_2 \rightleftharpoons C_2Cl_4Br + Br_2 \qquad (2) \text{ and } (2')$$
$$C_2Cl_4Br \rightleftharpoons C_2Cl_4 + Br \qquad (3) \text{ and } (3')$$
$$Br \longrightarrow Br\ (\text{wall}) \longrightarrow {}^1/_2Br_2 \qquad (4)$$
$$2Br + M \longrightarrow Br_2 + M \qquad (5)$$

This leads to the rate expression·

$$\frac{d(Br_2)}{dt} = \frac{-k_4 + \sqrt{k_4^2 + 16k_5(M)(I_{abs.})}}{4\,k_5(M)} \times \frac{[k_2k_3(C_2Cl_4Br_2) - k_{2'}k_{3'}(C_2Cl_4)(Br_2)]}{[k_3 + k_{2'}(Br_2)]}$$

At low intensities and sufficiently small values of $k_{2'}k_{3'}(C_2Cl_4)(Br_2)$ to make reverse reaction unimportant, the rate becomes

$$\frac{d(Br_2)}{dt} = \frac{2k_2(I_{abs.})}{k_4}\ \frac{k_3(C_2Cl_4Br_2)}{[k_3 + k_{2'}(Br_2)]}$$

The mechanism thus attributes inhibition by the products to the bromine. On the assumption that k_4 remained constant in a series of measurements on a given filling, then with $(C_2Cl_4Br_2)$ constant the quantum yield should be inversely pro-

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[7] H. J. Schumacher and E. O. Wiig, *Z. physik. Chem.*, **B11**, 50 (1930).

[8] M. Polissar, THIS JOURNAL, **52**, 956, 3132 (1930).

[9] Jost and Jung, *Z. physik. Chem.*, **B3**, 83 (1929).

portional to [1 + $k_{2'}(\mathrm{Br_2})/k_3$]. The data of Table III lead to a value of $k_{2'}/k_3$ of 0.016 mm.$^{-1}$ or 4 × 10^5 cc. × mole^{-1} at 135° and slightly higher values at lower temperatures.

The variation of rate with intensity for a mixture of given composition should be of the form $\mathrm{d(Br_2)/d}t = a(-1 + \sqrt{1 + bI_0})$. From experiments 48 to 55 of Table IV, the rates have, for each of four intensities covering a 250-fold range, been interpolated to the same composition (that where $p_{\mathrm{Br_2}} = 36.7$ mm.). These rates together with those calculated placing $a = 0.135$ mm/sec. and $b = 16$ are shown in Table V.

TABLE V

EFFECT OF LIGHT INTENSITY AT CONSTANT COMPOSITION

$I_0 = \tau_{\text{screen}}$	$\mathrm{dBr_2/d}t$, mm./sec. obsd.	$\mathrm{dBr_2/d}t$ mm./sec., calcd.
0.0038	0.0041	0.0041
.0132	.014	.014
.0900	.065	.075
1	.43	.42

A knowledge of b permits the calculation of the order of magnitude of the bromine atom concentration, for, if the variation of ($I_{\text{abs.}}$) over the reacting space at any moment be ignored, bI_0 evidently becomes equal to 16 $k_5(\mathrm{M})(I_{\text{abs.}})/k_4^2$. For experiments where the intensity is low enough so that $k_4(\mathrm{Br}) >> k_5(\mathrm{M})(\mathrm{Br})^2$, we may place $k_4(\mathrm{Br}) = 2(I_{\text{abs.}})$ and also $k_4(\mathrm{Br}) = 2(\mathrm{dBr_2/d}t)/\varphi$ where φ is the quantum yield. Making these substitutions

$$bI_0 = \frac{4\varphi k_5(\mathrm{M})(\mathrm{Br})^2}{\mathrm{d(Br_2)/d}t}$$

The value of k_5 may be taken as 2.9 × 10^{15} cc.^{2} mole^{-2} sec.$^{-1}$.[10] At, for example, the first intensity of Table V $bI_0 = 0.061$, (M) = 587 mm., $\mathrm{d(Br_2)/d}t = 0.0041$ mm./sec.; taking $\varphi = 10$ as a reasonable value, (Br) is calculated as 2 × 10^{-12} mole/cc. This is considerably larger than the thermal equilibrium value of (Br), 8 × 10^{-16} mole cc.$^{-1}$, as it should be if the proposed mechanism is to be tenable. The thermal equilibrium value was calculated from the results of Bodenstein and Cramer.[11] It may be added that the calculated (Br) can readily be shown to be much larger than is necessary to give sufficient collisions with dibromotetrachloroethane to account for the rate of reaction and also to be much larger than is necessary to give sufficient collisions with the wall to account for the chain breaking rate.

Summary

A bromine-sensitized photodecomposition of gaseous dibromotetrachloroethane has been found and measurements of the quantum yield made at temperatures up to 150°. The decomposition has been found to proceed as a chain reaction; the chain is presumed to be similar to that which has been suggested for the iodine-sensitized decomposition of ethylene iodide in carbon tetrachloride solution. The quantum yields have been found to be independent of the intensity at low intensities but to fall off at higher intensities. Photochemical recombination of bromine and tetrachloroethylene has been found to be comparatively slow.

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[10] Kassel, "Kinetics of Homogeneous Gas Reactions," Chemical Catalog Co., p. 248.

[11] Bodenstein and Cramer, *Z. Elektrochem.*, **22**, 327 (1916).