THE CHLORINE-SENSITIZED PHOTO-OXIDATION OF TETRACHLOROETHYLENE IN CARBON TETRACHLORIDE SOLUTION

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In 1821, Michael Faraday[1] found that a solution of chlorine in tetrachloroethylene yielded hexachloroethane when exposed to sunlight. This reaction should offer perhaps the simplest possible case for kinetic study of photochemical chlorination of a double bond; there is no opportunity for complication arising from simultaneous substitution, and there is little likelihood of the formation of more than one chlorination product; moreover, at room temperature dark reaction apparently does not occur. On the other hand, it has been found[2] that tetrachloroethylene and oxygen alone give on prolonged exposure to sunlight, trichloroacetyl chloride and phosgene. We have undertaken a study of the kinetics of the chlorination in carbon tetrachloride solution using light absorbed only by the chlorine; we have found: (1) that this photochlorination, in common with many others, is strongly inhibited by dissolved oxygen; and (2) that in the presence of sufficient oxygen, oxidation of the tetrachloroethylene occurs to the practical exclusion of the chlorination although chlorine remains the light absorber. The present paper is concerned mainly with the products and kinetics of this photochemical oxidation sensitized by chlorine.

Apparatus

The Reaction Vessel.—Most of the illuminations were carried out with the solution in the vessel shown in Fig. 1. This vessel consisted of two flat-windowed Pyrex cells so joined together that the solution could be transferred from one to the other by inverting the vessel: the solution was placed in the thin cell A for illumination and in the thick cell B for photometric analysis. The cell A, which was of 5 mm. internal thickness and about 35 mm. diameter, was made thin in order that light absorption in it be low and all parts of the solution under nearly the same intensity of illumination. The cell B, which was of 3.30 cm. internal thickness and of slightly smaller volume than A, gave a longer optical path through the solution. The light absorption measured with the solution in B was used to compute the chlorine concentration and to compute the smaller absorption occurring in the cell A. The vessel was filled through a ground-glass stopper C which was protected with a water-tight cap D, since the vessel was placed in a water thermostat for illumination.

The Light Thermostat.—This was a tank of water provided with a window, stirrer and heater; temperatures were kept constant to one-half degree or better. The reaction vessel was mounted in a position accurately reproducible from one experiment to another, and about 1 cm. from the window.

[1] M. Faraday, Ann. chim. phys., [2] 18, 55 (1821).

[2] M. A. Besson, Compt. rend., 121, 125 (1895).

In experiments in which the mercury radiation λ4358 was used, the intensity of the radiation was measured by means of a thermopile and galvanometer. This thermopile was mounted in a waterproof brass case with a glass window and was so arranged that after removing the reaction cell, the thermopile could be placed in a reproducible position approximating that occupied by the cell during illumination.

The Sources of Illumination.—For most experiments of a preliminary or of a qualitative nature, the source of illumination was a 500-watt projection lamp. The infra-red was removed by a water-cooled filter consisting of a 1-cm. layer of 6% copper sulfate solution. The light was approximately collimated by a 16-diopter lens of aperture about f 1.5. An ammeter and variable resistance were placed in series with the lamp to assist in securing reproducible intensities. This source was the one used in experiments with "white light" described below.

A series of experiments was made using the mercury line λ4358; this was obtained from an upright type quartz arc placed just outside the thermostat (in a reproducible position) about 6 cm. from the reaction vessel and used without collimating lenses. The radiation was passed through the copper sulfate filter mentioned above and then through the Corning glasses Noviol A and blue-purple ultra. Spectrographic examination of the transmitted radiation showed it to be entirely free from strong mercury lines other than λ4358. Similar filters were used in the photometer.

Fig. 1.—Cell employed for illuminating the solution and for measuring its light transmission.

The Photometer.—In order to determine chlorine concentrations without removing samples for analysis, and in order to compute the low absorption in the thin cell in the experiments with λ4358, its absorption in the thick cell (B) was determined with the aid of a photometer. This apparatus employed simultaneously two thermopiles and two galvanometers and a divided light beam in one branch of which the absorption cell was placed. Beer's law was used, the molal absorption coefficient of chlorine being taken as 2.26.[3]
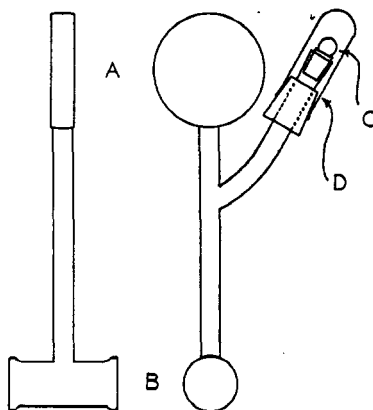
Materials

Carbon Tetrachloride.—The carbon tetrachloride was obtained from a c. p. sulfur-free product. This was given prolonged illumination with chlorine dioxide and chlorine; it was then refluxed, washed with sodium hydroxide solution, with water, dried over c. p. calcium chloride, and finally distilled in an all-glass apparatus. The product was found to give only negligible quantities of acid when its chlorine solution was subjected to more prolonged illumination than those used in the measurements. Two separate samples of carbon tetrachloride were used.

Tetrachloroethylene.—The tetrachloroethylene was obtained from Eastman's c. p. product. It was found that when a carbon tetrachloride solution of chlorine was mixed with an excess of the original tetrachloroethylene in the dark, a small fraction of the chlorine disappeared immediately but no more disappeared on standing; this indicated a small amount of easily chlorinated impurity in the tetrachloroethylene. It was accordingly further treated by passing chlorine into it and illuminating it. It was

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[3] Dickinson and Jeffreys, THIS JOURNAL, **52**, 4288 (1930).

washed with sodium hydroxide solution, and then with water, dried with calcium chloride, and fractionally distilled. The fraction coming over at 118.0–118.1° at 740 mm. was retained. (It constituted most of the sample.) The product (of which two different preparations were used) yielded a little acid on shaking with water but the amount was small enough to ignore in all experiments except at very high tetrachloroethylene concentrations; in these a small blank correction was applied.

Chlorine.—The chlorine was taken from a commercial tank. It was passed successively through glass-connected wash bottles containing potassium permanganate solution, dilute sulfuric acid, concentrated sulfuric acid, glass wool and finally desichlor. The effluent gas was passed directly into carbon tetrachloride in a glass-stoppered bottle. The chlorine solutions so prepared were found to be completely acid-free.

The Products of the Reaction

Inhibition of Chlorination.—The effect of oxygen in preventing the disappearance of free chlorine is shown by the following pair of experiments carried out with solutions initially 1.6 molal in tetrachloroethylene and 0.075 molal in chlorine. In one experiment, the reaction vessel (Fig. 1) was filled with oxygen and then enough solution introduced to fill cell A. The solution was illuminated in A for twenty minutes; the illumination was occasionally interrupted and the solution run back and forth between cells A and B to keep the solution supplied with oxygen. The chlorine concentration showed no detectable decrease in this time. A second sample was illuminated in the same way except that the cell was initially filled with nitrogen and was not disturbed during the illumination. At the end of five minutes most of the chlorine had disappeared; its molality was now 0.012. The non-disappearance of chlorine in solutions containing oxygen was verified in many experiments.

Formation of Hydrolyzable Product.—That oxygen not only inhibited the chlorination but also produced an oxidation was evident from the phosgene-like odor from the illuminated solution. It was shown more convincingly by the fact that when the illuminated solution was shaken with water and the free chlorine removed with iodide and thiosulfate, the water was found to be acid. The photochemical formation of oxidation products hydrolyzable to acid is the feature of which we have made use in following the reaction quantitatively.

Analysis for Acid.—In order to determine the number of equivalents of acid obtainable by hydrolysis of the illuminated solution, it was poured into a weighed, glass-stoppered flask containing water, and shaken for five minutes. Then potassium iodide was added and the color just discharged with thiosulfate. The acid was then determined by adding potassium iodate and titrating the iodine with thiosulfate. Special experiments were made to show that sufficient time was allowed for the hydrolysis.

Dark Reaction.—Several solutions similar to those used for illumination were allowed to stand in the dark for periods exceeding the times required for the light experiments; one solution was as high as 3.2 molal in

tetrachloroethylene, and another was kept at 36°. In no case was either chlorination or oxidation found.

Equivalents of Acid per Formula Weight of Tetrachloroethylene.— A series of experiments was made starting in each case with a solution of the same composition, viz., 0.0113 volume molal in tetrachloroethylene and 0.07 in chlorine. A supply of oxygen was maintained in the solution in the manner described above. (The oxygen present in the vessel was several times the amount needed to oxidize all the tetrachloroethylene to phosgene.) The samples were exposed for various times to the white light source under identical conditions of illumination, and were then hydrolyzed and titrated for acid. The results of this series are shown in curve A of Fig. 2 in which
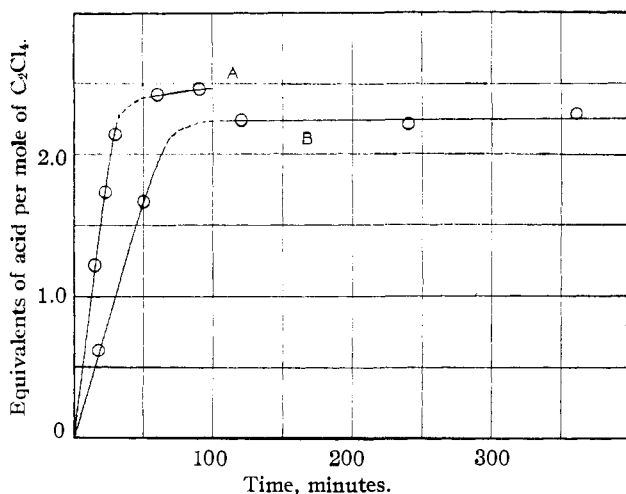

Fig. 2.—Amount of oxidation produced in various times of illumination.

the equivalents of acid found per formula weight of tetrachloroethylene taken are plotted as ordinates against the times of exposure in minutes as abscissas. It may be seen that in the early part of the reaction the amount of acid-producing material formed is nearly linear with the time; this suggests that the rate of oxidation is not strongly dependent on the tetrachloroethylene concentration. With continued illumination the formation of acid-producing material ceases abruptly and before the tetrachloroethylene is at all completely oxidized to phosgene; for complete oxidation to phosgene would give four equivalents of acid per formula weight of tetrachloroethylene in accordance with the equations

$$C_2Cl_4 + O_2 = 2COCl_2$$
$$2(COCl_2 + H_2O = CO_2 + 2HCl)$$
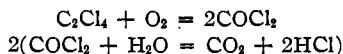
Oxidation to trichloroacetyl chloride would, however, give two equivalents of acid per formula weight of tetrachloroethylene

$$C_2Cl_4 + \frac{1}{2}O_2 = CCl_3COCl$$
$$CCl_3COCl + H_2O = CCl_3COOH + HCl$$
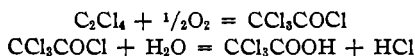
Since, in this series, the original solution was prepared volumetrically and the concentration of tetrachloroethylene was not known to better than a few per cent., two more experiments were made with solutions carefully prepared by weighing. These gave, after sixty minutes of the same exposure as before, the values 2.22 and 2.28 for the equivalents of acid per formula weight of tetrachloroethylene.

In another series of measurements a solution 0.0113 molal in tetrachloroethylene and 0.05 molal in chlorine was exposed in a larger cell (not shown) under slightly different conditions of illumination. The cell was provided with an oxygen reservoir into which the solution was occasionally run. Successive samples of solution were withdrawn and titrated. The illumination was continued for six hours although the initial reaction was apparently over in a little over one hour.

The results are shown in B of Fig. 2. The experiment makes it clear that the products of the oxidation of tetrachloroethylene undergo little if any further oxidation even on prolonged illumination. On the assumption that the oxidation is to trichloroacetyl chloride and phosgene, the average value of 2.25 equivalents of acid obtained per formula weight of tetrachloroethylene leads to the conclusion that 87.5% of the tetrachloroethylene oxidized goes to trichloroacetyl chloride.

Isolation of Trichloroacetic Acid.—In order to determine whether trichloroacetic acid could be isolated from the products of hydrolysis, an illuminated solution was shaken with water and both liquids were evaporated together at 40°. Drying in a desiccator yielded a hygroscopic solid. Two separate samples gave melting points of 55 and 56°, respectively; that of trichloroacetic acid is 57°. Furthermore the solid gave a strongly acid solution and an isocyanide odor when heated with potassium hydroxide and aniline.

Ratio of Acid to Chloride.—An independent estimate of the fraction of the oxidation leading to trichloroacetyl chloride was obtained from a determination of the ratio of equivalents of acid to equivalents of chloride in the hydrolysis products; this ratio would evidently be 2 were the oxidation completely to trichloroacetyl chloride and 1 were it completely to phosgene. We have accordingly, in certain experiments, supplemented the titration for acid with an electrometric titration for chloride on a separate sample. The procedure was as follows: twenty cc. of carbon tetrachloride solution was illuminated in white light (oxygen being present) until a suitable amount of reaction was judged to have occurred. The solution was then shaken with 10 cc. of water in a small separatory funnel and the carbon tetrachloride layer rejected. Separate distribution experiments showed that the aqueous layer should retain all of the trichloroacetic acid and hy-

drochloric acid but only a portion of the free chlorine. The aqueous layer was diluted to 30 cc. Ten cc. of this solution was titrated for free chlorine and then for acid using potassium iodide and potassium iodate and 0.01 N thiosulfate. To another 10-cc. sample was added 1 cc. of 0.1 N sodium sulfite to convert the free chlorine to chloride. The total chloride in this sample was then determined by electrometric titration with 0.01 N silver nitrate solution. The chloride in the original hydrolysis products was then obtained by subtracting from this total chloride the number of equivalents of free chlorine found in the first titration.

The results of these experiments are shown in Table I. The composition of the original carbon tetrachloride solution is shown in the first two columns; the results of the titrations are shown in the next two columns, and the ratio of acid to chloride in the hydrolysis products in the fifth column. In agreement with expectations, the value of this ratio is much greater than 1 but less than 2 in all cases. If x be the fraction of the reacting tetrachloroethylene which gives trichloroacetyl chloride and $(1-x)$ the fraction which forms phosgene, then per formula weight of tetrachloroethylene oxidized the hydrolysis products contain $2x + 4(1-x)$ equivalents of acid and $x + 4(1-x)$ equivalents of chloride; the ratio of acid to chloride is then $(4-2x)/(4-3x)$. With this relation, values of x were calculated from the observed acid to chloride ratio; these are given in the last column of Table I. The average value 0.86 agrees with that previously obtained (0.875) in indicating that the oxidation is mainly to trichloroacetyl chloride.

TABLE I

RATIO OF ACID TO CHLORIDE IN HYDROLYZED PRODUCTS

C_2Cl_4, mole/liter	Cl_2, mole/liter	Equiv. acid in 10-cc. sample	Equiv. chloride in 10-cc. sample	Ratio of acid to chloride	Fraction of oxidation to CCl_3COCl; x
0.097	0.07	12.69×10^{-5}	8.57×10^{-5}	1.48	0.79
.097	.07	11.18	6.84	1.63	.87
.097	.07	2.64	1.80	1.47	.78
.097	.07	4.27	2.57	1.66	.89
.485	.05	9.57	5.73	1.67	.89
.97	.05	7.43	4.04	1.84	.95
.97	.05	23.64	15.19	1.56	.84

Mean .86

The Kinetics of the Reaction

A considerable number of experiments on the effect of various factors on the reaction rate was made using white light since such experiments could be carried out with comparatively short exposures. Another series of experiments was then made using monochromatic radiation (λ 4358). In view of the facts that the latter experiments were more precise and unambiguous than those with white light, and that the experiments with white light

led to no conclusions at variance with those obtained with λ4358, we are giving in detail only the results of the latter experiments. They were all carried out by illuminating various solutions in cell A of Fig. 1, using the photometer to determine the absorption and chlorine concentration, and hydrolyzing the final solution and titrating the products for acid as described above. The results are given in Table II.

In column 5 is given the intensity of radiation in arbitrary units (cm. of galvanometer scale deflection). Since the thermopile as used was at the thermostat temperature, and since its sensitivity was found by separate experiment to decrease with rising temperature 0.24% per degree, the tabulated intensities for temperatures other than 20° have been reduced to the deflections which would have been obtained with the thermopile at 20°. In column 6 is given the fraction of radiation absorbed in the thin cell A as computed from measurements in cell B. These absorption measurements were all made at about 20°. However, we have found in a separate experiment that the absorption of a carbon tetrachloride solution 0.05 M in chlorine did not differ appreciably (*i. e.*, by more than 1%) at 7 and 30°; it is safe to take the values in column 6 as those actually prevailing in the experiments at other temperatures. In column 8 is given the amount of acid found by titration; and in column 9 the yield, *i. e.*, the amount of reaction per unit time per arbitrary unit of radiation absorbed. These data permit the following conclusions concerning the effect of various factors on the rate of oxidation.

TABLE II

RESULTS OF ILLUMINATING SOLUTIONS WITH λ4358

1	2	3	4	5	6	7	8	9
	C_2Cl_4, mole/	Cl_2, mole/	Temp.,	Intensity cm. defl. of galv.,	Fraction of rad. absorbed,	Exposure time, min.,	Equiv. acid per g. of soln.,	Yield,
Expt.	liter	liter	°C.	d	a	t	q	$\frac{q}{adt}$
1	0.0220	0.0619	20	2.11	0.149	60	0.876×10^{-5}	0.0465×10^{-5}
2	.0420	.0318	20	2.16	.081	120	1.022	.0489
3	.0420	.0658	20	2.23	.159	60	1.062	.0500
4	.0420	.0726	20	1.97	.172	60	1.059	.0520
5ᵃ	.0420	.0987	20	2.74	.226	30	0.977	.0527
6	.0420	.1147	19	0.567	.258	90	0.700	.0531
7	.0420	.1260	20	2.65	.283	30	1.164	.0517
8	.462	.0614	20	2.13	.150	60	1.558	.0813
9	.881	.0460	20	2.37	.113	60	1.593	.0994
10	1.615	.0629	20	2.52	.151	50	2.260	.1181
11	2.425	.0348	20	2.16	.086	60	1.950	.1758
12	3.235	.0213	20	2.33	.053	60	2.310	.3120
13	0.0420	.0476	3	1.09	.117	120	0.564	.0369
14	.0420	.0755	3	1.52	.178	90	0.905	.0372
15	.462	.0458	3	1.74	.112	90	1.033	.0589
16	.0420	.1026	36	2.00	.235	40	1.248	.0664
17	.462	.0582	36	2.18	.140	45	1.539	.1121

ᵃ Solution saturated with air instead of oxygen.

Oxygen Concentration.—That the concentration of oxygen, when not too low, has little effect on the rate of oxidation is suggested by the coherence of the results shown in Fig. 2 since there was no attempt to maintain constancy of oxygen concentration in those experiments. It is shown more directly by the equality in yield (column 9) in experiments 4, 5 and 7, which differ mainly in that air instead of oxygen was used to saturate the solution in experiment 5. Similar results have been obtained with white light. From the solubility of oxygen in carbon tetrachloride given in the "International Critical Tables," the concentration of oxygen in solutions saturated with air is calculated to be 0.002 molal.

Light Intensity.—The rate of oxidation is proportional to the first power of the intensity of the incident light. This is best shown by a comparison of experiments 6 and 7, which involve a nearly 5-fold intensity range but are otherwise similar. With white light, 4-fold changes in intensity have been made using calibrated screens with similar results.

Chlorine Concentration.—Experiments 2, 3, 4 and 7 differ mainly in chlorine concentration, which is here varied four-fold. The rates per unit absorption probably do not differ by more than the error of the experiments. For a thin layer of solution, then, the rate of oxidation is proportional to the chlorine concentration, i. e., the chlorine concentration affects the rate only by affecting the amount of absorption.

Tetrachloroethylene Concentration.—In experiments 1 to 10 inclusive, the concentration of tetrachloroethylene is increased 73-fold while the rate per unit absorption increases only 2.5-fold. At very high concentrations, the rate begins to increase much more rapidly. The results of the first ten experiments may be very satisfactorily represented by an empirical expression of the form

$$\text{Rate} = kI_{abs.} \, [1 + b(C_2Cl_4)^{1/2}]$$

but at very high tetrachloroethylene concentrations this expression leads to lower values than those observed.

Temperature.—Most of the experiments were made at 20°, but measurements have been made at 3° and at 36° at two different tetrachloroethylene concentrations. The yields under various conditions are summarized in Table III. In the third and fifth columns are given the ten-

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TABLE III

EFFECT OF TEMPERATURE ON THE RATE OF OXIDATION

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Temp., °C.	Yield at $(C_2Cl_4) = 0.0420$	$\dfrac{k_{T+10}}{k_T}$	Yield at $(C_2Cl_4) = 0.462$	$\dfrac{k_{T+10}}{k_T}$
3	0.0370×10^{-5}		0.0589×10^{-5}	
		1.21		1.21
20	.0514		.0813	
		1.17		1.22
36	.0664		.1121	

degree multiplications of the yield. In the range studied, *i. e.*, from 0.04 to 0.5 molal in tetrachloroethylene, the temperature coefficient shows no evident dependence on the yield. Since the absorption coefficient of the chlorine solutions is substantially independent of the temperature, these ten-degree multiplications may be regarded as applying either to the specific rate constants or to the quantum yields.

Quantum Yields

In view of the character of the dependence of the reaction rates on the tetrachloroethylene concentration and on the temperature, an extremely precise determination of quantum yield would appear to be without present interest; a fair estimate of the quantum yields can be had from the experiments already described.

The intensity of radiation at the front surface of the reaction cell corresponding to a deflection, d, in the experiments of Table II was found by locating the mercury arc and thermopile in the positions they occupied in those experiments, and comparing the deflection obtained with that obtained when a second calibrated thermopile was placed at the position normally occupied by the reaction cell. It was thus found that the intensity at the reaction cell was $56 \times 10^2 \, d$ ergs per sq. cm. per sec. If now A be the illuminated area of liquid (the entire liquid in the cell was illuminated) and a the fractional absorption, then since the number of einsteins per erg of radiation of wave length 4358 Å is 3.66×10^{-13}, the number of einsteins absorbed by the liquid in t minutes is $3.66 \times 10^{-13} \times 56 \times 10^2 \times adA \times 60t$. If q be the equivalents of acid produced per gram of solution, ρ the density of the solution (1.59 g./cc.), and l the thickness of the solution in the cell, the equivalents of acid per Al cc. of solution is $q\rho Al$. The quantum yield expressed in equivalents of acid per einstein absorbed is then $64 \times 10^5 \times q/adt$; *i. e.*, the quantum yields so expressed may be obtained by multiplication of the numbers in column 9 of Table II by 64×10^5. The values obtained in this way range from 2.4 in experiments 13 and 14 to 20 in experiment 12. The above calculation assumes that the illumination was (1) parallel and (2) spatially uniform; these conditions, particularly the first, were only approximately satisfied.

Two measurements of quantum yield largely independent of the above were made by illuminating the solution in cell B of Fig. 1, using a uniform collimated beam defined by a circular diaphragm with an opening only 1.00 cm. in diameter so that the entire beam was intercepted by the solution. The intensity was measured by a thermopile giving a deflection of 1 cm. for an intensity of 1.340 ergs per sq. mm. per sec. The results are given in Table IV.

The intensity given in column 3 has been corrected for reflection losses and represents the intensity of the radiation entering the solution. The

TABLE IV

QUANTUM YIELD DETERMINATIONS AT 20°—λ = 4358 Å.

C₂Cl₄, mole/ liter	Cl₂, mole/ liter	Intensity ergs/ sq. cm./sec.	Fraction absorbed	Time, min.	Total equivs. acid	Equivs. acid per einstein
0.0420	0.0761	2340	0.729	232	1.34×10^{-5}	1.95
.0420	.0779	1570	.737	301	1.36	2.25

yields of Table IV are only about 66% of those calculable from Table II, but are more reliable. For a solution having (C_2Cl_4) = 0.0420, our best estimate (good to 20%) of the quantum yield is 2.5 equivalents of acid per einstein. Assuming 87% of the oxidized tetrachloroethylene to form trichloroacetyl chloride, this corresponds to 1.1 mole of tetrachloroethylene oxidized per einstein absorbed at 20°. The values of the yields in Table II should be good to within a few per cent. relative to each other. If they are all multiplied by a constant factor so as to give the yield 1.1 mole of tetrachloroethylene per einstein at (C_2Cl_4) = 0.0420 and at 20°, the absolute yields shown in Fig. 3 are obtained.
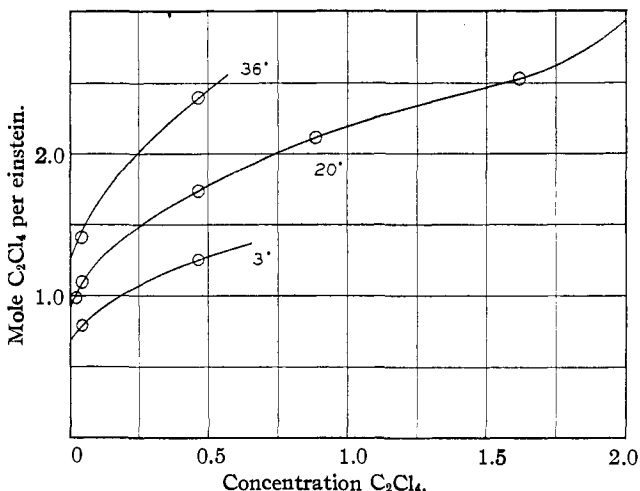

Fig. 3.—Moles of tetrachloroethylene oxidized per einstein of radiation λ4358 absorbed.

Discussion

As far as the present reaction has been studied, it is found to exhibit considerable similarity to the chlorine sensitized formation of carbon dioxide from gaseous carbon monoxide and oxygen. It is well known that carbon monoxide and chlorine unite under illumination and form phosgene;[4] when, however, oxygen is present the chlorination of carbon monoxide ceases, and oxidation to carbon dioxide occurs instead. The

[4] This reaction has been extensively studied by M. Bodenstein and his collaborators.

rate of formation of carbon dioxide is given by the expression $d(CO_2)/dt = k\, I_{abs.}(CO)^{1/2}$ when the pressures are low and when vessels with large surface are used.[5]   The kinetics of the tetrachloroethylene oxidation in solution and the carbon monoxide oxidation at low pressures agree with respect to the effect of intensity, chlorine concentration and oxygen concentration and further agree to the extent of involving no strong dependence on the concentration of tetrachloroethylene or carbon monoxide.

A mechanism has been given to account for the rate of carbon dioxide formation.   An essential feature of this mechanism is the achievement of first order dependence on the light intensity through wall recombination of the chlorine atoms.   It is difficult to suppose that wall recombination is of importance in the case of a solution reaction.   Accordingly, in spite of the formal resemblance of the tetrachloroethylene reaction to some aspects of the carbon monoxide reaction, we are unable to make direct use of the mechanism proposed for the latter.

We shall defer attempts to develop a mechanism for the oxidation of tetrachloroethylene until further experiments on the chlorination have been completed.

Summary

The photochemical chlorination of tetrachloroethylene in carbon tetrachloride solution has been found to be strongly inhibited by oxygen.

In the presence of both oxygen and chlorine, photosensitized oxidation to trichloroacetyl chloride and to phosgene occurs; most of the oxidation ($\sim 87\%$) leads to trichloroacetyl chloride.

With radiation of wave length 4358 Å. the rate of oxidation in a uniformly illuminated layer is found, in the ranges studied, to be proportional to the first power of the intensity of the incident radiation, the first power of the chlorine concentration, independent of the oxygen concentration and only moderately dependent on the tetrachloroethylene concentration except when this is very high.

Rates have been measured at 3, 20 and 36°; the ten-degree multiplication of the yield has been found to be 1.20.

Quantum yields for the oxidation have been determined.

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[5] H. J. Schumacher and G. Stieger, Z. physik. Chem., [B] 13, 169 (1931).