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## THE PHOTOKHLORINATION OF TETRACHLOROETHYLENE IN CARBON TETRACHLORIDE SOLUTION

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When a carbon tetrachloride solution of chlorine and tetrachloroethylene which has been made up without the exclusion of dissolved oxygen is illuminated with radiation absorbable by only the chlorine, oxidation of the tetrachloroethylene to trichloroacetyl chloride and phosgene occurs<sup>1</sup> while the chlorine concentration remains sensibly constant. The rate of this oxidation is fairly low, the quantum yield at 20° and tetrachloroethylene concentrations of 0.02 to 1.5 molal being from 1 to 2.5 moles of tetrachloroethylene oxidized per einstein absorbed. We have found that if the experiment is carried out in such a way that the liquid has no access to additional oxygen, then after a period of illumination which varies with the amount of oxygen originally present, the chlorine concentration suddenly begins to decrease. The rate of the chlorination is then comparatively high; a solution originally 0.05 molal in chlorine and 0.002 molal in oxygen and containing an excess of tetrachloroethylene may, with a certain illumination, require an hour for the reaction of the oxygen before chlorination sets in, and then only a few additional minutes to bleach.<sup>2</sup>

The present paper deals with some aspects of the kinetics of the photochlorination.

**Materials.**—The carbon tetrachloride, tetrachloroethylene and chlorine solution in carbon tetrachloride were prepared as previously described.<sup>1</sup> In the course of the present work several different preparations of each have been employed with concordant results.

**Apparatus and Procedure.**—The reaction cell is shown in Fig. 1. It was a cylindrical Pyrex vessel 2.0 cm. in diameter and 3.05 cm. long with plane ends. The side tubes were of small bore; the cell was filled with liquid well into these tubes to eliminate access of oxygen to the main body of solution. The cell was then mounted between a 500-watt lamp and a thermopile and given a preliminary illumination to remove oxygen; the light was filtered through blue glass and copper sulfate solution. Suitable stirring to keep the solution homogeneous was regarded as important; without it the oxygen might be used up at the front end of the cell and chlorination proceed there before chlorination had started at the rear end. Stirring without further admission of oxygen was accomplished with the aid of a glass bead which normally remained out of the light beam in a depression from which it could be shaken when needed; tests with permanganate showed the stirring to be efficient.

<sup>1</sup> R. G. Dickinson and J. A. Leermakers, *THIS JOURNAL*, **54**, 3852 (1932).

<sup>2</sup> This phenomenon affords a possible explanation of Faraday's observation [*Ann. chim. phys.*, [2] **18**, 55 (1821)] that the chlorination did not occur in ordinary daylight but did occur in sunlight: the exposure to diffuse light was probably insufficient to remove oxygen; once the chlorination starts its rate is appreciable even in comparatively weak light.

The preliminary illumination was continued with occasional stirring until the thermopile deflections began suddenly to increase; then with very frequent stirring a short additional exposure was made which reduced the chlorine concentration by about one-third of its original value. The cell was then transferred to a two-thermopile photometer which furnished both a monochromatic source for the chlorination and a means of following the chlorine concentration.

This apparatus is shown in Fig. 2.<sup>3</sup> Light from a mercury arc H passed through a hole 1.0 cm. in diameter fitted with a shutter S, and then through a compartment containing the light filters immersed in running water; the radiation selected was  $\lambda 4358$ . The light was rendered approximately parallel by the lenses L and then fell at about  $45^\circ$  on two thin plane plates of glass M; a portion of the light was reflected by M to the thermopile  $T_2$  (two plates were used in order to secure sufficient reflection). The beam transmitted by M was considerably stronger than that which was reflected, and in it was interposed the cell B containing the reacting solution. A second thermopile  $T_1$  was carefully adjusted to be the mirror image of  $T_2$  across the plane of M and this second thermopile received light transmitted by the solution. The absorption cell B was immersed in a glass-walled tank of xylene (this liquid was chosen because it is reasonably non-volatile and has about the same refractive index as carbon tetrachloride); a similar tank  $X_2$  of just the same thickness was placed in the other beam. The thermopiles were connected to two high-sensitivity

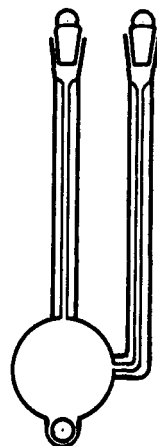


Fig. 1.—Cross section of cylindrical reaction cell.

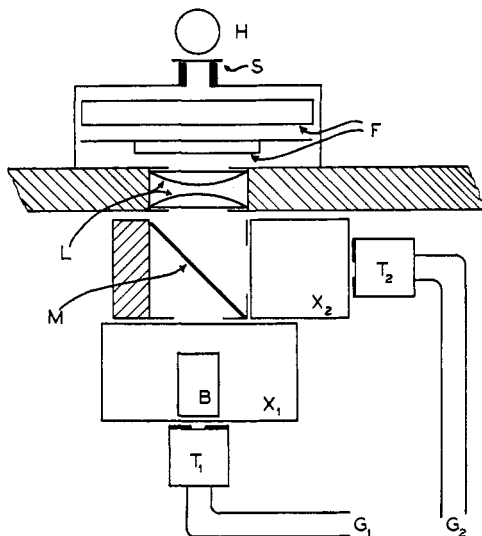


Fig. 2.—Photometer in which the chlorination was conducted and the chlorine concentration followed.

galvanometers  $G_1$  and  $G_2$  which could be read simultaneously.

The apparatus was calibrated for chlorine concentration measurements simply by measuring the ratio of the two galvanometer deflections with pure carbon tetrachloride in the cell and again with a chlorine solution of known concentration. The value of  $al$ , defined by the equation  $\ln_e \tau = -al(Cl_2)$  where  $\tau$  is the transmission, was found to be 14.7 liters per mole.

The apparatus was calibrated for quantum yield determination as follows. The thermopile  $T_1$  was calibrated against a Bureau of Standards carbon filament lamp.  $T_1$  was placed in the position normally occupied by the reaction vessel and the ratio of the readings of  $T_1$  and  $T_2$  determined. Making a small allowance for reflection and for the slight non-uniformity of the beam, it was found that a deflection of 1 cm. given

<sup>3</sup> The development of this apparatus was carried out mainly with the aid of Dr. E. P. Jeffreys.

by  $T_2$  corresponded to an intensity of  $6.4 \times 10^3$  ergs per  $\text{cm.}^2$  per sec. at the reacting solution.

At the end of the experiment, the solution was usually analyzed as previously described<sup>1</sup> to determine the amount of oxidation of tetrachloroethylene which had occurred in the preliminary illumination.

**Sample Run.**—The data of a typical run are given in some detail in Table I. In this table, the times of exposure in each successive interval of illumination are given under  $\Delta t$ . In the next three columns are given the transmission  $\tau$  of the solution, the deflection  $d_2$  given by the thermopile  $T_2$ , and the chlorine concentration; in each case the values are those prevailing at the beginning of the interval.

TABLE I  
DETAILS OF A SINGLE EXPERIMENT (No. 11)  
( $\text{Cl}_2$ ) before preliminary illumination, 0.1 mole per liter  
( $\text{C}_2\text{Cl}_4$ ) before preliminary illumination, 0.461 mole per liter

$\Delta t$ , sec.	$\tau$	$d_2$ , cm.	( $\text{Cl}_2$ ) mole/liter	( $\text{Cl}_2$ ) <sup>1/2</sup>	$\frac{\Delta t(1 - \sqrt{\tau})\sqrt{d_2}}{\times 7.2 \times 10^{-5}}$	$\Sigma$
	0.490	1.77	0.0485	0.220	0	0
225	.585	1.73	.0364	.191	$5.73 \times 10^{-3}$	$5.73 \times 10^{-3}$
292	.680	1.73	.0262	.162	5.70	11.43
360	.761	1.70	.0186	.136	5.13	16.56
352	.818	1.75	.0137	.117	3.69	20.25

Decrease in ( $\text{C}_2\text{Cl}_4$ ) due to oxidation, 0.0029 mole per liter.

Slope of ( $\text{Cl}_2$ )<sup>1/2</sup> vs.  $\Sigma = -kf = -5.10$ .

**Dark Reaction.**—When a solution in which photochlorination had been started was allowed to stand in the dark, a slow chlorination was found to occur. For example, in a solution having ( $\text{C}_2\text{Cl}_4$ ) = 0.83 *m*, the concentration of chlorine dropped in the dark from 0.0504 to 0.0487 in fifty-five minutes; from 0.0474 to 0.0451 in sixty minutes; and from 0.0380 to 0.0369 in thirty-three minutes. In the average photochemical run which consumed thirty minutes, the chlorine concentration fell from 0.05 to 0.01 molal. Thermal reaction was thus accountable for perhaps 3% of the total change. Since a correction for thermal rate would be small and, at present, uncertain of application, we have made none.

**Treatment of Measurements.**—A preliminary examination of measurements similar to those of Table I showed that the rate of disappearance of chlorine could be approximately represented by the equation

$$-\frac{d(\text{Cl}_2)}{dt} = \text{const.} \times (I_{\text{abs.}})^{1/2}(\text{Cl}_2) \quad (\text{I})$$

We shall assume that the local rate prevailing at any point in the solution can be represented by

$$-\frac{d(\text{Cl}_2)}{dt} = k(I_{\text{abs.}})^{1/2}(\text{Cl}_2) f \quad (\text{II})$$

where ( $I_{\text{abs.}}$ ) is the rate of absorption of radiation in einsteins per liter per second at that point and  $f$  is a function of the concentrations. We may then derive an expression for the (volume) average rate for the case where the absorption is too large to permit regarding ( $I_{\text{abs.}}$ ) as the same throughout the solution. For this purpose it may reasonably be supposed that: (1) the concentration of chlorine is kept uniform; (2) Beer's law applies;

(3) the rate at a given point is independent of the intensity prevailing at neighboring points (*i. e.*, the rate of diffusion of intermediate reactants is small); (4) the solution occupies a cylindrical space illuminated by light parallel to its axis and uniformly distributed over one end of the cylinder. Making use of Beer's law, we obtain from (II) the local rate in a layer at distance  $x$  from the front of the cylinder

$$-\left(\frac{d(\text{Cl}_2)}{dt}\right)_x = kI_0^{1/2} e^{-\alpha(\text{Cl}_2)x/2} (1000\alpha)^{1/2} (\text{Cl}_2)^{3/2} f \quad (\text{III})$$

where  $I_0$  is the intensity of the incident radiation in einsteins per sq. cm. per sec. The volume average of this rate is obtained by integration over the length,  $l$ , of the cell

$$\begin{aligned} -\left(\frac{d(\text{Cl}_2)}{dt}\right)_{\text{av.}} &= \frac{1}{l} \int_0^l kI_0^{1/2} e^{-\alpha(\text{Cl}_2)x/2} 10^{3/2} \alpha^{1/2} (\text{Cl}_2)^{3/2} f dx \\ &= 2 \times 10^{3/2} l^{-1} \alpha^{-1/2} kI_0^{1/2} (\text{Cl}_2)^{1/2} f [1 - \sqrt{\tau}] \quad (\text{IV}) \end{aligned}$$

where  $\sqrt{\tau}$  is written for  $e^{-\alpha(\text{Cl}_2)l/2}$ . Since  $(\text{Cl}_2)$  is uniform throughout the solution, we may drop the subscript av. and write

$$-\frac{d(\text{Cl}_2)^{1/2}}{dt} = -1/2 (\text{Cl}_2)^{-1/2} \frac{d(\text{Cl}_2)}{dt} = kf 10^{3/2} \alpha^{-1/2} l^{-1} I_0^{1/2} [1 - \sqrt{\tau}] \quad (\text{V})$$

From this it appears that if  $(\text{Cl}_2)^{1/2}$  be plotted against  $\int_0^t 10^{3/2} \alpha^{-1/2} l^{-1} I_0^{1/2} [1 - \sqrt{\tau}] dt$ , the slope of the curve at any point will give  $-kf$ ; and if  $f$  be only slightly dependent on the concentrations, the plot will be a nearly straight line.

The integral was approximated by the summation  $\sum 10^{3/2} \alpha^{-1/2} l^{-1} I_0^{1/2} [1 - \sqrt{\tau}] \Delta t$  taken over all intervals from the beginning of the measurements;  $I_0$  and  $\tau$  were given mean values prevailing in each short interval,  $\Delta t$ , of illumination. For numerical purposes we have taken  $l = 3.05$  cm.,  $\alpha = 4.81$  liters moles<sup>-1</sup>cm.<sup>-1</sup> and  $I_0 = 6.4 \times 10^2 \times 3.66 \times 10^{-13} d_2$  einsteins cm.<sup>-2</sup>sec.<sup>-1</sup>, and have accordingly plotted  $(\text{Cl}_2)^{1/2}$  against  $\sum 7.2 \times 10^{-5} \times d_2^{1/2} (1 - \sqrt{\tau}) \Delta t$ . A sample of this treatment of the data is given in Table I; plots obtained in this way are shown in Figs. 3 and 4; values of  $kf$  obtained from these slopes are given under  $kf_{\text{obs.}}$  in Table II.

**Discussion of Results.**—The plots in Fig. 3, which involve the higher values of  $(\text{C}_2\text{Cl}_4)$ , may be seen to be practically straight lines of substantially equal slope. This method of plotting has been developed on the assumption that the rate is everywhere proportional to the one-half power of the intensity. Justification of this is found in Expts. 7, 8, 9 and 10. During the intervals shown dotted on the plots a calibrated absorber was interposed before the reaction vessel; the absorber transmitted 45% in Expt. 7 and 10.5% in Expts. 8, 9 and 10. Were the rates proportional, for example, to the first power of the intensity, these plots would appear as broken lines with slopes in the dotted portions less than one-third (in 8,

TABLE II  
 SUMMARY OF SPECIFIC REACTION RATE DETERMINATIONS

Expt.	Composition of soln. before prelim. illum.		Concentration of Cl <sub>2</sub> during rate meas.		(C <sub>2</sub> Cl <sub>4</sub> ) oxidized mole/liter	$\left(\frac{(\text{Cl}_2)}{(\text{C}_2\text{Cl}_4)}\right)_{\text{Av.}}$	<i>k</i> <sub>obs.</sub>	<i>k</i> <sub>foaled.</sub>
	(C <sub>2</sub> Cl <sub>4</sub> ) <sub>0</sub> mole/liter	(Cl <sub>2</sub> ) <sub>0</sub> mole/liter	(Cl <sub>2</sub> ) <sub>initial</sub> mole/liter	(Cl <sub>2</sub> ) <sub>final</sub> mole/liter				
3	0.882	0.080	0.0406	0.0150	0.0024	0.033	4.77	5.09
4	.882	.080	.0302	.0110	.0027	.025	4.81	5.09
6	.882	.108	.0782	.0138	.0031	.054	5.07	5.06
7	.882	.108	.0739	.0143	.0029	.052	4.97	5.06
8	.882	.108	.0605	.0128	.0029	.045	5.10	5.08
9	.882	.108	.0582	.0137	.0031	.044	5.40	5.08
10	.882	.108	.0561	.0141	...	.044	5.47	5.08
18	.882	.108	.0466	.0160	.0005	.039	5.32	5.09
20	.882	.101	.0358	.0123	.0029	.030	4.80	5.09
21	.882	.108	.0268	.0122	.0720	.027	5.35	5.09
22	.882	.108	.0450	.0149	.0118	.039	5.23	5.09
26	.676	.100	.0525	.0142	...	.055	5.06	5.06
11	.461	.114	.0485	.0137	.0029	.081	5.10	5.03
17	.251	.110	.0629	.0150	...	.21	4.53	4.90
25	.180	.100	.0439	.0143	...	.26	4.35	4.85
12	.0989	.110	.0679	.0540	.0030	1.37	4.06	4.10
13	.0989	.109	.0540	.0433	...	1.66	3.83	3.96
13*						4.51	3.0	3.04
24	.0799	.097	.0524	.0400	.0032	1.94	3.60	3.84
24*						6.95	2.6	2.63

Temperature of all experiments, 22 = 1°.

Expt. 18; solution shaken with N<sub>2</sub> and cell first filled with N<sub>2</sub>.

Expt. 22; solution shaken with O<sub>2</sub> and cell first filled with O<sub>2</sub>.

Expt. 21; solution shaken with air to replenish O<sub>2</sub> several times during preliminary illumination.

Expt. 20; solution made 0.716 molal in C<sub>2</sub>Cl<sub>4</sub> at start.

Expt. 7; intensity was dropped 55% in some of the intervals of illumination.

Expts. 8, 9, 10; intensity was dropped 90% in some of the intervals of illumination.

Expts. 13\*, 24\*; *k*'s determined from later part of run.

9 and 10) of the slopes in the adjacent solid portions. There are, however, no indications of breaks in these plots.

Since the reacting solutions contained small amounts of the products of oxidation (corresponding to (C<sub>2</sub>Cl<sub>4</sub>) oxidized = 0.003 molal) experiments were made to see whether their quantity affected the rate. In Expt. 18 the solution as made up was shaken with nitrogen to remove most of the oxygen at the outset, and the reaction cell was filled with nitrogen before introducing the solution; the (C<sub>2</sub>Cl<sub>4</sub>) oxidized was only 0.0005 *m* but the rate of chlorination was not appreciably changed. In Expt. 22 a similar treatment was given with oxygen and the (C<sub>2</sub>Cl<sub>4</sub>) oxidized became 0.0118 *m*. In Expt. 21 the solution was frequently shaken with air during the preliminary illumination, so that the (C<sub>2</sub>Cl<sub>4</sub>) oxidized was 0.0720 *m*; the use of these larger amounts of oxygen did not, however, appear to affect the subsequent chlorination rates.

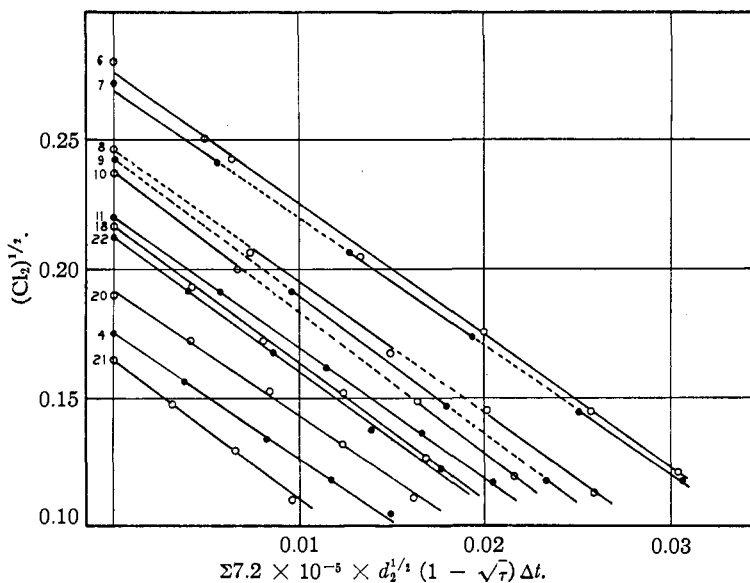


Fig. 3.—Results of runs at the higher tetrachloroethylene concentrations.

In Expt. 20 enough resublimed hexachloroethane was dissolved to make the solution 0.716 molal in hexachloroethane at the start; this was several

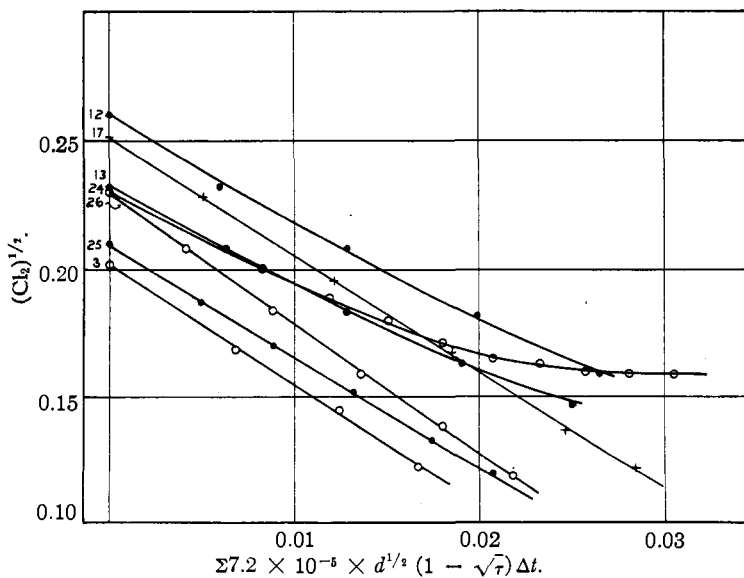


Fig. 4.—Results of runs at various tetrachloroethylene concentrations; the original tetrachloroethylene concentrations decrease in the order 3, 26, 17, 25, 12, 13, 24.

times the concentration ever built up in the ordinary runs, but had little if any effect on the rate.

Figure 4 shows plots for experiments with lower tetrachloroethylene concentrations (Nos. 3 and 26 with high  $(C_2Cl_4)$  are included here for comparison). At the lower values of  $(C_2Cl_4)$  the slopes, *i. e.*, the values of  $kf$ , are somewhat smaller; and in those experiments (for example, 24 and 13) where  $(C_2Cl_4)$  undergoes a considerable percentage change during the run the plotted lines show curvature. Thus  $f$  is to some extent dependent on concentrations; the nature of the dependence is discussed below.

**Quantum Yield.**—From Equation (II) it immediately follows that the local quantum yield expressed in moles of chlorine reacting per einstein absorbed is, for a given intensity and composition of solution

$$\text{Quantum yield} = - \frac{1}{(I_{\text{abs.}})} \frac{d(Cl_2)}{dt} = k(I_{\text{abs.}})^{-1/2}(Cl_2)f \quad (\text{VI})$$

At the beginning of sample Expt. 11 (Table I), the quantum yield was then 790, and at the end 430. The extreme variations in quantum yield occurring in the measurements made are from 2500 in the early part of Expt. 7 to about 300 near the end of Expt. 24.

**Temperature Coefficient.**—With a separate apparatus, we have measured rates at 0, 10, 20 and 30°. These measurements have not been sufficiently satisfactory to give in detail, but they make it possible to say that the temperature coefficient is not large; our present best value of the 10° multiplication of the specific rate constant is  $1.16 \pm 0.08$ .

**Products of the Reaction.**—In several experiments carried out with low tetrachloroethylene concentration and a slight excess of chlorine, the illumination was prolonged until the chlorination ceased. It was found that about 9% less chlorine disappeared than would correspond to complete reaction according to the equation:  $Cl_2 + C_2Cl_4 = C_2Cl_6$ . (Correction for oxidation of tetrachloroethylene in the preliminary illumination was applied but was small, usually about 3%, except in one case where 12% of the tetrachloroethylene was purposely oxidized without changing the corrected result.)

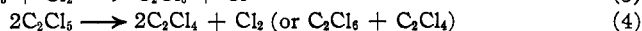
A series of experiments was made to determine the constancy of the ratio of the number of mols of chlorine used up to the number of mols of tetrachloroethylene taken (corrected for oxidation). The initial ratio of  $(Cl_2)$  to  $(C_2Cl_4)$  was varied two-fold; the light intensity was varied ten-fold; three independently purified samples of tetrachloroethylene were tried; the change in chlorine was determined both by the photometer and by direct titration. In no case was a significant variation of the ratio  $\Delta(C_2Cl_4)/\Delta(Cl_2)$  from 1.09 found.

Failure to use up enough chlorine could hardly be the result of a back reaction since large amounts of  $C_2Cl_6$  did not reduce the rate of chlorination. It may indicate a side reaction resulting in, for example,  $C_4Cl_8$  or

$C_4Cl_6$  ( $C_4Cl_{10}$  is not known). The residual solutions from these experiments were collected, washed with water, and the carbon tetrachloride layer allowed to evaporate. The white crystalline product gave a melting point  $4^\circ$  lower than a sample of resublimed hexachloroethane in the same bath (m. p.  $C_2Cl_6$   $185^\circ$ ). When mixed with hexachloroethane, the melting point was  $2^\circ$  below that of pure hexachloroethane.

If the failure to use up enough chlorine is due to the formation of some  $C_4Cl_8$ , the products must contain 4.2 mole per cent. of  $C_4Cl_8$ ; if due to  $C_4Cl_6$ , they must contain 2.9 mole per cent. Whether these results are to be attributed to the formation of a small amount of product containing a smaller proportion of chlorine than does tetrachloroethylene, or to some small unsuspected source of experimental error, there is no doubt that by far the main portion of the reaction results in the formation of hexachloroethane.

**Possible Mechanisms of the Chlorination.**—In analogy with what is known to occur when blue light is absorbed by gaseous chlorine, it may be assumed that the primary absorption process leads to the production of chlorine atoms. Starting with this, the following simple chain reaction scheme may be written

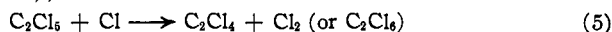


In 2' the compound  $C_2Cl_5$  is formed which may sometimes dissociate (2'') before forming the product,  $C_2Cl_6$ , according to 3; reactions 2' and 3 constitute the chain which is finally broken by 4. The products of 4 may be those suggested or any others which do not perpetuate the chain. This reaction scheme is essentially similar to that proposed by Berthoud and Beranek<sup>4</sup> for the brominations of cinnamic acid and stilbene, and leads, when the quantum yields are high, to the rate expression

$$-\frac{d(Cl_2)}{dt} = \frac{k_3}{\sqrt{k_4}} (I_{abs.})^{1/2} (Cl_2) \quad (VII)$$

which is of the form of (II) with  $f$  constant. Since  $f$  is found to vary only moderately, the mechanism accounts for the main features of our kinetic results.

Two additional chain-breaking reactions suggest themselves whose occurrence in addition to the above reactions leads to a decrease of the rate with decreasing ( $C_2Cl_4$ ); these reactions are



Applying the usual methods of treatment, and noticing that when the quantum yields are high

$$k_2'(Cl)(C_2Cl_4) = k_2''(C_2Cl_5) + k_3(Cl_2)(C_2Cl_5) \text{ nearly}$$

<sup>4</sup> A. Berthoud and J. Beranek, *J. chim. phys.*, **24**, 213 (1927).



the following rate expression may be obtained

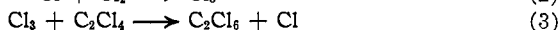
$$-\frac{d(\text{Cl}_2)}{dt} = \frac{k_3}{\sqrt{k_4}} (I_{\text{abs.}})^{1/2} (\text{Cl}_2) \left[ 1 + \frac{k_5[k_3(\text{Cl}_2) + k_2'']}{k_4 k_2' (\text{C}_2\text{Cl}_4)} + \frac{k_6[k_3(\text{Cl}_2) + k_2'']^2}{k_4 k_2'^2 (\text{C}_2\text{Cl}_4)^2} \right]^{-1/2} \quad (\text{VIII})$$

From this, the effect of suppressing one or more of the reactions 2'', 5 and 6 may be seen by setting the corresponding  $k$  equal to zero. It is probably not possible, with our data, to attribute the decrease in  $f$  with decreasing  $(\text{C}_2\text{Cl}_4)$  to any one of these causes to the exclusion of the others; satisfactory agreement with the data may be had by setting  $k_2''$  and  $k_6$  equal to zero,  $k_3/\sqrt{k_4}$  equal to 5.1, and  $k_5 k_3/k_4 k_2' = 0.4$  so that (VIII) becomes

$$-\frac{d(\text{Cl}_2)}{dt} = 5.1 (I_{\text{abs.}})^{1/2} (\text{Cl}_2) \left[ 1 + 0.4 \frac{(\text{Cl}_2)}{(\text{C}_2\text{Cl}_4)} \right]^{-1/2} \quad (\text{IX})$$

Values of  $kf_{\text{calcd.}}$  obtained by using the above numerical values for the  $k$ 's and the mean values of  $(\text{Cl}_2)/(\text{C}_2\text{Cl}_4)$  prevailing in the experiment, are given in the last column of Table II. Equation (IX), then, corresponds to a mechanism made up of reactions 1, 2', 3, 4 and 5.

It should be pointed out that another different but equally simple mechanism leads to types of rate expression similar to those obtained from the scheme just discussed. This mechanism is



Here, as before, 2 and 3 are chain carrying reactions while 4, 5 and 6 are chain breaking reactions. The scheme differs from the first in having the intermediate  $\text{Cl}_3$  instead of  $\text{C}_2\text{Cl}_5$  and in having (to secure agreement with the experiments) the uniting of 2 chlorine atoms instead of the reaction of  $2\text{C}_2\text{Cl}_5$  as the principal chain breaking step. Rollefson and Eyring<sup>5</sup> have given arguments based on quantum mechanics to show that halogen molecules of the type  $\text{X}_3$  are stable at room temperature with respect to decomposition into  $\text{X}_2$  and  $\text{X}$ .

Reactions 1, 2, 3 and 4 lead to the rate expression (VII) but with  $k_2$  replacing  $k_3$ . Reactions 1, 2, 3, 4 and 5 give, when the quantum yield is high

$$-\frac{d(\text{Cl}_2)}{dt} = \frac{k_2}{\sqrt{k_4}} (I_{\text{abs.}})^{1/2} (\text{Cl}_2) \left[ 1 + \frac{k_2 k_5}{k_3 k_4} \frac{(\text{Cl}_2)}{(\text{C}_2\text{Cl}_4)} \right]^{-1/2} \quad (\text{X})$$

which again is of the form of Equation (IX), and in agreement with the experiments. The further introduction of reaction 6 and of the reversal of 2, gives a complicated expression which may be put in a form resembling (VIII); while these reactions are not necessary in order to secure agreement, our data do not wholly exclude them.

\* G. K. Rollefson and H. Eyring, THIS JOURNAL, 54, 176 (1932).

### Summary

The photochemical chlorination of tetrachloroethylene in carbon tetrachloride solution has been studied in monochromatic light of wave length 4358 Å., and the specific rates have been expressed in absolute units. The rate has been found proportional to the square root of ( $I_{\text{abs.}}$ ), at least approximately proportional to the first power of ( $\text{Cl}_2$ ), and only moderately dependent on ( $\text{C}_2\text{Cl}_4$ ); Equation (IX) summarizes these results. Under the conditions of the experiments, the quantum yield has varied from 300 to 2500. Two alternative mechanisms, one involving  $\text{C}_2\text{Cl}_5$  and one involving  $\text{Cl}_3$ , have been discussed, and both found to account for the observations.

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## THE DENSITY AND MOLECULAR STATE OF RHENIUM TETRACHLORIDE AND RHENIUM HEXACHLORIDE IN THE GASEOUS STATE

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**Introduction.**—Previous experiments on the nature of the rhenium chlorides<sup>1</sup> have shown that more than one compound is formed when chlorine is passed over the heated metal. Some of the substances so formed are reported to be easily volatile. Hönigschmid,<sup>2</sup> in an attempt to determine the atomic weight of rhenium by the analysis of a chloride, found the best preparations to be mixtures since the proportions of rhenium and chlorine were not constant and led in the more reproducible cases to the formula  $\text{ReCl}_{4.3}$ . He also observed that this substance decomposed on heating in an atmosphere of nitrogen with the formation of a less volatile product, whereas similar treatment in the presence of chlorine resulted in complete volatilization without apparent change.

In the present article are presented the results of vapor density measurements made on various mixtures of rhenium and chlorine in order to determine the molecular state and composition of some of the rhenium chlorides.

**Experimental Method and Preparation of Materials.**—The vapor density measurements were carried out in the same manner as in a previous investigation,<sup>3</sup> the method consisting of heating weighed amounts of rhenium and chlorine in previously evacuated tubes until the contents were completely reacted and vaporized and then allowing the excess to escape

<sup>1</sup> W. Noddack, *Z. Elektrochem.*, **34**, 627 (1928).

<sup>2</sup> Hönigschmid and Sachtleben, *Z. anorg. Chem.*, **191**, 147 (1931).

<sup>3</sup> Yost and Hatcher, *THIS JOURNAL*, **53**, 2549 (1931).