energy of ionization and the heats of ionization. The latter are calculated on the very doubtful assumption that this magnitude remains constant between 0 and 25°.

TABLE I

Molality	—S— acid K (0°)	—S— acid K (25°)	—SO— acid K (0°)	—SO— acid K (25°)	—SO_2 acid— K (0°)	—SO_2 acid— K (25°)
0.00201	0.000297	0.000269	0.00261	0.00220	0.00444	0.00357
.00401	.000306	.000279	.00263	.00221	.00449	.00365
.0100	.000301	.000277	.00254	.00219	.00451	.00365
.0201	.000302	.000278	.00255	.00219	.00440	.00364

TABLE II

Acid	K (0°)	K (25°)	ΔF° (0°), cal.	ΔF (25°), cal.	ΔH, cal.
—S—	0.000302	0.000276	4400	4860	− 600
—SO—	.00258	.00220	3240	3630	−1000
—SO_2—	.00446	.00363	2940	3330	−1300

Table III gives the values for Λ_e for the acids at 25° for certain concentrations. This table is included to show the comparative values for the ion mobilities in the acids. It is to be noted that the —SO— ion has a decidedly lower mobility than either of the other ions. This may perhaps be due to hydration of the —SO— group.

TABLE III

Molality	—S—	—SO—	—SO_2—
0.001	375.8	373.2	375.1
.0025	372.3	370.2	372.2
.004	371.0	368.4	370.7

For the —S— and —SO— acids at 25° Behaghel obtained ionization constants of 0.0002971 and 0.002148. These are averages for three concentrations. His individual values differ more widely than ours.

It is seen that the addition of the oxygen atom to the —S— acid decreases the free energy of ionization far more than the addition of the oxygen atom to the —SO— acid. The heat of ionization is increased with the addition of oxygen.

Summary

1. The ionization constants in aqueous solutions at 0 and 25° of phenylthioglycolic acid, phenylsulfoacetic acid and phenylsulfonylacetic acid have been determined conductimetrically at 0 and 25°.

2. From the values obtained have been calculated the free energies and heats of ionization.

CHAPEL HILL, N. C. RECEIVED MARCH 24, 1934

[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 404]

The Photochlorination and the Chlorine-Sensitized Photo-oxidation of Gaseous Tetrachloroethylene

BY ROSCOE G. DICKINSON AND JAMES L. CARRICO

In the absence of oxygen, the illumination of a carbon tetrachloride solution of chlorine and tetrachloroethylene with blue light has been found to bring about chlorination which proceeds[1] as a chain reaction with a large quantum yield and at a rate proportional to the square root of the intensity of illumination. In the presence of oxygen, the chlorination is strongly inhibited and instead there occurs a chlorine-sensitized oxidation to trichloroacetyl chloride and phosgene; this reaction proceeds in solution with a comparatively small quantum yield and at a rate proportional to the first power of the light intensity.[2] It was found possible to account for the kinetics of the chlorination by either of two simple and plausible reaction schemes, one involving C_2Cl_5 and the other Cl_3.

In extension of this work we have found these reactions to occur in the gas phase and have made some preliminary observations on their kinetics. In order not to be too seriously involved with purely thermal reaction, the temperatures have been kept at 40° or below. The oxidation products are about as volatile as the reactants; but the solid chlorination product, hexachloroethane, has at 40° a vapor pressure of only 1 mm. Its precipitation on the vessel walls during an illumination might be expected to render satisfactory radiation measurements impossible. However, under the conditions of our experiments, the crystals formed were comparatively few and large; moreover, a very slight temperature difference prevented this formation on the part of the vessel through which illumination occurred. It was thus possible to carry on chlorination experiments without complication from this source.

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

(2) R. G. Dickinson and J. A. Leermakers, *ibid.*, **54**, 3852 (1932).

Materials

The tetrachloroethylene was an Eastman Kodak Company C. P. product treated as follows.[3] Chlorine was added and the liquid illuminated; it was then washed with sodium hydroxide, washed with water, dried with calcium chloride, and distilled. The fraction retained came over in an interval of 0.2° and was a large part of the sample.

The chlorine was taken from a commercial tank and dried with calcium chloride. It was liquefied into and sealed in small glass containers in weighed amounts.

The oxygen was taken from a commercial tank (source: liquid air) and dried with phosphorus pentoxide.

Apparatus and Procedure

A technique was chosen which would permit pressure changes during the reaction to be followed without exposure of the reacting gases to any material but glass. Details are shown in Fig. 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 conjunction with a mercury manometer which was read to 0.05 mm. That part of the apparatus shown within the dotted line of Fig. 1 was contained within a light-tight air thermostat which was maintained constant to 0.2° with the aid of a heater and fan.

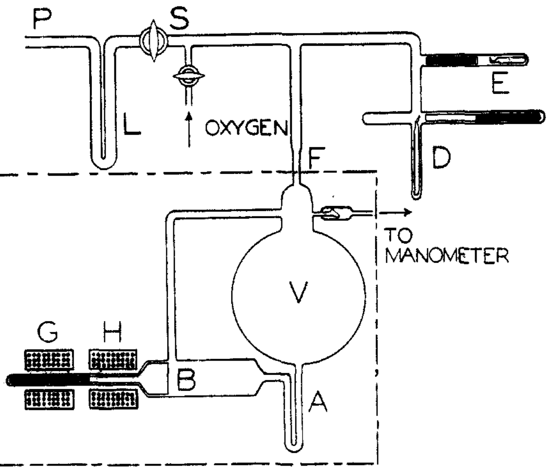

Fig. 1.—The reaction vessel and its connections.

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 4358 Å. 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.

Alternatively, by sliding the lamp system on tracks, the same beam could be allowed to fall on a Moll small surface thermopile connected with a high sensitivity galvanometer. The primary object of this was to determine the relative intensities of illumination from one experiment to another. It also served to give an approximate measure (within 10 to 20%) of the absolute amount of radiation shined into the reaction mixture. This involved: (a) calibration of the thermopile–galvanometer combination against a carbon filament lamp calibrated by the Bureau of Standards; (b) measurement of the ratio of the galvanometer deflections with the thermopile in its normal position and in the plane of the 3.0 cm. diaphragm; (c) appropriate correction for reflection losses. It was accordingly found that a galvanometer deflection of 1 cm. corresponded to an intensity of 1.00×10^2 ergs cm.^{-2} sec.^{-1} at the surface of the gaseous reactants or to a flux of 7.06×10^2 ergs sec.^{-1}. The fraction of the radiation absorbed was kept low (0.123 was the highest value in any chlorination experiment) and was not measured but was calculated from the known molal absorption coefficient of Cl_2,[5] which has been found to be little dependent on the temperature.[6] The expression used was $I/I_0 = 10^{-\alpha c d}$ with $\alpha = 1.64$, $d = 12$ cm. and c the concentration of chlorine in moles per liter; this was obtained from pressure measurements and the weight of chlorine taken.

Sample Runs

The results of a pure chlorination experiment at 40° are shown in Fig. 2, in which the total pressure in mm. is plotted against the time of illumination in minutes. In this run the initial chlorine pressure was 49.2 mm. and that of tetrachloroethylene 8.33 mm. The increase in slope at 56.6 mm. is presumably due to the beginning of precipitation of hexachloroethane whose vapor pressure was 1 mm. The decrease in slope at 50.5 mm. resulted from a reduction in the intensity of illumination to 35% of its previous value by the interposition of a wire screen. Attention should be drawn to the fact that the rate of chlorination continued with little change at small tetrachloroethylene pressures until the chlorination was complete at 41.9 mm.

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[3] Ref. 2, p. 3853.

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

[5] H. v. Halban and K. Siedentopf, *Z. physik. Chem.*, **103**, 81 (1922).

[6] Bodenstein and Schenk, *ibid.*, **B20**, 420 (1933).

The results of a run in which an excess of oxygen was present are shown in Fig. 3. The initial partial pressures were: chlorine, 65.5 mm.; oxygen, 13.8 mm.; tetrachloroethylene, 14.8 mm. The discontinuity at 90.6 mm. resulted from the interposition of the same screen as in Fig. 2; the change in slope is obviously much greater than in the chlorination experiment. It may be observed that in Fig. 3 the rate of reaction is not much dependent on the partial pressure of tetrachloroethylene.

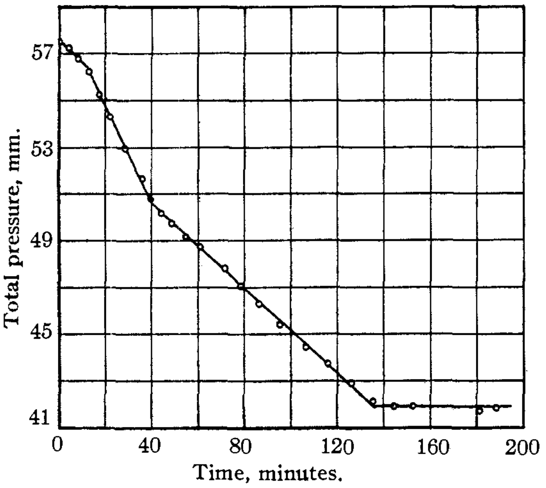

Fig. 2.—Sample run with only chlorine and tetrachloroethylene present at the start. The initial pressures were: Cl_2, 49.2 mm.; C_2Cl_4, 8.33 mm. After forty minutes the intensity was reduced to 35% of its previous value.

In Fig. 4 are shown the results of an experiment with insufficient oxygen to oxidize all of the tetrachloroethylene. The initial pressures were: chlorine, 53.75 mm.; oxygen, 2.45 mm.; tetrachloroethylene, 8.12 mm. The curve is characterized by three features: (1) an initial period of oxidation in which the rate remains fairly constant while the oxygen pressure falls off greatly; (2) a final period of chlorination similar to that of Fig. 2; (3) an intermediate period in which the rate of pressure decrease is for a time very much smaller than either before or afterward (too small and too prolonged to be accounted for by initial non-precipitation of hexachloroethane).

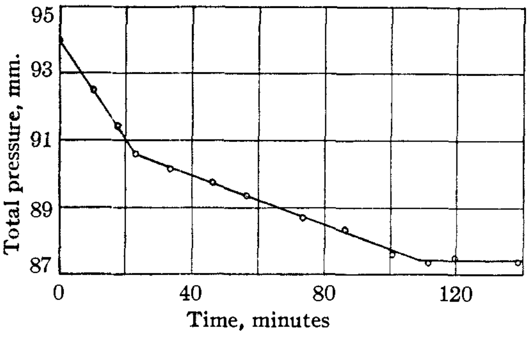

Fig. 3.—Sample run with chlorine, tetrachloroethylene and an excess of oxygen present at the start. The initial pressures were: Cl_2, 65.5 mm.; O_2, 13.8 mm.; C_2Cl_4, 14.8 mm. After twenty-two minutes the intensity was reduced as in Fig. 2.

The Reaction Products

In the absence of oxygen, chlorination of the tetrachloroethylene occurred; colorless crystals with the odor of hexachloroethane formed on the vessel walls. The magnitude of the pressure decrease agreed with the supposition that hexachloroethane was the chlorination product. For example, in the experiment of Fig. 2 at 40° with 4.74 × 10^{-4} mole of tetrachloroethylene and an excess of chlorine in a volume of 1110 cc., the observed total pressure decrease was 15.7 mm., while the calculated decrease (allowing 1.00 mm. for the vapor pressure of hexachloroethane) is 15.65 mm. In an experiment at 50°, the chlorination of 1.038 × 10^{-3} mole of tetrachloroethylene in a vessel of volume 1040 cc. gave a pressure drop of 38.3 mm. The vapor pressure of hexachloroethane at 50° is 2.12 mm. and the calculated pressure decrease assuming hexachloroethane to be the chlorination product is 38.1 mm.

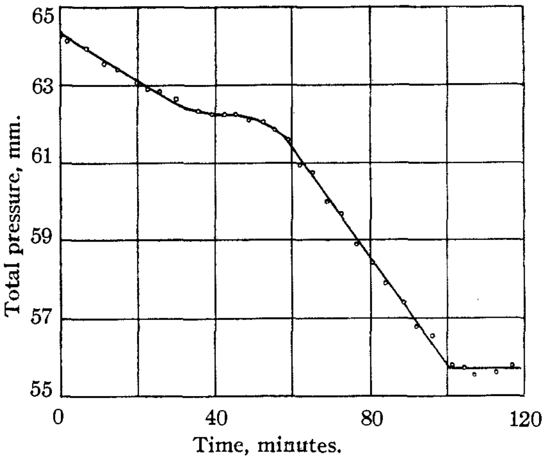

Fig. 4.—Sample run with chlorine, tetrachloroethylene and insufficient oxygen to oxidize all of the tetrachloroethylene. The initial pressures were: Cl_2, 53.75 mm.; O_2, 2.45 mm.; C_2Cl_4, 8.12 mm.

In the presence of oxygen, chlorination was inhibited almost completely, if not entirely so. This was best shown by a special series of experiments in which samples containing known amounts of chlorine and tetrachloroethylene and an excess of oxygen were given illuminations known to be adequate for the complete reaction of the tetrachloroethylene, and the free chlorine determined at the end with potassium iodide and thiosulfate. As shown by Table I, the final amount of chlorine found was nearly equal to the initial amount of chlorine taken, showing that little, if any, chlorination occurred during the oxidation.

Table I

Free Chlorine Present Before and After Oxidation

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

That phosgene was one of the products of the oxidation was evident from their odor. On the assumption that the oxidation products were trichloroacetyl chloride and phosgene, the fraction, x, of the oxidized tetrachloroethylene going to trichloroacetyl chloride was determined by two methods. The reaction products, in one series of experiments, were analyzed for acid produced by hydrolysis. This was accomplished by opening the flask under potassium iodide solution and, after shaking, titrating with thiosulfate. The solution was then boiled (to remove carbon dioxide which came from phosgene) and potassium iodate added after cooling; the liberated iodine was again titrated with thiosulfate. The number of equivalents of acid found in the last titration per mole of tetrachloroethylene oxidized is then equal to $4 - 2x$. The results of these measurements are shown in Table II.

Table II

Fraction of Oxidized Tetrachloroethylene Yielding Trichloroacetyl Chloride (Analytical Measurements)

Initial C_2Cl_4, mole × 10^3	Initial O_2, mole × 10^3	Initial Cl_2, mole × 10^3	Acid equivs. × 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

An independent determination of the fraction x was made by measuring the reduction in total pressure accompanying the complete oxidation of a known amount of tetrachloroethylene. For since oxidation to phosgene does not alter the total pressure, while oxidation to trichloroacetyl chloride involves a reduction $-\Delta p_t$ in total pressure equal to one-half the partial pressure of tetrachloroethylene so oxidized, it follows that $-\Delta p_t = x/2p_{C_2Cl_4}$ where $p_{C_2Cl_4}$ is the initial partial pressure of tetrachloroethylene. Values of the fraction x determined in this manner are given in the seventh column of Table III. They agree reasonably well with those of Table II in indicating about 90% conversion to trichloroacetyl chloride and 10% to phosgene. (In carbon tetrachloride solution about the same result, 87% to trichloroacetyl chloride, was obtained.[7])

Table III

Fraction of Oxidized Tetrachloroethylene Yielding Trichloroacetyl Chloride (Pressure Measurements)

T, °C.	$p_{C_2Cl_4}$, initial	p_{Cl_2}, initial	p_{O_2}, initial	p_t, initial	p_t, final	x	$-\Delta p_{O_2}$ obs.	$-\Delta p_{O_2}$ calcd.
24	7.95	60.7	18.75	87.4	84.15	0.82	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	..	...

As a final check on this percentage conversion to trichloroacetyl chloride and on the absence of chlorination during oxidation, the decrease in oxygen pressure has been calculated on the assumption of 90% conversion of tetrachloroethylene to trichloroacetyl chloride. A comparison of these calculated values with the observed decreases in oxygen pressure is given in the last two columns of Table III.

Dark Reaction

Gaseous mixtures of oxygen, chlorine and tetrachloroethylene did not show a perceptible rate of pressure change in the dark even at 40°, nor did mixtures containing no oxygen do so at 26°. At 40° mixtures containing no oxygen sometimes showed a dark rate amounting to a few per cent. of the photochemical rate; however, the dark rate was usually much smaller than this and was not reproducible. No correction for dark reaction has been attempted.

The Kinetics of the Chlorination

In Table IV are collected measurements of the rates of chlorination at various partial pressures and various light intensities. In compiling these results, plots were made of total pressure against time of illumination for periods during which the illumination was constant, and values of dp/dt at particular total pressures were obtained from the plots. The various partial pressures prevailing at any time were calculated from the total pressure and the initial composition of the gas on the assumption that during the initial oxidation process 90% of the oxidation was to

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(7) Ref. 2, p. 3856.

TABLE IV

RATE AND QUANTUM YIELDS OF CHLORINATION WITH λ 4358 Å.

	Initial pressure, mm.			Momentary pressure, mm.			I_0 ergs × cm.$^{-2}$ × sec.$^{-1}$	$I_{abs.}$ einsteins sec.$^{-1}$	$-dp/dt$ mm. sec.$^{-1}$	$-dN_{Cl_2}/dt$ mole sec.$^{-1}$	a	Quantum yield
Expt.	$p_{Cl_{2_0}}$	$p_{O_{2_0}}$	$p_{C_2Cl_{4_0}}$	p_{Cl_2}	$p_{C_2Cl_4}$	Total	× 10^{-2}	× 10^{10}	× 10^3	× 10^8	× 10^{-3}	
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	324
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°.

trichloroacetyl chloride and 10% to phosgene, and that the partial pressure of oxygen was zero during chlorination. The equations used were

$$p_{Cl_2} = p_{Cl_{2_0}} - {}^1/_2(p_{t_0} - p_t - 0.82p_{O_{2_0}} + p_{C_2Cl_6})$$

$$p_{C_2Cl_4} = p_{C_2Cl_{4_0}} - 1.82\,p_{O_{2_0}} - {}^1/_2(p_{t_0} - p_t - 0.82p_{O_{2_0}} + p_{C_2Cl_6})$$

In these equations p_t is the total pressure; the subscript zero indicates initial values of the total or partial pressures. The vapor pressure[8] of hexachloroethane is 0.35 mm. at 26° and 1.0 mm. at 40°. From the rate of pressure decrease, the rate of chlorination of C_2Cl_4 was calculated by the relation

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

where $N_{C_2Cl_4}$ is the number of moles of tetrachloroethylene present; v, the volume of the reaction mixture varied from one run to another within the limits 1093 to 1118 cc.

The rate of photochlorination is given satisfactorily by the equation

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

where $I_{abs.}$ is the total radiation absorbed per unit of time and a is a constant in part dependent on the dimensions of the apparatus. In Table IV are given values of the a of this equation computed using dN_{Cl_2}/dt in moles per second, $I_{abs.}$ in einsteins per second, and (Cl_2) in moles per cc. The mean of the values at 40° is 1.69 × 10^3 with no large divergence from this value. The mean for 26° is 1.35 × 10^3 but is less reliable than that for 40°. With respect to the effect of intensity on the rate, attention may be drawn especially to experiments 15 and 18 where large changes in intensity were made in the course of each run; assumption of a rate proportional to the first power of the intensity would lead here to very discordant a's.

Since the fraction of the radiation absorbed was never large, the above results imply that the local rate of chlorination at a point where the radiation absorbed per unit volume per unit time is $(I_{abs.})$ is given by[9]

$$-d(Cl_2)/dt = k(I_{abs.})^{1/2}(Cl_2) \qquad (II)$$

This expression (II) is the same as that found for the rate of photochlorination[10] in carbon tetrachloride solution when sufficient tetrachloroethylene was present. It is of interest to attempt a comparison of the value of k for the gaseous reaction with that for the solution reaction. Leermakers and Dickinson give 5.1 as the value of k in solution at 22° when the units employed are moles, einsteins, liters and seconds; this

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[8] O. A. Nelson, *Ind. Eng. Chem.*, **22**, 971 (1930).

[9] It will be noted that the symbol $(I_{abs.})$ is used to indicate a different kind of quantity from that indicated by $I_{abs.}$

[10] Ref. 1, p. 4656.

becomes 161 when the units are moles, einsteins, cc. and seconds. In order to estimate k for the gaseous reaction, it may be assumed that comparatively little reaction occurred outside of the illuminated region as a result of diffusion of transient intermediates; this may not be entirely correct but can hardly invalidate the order of magnitude of the results. On this assumption the k of (II) is evidently related to the a of (I) by the equation $k = a/V^{1/2}$ where V is the volume of gas actually illuminated. Supposing the illuminated volume to have been a cylinder 3 cm. in diameter and 12 cm. long, we obtain $k = 0.109\ a$. Taking a as 1.35×10^3 at 26°, the value $k = 147$ results. This is very close to the value 161 obtained in solution at 22°, closer, indeed, than the accuracy of the calculation could lead one to expect. It appears, then, that in the presence of sufficient tetrachloroethylene, the photochlorination in the gaseous state is very similar to that in carbon tetrachloride solution not only in its dependence on concentrations and intensity but also in absolute value.

Mechanism of the Photochlorination

Two about equally simple mechanisms of photochlorination of gaseous tetrachloroethylene can be given. These are

MECHANISM A

$Cl_2 + h\nu \longrightarrow 2Cl$ (1)
$Cl + C_2Cl_4 \longrightarrow C_2Cl_5$ (2)
$C_2Cl_5 + Cl_2 \longrightarrow C_2Cl_6 + Cl$ (3)
$2C_2Cl_5 \longrightarrow 2C_2Cl_4 + Cl_2$ (or $C_2Cl_6 + C_2Cl_4$) (4)

MECHANISM B

$Cl_2 + h\nu \longrightarrow 2Cl$ (1)
$Cl + Cl_2 \longrightarrow Cl_3$ (2)
$Cl_3 + C_2Cl_4 \longrightarrow C_2Cl_6 + Cl$ (3)
$2Cl \longrightarrow Cl_2$ (4)

Either of these mechanisms leads to equation (II) as an expression of the local rate of reaction; for mechanism A, $k = k_3/\sqrt{k_4}$ and for B, $k = k_2/\sqrt{k_4}$.

Reactions (2) and (4) of B presumably would usually require the coöperation of a third molecule in order to take place in the gas phase. Consequently with mechanism B some dependence of rate on the total concentration of all molecules present might be expected. The rate determining steps in A, (3) and (4), are not bimolecular associations and no dependence of rate on total concentration is expected with this mechanism. The fact that the rate in carbon tetrachloride solution (at sufficiently high tetrachloroethylene concentration) is not greatly different from that in the gas is thus evidence in favor of A as opposed to B unless the fact be regarded as fortuitous.

Enough information is now at hand to permit an examination of the collision numbers involved in these mechanisms. The specific rate, $k°$, at which bimolecular collisions between unlike spherical molecules of diameters, d_1 and d_2 and molar weights M_1 and M_2 occur in a gas at temperature T is given by

$$k° = 2\sqrt{2\pi} \times 6.06 \times 10^{23} \left(\frac{d_1 + d_2}{2}\right)^2 \sqrt{\frac{M_1 + M_2}{M_1 M_2} RT}$$
$$= 10^{28.443} \left(\frac{d_1 + d_2}{2}\right)^2 \sqrt{\frac{M_1 + M_2}{M_1 M_2} T}$$

In the numerical equation, $k°$ is the number of moles colliding per cc. per second when each concentration is 1 mole per cc.; d_1 and d_2 are expressed in cm. For like molecules

$$k° = 10^{28.292} d^2 \sqrt{T/M}$$

For the various molecular diameters involved in mechanism A, the following values are reasonable estimates: Cl_2, 4.8×10^{-8}; Cl, 3.8×10^{-8}; C_2Cl_5, 6.3×10^{-8}; C_2Cl_4, 6.2×10^{-8} cm.[11]

Employing these values the specific rate of collision of Cl_2 with C_2Cl_5 at 26° is found to be $k_3^\circ = 2.0 \times 10^{14}$, and that of collision between C_2Cl_5 molecules, $k_4^\circ = 9.5 \times 10^{13}$. Assuming reaction (3) to occur at the fraction r_3 of all collisions between Cl_2 and C_2Cl_5, we may write $k_3 = k_3^\circ r_3$; similarly, $k_4 = k_4^\circ r_4$. Now the k of equation II, whose experimental value is 147, is equal to $k_3/\sqrt{k_4}$. Hence we may place $k_3^\circ r_3/\sqrt{k_4^\circ r_4} = 147$. Substituting the above numerical values for k_3° and k_4° we get $r_3 = 7 \times 10^{-6} \sqrt{r_4}$. Since r_4 is presumably not greater than unity, reaction (3) then occurs at less than the fraction 7×10^{-6} of all collisions between Cl_2 and C_2Cl_5 at 26°; this result is consistent with the treatment of (3) as a rate determining step.

Since, in a steady state, chains are broken as often as they are formed, we may write $k_4(C_2Cl_5)^2 = (I_{abs.})$ or $(C_2Cl_5) = \sqrt{(I_{abs.})/k_4^\circ r_4}$. The concentration of C_2Cl_5 prevailing in any experiment may then be found (in terms of r_4) by substituting numerical values for $(I_{abs.})$ and k_4°. In no experiment did $(I_{abs.})$ exceed 10^{-11} einsteins

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(11) As far as possible these estimates have been based on the formula $d = 1.33 \times 10^{-8} v^{1/3}$ where v is the molar volume of the substance in the solid or liquid state. This formula is given by E. A. Moelwyn-Hughes, *Chem. Rev.*, **10**, 241 (1932).

per cc. per second, and consequently in no case was (C_2Cl_5) greater than $3 \times 10^{-13}/\sqrt{r_4}$. A concentration of $3 \times 10^{-13}/\sqrt{r_4}$ moles per cc. corresponds to a partial pressure of the order of $6 \times 10^{-6}/\sqrt{r_4}$ mm. Unless r_4 is excessively small the concentration of C_2Cl_5 was then negligible compared with the concentration of the reactants; and the treatment of C_2Cl_5 as a transient intermediate of comparatively low concentration is justified.

The rate of (2) is substantially equal to that of (3) so that $k_2(\text{Cl})(\text{C}_2\text{Cl}_4) = k_3(\text{Cl}_2)(\text{C}_2\text{Cl}_5)$ or

$$\frac{(\text{Cl})}{(\text{C}_2\text{Cl}_5)} = \frac{k_3}{k_2}\,\frac{(\text{Cl}_2)}{(\text{C}_2\text{Cl}_4)} = \frac{k_3^\circ \times \sqrt{r_4} \times 7 \times 10^{-6}}{k_2^\circ \times r_2} \times \frac{(\text{Cl}_2)}{(\text{C}_2\text{Cl}_4)}$$

Now $k_3^\circ/k_2^\circ = 0.9$; and the largest value of (Cl_2)/(C_2Cl_4) in any part of an experiment where the rate is known to fit equation (II) was not over 10^2. Hence the largest value of the ratio (Cl)/(C_2Cl_5) in the present experiments was $6 \times 10^{-4}\sqrt{r_4}/r_2$. Since ($C_2Cl_5$) has already been shown to be small, evidently no difficulty has arisen in assuming that (Cl) is likewise small compared with (Cl_2) and (C_2Cl_4).

These considerations do not, however, serve to differentiate between mechanisms A and B. When the latter is examined in a similar manner it is found that for it $r_2 = 7 \times 10^{-6}\sqrt{r_4}$; that the highest (Cl) occurring in the experiments was $3.5 \times 10^{-13}/\sqrt{r_4}$; and the highest ratio of (Cl_3) to (Cl), $7.5 \times 10^{-4}\sqrt{r_4}/r_3$. Thus mechanism B is equally self-consistent.

Kinetics of the Oxidation

Measurements of the rate of photo-oxidation under various conditions are given in Table V. The pressures given in the first four columns are those prevailing at the beginning of intervals during which the intensity of illumination was substantially constant and in which dp/dt was measured. These pressures were initial pressures except in the parts of the experiments marked b; here the partial pressures of chlorine, oxygen, and tetrachloroethylene were calculated from the total pressure on the assumption that 90% of the oxidized tetrachloroethylene yielded trichloroacetyl chloride and the other 10% phosgene. On this same assumption the quantum yields, expressed as moles of tetrachloroethylene oxidized per einstein absorbed, were calculated from the rate of total pressure change and rate of light absorption.

The quantum yields are somewhat erratic, undergoing an uncorrelated variation of about two-fold. Nevertheless, the results make it clear that there is no strong dependence of the yield on any of the partial pressures or on the total pressure within the ranges studied; the initial total pressure was varied three-fold, that of the chlorine four-fold, and of oxygen 100-fold. In runs with an excess of oxygen the partial pressure of tetrachloroethylene fell to low values before any change in rate was apparent. The quantum yields show no systematic variation

TABLE V

QUANTUM YIELDS AND RATES OF OXIDATION WITH λ 4358 Å.

Expt.	Pressure, mm. p_{Cl_2}	p_{O_2}	$p_{C_2Cl_4}$	Total	I_0 ergs cm.$^{-2}$ sec.$^{-1}$ × 10^{-2}	$I_{abs.}$ einsteins sec.$^{-1}$ × 10^{10}	$-dp/dt$ mm. sec.$^{-1}$ × 10^4	$-dN_{C_2Cl_4}/dt$ moles sec.$^{-1}$ × 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	145.6	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°.

with the intensity when this is changed several fold; this is taken to indicate a first-power dependence of the rate on intensity. In experiments 15 and 17 the intensity was changed about fourfold within each run.

In dilute carbon tetrachloride solution, the quantum yields of this reaction likewise showed little dependence on concentrations or intensity; but the yields were less than one one-hundredth as great as in the gas phase. The high yields in the gas phase leave no doubt as to the chain character of the reaction.

Concerning a possible mechanism of the oxidation, two remarks may be made. First, in view of the different dependence of rate on intensity in the oxidation and chlorination, the chain breaking step presumably differs in the two cases. Second, the fact that when the oxygen concentration has fallen to a low value the total rate of reaction is less than either that of the preceding oxidation or that of the subsequent chlorination suggests that oxygen enters in two different ways —a chain oxidation and a chain-breaking oxidation. For example, with sufficient oxygen present, Cl might usually form ClO_2 and this lead to chain oxidation; with little oxygen, Cl might usually form C_2Cl_5 and this be oxidized without the continuance of a chain.

Summary

A chlorine-sensitized photo-oxidation of tetrachloroethylene in the gaseous state has been carried out with radiation of the wave length 4358 Å. The products have been found to be largely trichloroacetyl chloride with some phosgene. Quantum yields of about 300 molecules of tetrachloroethylene oxidized per quantum absorbed have been obtained; no strong dependence of the yields on concentrations or light intensity has been found.

Chlorination to hexachloroethane in the absence of oxygen also has been found to go as a chain reaction with rates fairly well represented by the equation $-d(Cl_2)/dt = k(I_{abs.})^{1/2}(Cl_2)$. Possible mechanisms have been discussed.

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[CONTRIBUTION FROM WESTINGHOUSE RESEARCH LABORATORIES]

The Dielectric Properties of Cellulose

BY W. N. STOOPS

Cellophane has a number of properties which suggest that it would be superior to paper as a dielectric. It is not highly porous and has both a higher dielectric constant and a higher dielectric strength than paper. On account of these desirable properties, it was decided to undertake a rather thorough investigation of its electrical properties, particularly the dielectric constant and power factor, considering their variation with temperature, frequency and the presence of various materials with which cellophane may be impregnated. For example, it readily absorbs moisture from the air, and this adsorbed water profoundly affects its electrical properties. It is hoped to discuss this effect in a later paper, but here only dried glycerol-free cellophane will be considered.

Experimental

A modified Schering bridge was used for dielectric constant and power factor measurements at frequencies below 100,000 cycles and a resonance circuit at higher frequencies. The bridge is similar to the one reported on by Dr. A. V. Astin before the Baltimore meeting of the Committee on Insulation of the National Research Council in November, 1932. As in his bridge, the source and detector were interchanged with the result that the detector could be at ground potential, thus simplifying the shielding and permitting the use of a Wagner earthing device. However, it was found that this Wagner ground was not necessary except for measuring very small power factors—less than 0.01—and so the bridge was grounded directly without its use. The bridge was balanced entirely by variation in capacitance, General Radio precision condensers type 222 being used throughout. A two-stage capacity-resistance coupled amplifier was used on the output of the bridge and gave satisfactory amplification over the entire frequency range. A vibration galvanometer was used as detector at frequencies below 1000 cycles, headphones at 1000–3000, and a heterodyne method at higher frequencies. A General Radio variable frequency oscillator was used as a power source at all frequencies below 100,000 cycles. A resonance circuit recommended by the American Society for Testing Materials[1] was used for the capacity and power factor measurements at higher frequencies. It was modified by

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[1] Proc. A. S. T. M., Vol. 31, I, p. 877, and 1931, T. S., p. 642.