PHOTOCHEMICAL REACTIONS INVOLVING THE DOUBLE BOND BETWEEN CARBON ATOMS

I. THE PHOTOCHLORINATION and THE CHLORINE-SENSITIZED PHOTO-OXIDATION OF GASEOUS TETRACHLOROETHYLENE

II. THE BROMINE-SENSITIZED PHOTODECOMPOSITION OF GASEOUS DIBROMOTETRACHLOROETHANE

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I. OBJECT OF THE INVESTIGATIONS

The express purpose of the work to be presented was to determine, in so far as possible, the products formed, the intermediates formed, the factors controlling the rate, and the mechanism involved in the addition reaction of oxygen, on the one hand, and the addition of chlorine, on the other, at the double bond between the two carbon atoms of tetrachloroethylene, C_2Cl_4. Interest was centered, perhaps, on the intricacies of the oxidation, and still is.

In attempting to study the bromine addition at the double bond of tetrachloroethylene, experimental facilities accentuated the study of the elimination of two bromine atoms from dibromotetrachloroethane, $C_2Cl_4Br_2$, and the accompanying double bond formation between two carbon atoms rather than the addition reaction study. It was highly probable that a study of the elimination of two halogen atoms from two adjacent carbon atoms would elucidate the processes involved in the addition of the two halogen atoms to the adjacent carbon atoms.

To be more explicit concerning the intermediate compounds involved, it was desirable to establish evidence for or against the existence of a Cl_3 or a Br_3 molecule postulated as a transient intermediate by certain investigators.

II. LITERATURE SURVEY OF SOME PHOTOCHEMICAL REACTIONS CONCERNING THESE INVESTIGATIONS

The role of oxygen in photochemical processes is a variable and non-predictable one. Concerning the present investigations, the inhibitory action of oxygen is involved. Wildermann[1] and Dyson and Harden[2], independently, found that the photochemical formation of phosgene, $COCl_2$, from chlorine and carbon monoxide was retarded by the presence of oxygen. Schultze[3] observed that a chlorine-sensitized oxidation of the carbon monoxide to carbon dioxide was occurring and that small amounts of oxygen had relatively greater effects than larger amounts.

Bauer and Daniels[4] have found that the thermal bromination of cinnamic acid in carbon tetrachloride solution is critically inhibited by free oxygen and they have unknowingly studied the photobromination of an oxygen-inhibited reaction.

Dickinson and Leermakers[5] found that traces of oxygen almost completely inhibited the photochlorination of tetrachloroethylene in carbon tetrachloride solution and a chlorine-sensitized photo-oxidation occurred.

Chapman[6] found that free oxygen inhibited the photochlorination of chloroform in carbon tetrachloride solution and a chlorine-sensitized photo-oxidation occurred.

In contradistinction to these inhibitions by oxygen, however, Kharasch and Mayo[7] found that in the absence of oxygen or peroxides, hydrogen bromide adds slowly to allyl bromide, $CH_2 = CH - CH_2Br$, forming 1-2 dibromopropane; but in the presence of oxygen or peroxide, the addition is very rapid and 1-3 dibromopropane is the product. Though this is not a photochemical reaction, it has a place here since it shows that oxygen is capable of increasing the velocity of addition reactions at the double bonds between two carbon atoms.

The nature of the products of photo-oxidation reactions involving the double bonds between two carbon atoms is a point for investigation. Besson[8] found that tetrachloroethylene and oxygen on intensive illumination by sunlight produced trichloroacetyl chloride and phosgene. These same products were formed in chlorine-sensitized photo-oxidation of tetrachloroethylene in carbon tetrachloride solution.[5]

Horio and Yamashita[9] have investigated the oxidation of linseed oil and linoleic acid under the full radiation of a quartz Hg-arc. Peroxides were found to be present. The presence of a peroxide, phosgene, and hydrogen chloride in the products of the chlorine-sensitized photo-oxidation of chloroform in carbon tetrachloride solution was proven by Chapman[6]. Bowen and Steadman[10] found a peroxide, colorless and stable in solution, formed by illuminating a benzene solution of red rubrene, $C_{42}H_{28}$, and dissolved oxygen with visible radiation.

The dependence of oxidation rates on concentrations of reactants is manifold. The rate of photo-oxidation of linoleic acid, olive oil, and linseed oil is independent of the oxygen concentration and of the temperature but is proportional to the concentration of the acid (of oil) and to the square root of the light intensity[9] Dickinson and Leermakers[5] found that the rate of oxidation of tetrachloroethylene is proportional to the first power of the light intensity and of the chlorine concentration, independent of oxygen concentration, and also independent of the tetrachloroethylene concentration except when very high.

The rate of the chlorine-sensitized photo-oxidation of chloroform has practically these same respective dependencies[6].

The quantum yields of these photo-oxidation reactions may vary from values less than unity as is found in the case of rubrene oxidation at low rubrene concentrations[10] to the enormous yields of some 50,000 for oxidation of sulfite solutions as shown in work of Alyea and Backstrom[11].

The literature is pregnant with photochemical measurements involving various types of changes at the double bond between two carbon atoms. Three of these have a very direct bearing on the investigations at hand. Leermakers and Dickinson[12] have investigated the photochlorination of tetrachloroethylene in carbon tetrachloride solution. The essentials of this paper that concern the photochlorination of gaseous tetrachloroethylene are given in Chapter III.

The iodine-sensitized photodecomposition of ethylene iodide, $C_2H_4I_2$, in carbon tetrachloride solution has been studied by Schumacher and Wiig[13]. The rate expression, $d(C_2H_4I_2)/dt = k(I_{abs.})^{.5}(C_2H_5I_2)$ has been found, and a mechanism for the chain reaction has been given as

$$I_2 + h\nu = 2I \qquad (1)$$

$$C_2H_4I_2 + I = C_2H_4I + I_2 \qquad (2)$$

$$C_2H_4I \rightleftharpoons C_2H_4 + I \qquad (3) \text{ and } (3\ )$$

$$2I = I_2 \qquad (4)$$

The chain-breaking step (4) is second order with respect to the chain-carrier, I, and gives rise to the rate dependence on $\sqrt{I_{abs.}}$ The iodine atoms combine in ternary collision with the carbon tetrachloride molecules in solution.

Bodenstein, Jost, and Jung[14,15] have studied the photochemical hydrogen bromide formation with respect to its rate dependence on light intensity. At low intensities the rate is proportional to the first power of the light intensity, but at higher light intensities the rate is proportional to some power less than the first. This is attributed to two chain-breaking steps, (1), $Br = 1/2Br_2$ (wall), and (2), $2Br + M = Br_2 + M$ in the gas phase. The occurrence of step (2) becomes greater as the light intensity and total pressure increase and the dependence of rate on intensity becomes smaller since a square root dependence on light intensity would result were step (2) the sole chain-breaking step.

An intermediate molecule, X_3, in photoreactions involving the halogens has been a source of much discussion. Gohring[16] postulated the existence of Cl_3 in discussing the reaction between H_2 and Cl_2. Rollefson and Lehner[17] utilized Cl_3 in discussing the photochemical formation of phosgene. Rollefson and Eyring[18] used quantum mechanical methods to establish the statement that Cl_3 was stable with respect to decomposition into Cl_2 and Cl at room temperature. Leermakers and Dickinson[12] found that a suitable mechanism could be developed for the photochlorination of tetrachloroethylene in carbon tetrachloride solution if Cl_3 were employed; a second mechanism involving C_2Cl_5 was satisfactory. Berthoud and Beraneck[19] postulated a mechanism for the bromination of cinnamic acid which involved bromine atom chains and a $C_6H_5CHBrCHCOOH$ intermediate. Purakayastha and Ghosh[20] postulated a Br_3 molecule for the cinnamic acid bromination mechanism. Bauer and Daniels[21] discarded the Berthoud and Beraneck mechanism after a consideration of activation energies and temperature coefficients. Sherman and Sun[22] stated from quantum mechanical considerations that a diatomic bromine molecule, Br_2, will add to an ethylene double bond more rapidly than would a triatomic bromine molecule, Br_3. Rollefson[23] then produced the statement that the heat of dissociation of Cl_3 into Cl_2 and Cl at room temperature is 5000 calories. The existence of Cl_3 and Br_3 molecules is at present controversial.

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III. THE PHOTOCHLORINATION and THE CHLORINE-SENSITIZED PHOTO-OXIDATION OF GASEOUS TETRACHLOROETHYLENE

The combination of oxygen with gaseous tetrachloroethylene occurred as a chain reaction with practically complete inhibition of the addition of chlorine at the double bond between the two carbon atoms when gaseous mixtures of oxygen, chlorine, and tetrachloroethylene at temperatures of 25° to 40°C. were illuminated either with sunlight or with the three lines 4358Å, 4347Å, and 4339Å of the Hg-arc. The products of this chlorine-sensitized photo-oxidation of the tetrachloroethylene were phosgene, and trichloroacetyl chloride, the same products that were formed in the chlorine-sensitized photo-oxidation of tetrachloroethylene in carbon tetrachloride solution[1] Illumination of gaseous mixtures containing no oxygen produced photochlorination of the tetrachloroethylene, hexachloroethane being the colorless crystalline product of the chain reaction. This reaction was the same as the one occurring in the photochlorination of tetrachloroethylene in carbon tetrachloride solution[2]

Materials

The <u>oxygen</u> used was drawn from a commercial tank (liquid air source), dried over phosphorus pentoxide and stored in a liter bulb.

The <u>chlorine</u> supply was likewise drawn from a cylinder, dried over calcium chloride, and sealed off, after liquefying weighed amounts in small glass tubes with easily breakable tips.

The <u>tetrachloroethylene</u> was c.p. Eastman Kodak Company product, illuminated after having been saturated with chlorine, washed with sodium hydroxide solution, washed free of hydroxide with water, dried with calcium chloride, and distilled.[3] The large fraction of the distillate coming over within a 0.2°C. temperature interval was utilized. The tetrachloroethylene was stored in an atmosphere of nitrogen in brown glass-stoppered bottles until transferred in weighed quantities to glass bulbs with easily breakable tips.

Apparatus and Procedure

The equation for the reaction of oxygen and gaseous tetrachloroethylene to form phosgene,

$$C_2Cl_{4(g)} + O_{2(g)} = 2COCl_{2(g)}$$

shows no change in total pressure as a result of reaction since the total number of molecules present remain constant. On the other hand, the equation for the formation of trichloroacetyl chloride by these two reactants,

$$C_2Cl_{4(g)} + 1/2O_{2(g)} = CCl_3COCl_{(g)}$$

does show a pressure decrease as the result of reaction.

Furthermore, the equation of the photochlorination reaction,

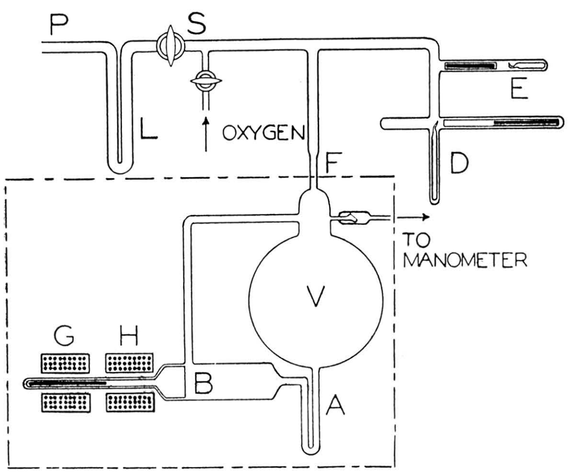
$$C_2Cl_{4(g)} + Cl_{2(g)} = C_2Cl_{6(g)}$$

or

$$C_2Cl_{4(g)} + Cl_{2(g)} = C_2Cl_{6\,(s)}$$

shows a pressure decrease as result of reaction. Therefore, it was possible to follow the progress of the two simultaneously occurring oxidation reactions or of the photochlorination reaction by decrease in total pressure. This was accomplished in the apparatus diagrammed in Figure 1, the gaseous mixture being in contact with glass only.

Figure 1



The reaction vessel V was a 1-liter spherical Pyrex flask; it was evacuated through P with a mercury vapor pump, liquid air being kept on the trap L. After evacuation the cock S was closed, liquid air applied at A, and weighed samples of chlorine and tetrachloroethylene released into A by magnetically breaking small bulbs, D and E, with glass-enclosed hammers. After the admission of oxygen to a measured pressure, the reaction vessel was sealed off at F and the liquid air removed from A. The reactants were evaporated and carried out from A by surges of gas created by the operation of a close-fitting plunger B which was given a reciprocating motion by the two solenoids G and H. The plunger was also frequently operated during the run in order to ensure uniformity of composition of the gas. Its use also permitted the measurement of residual oxygen pressure by again applying liquid air to A at the close of a run; condensation would have required a very long time had diffusion of the condensables into A been relied on in those cases where the residual oxygen pressure was several millimeters or more. The pressure measurements were made with the aid of a clicker type of glass diaphragm gage[4] used in conjuction with a mercury manometer which was read to 0.05 mm. That part of the apparatus shown within the dotted line of Figure 1 was contained within a light-tight air thermostat which was maintained constant to 0.2°C. with the aid of a heater and fan.

The thermostat wall was fitted with a window at the reaction vessel; illumination of the reacting gas occurred through this window. The light source was an upright quartz mercury arc. Radiation from it passed through a hole 1 cm. in diameter and then through filters to isolate the line 4358Å. The filters used were a 1-cm. layer of 6% copper sulfate, and Corning glasses "Noviol A" and "blue-purple ultra"; because of their proximity to the lamp, these were water-cooled. The radiation was collimated by a lens of 6.3 cm. focal length with the 1-cm. hole at its focus. Before entering the reaction vessel, the beam passed through a diaphragm 3.0 cm. in diameter.

The lamp system could be moved on tracks to a position which allowed the light beam to fall upon a Moll small surface thermopile connected to a high sensitivity galvanometer. This arrangement made possible the comparison of relative illumination intensities of different experiments, and afforded means of evaluating with reasonable accuracy the absolute amount of radiation entering the reaction mixture. This evaluation involved three considerations, namely, reflection losses at thermostat window, calibration of the thermopile-galvanometer system against a carbon filament lamp calibrated by the Bureau of Standards, and the ratio of galvanometer deflections for the same light-beam for the thermopile located in its normal position, and located in the plane of the 3.0 cm. beam-defining diaphragm. A galvanometer deflection of 1 cm. corresponded to an intensity of 1 x 10^2 ergs cm.$^{-2}$ sec.$^{-2}$ at the surface of the reacting gas mixture or to a flux of 7.06 x 10^2 ergs sec.$^{-1}$ The fraction of light absorbed was calculated from the relation $I/I_0 = 10^{-acd}$ where a, 1.64, is the molal extinction coefficient of chlorine,[5,6] d = 12 cm., and c the concentration of chlorine in moles per liter obtained from pressure measurements and the known weight of the chlorine sample charged into the reaction vessel. This fraction of incident radiation absorbed was kept small, the maximum in any photochlorination experiment being 0.123.

Sample Runs

The nature of total pressure changes during illumination are best described by plotting total pressure in mm. against the time of illumination in minutes. Figure 2 discloses the photochlorination resulting from illuminating an initial gaseous mixture of chlorine, 49.2 mm., and tetrachloroethylene, 8.33 mm. at 40°C. The increase in slope at 56.6 mm. was caused by the beginning of the precipitation of colorless crystals of hexachloroethane, the product of photochlorination very easily identifiable by characteristic odor, whose vapor pressure at 40°C. was

1.0 mm. The change in slope at 50.8 mm. was due to a decrease in incident light intensity by interposing a neutral wire screen of 35% transmission in the incident light beam. The rate of chlorination at small tetrachloroethylene pressures is independent of tetrachloroethylene pressure as shown by unchanging slope from 50.8 mm. to 41.9 mm. at which pressure photochlorination was complete.

Figure 2

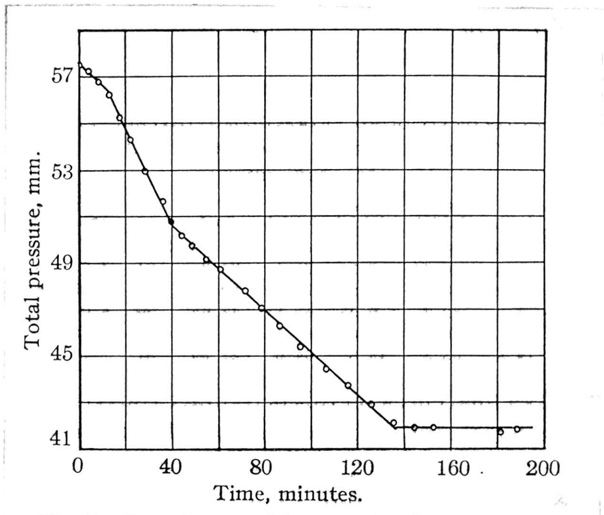


Figure 3 shows a characteristic experiment at 40° C. in which the initial gas mixture contained chlorine, 65.5 mm., tetrachloroethylene, 14.8 mm., and oxygen, 13.8 mm., an amount in excess of that required for oxidation of all the tetrachloroethylene present. The change of slope at 90.6 mm., was due to the decrease of intensity of incident radiation by interposition of the neutral wire screen of 35% transmission in the light beam. The change of slope with change of intensity is more marked in Figure 3 than was the case in Figure 2, showing that the oxidation rate had a greater dependence on light intensity than chlorination rate. The lack of dependence of the oxidation rate on the pressure of the tetrachloroethylene is an essential pointed out by the constancy of slope as oxidation neared completion.

Figure 3

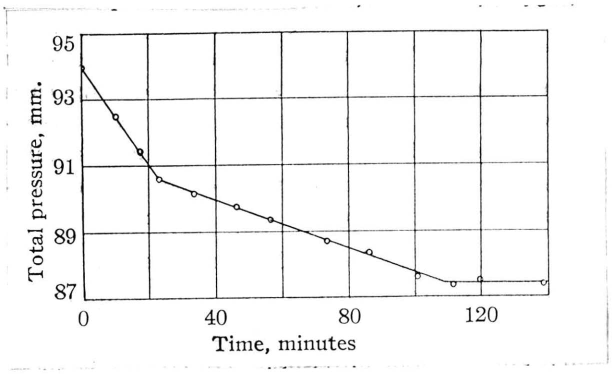
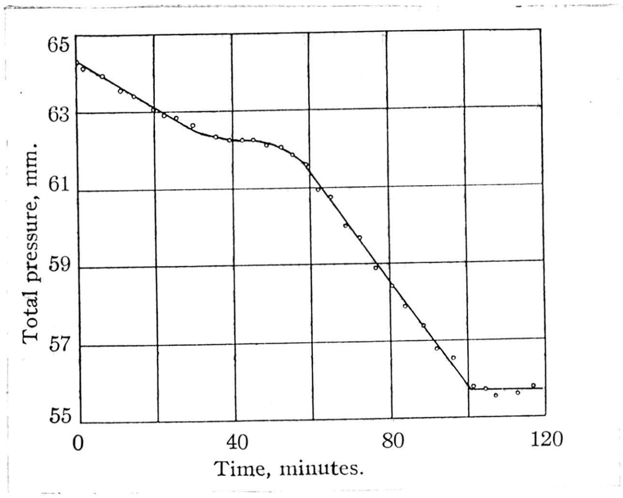


Figure 4 shows at 26° the course of an experiment having present, initially, chlorine, 53.75 mm., tetrachloroethylene, 8.12 mm., and oxygen, 2.45 mm., an amount insufficient to oxidize the total tetrachloroethylene present. The portion of the curve from 64.3 mm. to 62.6 mm. is interpretable as an oxidation proceeding at constant rate until the oxygen is practically used up, the oxidation rate being independent of oxygen pressure until only minute traces of oxygen remain. The region of very little change in total pressure found in the time interval between 30 and 50 minutes most likely involved the removal of the last traces of oxygen by slow oxidation of tetrachloroethylene, photochlorination being very critically if not entirely inhibited by traces of oxygen. Then in the pressure interval from 61.8 mm. to 55.6 mm. photochlorination proceeded until all the tetrachloroethylene had reacted.

Figure 4



Products of Oxidation Reaction

Practically total inhibition of chlorination by oxygen was shown by experiments in which gaseous mixtures containing a weighed quantity of chlorine and of tetrachloroethylene and excess oxygen were given illuminations known to be adequate for complete reaction of tetrachloroethylene, and the free chlorine determined by thiosulfate titration of the iodine liberated from potassium iodide solution by the free chlorine. Table 1 shows the results of these experiments.

Table 1

Free Chlorine Present Before and After Oxidation

Initial C_2Cl_4, mole x 10^3	Initial O_2, mole x 10^3	Initial Cl_2, mole x 10^3	Final Cl_2, mole x 10^3	Exposure time, minutes	
0.475	5.74	2.42	2.40	180	4358Å
.402	5.74	0.99	0.99	200	"
.399	0.394	2.55	2.53	60	sunlight
.454	.417	2.15	2.14	120	"

The agreement between initial and final amounts of free chlorine present in the gaseous mixtures indicates that little if any chlorination could have occurred during the oxidation.

The odor of phosgene was unmistakable evidence of its presence among the products of oxidation. The isolation of trichloroacetyl chloride from the reaction products was not deemed necessary in light of its isolation by Dickinson and Leermakers[1] from the oxidation products of tetrachloroethylene in carbon tetrachloride solution. The distribution of the tetrachloroethylene between the two oxidation products was determined. An analytical method of determination involved the titration of acids produced by the hydrolysis of the reaction products upon opening the reaction flasks under a potassium iodide solution. The iodine liberated from the potassium iodide by free chlorine was titrated with thiosulfate solution. The equation for the hydrolysis of trichloroacetyl chloride is

$$CCl_3COCl + H_2O = CCl_3COOH + HCl,$$

and for the hydrolysis of phosgene is

$$COCl_2 + 2H_2O = 2HCl + H_2CO_3.$$

The solution was boiled to remove the carbon dioxide produced by the phosgene hydrolysis, cooled and potassium iodate was added, liberating free iodine by the reaction

$$5I^- + IO_3^- + 6H^+ = 3I_2 + 3H_2O$$

The free iodine was titrated by thiosulfate solution. Letting $\underline{x}$ be the fraction of tetrachloroethylene oxidized to trichloroacetyl chloride, the oxidation of one mole of tetrachloroethylene produces $\underline{x}$ moles of trichloroacetyl chloride and $2(1 - \underline{x})$ moles of phosgene. Since $\underline{x}$ moles of trichloroacetyl chloride produce $2\underline{x}$ equivalents of acid, and $2 - 2x$ moles of phosgene produce $4 - 4\underline{x}$ equivalents of acid (the carbon dioxide was removed) by hydrolysis, each mole of tetrachloroethylene oxidized produced $4 - 2x$ equivalents of acid by hydrolysis of the oxidation products. Table II presents the results.

Table II

Fraction of Oxidized Tetrachloroethylene Yielding Trichloroacetyl Chloride (Analytical Measurements)

Initial C_2Cl_4, mole x 10^3	Initial O_2, mole x 10^3	Initial Cl_2, mole x 10^3	Acid equivs. x 10^3	Fraction of C_2Cl_4 to CCl_3COCl, x
0.475	5.74	2.42	0.990	0.96
.402	5.74	0.99	.872	.92
.454	4.17	2.15	.960	.94

The value of x was determined from the decrease in total pressure accompanying the oxidation of a known quantity of tetrachloroethylene. The oxidation of tetrachloroethylene to phosgene involved no change in total pressure but oxidation to trichloroacetyl chloride produced a pressure reduction equal to one-half the pressure of the tetrachloroethylene so oxidized. If $p_{C_2Cl_4}$ is pressure of the tetrachloroethylene oxidized, $xp_{C_2Cl_4}$ is the pressure of the tetrachloroethylene oxidized to trichloroacetyl chloride, and the accompanying reduction in total pressure, $-\Delta p_t$, equals $xp_{C_2Cl_4}/2$. The results of a series of such experiments are shown in Table III, given on the following page.

Table III

Fraction of Oxidized Tetrachloroethylene Yielding Trichloroacetyl Chloride (Pressure Measurements)

T, °C.	pC_2Cl_4, initial	pCl_2, initial	pO_2 initial	p_t, initial	p_t, final	x	$-\Delta pO_2$ obs.	$-\Delta pO_2$ calcd.
24	7.95	60.7	18.75	87.4	84.15	.82	4.3	4.4
24	7.3	60.05	7.74	75.1	71.8	.91	4.75	4.0
24	7.2	58.2	6.20	71.5	68.25	.90	4.05	4.0
26	7.3	32.2	6.95	45.83	42.65	.90	4.0	4.0
26	7.15	130.8	7.65	145.6	142.35	.91	4.15	4.0
40	14.8	65.5	13.8	94.0	87.55	.87		

It is seen that the values of x obtained by the pressure measurements agree substantially with the values obtained analytically. The value of x, 87%, obtained by Dickinson and Leermakers[1] for the oxidation of tetrachloroethylene in carbon tetrachloride solution is in good agreement with the value of x shown above.

Now the oxidation of one mole of tetrachloroethylene to trichloroacetyl chloride requires one-half mole of oxygen and the oxidation of one mole of tetrachloroethylene to phosgene requires one mole of oxygen; so knowing that 90% of the tetrachloroethylene is oxidized to trichloroactyl chloride, the oxidation of $p_{C_2Cl_4}$ mm. of tetrachloroethylene produces a decrease of oxygen partial pressure, $-\Delta p_{O_2}$, which is the sum of $xp_{C_2Cl_4}/2$ (for trichloroacetyl chloride formation) and $(1 - x)p_{C_2Cl_4}$

(for phosgene formation); i.e., $-\Delta p_{O_2} = (1 - x + x/2)p_{C_2Cl_4} = .55p_{C_2Cl_4}$. Listed in Table III are the calculated and observed decreases in oxygen partial pressures.

The Chlorination Product

The fact that the colorless, crystalline product of chlorination had the odor of hexachloroethane has been mentioned. Further evidence that hexachloroethane was the chlorination product is the agreement obtained between the calculated and observed decrease in total pressure upon chlorinating a known quantity of tetrachloroethylene in an excess of chlorine, assuming that the only product of chlorination was hexachloroethane, the partial pressure of which at 40° C. is 1.0 mm. and at 50° C. is 2.12 mm.[8] A calculated total pressure decrease of 15.7 mm. for the chlorination of 4.74×10^{-4} moles of tetrachloroethylene in a 1110 cc. reaction vessel at 40° C. agreed exceedingly well with a measured decrease of 15.65 mm. In an experiment in a 1040 cc. reaction vessel at 50° C., the calculated pressure decrease for the formation of hexachloroethane from 1.038×10^{-3} moles of tetrachloroethylene was 38.1 mm. and the observed decrease in total pressure was 38.3 mm.

Dark Reaction

Mixtures containing oxygen, chlorine, and tetrachloroethylene had no changes in total pressure after remaining for several hours in the dark at 25° C, as was the case at 40° C. Mixtures of chlorine and tetrachloroethylene showed no pressure changes on long standing in the dark at 25° C., but at 40° C. in some cases there was evidence of a thermal rate which amounted to such a small percent of the photochemical rate that there was no necessity for attempting a correction.

Kinetics of Oxidation

The sample runs discussed showed that the rate of oxidation of tetrachloroethylene induced by radiation of a wave length absorbed only by the chlorine present was very little dependent on the <u>oxygen</u> pressure, <u>total</u> pressure, or <u>tetrachloroethylene</u> pressure within the narrow range of pressures employed in those runs. Table IV shows that the same is true of oxidation rates measured under widely varying conditions.

The pressures listed are the initial pressures existing at the beginning of intervals of illumination having substantially constant intensity of incident

Table IV

Quantum Yields and Rates of Oxidation with λ 4358Å

Expt.	Pressure, mm. p_{Cl_2}	p_{O_2}	$p_{C_2Cl_4}$	Total	I ergs cm.$^{-2}$ sec.$^{-}$ x 10^{-2}	$I_{abs.}$ einsteins sec.$^{-1}$ x 10^{+10}	$-dp/dt$ mm. sec.$^{-1}$ x 10^4	$-dN_{C_2Cl_4}/dt$ moles sec.$^{-1}$ x 10^8	Q. Y. moles C_2Cl_4 einsteins^{-1}
2	59.0	82.6	6.6	148.2	3.92	1.36	5.3	7.10	522
3	60.7	18.8	7.9	87.4	12.60	4.50	17.2	22.95	510
4	60.0	7.8	7.3	75.1	11.8	4.15	15.0	20.00	482
5a	58.1	6.2	7.2	71.5	12.28	4.18	11.7	15.60	373
b	58.1	3.7	3.7	69.5	11.67	3.98	9.6	12.90	324
6a	32.2	6.9	7.3	45.8	14.20	2.75	5.3	7.05	256
b	32.2	4.7	3.2	44.0	15.08	2.92	5.6	7.48	256
7	130.8	7.7	7.1	146.6	13.00	9.20	23.2	30.80	335
8	50.3	0.8	7.3	58.3	4.50	1.34	4.1	5.42	405
9	53.7	2.5	8.1	64.3	13.95	4.48	9.4	12.30	274
10	48.6	2.4	7.2	58.3	10.33	2.99	5.9	7.77	260
11	50.1	2.4	7.4	59.8	2.84	0.85	1.7	2.48	292
13	56.0	2.3	7.5	66.0	9.23	2.94	5.3	6.70	228
14	60.0	2.0	22.8	84.7	8.66	2.91	4.7	5.95	204
15a	61.5	4.2	22.9	88.5	17.35	5.95	10.8	13.70	230
b	61.5	1.6	18.4	86.5	4.12	1.42	2.6	3.30	232
16	25.5	4.4	21.6	51.4	15.40	2.27	4.0	5.06	223
17a	65.5	13.8	14.8	94.0	22.40	8.08	24.9	31.50	390
b	65.5	8.8	5.9	90.0	6.74	2.44	6.0	7.60	311

Experiments 2-6 were at 24°; expts. 6-13 at 26°; and expts. 13-17 inclusive at 40°.

radiation. The assumption that 90% of the tetrachloroethylene oxidized to trichloroacetyl chloride and the remaining 10% to phosgene was used in calculating the initial partial pressures for experiments designated b. This same assumption was utilized in calculating quantum yields, i.e., moles of tetrachloroethylene oxidized per einstein absorbed, from the measured rate of decrease of total pressure and rate of radiation absorption. The veritable constancy of quantum yield shown in experiment 15a, b, in which there was substantially a four-fold decrease in intensity of incident radiation accompanied by a four-fold decrease in oxidation rate, is indication of the proportionality of the rate of oxidation and the first power of the incident light intensity. Further evidence for this statement is given by a comparison of experiment 10 with 11 and also by 17a, b.

The quantum yields undergo an uncorrelated two-fold change in a series of experiments involving a three-fold variation in initial total pressure, a five-fold variation in chlorine pressure, a hundred-fold change in oxygen pressure, and at least a hundred-fold change in tetrachloroethylene pressure (its partial pressure dropped nearly to zero before any measurable change in oxidation rate occurred). The high quantum yields lead definitely to the existence of a chain mechanism for the oxidation in gas phase. The quantum yields are much larger than those found in tetrachloroethylene oxidation in carbon tetrachloride solution.[1]

A satisfactory mechanism must lead to an oxidation rate expression having *no dependence* on *total pressure*, *oxygen pressure* (when oxygen concentration is greater than a mere trace), or *tetrachloroethylene pressure*, having a first power dependence on light intensity and no dependence on the chlorine pressure except in so far as it determines the fraction of incident radiation that is absorbed. Furthermore the mechanism must provide for the conversion of 90% of the tetrachloroethylene to trichloroacetyl chloride and the other 10% to phosgene, lead to high quantum yields, provide for inhibition of chlorination by traces of oxygen and for the rearrangement of chlorine atoms with respect to the carbon atoms in the oxidation of tetrachloroethylene to trichloroacetyl chloride. At present, no such mechanism has been written. The most pertinent statement that seems worthy of credence is that the chain-breaking step for the oxidation is not the same as the chain-breaking step in chlorination; for it has been pointed out that the oxidation had greater dependence on light intensity than did chlorination.

The Kinetics of Chlorination

It was pointed out in sample runs that, within the range of pressures used in those runs, the photochlorination rate was independent of the tetrachloroethylene pressure and was less dependent on light intensity than the oxidation rate which has been shown to have a first power dependence on intensity. The collected results of the photochlorination experiments are shown in Table V. The light intensities show a five-fold variation, the momentary partial pressures of chlorine a four-fold variation, and the momentary partial pressures of tetrachloroethylene a variation greater than fifteen-fold. Oxygen was present in the initial gas mixtures except in experiment 18a.

The momentary partial pressures at any time during chlorination were calculated with the use of the initial composition of the gas, the measured momentary total pressure, p_t, and the two assumptions that 90% of the oxidized tetrachloroethylene was converted to trichloroacetyl chloride and the other 10% to phosgene and that no oxygen was present during chlorination. The equations used in calculating these momentary partial pressures were:

(1) $p_{Cl_2} = p_{Cl_{2_0}} - 1/2(p_{t_0} - p_t - 0.82p_{O_{2_0}} + p_{C_2Cl_6})$,

and (2) $p_{C_2Cl_4} = p_{C_2Cl_{4_0}} - 1.82p_{O_{2_0}} - 1/2(p_{t_0} - p_t - 0.82p_{O_{2_0}} + p_{C_2Cl_6})$.

Table V

Rate and Quantum Yields of Chlorination with $\lambda 4358 Å$.

Expt.	Initial pressure, mm. $P_{Cl_{2_0}}$	$P_{O_{2_0}}$	$P_{C_2Cl_{4_0}}$	Momentary pressure P_{Cl_2}	$P_{C_2Cl_4}$	Total	I_0 ergs X cm.$^{-2}$ X sec.$^{-1}$ X 10^{-8}	$I_{abs.}$ einsteins sec.$^{-1}$ X 10^{10}	$-dp/dt$ mm. sec.$^{-1}$ X 10^3	$-dN_{Cl_2}/dt$ mole sec.$^{-1}$ X 10^8	a X 10^{-3}	Quantum yield
8	50.3	0.8	7.3	47.3	2.9	52.0	3.28	0.96	1.45	4.36	1.75	453
9	53.7	2.5	8.1	51.9	1.8	59.0	13.68	4.21	2.33	6.83	1.19	163
10	48.6	2.4	7.2	47.0	1.3	53.5	9.39	2.65	1.61	4.84	1.17	183
11	50.1	2.4	7.4	48.5	1.5	55.0	2.85	0.82	1.00	2.99	1.27	366
										Mean	1.35	
13	56.1	2.4	7.6	54.0	1.3	61.0	9.30	2.87	2.62	7.44	1.58	259
14a	60.0	2.0	22.8	56.3	15.2	76.5	8.20	2.61	2.98	8.45	1.81	325
b				52.5	11.4	69.0	7.73	2.30	2.62	7.44	1.82	323
c				44.0	2.9	52.0	8.60	2.18	1.90	5.40	1.62	247
15a	61.5	4.2	22.9	58.4	11.3	79.5	20.65	6.85	5.04	14.25	1.82	209
b				53.7	6.5	70.0	6.38	1.97	2.45	6.96	1.80	354
c				51.2	4.0	65.0	19.80	5.74	3.62	10.25	1.63	179
16a	25.5	4.4	21.6	22.4	11.2	43.0	22.40	2.96	1.23	3.51	1.77	118
b				18.2	6.9	34.5	21.70	2.36	0.83	2.37	1.66	100
c				15.2	3.9	28.5	22.70	2.05	0.63	1.80	1.62	88
d				13.2	1.9	24.5	22.30	1.73	0.50	1.42	1.59	82
18a	49.2	0	8.3	46.7	5.8	53.5	21.10	5.66	3.40	9.67	1.69	171
b				43.2	2.3	46.5	5.97	1.47	1.48	4.22	1.57	287
										Mean	1.69	

Experiments 8, 9, 10, and 11 were at 26°; the rest were at 40°.

The subscript $_o$ designates initial values of partial pressures and the total pressure. The total pressure is designated by p_t. The derivation of equations (1) and (2) follows. From the oxidation equations,

$$C_2Cl_{4(g)} + O_{2(g)} = 2COCl_{2(g)}$$

$$C_2Cl_{4(g)} + 1/2O_{2(g)} = CCl_3COCl_{(g)},$$

it is evident that the total pressure decrease, $-\Delta p_t$, occurring during oxidation is equal to the pressure of the oxygen used in trichloroacetyl chloride formation which is 82% of all the oxygen used in the oxidation process, i.e., 82% of the initial oxygen present.

$$-\Delta p_t(\text{for oxidation}) = .82p_{O_{2_0}}$$

From the equation of chlorination,

$$C_2Cl_{4(g)} + Cl_{2(g)} = C_2Cl_{6(g)}\text{ or }_{(s)},$$

it is seen that the decrease in total pressure, $-\Delta p_t$, equals twice the decrease in chlorine partial pressure, $-2\Delta p_{Cl_2}$, less the partial pressure of the hexachloroethane, $p_{C_2Cl_6}$. (If solid hexachloroethane were present at 26° C., its partial pressure was .35 mm.[8])

$$-\Delta p_t(\text{for chlorination}) = -2\Delta p_{Cl_2} - p_{C_2Cl_6}$$

Let $-\Sigma\Delta p_t = -\Delta p_t(\text{for chlorination}) -\Delta p_t(\text{for oxidation})$

$$= -2\Delta p_{Cl_2} - p_{C_2Cl_6} + .82p_{O_{2_0}}$$

Also, $-\Sigma\Delta p_t = p_{t_0} - p_t$;

Substituting and rearranging,

$$-\Delta p_{Cl_2} = 1/2(p_{t_0} - p_t - .82p_{O_{2_0}} + p_{C_2Cl_6}).$$

Now, $-\Delta p_{Cl_2} = p_{Cl_{2_0}} - p_{Cl_2}$.

Therefore, $p_{Cl_2} = p_{Cl_{2_0}} - 1/2(p_{t_0} - p_t - .82p_{O_{2_0}} + p_{C_2Cl_6})$, which is equation (1).

For the derivation of equation (2), let

$$-\Sigma\Delta p_{C_2Cl_4} = -\Delta p_{C_2Cl_4}\text{(for oxidation)}$$
$$-\Delta p_{C_2Cl_4}\text{(for chlorination)}.$$

Also, $-\Sigma\Delta p_{C_2Cl_4} = p_{C_2Cl_{4_0}} - p_{C_2Cl_4}$.

It has been shown previously that in the oxidation process the decrease in the oxygen pressure equals 55% of the tetrachloroethylene pressure decrease. Therefore,

$-\Delta p_{C_2Cl_4}\text{(for oxidation)} = -1.82\Delta p_{O_2} = 1.82p_{O_{2_0}}$.

Also, from the equation for chlorination, it is seen that

$$-\Delta p_{C_2Cl_4}\text{(for chlorination)} = -\Delta p_{Cl_2}$$
$$= 1/2(p_{t_0} - p_t - .82p_{O_{2_0}} + p_{C_2Cl_6}).$$

Thus, $-\Sigma\Delta p_{C_2Cl_4} = 1.82p_{O_{2_0}} - 1/2(p_{t_0} - p_t - .82p_{O_{2_0}} + p_{C_2Cl_6})$.

So, $p_{C_2Cl_4} = p_{C_2Cl_{4_0}} - 1.82p_{O_{2_0}}$
$$- 1/2(p_{t_0} - p_t - .82p_{O_{2_0}} + p_{C_2Cl_6}),$$

which is equation (2).

A plot of total pressure against time of illumination for an interval of constant incident radiation was made for each experiment. A momentary total pressure whose value approximated the average of the total pressures prevailing at the beginning and end of the interval was selected and the value of -dp/dt at the chosen momentary total pressure was read from the plot. This -dp/dt was converted into $-dN_{C_2Cl_4}/dt$ by the relation

$$\frac{-dN_{C_2Cl_4}}{dt} = \frac{v}{2RT} \times \frac{-dp}{dt}$$

in which $N_{C_2Cl_4}$ is the number of moles of tetrachloroethylene present, and v is the volume of the reaction vessel. This equation was developed from the perfect gas equation,

$$p_{C_2Cl_4}v = N_{C_2Cl_4}RT.$$

At constant temperarure, T, and constant volume

$$\frac{-vdp_{C_2Cl_4}}{dt} = \frac{-RTdN_{C_2Cl_4}}{dt}.$$

In the chlorination of tetrachloroethylene when solid hexachloroethane was being formed,

$$-dp/dt = 2dp_{C_2Cl_4}/dt,$$

since one-half of the total molecules disappearing were tetrachloroethylene molecules. Then by substitution,

$$\frac{-dN_{C_2Cl_4}}{dt} = \frac{-v}{2RT} \times \frac{dp}{dt}.$$

The quantum yields given are moles of tetrachloroethylene chlorinated per einstein absorbed and were obtained by dividing the rate of tetrachloroethylene disappearance by the rate of absorption of radiation. The variation of these quantum yields with changing light intensity as shown in 15a, b, c, and 18a, b of Table V is definite proof that the chlorination rate does not have a first power dependence on light intensity. A very satisfactory expression for the rate of chlorination is given by

$$-dN_{C_2Cl_4}/dt = \underline{a}V\sqrt{I_{abs.}}\,(Cl_2)$$

where $I_{abs.}$ is the einsteins absorbed per second, and (Cl_2) is the concentration of chlorine in moles per cc. The mean value of $\underline{a}$ is 1.69 x 10^3 cc. moles$^{-.5}$ sec.$^{-.5}$ at 40° and less reliably, 1.35 x 10^3 cc. mole$^{-.5}$ sec.$^{-.5}$ at 26°. The values obtained for $\underline{a}$ were very erratic when rate expressions involving different dependencies on $I_{abs.}$ and (Cl_2) were applied to the data of Table V.

Since the fraction of absorbed radiation was always small, it is possible to convert the rate expression

$$-dN_{C_2Cl_4}/dt = a\sqrt{I_{abs.}}\,(Cl_2)$$

to an expression for local rate

$$-d(C_2Cl_4)/dt = k\ (I_{abs.})^{.5}\ (Cl_2)$$

in which the concentrations are expressed as moles per cc. and $(I_{abs.})$ is the <u>local</u> rate of absorption of radiation expressed as einsteins <u>per</u> <u>cc</u>. per second. It is <u>necessary</u> to assume that no reaction occurred outside the region illuminated by the light beam. The illuminated region was a cylinder of 3 cm. diameter and 12 cm. length, giving a volume of reaction region, V, equal to 85 cc. To find $\underline{k}$ in terms of $\underline{a}$, divide

$$-dN_{C_2Cl_4}/dt = \underline{a}\sqrt{I_{abs.}}\,(Cl_2)$$

by V, and the expression

$$\frac{-dN_{C_2Cl_4}}{Vdt} = \frac{a\sqrt{I_{abs.}}\,(Cl_2)}{V} = \frac{-d(C_2Cl_4)}{dt} = \frac{k(I_{abs.})^{.5}(Cl_2)}{}$$

results. From this expression comes

$$a\sqrt{I_{abs.}}/V = k(I_{abs.})^{.5}.$$

As

$$I_{abs.} = (I_{abs.})V,$$

$$a\sqrt{(I_{abs.})V}/V = k(I_{abs.})^{.5}$$

and

$$\underline{a} = \underline{k}V^{.5}.$$

Now $\underline{a}$ at 26° has a value of 1.35×10^3, so $\underline{k}$ has a value of $1.35 \times 10^3/85^{.5} = 148$.

The same dependence of chlorination rate on intensity and chlorine concentration was found by Leermakers and Dickinson[9] for the chlorination of tetrachloroethylene in carbon tetrachloride solution at sufficiently high tetrachloroethylene concentrations. The expression given for the rate of local reaction at 22° was

$$\frac{-d(Cl_2)}{dt} = 5.1(I_{abs.})^{.5}(Cl_2)\left[\frac{1 + .4(Cl_2)}{(C_2Cl_4)}\right]^{.5}$$

which at sufficiently high tetrachloroethylene concentrations becomes

$$-d(Cl_2)/dt = 5.1(I_{abs.})^{.5}(Cl_2).$$

In this equation the concentrations are expressed as moles per liter and $(I_{abs.})$ is the local rate of absorption of radiation expressed as einsteins per liter per second. To convert the volume units from liters to cc., the right hand side of the above equation is multiplied by $1000^{.5}$, the value of the constant, 5.1, becoming 161. The agreement of this value with the value of $\underline{k}$, 148, obtained for the local reaction rate expression for the gaseous photochlorination is surprisingly good, and indicates that the dependence on concentrations and intensity at sufficiently high tetrachloroethylene concentrations has the same absolute value in each case.

Mechanism of Photochlorination

A satisfactory mechanism, *A*, developed for photochlorination follows:

$$Cl_2 + h\nu = 2Cl \tag{1}$$

$$C_2Cl_4 + Cl = C_2Cl_5 \tag{2}$$

$$C_2Cl_5 + Cl_2 = C_2Cl_6 + Cl \tag{3}$$

$$2C_2Cl_5 = 2C_2Cl_4 + Cl_2 \tag{4}$$

$$(\text{or } C_2Cl_6 + C_2Cl_4)$$

The primary absorption process leads to dissociation of the chlorine molecules into chlorine atoms. There is no difficulty arising from energetics on this score, since an einstein of 4358Å radiation has an energy of 65,250 calories while the heat of dissociation of chlorine into chlorine atoms is some 57,000 calories.[11] Step (2) involves a postulated intermediate molecule, C_2Cl_5. Step (2) and (3) are the chain-carrying steps. Chain-breaking step (4) is second order with respect to the chain carrier; and, since the chains are long as shown by the large quantum yields, the nature of the products of step (4) is immaterial (except that the products must contain no chain-carrying component).

This mechanism leads to a local reaction rate expression

$$-d(Cl_2)/dt = k(I_{abs.})^{.5}(Cl_2)$$

in which $k = k_3/k_4^{.5}$; thus steps (3) and (4) of the mechanism are the rate determining steps. The derivation of the local reaction rate expression follows.

At the <u>steady state</u>,

$$-d(Cl_2)/dt = d(C_2Cl_6)/dt,$$

since the equation for the overall reaction is

$$C_2Cl_{4\,(g)} + Cl_{2\,(g)} = C_2Cl_{6\,(g)}$$

before the precipitation of solid hexachloroethane begins.

Now, $-d(Cl_2)/dt = (I_{abs.}) + k_3(C_2Cl_6)(Cl_2) - k_4(C_2Cl_5)^2$

$$d(C_2Cl_6)/dt = k_3(C_2Cl_5)(Cl_2).$$

Equating,

$$(I_{abs.}) + k_3(C_2Cl_5)(Cl_2) - k_4\ (C_2Cl_5)^2 = k_3(C_2Cl_5)(Cl_2)$$

and rearranging,

$$(C_2Cl_5) = (I_{abs.})^{.5}/k_4^{.5}.$$

Substituting for (C_2Cl_5),

$$d(C_2Cl_6)/dt = k_3(I_{abs.})^{.5}(Cl_2)/k_4^{.5} = -d(Cl_2)/dt,$$

which is the expression desired.

Some information is forthcoming from a consideration of the collision frequencies involved in the mechanism.

$$k^\circ = 2 \quad \times 6.06 \times 10^{23} \times .25(d_1 + d_2)^2(RT(M_1 + M_2)/M_1M_2)^{.5}$$

$$= 10^{28.443} \times .25(d_1 + d_2)^2(T(M_1 + M_2)/M_1M_2)^{.5}\text{ cc/mole/sec}$$

This is the expression for calculating the specific rate, k°, at which bimolecular collisions between unlike molecules of diameters d_1 and d_2 cm. and of molecular weights M_1 and M_2 occur in gas phase at the temperature T, when the concentration of each of the gases is one mole per cc. For like molecules,

$$k^\circ = 10^{28.292} d^2 (T/M)^{.5} \text{ cc/mole/sec}$$

The molecular diameters[10] involved in the following considerations have been taken as: Cl_2, 4.8×10^{-8}; C_2Cl_4, 6.2×10^{-8}; C_2Cl_5, 6.3×10^{-8}, Cl, 3.8×10^{-8}cm.

The value of k_3^0, the specific binary collision rate between Cl_2 and C_2Cl_5 molecules at 26°, is 2.0×10^{14}. Now $k_3 = k_3^0 f_3$, where f is the fraction of the binary collisions leading to reaction. The value of k_4^0, the specific binary collision rate of C_2Cl_5 molecules at 26°, is 9.5×10^{13}, and $k_4 = k_4^0 f_4$, f_4 being the fraction of collisions leading to reaction.

$$k_3/k_4^{.5} = 148 = k_3^0 f_3/(k_4^0 f_4)^{.5}$$

Substituting values of k_3^0 and k_4^0,

$$f_3 = 7 \times 10^{-6} (f_4)^{.5}.$$

Since f_4 can not be greater than unity, f_3 has a maximum value of 7×10^{-6}, the fraction of binary collisions of Cl_2 and C_2Cl_5 leading to reaction thus being small as expected since step (3) is rate determining. Now, as stated

$$(C_2Cl_5) = ((I_{abs.})/k_4^0)^{.5} = ((I_{abs.})/k_4^0 f_4)^{.5}.$$

It is possible to calculate (C_2Cl_5) in terms of f_4. The maximum value of ($I_{abs.}$) was some 10^{-11} einsteins per cc. per second. Then the maximum value of (C_2Cl_5) was $(10^{-11}/9.5 \times 10^{13} f_4)^{.5} = 3 \times 10^{-13}/f_4^{.5}$ moles per cc., which corresponds to a pressure (at 26°) of some $7 \times 10^{-6}/f_4^{.5}$ mm. This value of $p_{C_2Cl_5}$ is in agreement with the postulated existence of C_2Cl_5 as a transient intermediate, unless the value of $\underline{f_4}$ was exceedingly low.

It is also possible to show that (Cl) is small in comparison with (Cl_2) and (C_2Cl_4). At the <u>steady state</u>,

$$-d(C_2Cl_4)/dt = k_2(Cl)(C_2Cl_4) - 2k_4(C_2Cl_5)^2$$
$$= k_2(Cl)(C_2Cl_4) \text{ nearly,}$$

since $k_2(Cl)(C_2Cl_4) >> 2k_4(C_2Cl_5)^2$, as the chains were long;

$$-d(C_2Cl_4)/dt = d(C_2Cl_6)/dt = k_3(C_2Cl_5)(Cl_2)$$
$$= k_2(Cl)(C_2Cl_4).$$

Rearranging, $(Cl)/(C_2Cl_5) = (k_3(Cl_2))/(k_2(C_2Cl_4))$
$$= k_3^o f_3(Cl_2))/(k_2^o f_2(C_2Cl_4)).$$

Now $\underline{k_2^o}$ equals 2.2×10^{14} at 26°, and the ratio $k_3^o/k_2^o = 0.9$. The maximum ratio of $(Cl_2)/(C_2Cl_4)$ found in Table V does not exceed 10^2. Employing these numerical values for k_3^o/k_2^o and $(Cl_2)/(C_2Cl_4)$, and substituting $7 \times 10^{-6} f_4^{.5}$ for f_3,

$(Cl_2)/(C_2Cl_5) = .9f_3/f_2 \times 10^2 = 6 \times 10^{-4} f_4^{.5}/f_2.$

Now $(C_2Cl_5) \ll (Cl_2)$, hence $(Cl) \ll (Cl_2)$.

A second mechanism, B, involving the Cl_3 molecule as an intermediate leads to the local reaction rate expression

$$-d(Cl_2)/dt = \underline{k}(I_{abs.})^{.5}(Cl_2).$$

The mechanism B follows

$$Cl_2 + h\nu = 2Cl \qquad (1)$$

$$Cl_2 + Cl = Cl_3 \qquad (2)$$

$$C_2Cl_4 + Cl_3 = C_2Cl_6 + Cl \qquad (3)$$

$$2Cl = Cl_2 \qquad (4)$$

The primary absorption process is the same as for the mechanism A. The chain-carrying steps are (2) and (3). The chain-breaking step (4) is second order with respect to the chlorine atom. The value of k for this mechanism is $k_3/k_4^{.5}$, derived from the steady state relations;

$$2k_4(Cl)^2 = 2(I_{abs.})$$

for a chain must be broken as frequently as one initiated. Then,

$$(Cl) = (I_{abs.})^{.5}/k_4^{.5}$$

Now, $-d(Cl_2)/dt = (I_{abs.}) + k_2(Cl_2)(Cl) - k_4(Cl)^2$

Substituting, $-d(Cl_2)/dt = k_2(I_{abs.})^{.5}(Cl_2)/k_4^{.5}$;

that is, $\underline{k} = k_2/k_4^{.5}$.

The rate determining steps are (2) and (4), each of which is a bimolecular association and in gas phase requires a stabilizing third molecule in ternary collision. This would lead to some dependence of the rate on the total concentration of all molecules. The rate determining steps, (2) and (4), of the mechanism A (in which C_2Cl_5 was postulated) were not bimolecular associations and should have no expected dependence on total pressure. In view of this fact, there is no difficulty arising from the equality of rates of chlorination at sufficiently high tetrachloroethylene concentrations in carbon tetrachloride solution and in the gas phase when mechanism A is employed. This equality of rates is contrary to expectation on the basis of mechanism B, and mechanism A is to be favored.

So far as this investigation is concerned, this is the only evidence for a choice of mechanism A; for in another respect, namely the smallness of concentration of its postulated intermediates in comparison with prevailing chlorine and tetrachloroethylene concentrations, mechanism B is quite consistent. Without giving the details of calculation, which are quite similar to those previously given, the results are stated. The fraction, f_2, of collisions between Cl and Cl_2 leading to reaction, is related to f_4, the fraction of collisions of chlorine atoms leading to reaction, by the equation

$$f_2 = 7 \times 10^{-6} f_4^{.5}.$$

This fraction, f_2, has a maximum value, 7×10^{-6} (if f_4 equals unity) which is consistent with the fact that step (2) is a rate determining step of mechanism B.

The maximum value of (Cl), moles per cc., is 3.5 x $10^{-13}/f_4^{.5}$, which is small in comparison with the (Cl_2) and (C_2Cl_4) prevailing, and the maximum value of (Cl_3)/(Cl) is 7.5 x $10^{-4}f_4^{.5}/f_3$. Since $(Cl) \ll (Cl_2)$, $(Cl_3) \ll (Cl_2)$.

Summary

The photochlorination of gaseous tetrachloroethylene illuminated by radiation 4358Å is practically entirely inhibited by free oxygen. A chlorine-sensitized photo-oxidation occurs instead. The tetrachloroethylene is 90% converted to trichloroacetyl chloride and 10% to phosgene. The quantum yields are about 300 molecules of tetrachloroethylene oxidized per quantum absorbed. The oxidation rate is independent of oxygen concentration and tetrachloroethylene concentration and is proportional to the first power of the intensity of absorbed radiation.

The photochlorination yields hexachloroethane and the local reaction rate expression found is

$$-d(Cl_2)/dt = k(I_{abs.})^{.5}(Cl_2).$$

The quantum yields indicate a chain reaction for which two possible mechanisms, each involving chlorine atoms, have been developed.

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IV. THE BROMINE-SENSITIZED PHOTODECOMPOSITION OF GASEOUS DIBROMOTETRACHLOROETHANE

In pursuing further study of the photohalogenation of the double bond existing between two carbon atoms, the investigation of the bromine addition to tetrachloroethylene was attempted. Since the bromination would produce solid dibromotetrachloroethane, $C_2Cl_4Br_2$, a pressure decrease would result from the reaction as shown by the equation

$$C_2Cl_4(g) + Br_2(g) = C_2Cl_4Br_2(s);$$

the reaction could be followed by pressure change. A gas mixture of bromine, 85 mm., and tetrachloroethylene 26 mm., was charged into a liter Pyrex bulb by use of an apparatus quite like the one shown in Fig. 1 of the preceding chapter.[1] Illumination of the mixture at 60°C. with 4358Å from the Hg-arc produced a very slow pressure decrease with the formation of colorless crystals; white light from two 60-watt incandescent lamps was then used and a pressure decrease of some 3 mm. per hour resulted. Anticipating an increased rate at higher temperatures, a mixture of 26.2 mm. of bromine and 15.2 mm. of tetrachloroethylene was illuminated strongly with the unfiltered radiation of a 500-watt projection lamp at 100°. The pressure decreased from 41.4 mm. to 40.4 mm. after several hours irradiation. The temperature of the mixture was lowered to 30° C. and illumination produced a slow, steady decrease in total pressure with the formation of colorless crystals.

These results indicated that a bromine-sensitized photodecomposition of dibromotetrachloroethane might occur at 100° and higher temperatures. A reaction of this nature materialized.

Materials

Bromine was prepared from potassium bromate and potassium bromide reaction in concentrated sulfuric acid. Solid potassium bromate was added to a saturated solution of potassium bromide and then concentrated sulfuric acid was added. The bromine was distilled off, allowed to stand over anhydrous calcium bromide, distilled off, dried with anhydrous calcium bromide a second time, and redistilled. The potassium bromate, potassium bromide, and calcium bromide were twice recrystallized salts; the calcium bromide was rendered anhydrous by prolonged heating at 145° C.

The tetrachloroethylene was treated as described in Chapter III.[2]

Dibromotetrachloroethane was prepared by the illumination of a liquid bromine-tetrachloroethylene mixture with white light. The slight excess of bromine remaining after prolonged illumination was pumped off and the solid, white, crystalline, lachrymatory dibromotetrachloroethane purified by sublimation in vacuo. From the mode of preparation symmetrical 1,1,2,2-tetrachloro-1,2-dibromo-ethane is assumed to have been produced.

Apparatus

The equations for the decomposition of dibromotetrachloroethane

$$C_2Cl_4Br_{2(s)} = C_2Cl_{4(g)} + Br_{2(g)}$$

and

$$C_2Cl_4Br_{2(g)} = C_2Cl_{4(g)} + Br_{2(g)}$$

disclose an increase in total pressure as the result of reaction. The apparatus was designed to follow the reaction by means of this pressure increase. The reaction vessel was a Pyrex cylindrical cell with flat ends; internally, the diameter was 6.2 cm., the length, 4.0 cm. The vessel had a small side arm to be used for freezing out condensible gases by applying liquid air or carbon dioxide-acetone mush. A clicker type glass diaphragm gage[4] to be used in conjunction with a mercury manometer in pressure measurements was also attached to the reaction cell. The cell was attached to a mercury diffusion pump for evacuation. Furthermore, there were side arms which held small glass bulbs containing weighed quantities of bromine, tetrachloroethylene, and dibromotetrachloroethane. These bulbs could be broken by glass-enclosed hammers operated magnetically, and the contents of the bulbs moved into the reaction cell by applying liquid air to the freezing-out side arm. (Dibromotetrachloroethane was sublimed into the reaction cell). Then the side arms which contained the broken sample bulbs were removed by sealing off. The solid dibromotetrachloroethane was sublimed onto the reaction vessel side walls and the flat end faces kept free of solid. The attachment to the pumps was sealed off prior to illumination. The reaction volume remaining was consistently 132 cc. A gas furnace was employed for baking out the evacuated reaction cell before admitting the reactants.

After having been filled with rectants, the reaction cell, freezing-out side arm, and clicker were surrounded by a metallic chimney and covered by a light-tight air thermostat. The chimney facilitated the circulation of air maintained by a fan and the heating coils. The front wall of the thermostat box had a window through which illumination of the reactants occurred. The back thermostat wall had a window which was used only when actual measurement was made of the fraction of the incident 4358Å radiation absorbed by the bromine present.

The incident radiation beam was well collinated and its defining diaphragm was 4.0 cm. in diameter. Quantum yields were made with 4358Å radiation from an upright quartz mercury arc. The color filters used for monochromatization were those described in Chapter III, with the exception that 10% cupric chloride solution was used instead of 6% copper sulfate solution. When higher light intensities were desired, a 500-watt projection lamp, operated at constant voltage, was used instead of the mercury arc.

A Moll small surface thermopile in conjuction with a high sensitivity galvanometer was calibrated bare against a carbon-filament Bureau of Standards standard lamp. This thermopile could be placed in the center of the 4.0 cm. beam-defining diaphragm for frequent measurement of intensity of incident radiation. In evaluating the absolute amount of radiation entering the gaseous reactants, three points of consideration arose; (a) appropriate correction for reflection losses, (b) slight lack of uniformity of the light beam over the area of the defining diaphragm, and (c) non-linearity of the galvanometer. It was found that 1 cm. of corrected galvanometer deflection corresponded to a flux of 623 ergs per second or 2.28 x 10^{-10} einsteins per second of 4358Å radiation entering the gaseous reactants.

The fraction of incident radiation absorbed, ordinarily, was calculated from known bromine partial pressures and the relation, $\tau = I/I_0 = 10^{-acd}$, where d = 4.0 cm., c is the concentration of bromine in moles per liter, and a, the molal extinction coefficient of bromine, taken as 154. This value was determined by Dr. P. G. Murdoch at this laboratory. Its agreement with the value of Gray and Style[5], 160, and the value of Ribaud's 149.5 is substantial. The temperature coefficient of *a* has been considered negligible. In making actual measurements of fractional absorption, the thermopile was placed in the light beam emerging from the back window of the thermostat after passage through the reaction cell. Alternate galvanometer deflection readings with and without liquid air applied to the freezing-out side arm of the reaction vessel were made. The ratio of corrected galvanometer deflections with the contents of reaction cell gaseous to corrected galvanometer deflections with the contents of the reaction cell frozer down was taken as $I/I_0 = \tau$, the fraction of incident radiation transmitted.

In quantum yield evaluation, it was necessary to make a correction for the radiation reflected into the gas by the back wall of the reaction vessel and back window of the thermostat. The derivation of the correction factor follows.

Invoke Fresnel's Law for finding the reflected fraction of parallel, monochromatic radiation incident normally at the plane interface of two media.

$$R = ((n - 1)/(n + 2))^2$$

in which *R* is the fraction of incident radiation reflected, *n* is the refractive index of the interface. Letting n = 1.65 for a Pyrex glass-air interface,

$$R = .035$$

τ is the transmission of the gas mixture and $(1 - \tau)$

is the fraction of incident radiation absorbed in a single passage through the gas mixture. The total interfaces involving the back wall of the reaction cell and the back window of the thermostat are four in number; namely, *a*, *b*, *c*, and *d*, progressively taken from front to back through reaction vessel and thermostat window. As a close *approximation*, it can be stated that if I_0 be the radiation incident at the front layer of the gas mixture, the fraction of I_0 incident at each interface is, respectively

a, τ ; *b*, $\tau(1 - R)$; *c*, $\tau(1 - R)^2$; *d*, $\tau(1 - R)^3$

Since each interface reflects the fraction, R, of the radiation incident on it, the fraction of I_0 reflected from each interface is, respectively,

a, $R\tau$; *b*, $R\,\tau(1 - R)$; *c*, $R\,\tau(1 - R)^2$; *d*, $R\,\tau(1 - R)^3$.

The total fraction of I_0 reflected into the gas is

$R\tau(1 + (1 - R) + (1 - R)^2 + (1 - R)^3)$.

The fraction of this reflected radiation absorbed by the gas is $(1 - \tau)$. Thus the fraction of I_0 absorbed by the gas due to reflections by interfaces of the back wall of the reaction cell and back window of the thermostat is

$(1 - \tau)R\tau(1 + (1 - R) + (1 - R)^2 + (1 - R)^3)$.

The total absorption fraction, A, of I_0 absorbed by the gas as a result of direct illumination and reflection is then

$$A = (1 - \tau) + (1 - \tau)R\tau(1 + (1 - R) + (1 - R)^2 + (1 - R)^3)$$
$$= (1 - \tau)(1 + R\tau(1 + (1 - R) + (1 - R)^2 + (1 - R)^3)).$$

Since R = .035,

$$\underline{A} = (1 - \tau)(1 + 0.13\tau)$$

The Vapor Pressure of Solid Dibromotetrachloroethane

The vapor pressure of solid dibromotetrachloroethane was determined by subliming the solid into the evacuated reaction vessel, pumping down, and sealing off, thermostating the reaction vessel at various temperatures. The pressures were measured 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 presents the best values obtained for the vapor pressure of dibromotetrachloroethane.

Table I

Vapor Pressure of Solid Dibromotetrachloroethane

Temperature °C	Vapor Pressure mm. Hg
50	0.4
75	1.3
90	3.5
100	6.0
110	9.8
125	19.6
135	29.4
150	50.9

The Nature of the Reaction

A comparison was made of the observed final pressures produced by illuminating mixtures containing known quantities of dibromotetrachloroethane , bromine, and tetrachloroethylene at 135° until no further pressure increase occurred and the final pressures calculated on the assumption that dibromotetrachloroethane would decompose into bromine and tetrachloroethylene until the dibromotetrachloroethane was almost completely gone if the bromine and tetrachloroethylene pressures were not too high. The agreement of the observed and calculated values shown in Table II indicate that the assumption was valid.

Table II

Extent of Photodecomposition at 135°

Initial Composition			Final Total Pressure	
$C_2Cl_4Br_2$ mg.	C_2Cl_4 mg.	Br_2 mg.	Observed mm.	Calculated 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

In agreement with the preliminary experiments, it was found that a mixture which had shown a pressure increase with disappearance of solid dibromotetrachloroethane on illumination at temperatures greater than 100° would give steady pressure decreases with colorless crystal formation when illuminated strongly at room temperature. Thus a series of decomposition measurements could be made with a mixture at elevated temperatures, recombination be produced by illumination at room temperature, and then a second set of decomposition measurements over the same pressure range as the first be made.

As a check on the indication that these pressure increases and decreases were really the decomposition and formation of dibromotetrachloroethane, respectively, a comparison was made of partial bromine pressures calculated in two different ways. One method of calculation was based on known initial composition of the reaction mixture and the final total pressure of the mixture after illumination. The other method involved the direct measurement of transmission of the mixture for 4358Å radiation.

A sample calculation illustrates the method and agreement. At 50° an initial gas mixture contained bromine, 3.8 mm., dibromotetrachloroethane, .4 mm. After illumination at various temperatures, the resulting mixture was found to have a total pressure of 21.7 mm. at 50°. The measured transmission of the mixture for 4358Å was 0.427. Solid dibromotetrachloroethane was present at all times.

(a). Since, $C_2Cl_4Br_{2(s)} = C_2Cl_{4(g)} + Br_{2(g)}$ on illumination at temperatures above 100° and the reverse occurred on illumination at room temperature,

$$\Delta p_{Br_2} = \Delta p_{C_2Cl_4} \text{ during reaction.}$$

At 50°, $p_{C_2Cl_4Br_2} = .4$ mm.

$p_{total} - p_{C_2Cl_4Br_2} = p_{Br_2} + p_{C_2Cl_4} = 21.7 - .4 = 21.3$ mm.

$$p_{Br_2} = 3.8 + p_{Br_2} = 21.3 - p_{C_2Cl_4}$$

Then, $3.8 + \Delta p_{Br_2} = 21.3 - \Delta p_{Br_2}$

$$\Delta p_{Br_2} = 8.7$$

$$p_{Br_2} = 12.5 \text{ mm.}$$

(b). In the calculation of p_{Br_2} from transmission of 4358Å,

$$= 0.427 = 10^{-acd} = 10^{-154 \times 4.0\underline{c}}$$

$$\log 0.427 = \bar{1}.6305 = 1.3695$$

$$-616\underline{c} = .3695$$

$$\underline{c} = 6.0 \times 10^{-4} \text{ moles/liter}$$

$$p_{Br_2} = 12.1 \text{ mm.}$$

Here, the agreement between the bromine pressure calculated from pressure measurements and from transmission measurements is seen to be satisfactory. In other instances the agreement was usually within 1 mm.

When mixtures containing relatively high concentrations of tetrachloroethylene and bromine, but no dibromotetrachloroethane were illuminated at 135°, a slow pressure decrease occurred which ceased in a photostationary state. Thus a mixture of 124.5 mm. of bromine and 155.1 mm. of tetrachloroethylene showed a total pressure decrease of 13.4 mm. after 36 hours illumination. Assuming that this pressure decrease resulted solely from the formation of dibromotetrachloroethane and using the perfect gas laws and the vapor pressure of solid dibromotetrachloroethane, the predicted pressure of the mixture cooled to 100° in the dark was 237.2 mm. and the observed pressure at 100° was 243.4 mm. To eliminate the possiblity that this discrepancy was due to a supersaturation, a CO_2-acetone freezing mixture was applied to the freezing-out side arm and left for twelve hours. Upon evaporation of the condensed gases a pressure of 243.4 mm. was again measured at 100°. The quantum yield at the start of this experiment was only .3 mole of dibromotetrachloroethane produced per einstein absorbed. A second gaseous mixture containing initially bromine, 203.5 mm., and tetrachloroethylene, 147.5 mm. at 135° showed a total pressure drop of 15.7 mm. on prolonged illumination. The predicted pressure for this mixture when cooled in the dark to 100° was 298.0 mm. and the observed pressure was 304.2 mm. This discrepancy indicates that the pressure decrease on prolonged illumination at 135° was not due solely to dibromotetrachloroethane formation, but probably was due to an isomerization. These two mixtures when illuminated at 100° C gave further pressure decreases with the formation of colorless crystals with the odor of dibromotetrachloroethane. A photostationary state was reached in each case, the final total pressures being 231.6 mm. and 227.0 mm., respectively.

In order to make the rate of formation of dibromotetrachloroethane negligible in the study of the rate of decomposition, the partial pressures of bromine and tetrachloroethylene employed were much smaller than those in the above experiments.

The alteration of temperatures on mixtures in which decomposition had occurred gave pressure changes in good agreement with those expected from the gas laws and the vapor pressure of solid dibromotetrachloroethane. Table III shows some examples of such cases.

Table III

Effect of Temperature Alteration on Total Pressure

Initial Conditions		Final Conditions		
Temp. °C	Pressure mm. Hg	Temp. °C	Pressure, mm. Obs.	Calc.
100	69.2	50	55.3	55.1
100	38.1	125	53.2	53.8
100	61.2	135	87.5	89.8
100	25.7	135	49.9	51.0
26	19.6	135	56.6	56.2
90	216.4	100	225.1	225.0

Table IV

Quantum Yield of Decomposition of Dibromotetrachloroethane 4358 Å

<table>
<tr><th>No.</th><th>Mean pressure of bromine; mm. Hg</th><th>Δp_{total} mm. Hg</th><th>Corrected galvanometer deflections;</th><th>Absorption; fraction</th><th>Time of illumination; seconds</th><th>Quantum yield; moles of $C_2Cl_4Br_2$ decomposed per einstein</th></tr>
<tr><td>1</td><td>4.7</td><td>3.3</td><td>25.4</td><td>0.274</td><td>12090</td><td>0.490</td></tr>
<tr><td>2</td><td>13.0</td><td>12.8</td><td>22.4</td><td>.579</td><td>24600</td><td>.497</td></tr>
<tr><td>3</td><td>17.9</td><td>7.0</td><td>21.9</td><td>.693</td><td>10920</td><td>.527</td></tr>
<tr><td>4</td><td>22.8</td><td>4.6</td><td>22.5</td><td>.776</td><td>7500</td><td>.438</td></tr>
<tr><td>5</td><td>31.7</td><td>7.2</td><td>19.9</td><td>.869</td><td>14760</td><td>.352</td></tr>
<tr><td>6</td><td>46.2</td><td>3.9</td><td>21.0</td><td>.946</td><td>9000</td><td>.272</td></tr>
<tr><td colspan="7">Nos. 1 to 6: T= 100°; $p_{C_2Cl_4Br_2} = 6.0$ mm.; $p_{C_2Cl_4} = p_{Br_2} - 3.9$ mm.</td></tr>
<tr><td>7</td><td>18.7</td><td>13.8</td><td>28.4</td><td>0.685</td><td>2160</td><td>3.83</td></tr>
<tr><td>8</td><td>24.4</td><td>9.1</td><td>6.9</td><td>.775</td><td>5400</td><td>3.68</td></tr>
<tr><td>9</td><td>29.0</td><td>9.4</td><td>26.7</td><td>.832</td><td>1410</td><td>3.50</td></tr>
<tr><td>10</td><td>33.3</td><td>7.8</td><td>26.7</td><td>.865</td><td>1200</td><td>3.29</td></tr>
<tr><td>11</td><td>37.3</td><td>8.0</td><td>26.7</td><td>.895</td><td>1200</td><td>3.26</td></tr>
<tr><td>12</td><td>42.8</td><td>14.4</td><td>26.7</td><td>.925</td><td>2400</td><td>2.84</td></tr>
<tr><td colspan="7">Nos. 7 to 12: T = 125°; $p_{C_2Cl_4Br_2} = 19.6$ mm.; $p_{C_2Cl_4} = p_{Br_2} - 4.0$ mm.</td></tr>
<tr><td>13</td><td>18.1</td><td>10.0</td><td>20.5</td><td>0.665</td><td>1140</td><td>7.30</td></tr>
<tr><td>14</td><td>23.6</td><td>11.7</td><td>20.5</td><td>.756</td><td>1255</td><td>6.84</td></tr>
<tr><td>15</td><td>29.6</td><td>12.2</td><td>20.8</td><td>.827</td><td>1260</td><td>6.39</td></tr>
<tr><td>16</td><td>35.7</td><td>12.1</td><td>20.8</td><td>.877</td><td>1260</td><td>6.00</td></tr>
<tr><td>17</td><td>40.3</td><td>6.1</td><td>5.3</td><td>.905</td><td>2400</td><td>6.04</td></tr>
<tr><td>18</td><td>45.3</td><td>14.0</td><td>20.8</td><td>.930</td><td>1500</td><td>5.49</td></tr>
<tr><td colspan="7">Nos. 13 to 18: T = 135°; $p_{C_2Cl_4Br_2} = 29.4$ mm.; $p_{C_2Cl_4} = p_{Br_2} - 4.1$ mm.</td></tr>
<tr><td>19</td><td>7.9</td><td>11.7</td><td>24.4</td><td>0.386</td><td>966</td><td>14.7</td></tr>
<tr><td>20</td><td>13.2</td><td>9.5</td><td>6.1</td><td>.554</td><td>1914</td><td>16.8</td></tr>
<tr><td>21</td><td>17.0</td><td>5.8</td><td>6.2</td><td>.645</td><td>960</td><td>17.3</td></tr>
<tr><td colspan="7">Nos. 19 to 21: T = 135°; $p_{C_2Cl_4Br_2} = 29.4$ mm.; $p_{C_2Cl_4} = p_{Br_2}$; 484 mm. $= p_{N_2}$</td></tr>
<tr><td>22</td><td>6.3</td><td>7.6</td><td>19.1</td><td>0.323</td><td>300</td><td>46.7</td></tr>
<tr><td>23</td><td>10.35</td><td>8.6</td><td>19.1</td><td>.470</td><td>240</td><td>45.4</td></tr>
<tr><td>24</td><td>14.9</td><td>9.6</td><td>19.1</td><td>.594</td><td>240</td><td>40.2</td></tr>
<tr><td>25</td><td>21.1</td><td>15.2</td><td>19.1</td><td>.719</td><td>330</td><td>38.2</td></tr>
<tr><td>26</td><td>27.0</td><td>8.4</td><td>19.0</td><td>.800</td><td>180</td><td>34.9</td></tr>
<tr><td>27</td><td>32.55</td><td>13.8</td><td>18.9</td><td>.855</td><td>300</td><td>32.3</td></tr>
<tr><td colspan="7">Nos. 22 to 27: T = 135°; $p_{C_2Cl_4Br_2} = 29.4$ mm.; $p_{C_2Cl_4} = p_{Br_2}$</td></tr>
<tr><td>28</td><td>6.3</td><td>6.7</td><td>14.9</td><td>0.323</td><td>600</td><td>26.4</td></tr>
<tr><td>29</td><td>10.05</td><td>8.2</td><td>14.5</td><td>.461</td><td>540</td><td>25.9</td></tr>
<tr><td>30</td><td>14.2</td><td>8.4</td><td>14.4</td><td>.580</td><td>480</td><td>23.85</td></tr>
<tr><td>31</td><td>18.3</td><td>8.0</td><td>14.6</td><td>.670</td><td>420</td><td>22.2</td></tr>
<tr><td colspan="7">Nos. 28 to 31: T = 135°; $p_{C_2Cl_4Br_2} = 29.4$ mm.; $p_{C_2Cl_4} = p_{Br_2} + 25.8$ mm.</td></tr>
<tr><td>32</td><td>33.4</td><td>18.8</td><td>22.3</td><td>0.857</td><td>600</td><td>17.2</td></tr>
<tr><td>33</td><td>41.1</td><td>9.6</td><td>5.64</td><td>.902</td><td>1200</td><td>14.4</td></tr>
<tr><td>34</td><td>46.7</td><td>10.5</td><td>22.3</td><td>.932</td><td>600</td><td>15.2</td></tr>
<tr><td colspan="7">Nos. 32 to 34: T = 150°; $p_{C_2Cl_4Br_2} = 50.9$ mm.; $p_{C_2Cl_4} = p_{Br_2} - 4.3$ mm.</td></tr>
</table>

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

Quantum Yields of Dibromotetrachloroethane Decomposition

In Table IV some of the quantum yield measurements of dibromotetrachloroethane decomposition are shown. The mean partial pressures shown in each experiment are the averages of the values prevailing at the beginning and end of suitably short illumination intervals. The total pressure increase, Δp_{total}, and duration of illumination in seconds, Δt, are shown. The fraction of absorption of incident radiation, A, are the values of $(1 - \tau)(1 + .13\tau)$, the derivation of which has been previously given. The bromine pressures used in the calculations of τ are those listed. From the rate of total pressure change and the rate of absorption of radiation, the quantum yields expressed as moles of dibromotetrachloroethane decomposed per einstein absorbed have been calculated. The quantum yields are high enough to show definitely that the decomposition is a chain reaction.

Solid dibromotetrachloroethane was present in the reaction cell in all these experiments. In Nos. 1 to 27 and 32 to 61 a large excess (about 2g.) of the solid was present; in Now. 28 to 31 a smaller amount was present. Illuminated gas mixtures were saturated with the vapor of dibromotetrachloroethane; for when illumination was stopped, the pressure of the mixture was immediately measured and found to be constant throughout long subsequent intervals in the dark at temperatures up to 135°.

Thermal reaction rate was negligible at 135°. At 150°, the dark rate was appreciable. The quantum yields at this temperature are corrected for thermal rate. This was done by subtracting the dark rate from the total rate measured during illumination. The validity of such a correction depends on the independence of actual photochemical and thermal rates. It is not known if the two rates are independent, hence the validity is doubtful; the correction is of little consequence.

An inspection of the quantum yields shows, in some cases, a five-fold variation in the results obtained in the same range of partial pressures from measurements made on different fillings of the reaction cell. To avoid the uncertainties arising from the comparison of runs made on different fillings, several decomposition runs were made in the same pressure range on one filling by the expedient photochemical recombination of the decomposition products at room temperature.

In Table IV Nos. 1 to 18 and 32 to 34 were made on the same filling and the quantum yields of these experiments show a consistent increase with increasing temperature.

Effect of Bromine and Tetrachloroethylene

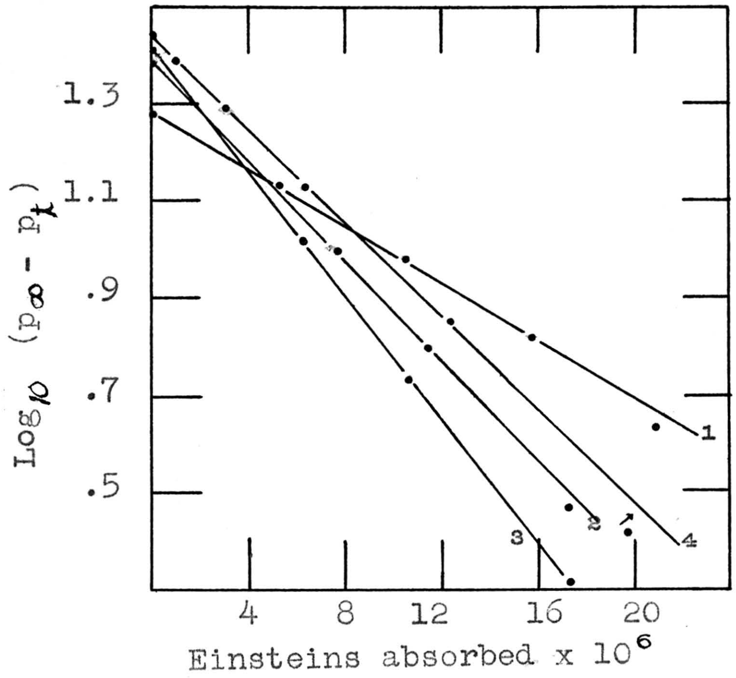
The effects of the decomposition products on the rate were not extensive. However, within a series of consecutive measurements on single fillings, as Nos. 7 to 12 at 125°, and 28 to 31, 13 to 18, 22 to 27 at 135°, the quantum yields show a decrease with increasing concentrations of the decomposition products. The magnitude of this effect in Nos. 22 to 27 is a concurrence of 30% decrease in quantum yield and five-fold increase in partial pressures of the products. In view of the *small* quantum yields of dibromotetrachloroethane *formation* at *higher* concentrations of bromine and tetrachloroethylene than were employed in these runs, it is hardly probable that this falling off in value of the quantum yields is due to a combination of bromine and tetrachloroethylene.

The decrease might be attributed to an inhibition of decomposition by one or both of the products.

Effects of Dibromotetrachloroethane

In order to determine the effect of dibromotetrachloroethane pressure on the decomposition rate, runs were made at 135° without the presence of solid dibromotetrachloroethane. The quantum yields decreased as the dibromotetrachloroethane pressure became less; the quantum yields were approximately linear with the pressure of the dibromotetrachloroethane. This linear dependence of rate of decomposition on dibromotetrachloroethane pressure is shown in Figure I by plotting the $\log_{10}(p_\infty - p_t)$ against $E_{abs.}$; p_∞ is the constant final total pressure and p_t is the momentary value of the total pressure. $E_{abs.}$ is the total 4358Å radiation absorbed expressed in einsteins and equals $I_{abs.}t$, einsteins absorbed per second x seconds of illumination.

Figure 1



	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	129.6	51.1	76.8
4	130.9	52.4	78.1

The concentrations of bromine and tetrachloroethylene in these runs were low enough that practically all the dibromotetrachloroethane decomposed and its pressure at p_∞ is assumed to be zero. Let the partial pressure of dibromotetrachloroethane be $p_{C_2Cl_4Br_2}$ mm. when the total pressure is p_t. Let the final constant total pressure be p_∞ after the $p_{C_2Cl_4Br_2}$ mm. have been decomposed. Since 1 mm. of dibromotetrachloroethane decomposing in the absence of the solid produces an increase of 1 mm. in total pressure,

$$p_\infty = p_t + p_{C_2Cl_4Br_2}$$

Then, $p_{C_2Cl_4Br_2} = p_\infty - p_t$.

In essence, $\log_{10} p_{C_2Cl_4Br_2}$ was plotted against $E_{abs.}$ in Fig. 1 and the linear relation between the two indicates a linear dependence of the rate of decomposition on dibromotetrachloroethane as shown by the following consideration. Assume the linear relation,

$$\ln p_{C_2Cl_4Br_2} = kI_{abs.}t + C,$$

k being negative. Assume that

$$I_{abs.} \neq f(p_{C_2Cl_4Br_2});$$

this is not too serious since the lamp intensity was constant, and the initial bromine concentration was high enough that the fraction of incident radiation absorbed was not changed critically as dibromotetrachloroethane decomposition progressed. Differentiating,

$$dp_{C_2Cl_4Br_2}/dt = kI_{abs.}p_{C_2Cl_4Br_2}$$

Effect of Incident Light Intensities

Quantum yields obtained at relatively low incident light intensities of 4358Å radiation were substantially constant when the incident light intensity was varied four-fold by use of neutral wire screens. This is shown in Table IV; Nos. 7, 8, 9, and 16, 17, 18 are consecutive measurements in which a quantum yield determination at low incident intensity is bracketed by determinations at an incident intensity four-fold higher. This constancy indicates that the decomposition rate is proportional to the first power of the incident light intensity *at these relatively low intensities*.

The dependence of rate on intensity was examined at somewhat higher light intensities by substituting the 500-watt projection lamp for the mercury arc. The same filters were used and the spectral region isolated was about 4100-4800Å. Results of such experiments are Nos. 42 to 47 of Table V. 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. Nos. 48 to 52 give results of such measurements; and 11-fold decrease in the light intensity produced a 1.66-fold increase in $\Delta p/\tau\Delta t$. Nos. 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 4-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 IV 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 V

Effect of Light Intensity on Rate of Decomposition.

No.	Mean p_{Br_2} mm. Hg	Time Δt secs	Pressure Increase Δp mm.Hg	I_0= screen τ	$\Delta p/\tau\Delta t$
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.

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.

(a) Illumination in consecutive seconds.

(b) Illumination in single seconds separated by 2-minute dark intervals.

Mechanism of the Reaction

The mechanism must provide for both decomposition and formation of dibromotetrachloroethane. When the rate of <u>formation</u> is negligible, the <u>rate of decomposition</u> must depend on the first power of the dibromotetrachloroethane pressure and must depend on the first power of the intensity of absorbed radiation at extremely low incident light intensities but on a lesser power as the incident intensities become higher. The mechanism must provide for a decrease in rate of decomposition as the partial pressures of the products increase, the decrease hardly being attributable to reversal of decomposition. Such a mechanism follows.

$$
\begin{array}{rcllr}
Br_2 + h\nu & \longrightarrow & 2Br & & (1) \\
Br + C_2Cl_4Br_2 & \rightleftarrows & C_2Cl_4Br + Br_2 & & (2) \text{ and } (2') \\
C_2Cl_4Br & \rightleftarrows & C_2Cl_4 + Br & & (3) \text{ and } (3') \\
Br & \longrightarrow & Br(\text{wall}) & 1/2Br_2 & (4) \\
2Br + M & \longrightarrow & Br_2 + M & & (5)
\end{array}
$$

Here the primary absorption process is the dissociation of the bromine molecule into atoms. The postulated intermediate molecule is C_2Cl_4Br. Two chain-breaking steps are provided. Step (4) provides for the disappearance of bromine atoms at the wall by a process which is first power with respect to bromine atoms, while step (5) provides for the recombination of bromine atoms in the gas phase by ternary collision with a required stabilizing third molecule, M.

This mechanism leads to the rate expression, 1,

$$\frac{d(Br_2)}{dt} = \frac{-k_4 + (k_4^2 + 16k_5(M)(I_{abs.}))^{.5}}{4\,k_5(M)}$$

$$\times\ \frac{k_2k_3(C_2Cl_4Br_2) - k_2'k_3'(C_2Cl_4)(Br_2)}{k_3 + k_2'\,(Br_2)}\ .$$

The derivation follows. To simplify, let (A) represent $(C_2Cl_4Br_2)$, (B) represent (C_2Cl_4Br), and (C) represent (C_2Cl_4).

$-d(A)/dt = k_2(Br)(A) - k_2'\,(B)(Br_2) = d(Br_2)/dt$

At the steady state

$$2(I_{abs.}) = k_4(Br) + 2k_5(M)(Br)^2,$$

since a chain must be terminated as frequently as initiated;

$(Br) = (-k_4 + (k_4^2 + 16k_5(m)(I_{abs.}))^{.5})/4k_5(M).$

Set, $d(B)/dt = k_2(Br)(A) - k_2'\,(B)(Br_2) - k_3(B) + k_3'\,(C)(Br)$

$$= 0;$$

$$(B) = \frac{(Br)(k_3'\,(C) + k_2(A))}{k_3 + k_2'\,(Br_2)}$$

Substituting these values of (B) and (Br) in expression for $-d(A)/dt$, rate expression 1 results.

At relatively low incident intensities, the bromine atom concentrations might be so low that recombination in the gas phase would be neglibible in comparison with recombination at the wall. Step (4) would then be the chain-breaking step and the rate expression would become, 2,

$$\frac{d(Br_2)}{dt} = \frac{2(I_{abs.})}{k_4}\ \frac{k_2k_3(C_2Cl_4Br_2) - k_2'\,k_3'\,(C_2Cl_4)(Br_2)}{k_3 + k_2'\,(Br_2)}$$

When $k_2'\,k_3'\,(C_2Cl_4)(Br_2) \ll k_2k_3(C_2Cl_4Br_2)$, this being the case when the reverse reaction was negligible,

$$\frac{d(Br_2)}{dt} = \frac{2(I_{abs.})}{k_4}\ \frac{k_2k_3(C_2Cl_4Br_2)}{k_3 + k_2'\,(Br_2)}$$

This expression, 3, shows the expected dependence of rate on dibromotetrachloroethane concentration and on the first power of the light intensity.

The mechanism has attributed the observed inhibition by the products of decomposition to the bromine. An inspection of expression 3 shows that should k_4 be a constant, the quantum yields, ϕ, should be inversely proportional to $(1 + k_2' (Br_2)/k_3)$ at constant $(C_2Cl_4Br_2)$; for,

$$\phi = \frac{d(Br_2)}{(I_{abs.})\,dt} = \frac{K}{1 + k_2'(Br_2)/k_3} .$$

Then, $\phi(1 + \underline{b}p_{Br_2}) = K$

The validity of this last equation has been examined. Assuming that k_4 is a constant for a single filling of the reaction cell, various values of $\underline{b}$ have been used in examining consecutive measurements on single fillings shown in Table IV. The best values of $\underline{b}$ found were .016 mm^{-1} at 135° and .020 mm^{-1}. The constancy of $\phi(1 + \underline{b}p_{Br_2})$ is shown in Table VI.

Thus the constancy of $\phi(1 + bp_{Br_2})$ for consecutive measurements on the same filling is seen to be satisfactory and there is no difficulty arising from the attribution of inhibition to bromine. At 135° the value of $\underline{b}$ in $moles^{-1}cc.$ is 4×10^5 which is the value of k_2'/k_3.

Table VI

Inverse Proportionality of Quantum Yield and The Expression $(1 + \underline{b}p_{Br_2})$

(A)		(B)		(C)		(D)	
No.	K	No.	K	No.	K	No.	K
7	5.27	13	9.40	22	51.5	28	29.1
8	5.47	14	9.41	23	52.7	29	30.1
9	5.53	15	9.42	24	49.6	30	29.4
10	5.43	16	9.44	25	51.5	31	28.4
11	5.69	18	9.46	26	50.0		
12	5.27			27	49.0		

No. is the number of measurement in Table IV.

K is $(1 + bp_{Br_2})$.

(A) at 125°, $\underline{b} = .020$; (B), (C), (D) at 135°, $\underline{b} = .016$

For a mixture of given composition, expression $\underline{1}$ reduces to $d(Br_2)/dt = K(1 + \sqrt{1 + \underline{d}I_0})$, in which $\underline{K} = \dfrac{k_2k_3k_4(C_2Cl_4Br_2)}{4k_5(k_3 + k_2'(Br_2))(M)}$ and $\underline{d}\,I_0 = \dfrac{16k_5(M)(I_{abs.})}{k_4^2}$

This equation may be used to study the variation of rate with intensity for mixtures of the given composition. From Nos. 48 to 55 of Table V, rates for each four intensities covering a 250-fold range have been interpolated to the same composition; namely, that of the mixture having $p_{Br_2} = 36.7$ mm. In Table VII are shown the interpolated rates and those calculated by setting K = 0.135 mm./sec. and $\underline{d} = 16$, values obtained from the first two rows of the table.

Table VII

Effect of Light Intensity at Constant Concentration

I_0 = γ screen	dp_{Br_2}/dt mm./sec. observed	dp_{Br_2}/dt mm./sec. calculated
0.0038	0.0041	.0041
0.0132	.014	.014
0.0900	.065	.075
1.	.43	.42

It is possible to estimate the value of (Br). In these considerations it is necessary to ignore the variation of ($I_{abs.}$) over the reaction zone and likewise the variation of reaction rate over the reaction zone. It has been shown

$$\underline{d}I_0 = 16k_5(M)(I_{abs.})/k_4^2$$

Consider an experiment at low incident intensity where a linear relation exists between rate and the first power of the light intensity; i.e., $k_4(Br) \gg 2k_5(M)(Br)^2$.

Since $2(I_{abs.}) = k_4(Br) + 2k_5(Br)^2(M)$ at steady state,

$$2(I_{abs.}) \cong k_4(Br)$$

Also $d(Br_2)/(I_{abs.})dt = \varphi$ the quantum yield.

Therefore, $k_4(Br) = 2(d(Br_2)/dt)/\varphi$,

and substituting in the expression for $\underline{d}I_0$ above,

$$dI_0 = 4k_5(M)(Br)^2\varphi/(d(Br_2)/dt).$$

The value[7] of k_5 used is 2.9×10^{15} cc.^{2} mole^{-2} sec.$^{-1}$.

In Table V , No. 54, the value of $\underline{d}\ I_0 = 0.061$, $(M) \doteq 587$mm.,

$d(Br_2)dt = .0041$ mm./sec., taking $\phi = 10$, the value of (Br) is calculated as 2×10^{-12} mole/cc.

This value of (Br) is much larger than the value of (Br) at thermal equilibrium at 135°. From the data of Bodenstein and Cramer[8], $\log K_p = -10100/T + 1.75\log T + .548 - .0_3409T + 4.726 \times 10^{-8}T^2$ for the reaction $Br_{2(g)} \rightleftarrows 2Br_{(g)}$. In this expression K_p is the equilibrium constant, p^2_{Br}/p_{Br_2}, for the reaction in question and T is the absolute temperature. At 135°

$$K_p = 1.6 \times 10^{-20}.$$

For $p_{Br_2} = 36.7 \text{ mm.} = 4.83 \times 10^{-2}\text{atm.},$

$$p_{Br} = (1.6 \times 10^{-20} \times 4.83 \times 10^{-2})^{.5} = 2.8 \times 10^{-11}\text{atm.}$$

$$(Br) = 8.4 \times 10^{-16} \text{ mole/cc.}$$

Thus the mechanism employed leads to no fallible results concerning the comparative equilibrium and photochemical concentrations of bromine atom.

In No. 54 of Table V, it becomes possible to compare the rate of bromine atom *disappearance* at the wall with the rate of bromine atom *collision* with the wall. It has been stated that

$$k_4(Br) = 2(I_{abs.});$$

i.e. the rate of bromine atom disappearance equals rate of formation. Also $(I_{abs.}) = (d(Br_2)/dt)/\phi$. ϕ has been taken as 10; $dp_{Br_2}/dt = .0041$mm./sec. corresponds to $d(Br_2)/dt = 1.6 \times 10^{-10}$ moles/cc./sec.

$2(I_{abs.}) = 3.2 \times 10^{-11}$ einsteins/cc./sec;

$-d(Br)/dt = 3.2 \times 10^{-11}$ moles/cc./sec.

$Vd(Br)/dt = 3.2 \times 10^{-11} \times 132 = \underline{4.2 \times 10^{-9}}$ moles of bromine atom <u>dying</u> on the wall per second, $\underline{V}$, the volume of the reaction cell being 132 cc.

To calculate the number of moles of bromine atom striking the wall of the reaction vessel per second employ the expression

$Z = \underline{c}\sqrt{RT}/\sqrt{2\ M} = 8.21 \times 10^{-3}\underline{c}$, where Z is the number of moles striking 1 sq. cm. of the wall per second when $\underline{c}$ is the concentration of bromine atoms in mole per cc., R the gas constant in ergs/mole/°C. and M the atomic weight of bromine. Then, ZS = total number of moles striking wall-surface $\underline{S}$ per sec. S = 138 cm^2 for the reaction vessel, $\underline{c}$ has been given above as 2×10^{-12} mole/cc.

$ZS = 8.21 \times 10^{3} \times 138 \times 2 \times 10^{-12} = \underline{2.3 \times 10^{-6}}$ moles of bromine atom <u>striking</u> the walls of the reaction vessel per second. This value is much larger than the numberof moles of bromine atoms dying on the walls per second; hence, there is a sufficient number of collisions at the wall to account for the chain-breaking rate.

It may be shown that the number of moles of bromine atom colliding with dibromotetrachloroethane is sufficient to account for the rate of decomposition. Let k° be the specific rate at which bimolecular collisions between unlike molecules of diameters d_1 and

d_2 cm. and of molecular weights M_1 and M_2 occur in the gas phase at the temperature T, when the concentration of each is one mole per cc. Then,

$$k^\circ = 10^{28.443} \times .25(d_1 + d_2)^2 (T(M_1 + M_2)/(M_1M_2)^{.5}) \text{ cc./mole/sec.}$$

The molecular diameters[9] have been taken as: Br, 3.9×10^{-8}; and $C_2Cl_4Br_2$, 6.6×10^{-8} cm.

$$k^\circ = 1.9 \times 10^{14} \text{ cc/mole/sec.}$$

In No. 54, Table V, $(Br) = 2 \times 10^{-12}$ mole/cc. and $(C_2Cl_4Br_2) = 1.16 \times 10^{-6}$ mole/cc.

$k^\circ(Br)(C_2Cl_4Br_2) = 6.4 \times 10^{-4}$ moles $C_2Cl_4Br_2$ and Br colliding per cc. per sec. This value is much larger than the 1.6×10^{-10} moles/cc./sec. of dibromotetrachloroethane decomposing and the postulated mechanism gives rise to no discrepancy from this stand point.

The mechanism chosen for this decomposition is similar to that for the iodine-sensitized decomposition of ethylene iodide in carbon tetrachloride solution[10] which was discussed in Chapter II. Furthermore, the decrease of the dependence of rate on light intensity as the light intensities are made higher is not unique, as the same feature was observed in the photochemical formation of hydrogen bromide;[11] also mentioned in Chapter II.

Summary

Quantum yields of the bromine-sensitized photo-decomposition of debromotetrachloroethane have been measured with 4358Å radiation between 100-150° C. and establish the chain nature of the reaction. Conditions have been chosen to render the reverse reaction more or less negligible. The rate of decomposition has been found proportional to the dibromotetrachloroethane pressure and proportional to the first power of the light intensity at relatively low intensities but to a power less than the first when the light intensities become higher. A satisfactory mechanism involving bromine atoms and a C_2Cl_4Br intermediate has been developed. This mechanism attributes an inhibition to the bromine.

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