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John Andrews Leermakers

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**THE THERMAL DECOMPOSITION OF DIMETHYL-TRIAZENE.
A HOMOGENEOUS UNIMOLECULAR REACTION**

By H. C. RAMSPERGER AND J. A. LEERMAKERS

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During the past four years a considerable amount of experimental data has given support to certain theories of unimolecular reaction velocity which postulate that activation occurs by kinetic theory collisions. The rate of production of activated molecules by collisions is a second order process but if only a very small fraction of those molecules which become activated decompose spontaneously the rate of decomposition is first order. At sufficiently low pressures collisions can no longer maintain the Maxwell-Boltzmann quota of activated molecules; consequently the rate falls off until finally at still lower pressures the rate approaches the rate of activation and is second order.

Now that the rate of decomposition of nitrogen pentoxide has at last also been shown to decrease at very low pressures,^{1,2} every example of a homogeneous unimolecular reaction shows such a decrease or else theory does not require it in the pressure range studied.

We have now studied the decomposition of dimethyl-triazene and find that this reaction also is first order at high pressures but falls off in rate at pressures below about one centimeter. Rate measurements have been made at temperatures from 200 to 230° and at pressures from 0.02 to 8.0 cm. of mercury.

Preparation of Dimethyl-triazene.—Dimethyl-triazene was prepared by the method of Dimroth.³

The copper salt of dimethyl-triazene was first prepared. Methyl azide was formed by dropping dimethyl sulfate upon a stirred and refluxed aqueous solution of sodium azide. The gas was passed through a warm tube containing calcium chloride and into an ice cooled solution of methylmagnesium iodide ($\text{CH}_3\text{—N=N=N} + \text{CH}_3\text{MgI} = \text{CH}_3\text{—N=N—NCH}_3\text{MgI}$). The resulting ether solution was hydrolyzed at zero degrees with an aqueous solution of ammonium chloride and ammonium hydroxide, and the dimethyl-triazene so formed was converted to its copper salt by shaking with ammoniacal cuprous chloride solution. The copper salt was separated from the water layer by repeated extraction with ether; the ether solution was dried with anhydrous sodium sulfate and the ether distilled from the salt. The solid green copper salt was recrystallized from warm anhydrous ether and dried over concentrated sulfuric acid.

The free dimethyl-triazene was prepared from its copper salt by warming it with solid diazoaminobenzene prepared according to Fischer.⁴ The liberation and purification of the dimethyl-triazene was carried out on a vacuum line.

The vacuum system was of Pyrex glass and consisted of a 30-cc. flask connected in series with a 3 × 1-cm. tube filled with c. p., ground, fused calcium chloride; a receiver of 3-cc. capacity; a 12 × 1-cm. tube filled with calcium chloride; and a small combination distilling flask of 3-cc. capacity and water-cooled reflux column. The exit tube of the reflux column led to another 3-cc. receiver which was separated from the high-vacuum line by a stopcock. Equivalent quantities, 2 g. of the copper salt and 3 g. of diazoaminobenzene, were mixed and introduced into the flask and the latter was sealed off at the neck. The system was evacuated and the flask heated slowly to a temperature of 90° by means of a glycerin bath. The dimethyl-triazene vapor was allowed to pass through the first tube of calcium chloride and was condensed in the first receiver by a mixture of solid carbon dioxide and ether at -78°. When the vapor had all been condensed the receiver was sealed off from the flask and its contents were allowed to distil through the second larger calcium chloride tube into the distilling flask, where they were recondensed with the ether-carbon dioxide mixture. The liquid was allowed to distil back to the receiver in the same manner, this process was repeated several times, and with the liquid finally frozen out in the distilling flask the latter was sealed off from the calcium chloride tube. The amount of liquid dimethyl-triazene was about 1.5 cc. Air was then let into the system at a pressure of 75 mm. and the liquid was slowly distilled into the second receiving flask, which was cooled as before to -78°. During the distilla-

¹ Ramsperger and Tolman, *Proc. Nat. Acad. Sci.*, 16, 6 (1930).

² Schumacher and Sprenger, *ibid.*, 16, 129 (1930).

³ Dimroth, *Ber.*, 39, 3905 (1906).

⁴ Fischer, *ibid.*, 17, 641 (1884).

tion a glycerin bath served to control the temperature of the distilling flask, and water was run into the condenser around the reflux column to insure careful fractionation. About three drops of a liquid which did not solidify at -78° came over below 40° . These were pumped out and rejected. With the exception of the last several drops, which were also rejected, the remainder of the liquid boiled between 43.0 and 43.1° under 75 mm. pressure. The distilling flask was finally sealed off from the receiver. The solid in the receiving flask melted fairly sharply at about -12.0° to give a perfectly clear, colorless liquid. In order to free the dimethyl-triazene from any dissolved air, the liquid was distilled into the top of the container by means of a bath of solid carbon dioxide and the flask was evacuated. This process was repeated several times. The sample was used for the rate determinations without further treatment.

Nature of Reaction

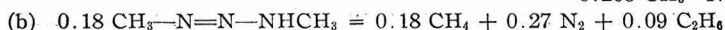
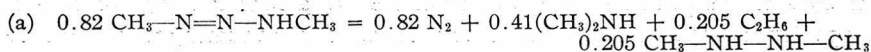
When dimethyl-triazene is completely decomposed at constant volume, the final pressure is 2.175 times the initial pressure. This fact, together with a titration for basic constituents and some freezing-out data, make possible a rough estimate of the reaction products.

The gas resulting from the complete decomposition of dimethyl-triazene was collected in a 120-cc. bulb at 9.60 cm. pressure. A tube sealed to the bottom of the bulb was surrounded with baths at various temperatures and the pressure was read on an attached mercury manometer. The following readings (corrected for the lower temperature of the gas in the cold bath) were obtained.

$t, ^{\circ}\text{C.}$	$P, \text{cm.}$	% Uncondensed
20	9.60	100
-20	9.05	94
-79	6.80	71
-111	6.25	65
-183	5.25	55

Titration with $0.01 N$ hydrochloric acid and phenolphthalein showed that 29.6% of the gas was basic, assuming one equivalent of acid per mole of base.

When dimethyl-triazene spontaneously decomposes it may be expected to break up into various radicals which may combine with one another or react with one another so as to give the reaction products. We shall try to represent the reaction products which seemed likely to form from such a process by stoichiometric equations and then test these equations with the above data.



The number of moles in each equation (0.82 and 0.18) has been so chosen that a combination of equation (a) with (b) or of (a) with (c) will give the correct ratio of final to initial pressure. Equation (a) gives some dimethylhydrazine (supposedly by a combination of two CH_3NH radicals) and thus

accounts for the gas which freezes out at -20° . With phenolphthalein it would neutralize an equivalent of acid and together with the $(\text{CH}_3)_2\text{NH}$ accounts for 27% of the gas which is nearly equal to the 29.6% observed. The combination of (a) with (b) gives 58% non-condensable with liquid air ($\text{N}_2 + \text{CH}_4$), while (a) with (c) gives 54% ($\text{N}_2 + \text{H}_2$), both of which are close to the value found (55%). Evidently no choice can be made between (b) and (c). It is not claimed that the agreement found with these stoichiometric equations is a very accurate description of the nature of the reaction.

Apparatus and Procedure

The rate of decomposition was followed by the increase in pressure at constant volume. The 250-cc. Pyrex reaction flask was placed in an oil-bath the temperature of which was automatically controlled to 0.05° . The thermometer used was calibrated against a Bureau of Standards thermometer.

In the high-pressure runs Nos. 39 to 50 the supply bulb was connected to a metal stopcock of the Bodenstein type,⁵ which was connected directly to the cell. One arm of a mercury U-trap was sealed to this connecting tube and the other arm led to the high-vacuum line. The stopcock and mercury trap were surrounded by a cardboard structure containing a glass window. Warm air was circulated through this structure so as to maintain a temperature of about 50° . This was necessary to prevent condensation of dimethyl-triazene in the system outside the thermostat. The volume outside the thermostat was at most 1% of the total volume. In making a run the cell was evacuated to about 1×10^{-5} mm., mercury was let up into the trap, the desired amount of gas let into the reaction vessel through the metal stopcock and the stop watch started. The pressure in the U-trap was read immediately and at intervals during the course of the run.

The low-pressure measurements were made with a clicker system.⁶ The supply was connected to an ordinary vacuum stopcock. This led to one arm of a mercury trap, the other arm of which was connected directly to the cell. A lead to vacuum was sealed in about 3 cm. above the bottom of the U-tube on the reaction vessel side. This lead had a stopcock separating it from the vacuum line. The clicker of about 0.5-cc. capacity and having a click constant of 0.150 cm. pressure was sealed by a small tube to the reaction vessel. A larger tube fitting around the clicker, and sealed to it by a ring seal at its base, was connected to a McLeod gage of 130-cc. capacity and to a number of capillary tubes. By evacuating through these capillary tubes it was possible slowly to change the pressure on the clicker as the critical clicking pressure was approached. Air could be let in through another capillary to reset the clicker. The limit of accuracy of this pressure measurement system was the reproducibility of the clicker,

⁵ Bodenstein and Dux, *Z. physik. Chem.*, **85**, 305 (1913).

⁶ Smith and Taylor, *THIS JOURNAL*, **46**, 1393 (1924).

which appeared to be better than 0.001 cm. The outside volume was less than 1% of the total volume of the reaction vessel. After letting the desired amount of gas into the reaction cell the mercury was raised in the U-trap and the air pressure surrounding the clicker was adjusted to get the click. Due to the fact that a short time was required to obtain the first click it was necessary to extrapolate the pressure readings back to zero time. The extrapolation was usually only about 2 to 3%, even at the higher temperatures. A similar extrapolation was sometimes necessary for the high pressure experiments.

Experimental Data

The partial pressure of dimethyl-triazene (P_T) was calculated for each reading by the expression $P_T = (2.175P_0 - P)/1.175$, where P_0 is the initial pressure at zero time and P is the total pressure at that reading. The factor of 2.175 is required because the final pressure is 2.175 times the initial pressure. First order rate constants were calculated by the interval method, that is, by using the equation

$$k_1 = \log_{10} P_{T_t}/P_{T_{t'}} \times 2.303/(t' - t)$$

where P_{T_t} is the partial pressure of dimethyl-triazene at time t , and $P_{T_{t'}}$ is its partial pressure at the following reading taken at time t' . First order

TABLE I

DATA FOR RUNS

Run number 17; $P_{\text{final}}/P_0 = 2.175$; $T = 210.0^\circ$; $P_0 = 0.2340$ cm.

p , cm.	P_T	t , sec.	$k_1 \times 10^4$ (sec. ⁻¹)
0.2340	0.2340	0	
.2410	.2280	120	1.76
.2648	.2078	645	1.38
.2935	.1835	1510	1.39
.3128	.1670	2190	1.35
.3298	.1525	2865	1.41
.3623	.1250	4380	1.37
.3815	.1088	5415	1.37
.4010	.0915	6675	1.59
.4348	.0560	9750	
.5090	.0000	∞	

Run number 35; $P_{\text{final}}/P_0 = 2.175$; $T = 200.0^\circ$; $P_0 = 2.987$ cm.

p , cm.	P_T	t , sec.	$k_1 \times 10^6$ (sec. ⁻¹)
2.987	2.987	0	
3.087	2.902	290	
3.550	2.508	1710	10.25
4.006	2.119	3360	10.21
4.438	1.752	5320	9.71
4.791	1.451	7290	9.56
5.106	1.187	9340	9.80
5.400	0.937	12060	8.68
5.700	0.682	15300	9.78

TABLE I (Concluded)

Run number 31; $P_{\text{final}}/P_0 = 2.175$; $T = 230.0^\circ$; $P_0 = 0.0400$ cm.

p , cm.	P_T	t , sec.	$k_1 \times 10^4$ (sec. ⁻¹)
0.0400	0.0400	0	
.0413	.0389	75	
.0475	.0336	635	2.62
.0528	.0291	1070	3.28
.0571	.0254	1600	2.58
.0619	.0214	2185	2.94
.0663	.0176	2855	2.88
.0711	.0135	3600	3.57
.0750	.0107	4595	2.79

rate constants were calculated for from five to twelve intervals so chosen as to give nearly equal pressure increases and until decomposition was 70 to 80% complete. The complete data of three typical runs are given in Table I.

In Table II is a summary of all of the runs with the exception of the first thirteen and runs 45 to 48, inclusive.

TABLE II
SUMMARY OF ALL RUNS

Number	Temp., °C.	Initial press., cm.	Number of constants	Average deviation	k_1 (sec. ⁻¹)
35	200.0	2.987	7	0.31×10^{-5}	9.71×10^{-5}
36	200.0	1.595	6	.56	9.98
37	200.0	0.2995	8	.21	6.62
34	200.0	.1464	6	.24	5.19
38	200.0	.0794	8	.23	4.27
33	200.0	.0317	5	1.08	4.15
18	210.05	1.520	11	0.14×10^{-4}	2.07×10^{-4}
16	210.0	0.956	9	.12	1.97
19	210.05	0.5825	12	.10	1.70
17	210.0	.2340	8	.11	1.45
21	219.9	1.520	7	.21	4.03
20	219.9	0.2620	10	.17	2.60
14	225.4	.763	7	.21	4.54
15	225.4	.111	5	.26	3.06
26	230.0	2.946	9	.42	8.35
25	230.0	1.505	6	.27	8.62
24	230.0	0.683	7	.26	7.40
29	230.0	.2945	7	.50	6.25
23	230.0	.2500	7	.26	5.23
27	230.0	.1652	6	.57	6.05
28	230.0	.0980	7	.34	4.59
22	230.0	.0560	4	.16	3.44
31	230.0	.0400	7	.24	2.95
32	230.0	.0296	5	.24	2.88
30	230.0	.0192	5	.23	2.93

TABLE II (Concluded)

Number	Temp., °C.	New Compound		Average deviation	k_1 (sec. ⁻¹)
		Initial press., cm.	Number of constants		
44	200.0	4.84	8	0.99×10^{-5}	9.12×10^{-5}
43	200.0	2.10	7	1.01	9.28
42	230.0	8.00	4	0.62×10^{-4}	7.02×10^{-4}
41	230.0	2.25	5	1.01	6.71
40	230.0	2.18	4	1.54	7.03
39	230.0	1.75	4	0.59	7.11
Added Surface 11.5 Times Original					
49	200.0	2.46	5	1.05×10^{-5}	8.93×10^{-5}
50	230.0	2.24	7	0.87×10^{-4}	7.09×10^{-4}

The first thirteen preliminary runs were carried out with an impure sample and a rough method of following the pressure. They differed but little from the later runs. Runs 45 to 48 will be discussed later.

While no trend in the constants during a given run was common to all of the runs, there seems often to have been a slightly higher rate at the start of the run as shown by run 17.

In runs 45 to 50 the surface was increased by adding Pyrex tubing, thus increasing the surface to volume ratio by 11.5 fold. The first run made after introducing the extra surface (Run 45) was 12% higher in rate but this effect disappeared gradually during the next three runs and then the rate constants were identical with runs made without extra surface. Earlier preliminary runs had likewise shown that opening the cell to the air or washing it out gave a slightly higher rate for the next two or three runs, so that apparently some conditioning of the surface or removal of impurities was necessary to eliminate catalysis completely. We conclude that the reaction rates reported were not influenced by the extent of wall surface and that the reaction is therefore homogeneous.

Runs 39 to 50 were made with a different sample of dimethyl-triazene and were made with the arrangement of apparatus described for the high-pressure measurements, while all the others reported were made with the low-pressure arrangement. Although the initial pressure to final pressure ratio was uniformly 2.175 for the first sample, it was not constant for these later runs but varied from 2.06 to 2.19. The experimental accuracy was not quite as good and they are all uniformly lower in rate than the earlier runs at similar pressures. It seems likely that this sample was impure. The metal stopcock became discolored and may have affected the sample. These runs show, however, that the first order rate constant has become independent of pressure above about 1 cm.

Interpretation of the Data

This reaction has the same characteristics as many other unimolecular reactions, namely, a true first order rate only at high pressures and a

falling of the first order rate constant at lower pressures. In Fig. 1 is plotted the log of the rate constant against the reciprocal of the absolute temperature. Only the rate constants at the higher pressures where the first order rate is independent of pressure have been used in this plot. From the slope of the best straight line through the points we find for the heat of activation $Q = 33,800$ cal. per mole. The equation for the high pressure rate constant is given by the expression $k_{\infty} = 4.05 \times 10^{11} e^{-33,800/RT}$.

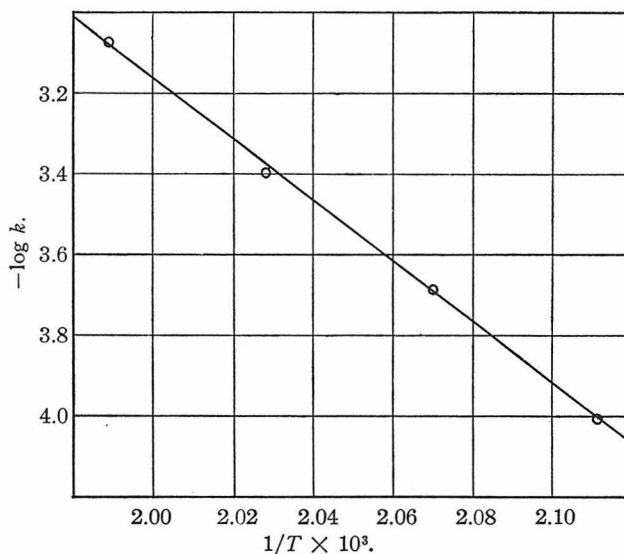


Fig. 1.

Figure 2 shows the usual plot of $\log k/k_{\infty}$ against $\log P$. The curves are theoretical and the points are the experimental values for the runs at 200 and 230° with the first sample. The lower curve is for Theory I and the upper two curves are for Theory II.⁷ The uppermost curve is for 200° and the other one close to it is for 230°. The number of squared terms chosen to fit the data best was 14 and the diameter of the molecule 10.0×10^{-8} cm. for Theory I and 6.0×10^{-8} cm. for Theory II. For Theory I the critical energy ϵ_0 is 39,800 cal. per mole and for Theory II $\epsilon_0 = 33,300$ cal. per mole. It is evident that it is not possible to decide definitely between the two theories on the basis of the data shown.

Discussion

During the past six years the experimental data on unimolecular reactions have been increased from one single reaction, namely, the decomposition of nitrogen pentoxide, to at least thirteen reactions that are

⁷ Rice and Ramsperger, *THIS JOURNAL*, 49, 1617 (1927).

now definitely recognized as being of this type. These reactions are listed in Table III. The pressure and temperature range over which they have been investigated are given and the constants in the rate expression $k_{\infty} = Ae^{-Q/RT}$ are listed. The values given for n designate the number of squared terms required to fit the data with either Theory II⁷ or Theory III.⁸ Ordinary kinetic theory diameters are used throughout.

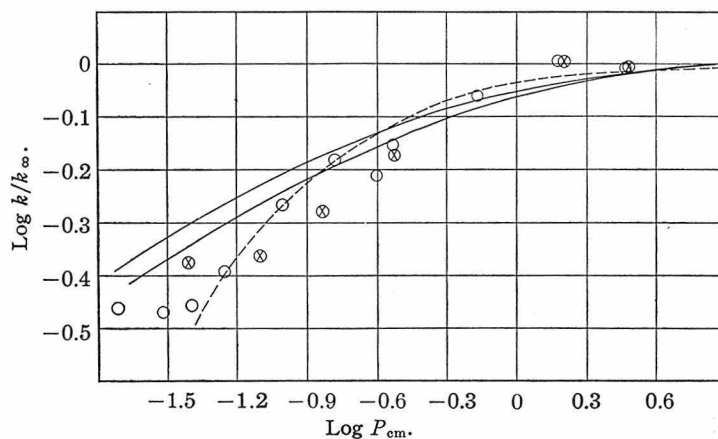


Fig. 2.

All but three of these thirteen reactions show a falling off in rate at low pressures. Of these three, ethylene oxide and pinene have not been investigated at sufficiently low pressures and azoisopropane is sufficiently complex a molecule that it is not required that its rate of decomposition fall off until very low pressures are reached. Thus from a qualitative point of view the experimental data are in complete accord with the present theoretical method of treatment. Furthermore, with the possible exception of the decomposition of nitrogen pentoxide, there is no quantitative disagreement with Theories II or III or their modified quantum treatments. As Kassel⁹ has indicated, it is possible even to account for the rate of decomposition of nitrogen pentoxide if one uses Kassel's quantum treatment¹⁰ and permits the use of a vibrational specific heat of at least 20 cal./mole and a molecular diameter of 17×10^{-8} cm. There are no specific heat data for nitrogen pentoxide but it seems likely that 20 cal./mole of vibrational specific heat will be found too high. In this connection it must be remembered that the requirement of an exact numerical agreement can be carried too far, since any actual molecule is not exactly of the type postulated either by the classical or quantum theory.

⁸ Kassel, *J. Phys. Chem.*, **32**, 225 (1928).

⁹ Kassel, *THIS JOURNAL*, **52**, 3972 (1930).

¹⁰ Kassel, *J. Phys. Chem.*, **32**, 1065 (1928).

TABLE III

Substance reacting	DATA FOR UNIMOLECULAR REACTIONS				
	P, cm.	T, °C.	A	Q, cal./mole	n
C ₂ H ₅ CHO ¹¹	2.0 to 40.0	450 to 600	$>1.38 \times 10^{12}$	54000	11
C ₂ H ₅ —O—C ₂ H ₅ ¹²	2.5 to 50.0	426 to 588	$>3.09 \times 10^{11}$	53000	6-8
CH ₃ —O—CH ₃ ¹³	3.0 to 90.0	422 to 552	1.52×10^{13}	58500	11-12
CH ₃ —O—C ₂ H ₅ ¹⁴	2.6 to 54.0	386 to 460	$>9.23 \times 10^{11}$	47000	9
CH ₃ —O—C ₃ H ₇ ¹⁴	2.2 to 33.6	400 to 450	$>2.21 \times 10^{12}$	49000	12
CH ₃ —N=N—CH ₃ ^{15,16}	0.026 to 70.79	278 to 327	1.07×10^{16}	51200	25
CH ₃ —N=N—C ₂ H ₇ ¹⁷	0.0058 to 13.12	250 to 332	2.80×10^{15}	47480	33
C ₃ H ₇ —N=N—C ₃ H ₇ ¹⁸	0.025 to 4.60	250 to 290	5.6×10^{13}	40900	>40
CH ₃ —N=N— NHCH ₃ ¹⁹	0.019 to 8.0	200 to 230	4.05×10^{11}	33800	14
d-Pinene ^{20,21}	17.0 to 116.0	184 to 237	5.40×10^{14}	43700	>20
Ethylene oxide ²²	2.4 to 90.5	378 to 445	9.9×10^{12}	52000	>14
N ₂ O ₅ ^{23,24,25}	0.00056 to 70.0	0 to 65	4.5×10^{13}	24700	30 ⁹
N ₂ O ^{26,27}	8.1 to 800	560 to 667	4.0×10^9	53000	2

The mass of evidence so far presented indicates strongly that activation is by collision and that reaction occurs when the critical energy becomes localized in a particular part of the molecule.

Summary

The thermal decomposition of dimethyl-triazene has been studied at temperatures from 200 to 230° and at pressures of 0.019 to 8.0 cm.

The reaction has been found to be homogeneous and first order at high pressures, but the rate begins to decrease at pressures below about 1 cm. and has dropped to about one-third of the high pressure value at the lowest pressures studied. The high pressure rate constant is given by the expression $k_{\infty} = 4.05 \times 10^{11} e^{-33,800/RT}$.

¹¹ Hinshelwood and Thompson, *Proc. Roy. Soc. (London)*, **A113**, 221 (1926).

¹² Hinshelwood, *ibid.*, **A114**, 84 (1927).

¹³ Hinshelwood and Askey, *ibid.*, **A115**, 215 (1927).

¹⁴ Glass and Hinshelwood, *J. Chem. Soc.*, 1805 (1929).

^{15,16} Ramsperger, *THIS JOURNAL*, **49**, 912, 1495 (1927).

¹⁷ Ramsperger, *ibid.*, **51**, 2134 (1929).

¹⁸ Ramsperger, *ibid.*, **50**, 714 (1928).

¹⁹ Ramsperger and Leermakers, *ibid.*, **53**, 2061 (1931).

²⁰ D. F. Smith, *ibid.*, **49**, 43 (1927).

²¹ Kassel, *ibid.*, **52**, 1935 (1930).

²² Heckert and Mack, *ibid.*, **51**, 2706 (1929).

²³ Daniels and Johnson, *ibid.*, **43**, 53 (1921).

²⁴ Ramsperger and Tolman, *Proc. Nat. Acad. Sci.*, **16**, 6 (1930).

²⁵ Schumacher and Sprenger, *ibid.*, **16**, 129 (1930).

²⁶ Volmer and Kummerow, *Z. physik. Chem.*, **9B**, 141 (1930).

²⁷ Nagasako and Volmer, *ibid.*, **10B**, 414 (1930).

The data can be fitted equally well by either Theories I or II of Rice and Ramsperger by using fourteen squared terms.

A table summarizing the present data on unimolecular reactions is given and discussed.

PASADENA, CALIFORNIA

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**THE GAS PHASE EQUILIBRIUM BETWEEN METHYL NITRITE,
HYDROGEN CHLORIDE, METHYL ALCOHOL, AND
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SPECTRUM OF NITROSYL CHLORIDE**

BY J. A. LEERMAKERS AND H. C. RAMSPERGER

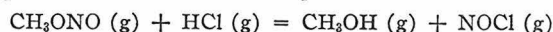
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Free energy values of organic substances will probably most often be obtained from heats of combustion and specific heat data by use of the third law of thermodynamics. They may, of course, be obtained with considerable accuracy from equilibrium data, but often a good equilibrium free from side reactions cannot be obtained with organic compounds. It is still more unusual to establish a gas phase equilibrium at room temperature. In the course of an investigation by the junior author to locate a gas phase reaction suitable for reaction rate research it was found that an equilibrium was very rapidly established between the gases listed in the title at room temperature. This was shown by the immediate partial disappearance of the color of nitrosyl chloride gas when added to an excess of methyl alcohol gas, and the appearance of the same color when hydrogen chloride gas was added to methyl nitrite gas. The thermodynamic data for the three gases, methyl alcohol, nitrosyl chloride and hydrogen chloride are quite accurately known so that from equilibrium measurements at two temperatures we are able to calculate the free energy of formation, the heat of formation and entropy of methyl nitrite.

Experimental Method

The equilibrium concentrations were obtained by quantitative measurements of the absorption of light in the spectral region 4000 to 5000 Å., where the absorption of nitrosyl chloride is quite strong. Of the other substances only methyl nitrite absorbs light in this region and then only faintly between 4000 and 4200 Å. From our determination of the absorption of pure nitrosyl chloride and methyl nitrite, the absorption of an equilibrium mixture of the four substances and the initial pressures of two of them it is possible to calculate an equilibrium constant for the reaction



Preparation and Purification of the Compounds.—Nitrosyl chloride was prepared by passing hydrogen chloride into nitrosyl sulfuric acid obtained from sulfur dioxide and fuming nitric acid.¹ The nitrosyl chloride was repeatedly distilled and collected at -20° to remove traces of hydrogen chloride and finally fractionally distilled through a column surrounded by a bath at -25° . The middle fraction boiling at $-6.0 \pm 0.2^\circ$ was used. This was distilled at a low temperature on a high vacuum line into a number of small tubes each drawn down to a capillary and maintained at -78° . When sufficient nitrosyl chloride had collected in a small tube, the supply was also cooled to -78° stopping the distillation and the tube was sealed off.

Methyl nitrite was prepared by dropping sulfuric acid into a stirred and gently heated mixture of sodium nitrite and methyl alcohol. The evolved gas was passed through fused calcium chloride and collected at -78° . The liquid was fractionally distilled through a column surrounded by ether cooled by solid carbon dioxide to about -30° and was collected at -78° . It boiled at a constant temperature of -17.0° and the middle portion was used. It was found necessary to eliminate traces of nitrogen dioxide since the strong characteristic absorption bands of this substance interfered with the measurements. A supply of pure methyl nitrite was obtained by allowing the gas to pass through a long tube containing soda lime into a one-liter storage flask sealed onto the vacuum system and previously evacuated. No bands of nitrogen dioxide were then found in the sample even when a pressure of the gas as high as 40 cm. was in the absorption tube.

The methyl alcohol used was Baker's Analyzed absolute methyl alcohol. This was further dried by refluxing over aluminum amalgam and was then fractionally distilled. It was placed in a small receiver equipped with a stopcock, sealed to the vacuum system, and enough of the vapor pumped off to displace all of the air.

Hydrogen chloride was obtained by dropping c. p. hydrochloric acid on concentrated c. p. sulfuric acid. The hydrogen chloride gas was passed through wash bottles containing concentrated c. p. sulfuric acid, then through a tube filled with c. p. anhydrous calcium chloride, and was collected in a half-liter flask equipped with a stopcock and a tube sealed to the bottom. When gas sufficient to displace the air had passed through the flask the stopcock was closed and the entrance tube sealed off. The flask was sealed to the vacuum system and the hydrogen chloride was frozen down by means of liquid air into the tube at the bottom. Any air left in the flask was then pumped off, the stopcock was closed, and the solid hydrogen chloride allowed to evaporate into the flask. It was used without further treatment.

The Absorption Curve of Nitrosyl Chloride and Methyl Nitrite.—A Pyrex absorption cell 4 cm. in diameter and 40.0 cm. long with plane parallel windows was filled with ni-

¹ Scott and Johnson, *J. Phys. Chem.*, **33**, 1975 (1929).

nosyl chloride or methyl nitrite gas as shown in Fig. 1. The absorption cell A was evacuated with a mercury diffusion pump through G. It was filled with nitrosyl chloride by breaking the capillary end of the tube B containing liquid nitrosyl chloride with the magnetic hammer C, or filled with methyl nitrite from the supply D.

The pressure was measured by a "clicker" system. The pressure on the "clicker"² sealed in the bottom of the bulb F was controlled by the variable leaks J and was measured by a McLeod gage having a compression of about eight-fold so as to read accurately pressures of several cm.

The absorption cell was then immediately sealed off just above the side tube. Capillary tubing was used to prevent too much reaction of nitrosyl chloride with the grease of the stopcock before sealing off.

Figure 2 shows the apparatus for photographing the absorption spectrum. Light from the 40-watt mazda lamp B operating under constant voltage passes through the diaphragm C which is covered with a ground glass, then through the partition D, the shutter E, the diaphragm F, the absorption cell H containing the absorbing substance, the diaphragm F', and finally into the slit of the spectrograph N. The cell is attached to the galvanized iron thermostat by the large rubber tubes at G and G' which slip over the brass tubes soldered into the ends of the thermostat. The cell has a side tube J (not shown in Fig. 1) used for freezing out the contents of the cell with liquid air. K is a heater and stirrer, L the mercury thermo-regulator and M is a thermometer which was calibrated against a Bureau of Standards thermometer.

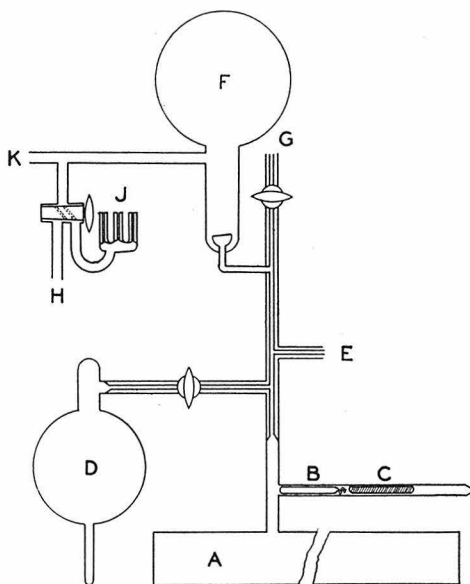


Fig. 1.

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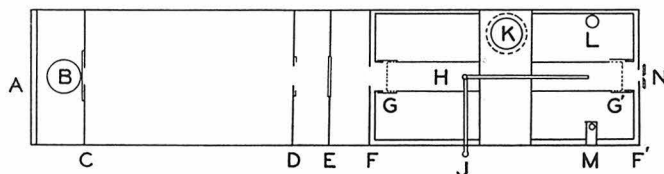


Fig. 2.

A series of spectra are photographed with the absorbing medium in the cell, the cell contents are frozen out, and then a series of photographs are taken on the same plate in between the first exposures. These latter exposures are given the same exposure time but are uniformly reduced in intensity for all wave lengths by placing screens of known absorption in the light path at D. The blackening of the photographic plate on two adjacent spectra is the same for those wave lengths for which the particular screen and the gas in the cell have the same absorption. Positions of equal intensity were deter-

² Smith and Taylor, THIS JOURNAL, 46, 1393 (1924).

mined by a method similar to that used by Ramsperger and Porter.³ The photometer system for this purpose is shown in Fig. 3. The photographic lens D projects an image of the plate in the holder C on the screen L with a magnification of about eight times. A high light intensity is obtained by the 500-watt projection lamp A and the condensing lenses B. A slit in the screen 2 cm. long and 2 mm. wide allows the light from a very narrow region of the spectrum to fall onto a cesium photoelectric cell E. F is a 45-volt battery, G a 10-megohm resistance, H a Leeds and Northrup high-sensitivity galvanometer with critical damping resistance J. With a scale at two meters, deflections of 6 to 20 cm. were obtained. The plate in the holder C could be moved either vertically or horizontally so as to bring the image of the spectra on the slit at any wave length. Points of equal deflection could be located with an accuracy of 2 to 5 Å. An iron arc spectrum served as a wave length reference. We wish to thank Professors Dickinson and Beckman of this Laboratory for the use of the screens which were constructed and calibrated by them. They determined the transmission of the screens by use of a thermopile and a constant light source.

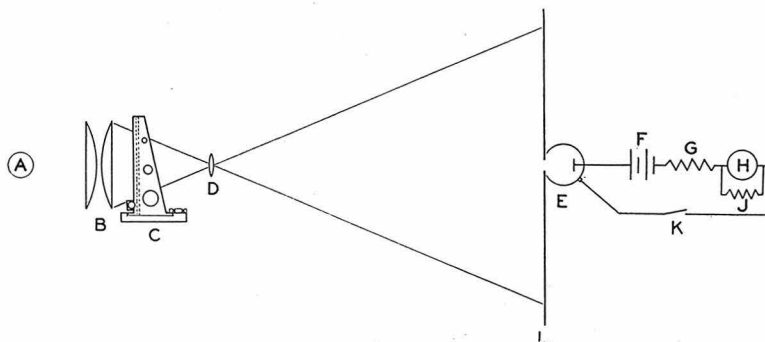


Fig. 3.

Table I gives the data obtained for the absorption of nitrosyl chloride and methyl nitrite at temperatures of 25 and 50°. The pressures are calculated to 25°. The absorption coefficients at the wave lengths listed are then calculated by assuming that Beer's law is obeyed over the range of pressure investigated. The relation used was $I_t/I_0 = 10^{-\epsilon cd}$ where I_t/I_0 is the fraction of light transmitted, c is the concentration expressed in cm. of mercury pressure at 25°, d is the length of the absorption cell (40.0 cm.) and ϵ is the absorption coefficient. Values of ϵ are plotted against the wave length in Fig. 4.

The small circles on the dotted line portion of the curve at 25° were estimated from the difference in galvanometer deflections from the nearest points of equal intensity on one of the plates. This region of the curve was not used in determinations of the equilibrium concentrations of nitrosyl chloride. The coincidence of several points at different pressures indicates that Beer's law is obeyed fairly well in the range studied.

The Partial Pressure of Nitrosyl Chloride at Equilibrium.—When nitrosyl chloride of concentration c and of absorption coefficient ϵ_1 is present

³ Ramsperger and Porter, THIS JOURNAL, 48, 1267 (1926).

TABLE I
POINTS OF EQUAL INTENSITIES (ÅNGSTRÖM UNITS) ON PHOTOGRAPHS TAKEN THROUGH SCREENS AND THROUGH NITROSYL CHLORIDE AND METHYL NITRITE AT VARIOUS TEMPERATURES AND PRESSURES

Screen no.	Light transmitted by screen	3.86 cm.		NOCl 11.02 cm.		8.44 cm.		CH ₂ ONO 41.84 cm.	
		25°	50°	25°	50°	25°	50°	25°	50°
2	0.459	4960	4940					4108	4115
		4530	4543						
		4520							
3	.2395	4170	4190					4065	4080
		4168 ^a							
4	.1032	4005	4010	4960	4945	4862	4855	4037	4045
		4007 ^a		4550		4255	4642		
				4505		4653	4432		
5	.0553			4850	4847	4186	4208	4018	4025
				4650	4647				
				4263	4406				
						4340			
						4295			

^a Duplicate plate to check accuracy.

in the same cell with methyl nitrite of concentration c_2 and absorption coefficient ϵ_2 the Beer's law expression becomes $I_t/I_0 = 10^{-(\epsilon_1 c_1 + \epsilon_2 c_2)d}$. If

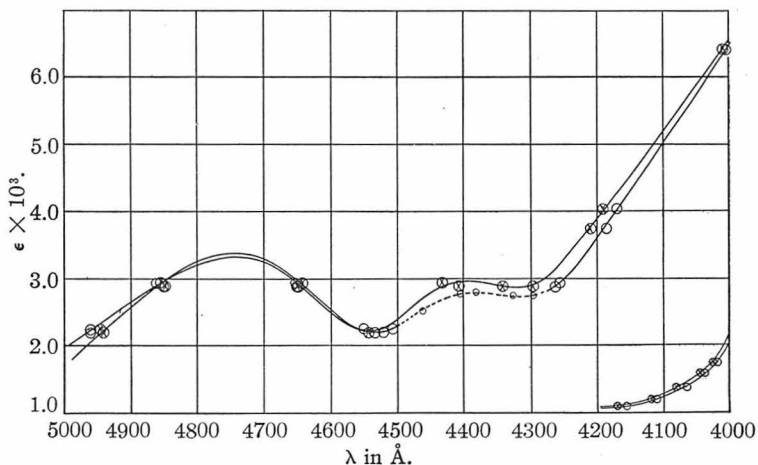


Fig. 4.—Absorption coefficients of nitrosyl chloride and of methyl nitrite plotted against wave lengths. The two upper curves are for nitrosyl chloride; those in the lower right-hand corner are for methyl nitrite. The open circles are for 25°, the circles enclosing crosses are for 50°.

the initial concentration of nitrosyl chloride is a and its equilibrium concentration after adding methyl alcohol is x , the expression becomes $I_t/I_0 = 10^{-\{\epsilon_1 x + \epsilon_2(a - x)\}d}$.

The same expression results if, in starting with methyl nitrite and hydro-

gen chloride, a is the initial concentration of methyl nitrite. The equilibrium concentration x can then be calculated from values of ϵ_1 and ϵ_2 obtained from the absorption curve for the wave length at which I_t/I_0 is measured.

The cell was filled with the two initial substances and their pressures were determined as described before and shown in Fig. 1. Methyl alcohol or hydrogen chloride was attached at E. Capillary tubing was used as indicated so that when the cell was sealed off just above the side tube no appreciable error was made in the partial pressures of gases admitted even though perfect mixing in the tubing had not taken place. The procedure in making the exposures and finding the points of equal intensity was similar to that for determining the absorption curves for the pure gases. Table II gives the complete data of two experiments. Table III gives a summary of all of the experiments.

TABLE II
SAMPLE EXPERIMENTS

Exposure	Absorbing medium	Points of equal intensity, Å.	Pressure NOCl
Expt. 4b. CH ₃ ONO, 4.03 cm.; HCl, 7.45 cm.; T, 50°			
1	Cell and contents	4235	2.43
2	Screen No. 2	4230	2.39
3	Cell and contents		
4	Iron arc source		
5	Cell and contents	4043	2.47
6	Screen No. 3	4037	2.44
7	Cell and contents		
			Average 2.43
Expt. 5a. CH ₃ ONO, 5.90 cm.; HCl, 3.07 cm.; T, 25°			
1	Cell and contents		
2	Screen No. 2	4125	1.69
3	Cell and contents	4123	1.69
4	Iron arc source		
5	Cell and contents		
6	Screen No. 3	4000	1.72
7	Cell and contents	4003	1.73
			Average 1.71

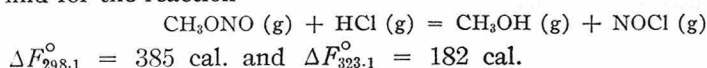
TABLE III
SUMMARY OF EXPERIMENTS

Expt. no.	Initial pressures, cm.				Pressure of NOCl at equilibrium		K_{298}	K_{323}
	CH ₃ ONO	HCl	NOCl	CH ₃ OH	25°	50°		
4	4.03	7.45			2.26 ± 0.04	2.43 ± 0.02	0.556	0.735
5	5.90	3.07			1.71 ± .01	1.88 ± .02	.513	.739
6			4.58	2.87	2.47 ± .02		.422	
7			4.56	4.14	2.04 ± .03	2.26 ± .03	.520	.785
8			12.70	3.44	9.64 ± .10	9.78 ± .09	.391	.596
12			6.02	4.06		3.44 ± .10		.764
13			4.75	4.19	2.14 ± .01	2.26 ± .06	.497	.620
14			4.20	3.76		2.07 ± .03		.744

Experiments 1 and 2 are not included because they were preliminary experiments made before the apparatus was in its final form. In Expts. 3, 9, 10 and 11 the total pressure in the cell was sufficiently high so that there was some evidence of condensation in each case. The equilibrium pressures of nitrosyl chloride are generally the average of four points. The average deviation from the average is shown by the \pm sign in columns 6 and 7. Equilibrium constants have been calculated by assuming the fugacities of the gases equal to their pressures. Experiments 6 and 8 deviate rather badly from the others listed. In these cases the concentration of methyl alcohol at equilibrium is very low, in fact so low that the estimated experimental error in the measurement of the nitrosyl chloride pressure will produce a very large error in the equilibrium constant. These experiments have not been used in obtaining an average equilibrium constant. Experiment 13 at 50° gives a constant which differs widely from the remaining constants at this temperature. No explanation is known for this discrepancy. The probable error of the average constant at 50°, if this value is excluded, is about equal to the probable error introduced by the probable errors in the measured pressures of nitrosyl chloride, while if this value be included the probable error of the average equilibrium constant is increased three-fold. We feel therefore that this value should likewise be excluded in obtaining an average equilibrium constant. When these values are excluded the average value of $K_{298.1} = 0.521$ and $K_{323.1} = 0.753$.

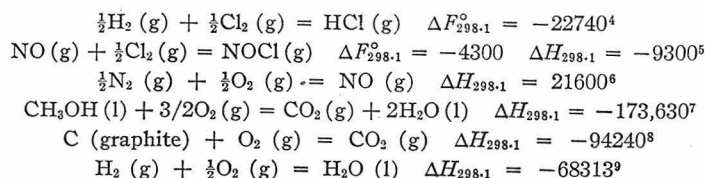
Evidence of a True Equilibrium.—We may present the following evidence that a true equilibrium free from side reactions has been obtained. The data of Table III show that the equilibrium constant is independent of the direction from which the equilibrium is established. It is independent of moderate variations in the partial pressure of the starting materials. No light-absorbing gas other than nitrosyl chloride or methyl nitrite (such as nitrogen dioxide) is likely to be present in appreciable amounts since the calculated concentration of nitrosyl chloride was the same at several wave lengths and any other absorbing gas would not likely have a characteristic absorption curve so very much like nitrosyl chloride. An experiment was carried out in which definite amounts of hydrogen chloride and methyl nitrite were mixed and the calculated pressure was obtained showing that no change in pressure occurred during the reaction. The equilibrium pressure of nitrosyl chloride as determined by its light absorption was found not to be changed on standing in the dark for an hour or on being illuminated for two hours.

Thermodynamic Calculations.—From the equilibrium constants we find for the reaction



Assuming ΔC_p zero over the range of temperature investigated $\Delta H_{298.1} = 2805$ cal. Then $\Delta S_{298.1}^\circ = 8.12$. The error in ΔF is quite small. The probable error of ΔH may be estimated roughly at 300 to 400 cal. and of ΔS about 1.0 entropy unit.

To calculate $\Delta F_{298.1}^\circ$, $\Delta H_{298.1}$ and $\Delta S_{298.1}^\circ$ for the reaction of formation of methyl nitrite from the elements and the entropy of methyl nitrite it will be necessary to make some choice of the available thermodynamic data of the other three substances occurring in the equilibrium. We have chosen the following data



Vapor pressure of $\text{CH}_3\text{OH}(\text{l})$ at $298.1^\circ = 122.2$ mm.¹⁰



The following values of the molal entropy at $T = 298.1^\circ$ and one atmosphere have been used for third law calculations

$\text{H}_2(\text{g}) = 31.23$	Giauque, THIS JOURNAL, 52, 4825 (1930)
$\text{C}(\text{graphite}) = 1.3$	Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, 1923, p. 464
$\text{N}_2(\text{g}) = 45.78$	Giauque, private communication
$\text{O}_2(\text{g}) = 49.03$	Giauque and Johnson, THIS JOURNAL, 51, 2300 (1929)
$\text{Cl}_2(\text{g}) = 53.3$	McMorris and Yost, <i>ibid.</i> , 53, 2625 (1931), footnote 2631
$\text{NO}(\text{g}) = 50.43$	Johnson and Giauque, <i>ibid.</i> , 51, 3194 (1929)
$\text{HCl}(\text{g}) = 44.64$	Giauque and Wiebe, <i>ibid.</i> , 50, 101 (1928)
$\text{CH}_3\text{OH}(\text{l}) = 30.3$	Kelley, <i>ibid.</i> , 51, 180 (1929)

The resulting data for the free energy, heat and entropy of formation at 298.1° and one atmosphere and the entropy of the four substances occurring in the equilibrium are listed in Table IV.

⁴ "International Critical Tables," McGraw-Hill Book Co., Inc., New York, 1930, Vol. VII, p. 233.

⁵ Dixon, *Z. physik. Chem.*, Bodenstein Festband, p. 679, July 15 (1931).

⁶ Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, 1923, p. 560.

⁷ Rossini, *Proc. Nat. Acad. Sci.*, 17, 343 (1931).

⁸ Roth and Naeser, *Z. Electrochem.*, 31, 461 (1925).

⁹ Rossini, *Bur. Standards J. Research*, 6, 1 (1931).

¹⁰ "International Critical Tables," McGraw-Hill Book Co., Inc., New York, 1928, Vol. 3, p. 216.

¹¹ Fiock, Ginning and Holton, *Bur. Standards J. Research*, 6, 881 (1931).

TABLE IV
CONSTANTS AND DATA FOR COMPOUNDS

	HCl (g)	NOCl (g)	CH ₃ OH (g)	CH ₃ ONO (g)
$\Delta F_{298.1}^{\circ}$	-22,740	16,400	-38,870	-100
$\Delta H_{298.1}^{\circ}$	-22,030	12,300	-48,290	-16,750
$\Delta S_{298.1}^{\circ}$	2.38	-13.8	-31.6	-55.9
$S_{298.1}^{\circ}$	44.64	60.3	56.7	64.2

Summary

Quantitative measurements of the light absorption of nitrosyl chloride and methyl nitrite have been made. Measurements of the light absorption due to nitrosyl chloride present in the gas phase equilibrium $\text{CH}_3\text{ONO (g)} + \text{HCl (g)} = \text{CH}_3\text{OH (g)} + \text{NOCl (g)}$ have been made and equilibrium constants calculated for the temperatures of 25 and 50° for both the forward and reverse reactions. The equilibrium is instantly established, is independent of the direction from which it is established and is free from side reactions. The equilibrium constants are $K_{298.1} = 0.521$ and $K_{323.1} = 0.753$. From these values and from thermodynamic data in the literature for hydrogen chloride, nitrosyl chloride and methyl alcohol we have calculated the free energy, the heat and the entropy of formation and the entropy of methyl nitrite.

PASADENA, CALIFORNIA

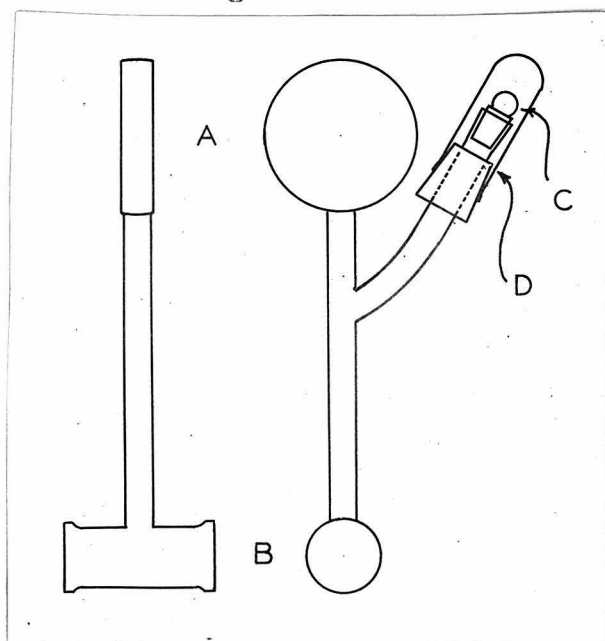
THE CHLORINE-SENSITIZED PHOTO-OXIDATION OF
TETRACHLOROETHYLENE IN CARBON TETRACHLORIDE SOLUTION

In 1821, Michael Faraday¹ 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 found² 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 by only the chlorine; it has been 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 work here described 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 Figure 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 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.

Figure 1



The Light Thermostat.- The thermostat was a galvanized iron tank of water provided with a motor-driven stirrer and an electric immersion heater; temperatures were read on a standardized thermometer and were kept constant to one-half degree or better. Light was admitted to the thermostat through a glass window built into one end. The reaction vessel was placed about 1 cm. from this window; it was so mounted that its position in the thermostat could be accurately reproduced from one experiment to another.

In experiments in which the mercury radiation $\lambda 4358$ 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-centimeter layer of 6% CuSO_4 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.

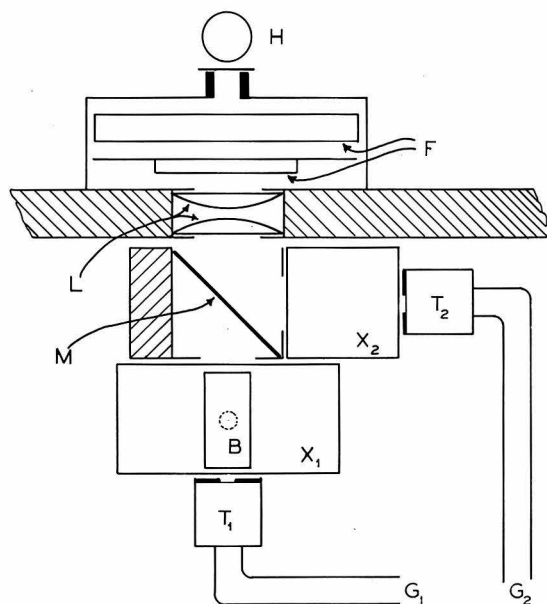
A series of experiments was made using the mercury line $\lambda 4358$; this was obtained from an upright type quartz arc placed just outside the thermostat (in a reproducible position) about

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 other strong Hg lines than λ 4358. Similar filters were used in the photometric analyzer.

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 monochromatic light experiment, the absorption of the solution for λ 4358 when in the thick cell (B) was measured with the apparatus shown in plan in Figure 2. The apparatus was designed to eliminate the effect of fluctuations of intensity of the light source.³ Light from a mercury arc H passed through a hole 1.0 cm. in diameter and then through a compartment containing the light filters immersed in running water. The light was rendered approximately parallel by the lenses L and then fell at about 45° 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 absorbing 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 absorber. 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 CCl_4); a tank X_2 of just the same thickness was placed in the other

beam. The thermopiles were connected to two high-sensitivity galvanometers G_1 and G_2 which could be read simultaneously.

Figure 2



The apparatus was used by determining, once for all, the ratio r_0 of the deflection of G_1 to that of G_2 when the absorption cell contained pure carbon tetrachloride, and later determining similarly this ratio r when the cell contained an absorbing solution. The transmission τ of the absorbing solution is evidently given by $\frac{r}{r_0}$. The concentration C of chlorine in mols per liter in the solution was obtained from the relation $C = -1/\epsilon d(\log \tau)$ where d , the cell thickness, was 3.30 cm., and ϵ , the molal absorption coefficient, was taken as 2.26.⁴ The transmission τ' of this solution in another cell of thickness d' is evidently given by $\tau' = (\tau)^{\frac{d'}{d}}$

MATERIALS

Carbon Tetrachloride.- The CCl_4 was obtained from Eastman's C. P. sulfur-free product. This was saturated with ClO_2 and allowed to stand 12 hours; it was then refluxed, washed with NaOH solution, washed several times with water, dried over C.P. calcium chloride and finally distilled using an all-glass fractionating column and condenser. When chlorine was dissolved in the product and illuminated, the solution gave a small amount of acid on shaking with water. The CCl_4 was therefore further treated by dissolving Cl_2 in it and illuminating for from 10 to 36 hours with a 500-watt lamp. After washing and treating as before the product was now 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 CCl_4 were used.

Tetrachloroethylene.- The C_2Cl_4 was obtained from Eastman's C.P. product. It was found that when a CCl_4 solution of Cl_2 was mixed with an excess of the original C_2Cl_4 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 C_2Cl_4 . It was accordingly further treated by passing Cl_2 into it and illuminating it. It was washed with NaOH 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 C_2Cl_4 concentrations; in these a small blank correction was applied.

Chlorine. The Cl_2 was taken from a commercial tank. It was passed successively through glass-connected wash bottles containing KMnO_4 solution, dilute H_2SO_4 , concentrated H_2SO_4 , glass wool, and finally desicchlora. The effluent gas was passed directly into CCl_4 in a glass-stoppered bottle. The chlorine solutions so prepared were found to be completely acid-free.

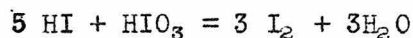
THE PRODUCTS OF THE REACTION

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 C_2Cl_4 and 0.075 molal in Cl_2 . 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 20 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 which we have made use of in following the reaction quantitatively.

Analysis for Acid. The method used in determining the number of equivalents of acid obtainable by hydrolysis of the illuminated solutions was as follows. The illuminated solution (containing, of course, free chlorine) was poured from the reaction vessel directly into a weighed, glass-stoppered flask containing about 30 cc. of water; the weight of the sample was obtained by difference. The solution and water were shaken together for five minutes. Fifteen cc. of 2% KI solution were added and the flask again shaken. The liberated iodine was just removed with 0.1 N thiosulfate using the disappearance of pink color from the carbon tetrachloride as end-point. Then 5 cc. of 4% KIO₃ solution were added, iodine being set free presumably according to the equation:



The number of cc. of standard thiosulfate necessary to discharge the color due to this additional iodine was determined.

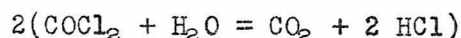
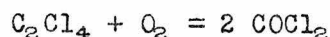
That any carbon dioxide (arising from the hydrolysis of phosgene) would have no effect on the titration was shown by the fact that an aqueous solution saturated with CO₂ gave no free iodine with KI and KIO₃. That sufficient time was allowed for the hydrolysis of the products of the photochemical reaction was shown by taking three equal samples from an illuminated solution. The first sample was shaken with water and treated as usual; the second was shaken with water containing a measured amount of dilute NaOH; the third was allowed to stand 18 hours with NaOH. In the last two cases,

the excess NaOH was removed by an excess of standard HCl and the titration finished with KI and KIO_3 as usual. The three samples yielded results in satisfactory agreement.

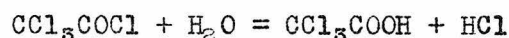
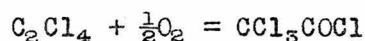
Dark Reaction.- Several solutions similar to those used for illumination were allowed to stand in the dark for periods exceeding the times required for the light experiments; one solution was as high as 3.2 molal in C_2Cl_4 , and another was kept at 36° . In no case was either chlorination or oxidation found.

Equivalents of Acid per Formula Weight of C_2Cl_4 . A series of experiments was made starting in each case with a solution of the same composition, viz. 0.0113 volume molal in C_2Cl_4 and 0.07 in Cl_2 . 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 C_2Cl_4 to COCl_2 .) 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. 3, in which the equivalents of acid found per formula weight of C_2Cl_4 taken are plotted as ordinates against the times of exposure in minutes as abscissae. 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 C_2Cl_4 concentration. With continued illumination the formation of acid-producing material ceases abruptly and before the C_2Cl_4 is at all completely oxidized to phosgene; for complete oxidation to COCl_2 would give four equivalents of acid per formula

weight of C_2Cl_4 in accordance with the equations:



Oxidation to trichloroacetyl chloride would, however, give two equivalents of acid per formula weight of C_2Cl_4 :

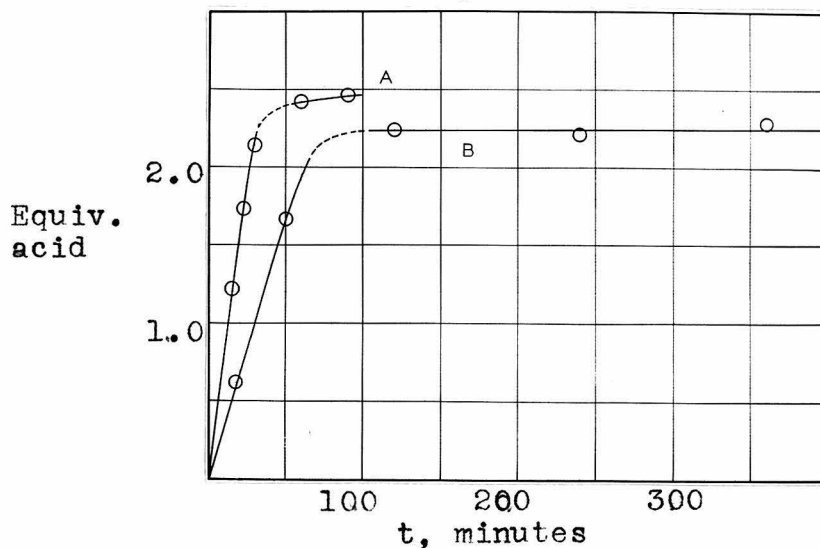


Since, in this series, the original solution was prepared volumetrically and the concentration of C_2Cl_4 was not known to better than a few percent, two more experiments were made with solutions carefully prepared by weighing. These gave, after 60 minutes of the same exposure as before, the values 2.22 and 2.28 for the equivalents of acid per formula weight of C_2Cl_4 .

In another series of measurements a solution 0.0113 molal in C_2Cl_4 and 0.05 molal in Cl_2 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. 3. The experiment makes it clear that the products of the oxidation of C_2Cl_4 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 C_2Cl_4 leads to the conclusion that 87.5% of the C_2Cl_4 oxidized goes to trichloroacetylchloride.

Figure 3 .



Isolation of Trichloroacetic Acid. An experiment was made to determine whether trichloroacetic acid could be isolated from the products of hydrolysis of an illuminated solution. Twenty cubic centimeters of a solution approximately 0.1 molal in C_2Cl_4 and 0.1 molal in Cl_2 were illuminated with the visible radiation from a mercury arc for 2 hours (the ultra violet was removed by a filter); the solution was frequently shaken with oxygen. At the end, the solution was shaken with 5 cc. of water and both liquids evaporated together at 40° ; When the volume had become small, the residual solution was placed in a desiccator over sulfuric acid. An extremely hygroscopic solid was finally obtained. A small amount of this was placed in a capillary tube which was then evacuated to remove water, and sealed off. Two separate samples so treated melted at 55° and 56° respectively; trichloroacetic acid melts at 57° . Furthermore, the solid gave a solution which was strongly

acid toward litmus. When heated with KOH solution and aniline it gave a distinct isocyanide odor.

Ratio of Acid to Chloride. An independent estimate of the fraction of the oxidation leading to trichloroacetylchloride 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 trichloroacetylchloride 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 CCl_4 solution were 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 hydrochloric acid but only a portion of the free chlorine. The aqueous layer was diluted to 30 cc. Ten cc. of this solution were titrated for free chlorine and then for acid using KI and KIO_3 and 0.01 normal thiosulfate. To another 10-cc. sample was added 1 cc. of 0.1 normal sodium sulfite to convert the free chlorine to chloride. The total chloride in this sample was then determined by electrometric titration with 0.01 normal AgNO_3 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 CCl_4 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 C_2Cl_4 which gives CCl_3COCl and $(1-x)$ the fraction which forms COCl_2 , then per formula weight of C_2Cl_4 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 values of x 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 trichloroacetylchloride.

TABLE I

Ratio of Acid to Chloride in Hydrolyzed Products

C_2Cl_4	Cl_2	Equiv. Acid in 10 cc. sample	Eq. 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
.0977	.07	11.18	6.84	1.63	.87
.097	.07	2.64	1.80	1.48	.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	<u>.84</u>
				Mean	0.86

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 λ 4358, 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 CCl_4 solution 0.05 molal in Cl_2 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 λ 4358

1 Expt. No.	2 C_2Cl_4 m/l	3 Cl_2 m/l	4 Temp.	5 Intensity cm. defl. of galv. $\frac{d}{t}$	6 Fraction or rad. absorbed $\frac{a}{t}$	7 Exposure time. min. $\frac{t}{t}$	8 Equivs. acid per g. soln $\frac{q}{g}$	9 Yield $\frac{q}{adt}$
1	0.0220	0.0619	20°	2.11	0.149	60	0.876×10^{-5}	0.0465×10^{-5}
2	0.0420	.0318	20	2.16	.081	120	1.022	.0489
3	0.0420	.0658	20	2.23	.159	60	1.062	.0500
4	0.0420	.0726	20	1.97	.172	60	1.059	.0520
5*	0.0420	.0987	20	2.74	.226	30	0.977	.0527
6	0.0420	.1147	19	0.567	.258	90	0.700	.0531
7	0.0420	.1260	20	2.65	.283	30	1.164	.0517
8	0.462	.0614	20	2.13	.150	60	1.558	.0813
9	0.881	.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	0.0420	.0755	3	1.52	.178	90	0.905	.0372
15	0.462	.0458	3	1.74	.112	90	1.033	.0589
16	0.0420	.1026	36	2.00	.235	40	1.248	.0664
17	0.462	.0582	36	2.18	.140	45	1.539	.1121

*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 constance 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 O_2 in CCl_4 given in the International Critical Tables, the concentration of O_2 in solutions saturated with air is calculated to be 0.002 molal.

Light Intensity. The rate of oxidation is proportional to 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 4-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:

$$\text{Rate} = kI_{\text{abs}}(1 + b(C_2Cl_4)^{\frac{1}{2}})$$

but at very high C_2Cl_4 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 C_2Cl_4 concentrations. The yields under various conditions are summarized in Table III. In the third and fifth columns are given the ten-degree multiplications of the yield. In the range studied, i.e., from 0.04 to 0.5 molal in C_2Cl_4 , 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 to either the specific rate constants or to the quantum yields.

TABLE III

Effect of Temperature on the Rate of Oxidation

Temperature	Yield at (C_2Cl_4) = 0.0420	$\frac{k_{T+10}}{k_T}$	Yield at (C_2Cl_4) = 0.462	$\frac{k_{T+10}}{k_T}$
3	0.0370×10^{-5}	1.21	0.0589×10^{-5}	1.21
20	0.0514	1.17	0.0813	1.22
36	0.0664		0.1121	

QUANTUM YIELDS

In view of the character of the dependence of the reaction rates on the C_2Cl_4 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, \underline{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 $56 \times 10^2 \underline{d}$ ergs per sq. cm. per sec. If now \underline{A} be the illuminated area of liquid (the entire liquid in the cell was illuminated) and \underline{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 \underline{t} minutes is $3.66 \times 10^{-13} \times 56 \times 10^2 \times \underline{a} \underline{d} \underline{A} \times 60 \underline{t}$. If \underline{q} be the equivalents of acid produced per gram of solution, $\underline{\rho}$ the density of the solution (1.59 g/cc), and \underline{l} the thickness of the solution in the cell, the equivalents of acid per $\underline{A} \underline{l}$ cc. of solution is $\underline{q} \underline{\rho} \underline{A} \underline{l}$. The quantum yield expressed in equivalents of acid per Einstein absorbed is then $64 \times 10^5 \times \underline{q} / \underline{a} \underline{d} \underline{t}$; 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 satisfactory.

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.cm. per sec. The results are given in Table IV.

TABLE IV

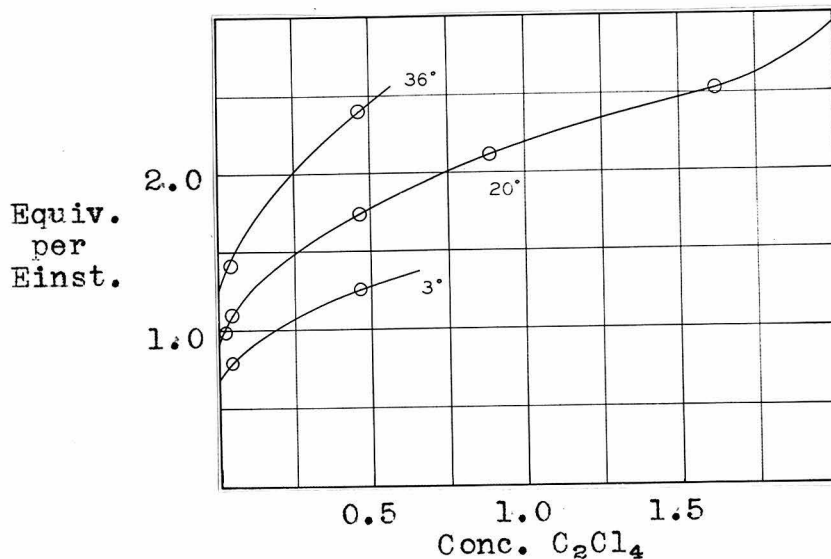
Quantum Yield Determinations at 20° - $\lambda = 4358 \text{ \AA}$

C_2Cl_4 m/l	Cl_2 m/l	Intensity ergs/cm. sq/sec	Fraction absorbed	Time min.	Total equivs. acid	Eq. Acid per Einstein
0.0420	0.0761	2340	0.729	232	1.34×10^{-5}	1.95
0.0420	0.0779	1570	0.737	301	1.36	2.25

The intensity given in column 3 has been corrected for reflection losses and represents the intensity of the radiation entering the solution. The 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 C_2Cl_4 to form CCl_3COCl this corresponds to 1.1 mols of C_2Cl_4 oxidized per Einstein absorbed at 20°. The values of the yields in Table II should be good to within a few percent relative to each other.

If they are all multiplied by a constant factor so as to give the yield 1.1 mols C_2Cl_4 per einstein at $(C_2Cl_4) = 0.0420$ and at 20° , the absolute yields shown in Fig. 4 are obtained.

Figure 4



DISCUSSION

As far as the present reaction has been studied, it is found to exhibit considerably 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;⁵ when, however, oxygen is present the chlorination of carbon monoxide ceases, and oxidation to carbon dioxide occurs instead. The rate of formation of carbon dioxide is given by the expression $\frac{d(CO_2)}{dt} = k I_{abs} (CO)^{\frac{1}{2}}$ when the pressures are low and when vessels with large surface are used.⁶

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 C_2Cl_4 or CO.

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.

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 trichloroacetylchloride and to phosgene occurs; most of the oxidation ($\approx 87\%$) leads to trichloroacetylchloride.

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 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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