[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 437]

The Chlorine-Sensitized Photochemical Oxidation of Gaseous Chloroform

BY ALAN T. CHAPMAN[1]

In the presence of oxygen, the chlorination of chloroform in carbon tetrachloride solution is very strongly inhibited. Instead the chlorine-sensitized oxidation to phosgene and hydrogen chloride occurs proceeding at a rate proportional to the first power of the light intensity and the chlorine concentration, but independent over wide variations of both the chloroform and the oxygen concentrations.[2]

Preliminary qualitative experiments indicated that this sensitized oxidation occurred with even greater rapidity in the gaseous state. The relatively high vapor pressure of chloroform at room temperature coupled with the lack of any but gaseous products insured the opportunity of investigating this reaction over a wide range of conditions. In addition the study suggested itself as a means of a more thorough understanding of the oxidation process of comparatively simple organic compounds.

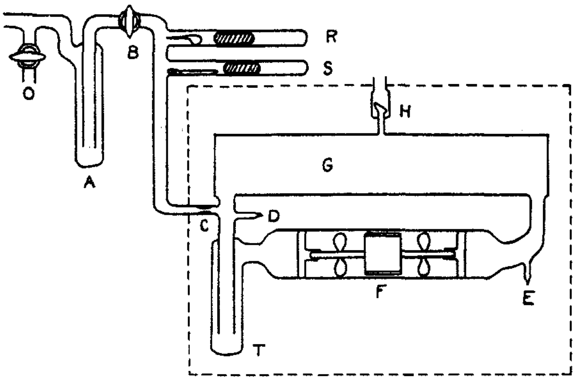

Fig. 1.—Reaction vessel and accessories.

Reagents.—A good grade of chloroform was carefully purified free from alcohol, dried over C. P. calcium chloride, and twice distilled in the dark in an all-glass distilling apparatus. The product was introduced immediately into small weighed glass bulbs whose tips were then sealed. The chlorine was freed from traces of hydrogen chloride, thoroughly dried over several desiccating agents, and then liquefied in small weighed glass tubes provided with tips which could be readily broken. Bottles containing concentrated sulfuric acid and calcium chloride were used to dry the oxygen taken from a commercial cylinder before introducing directly into the system.

Apparatus and Procedure.—In order to prevent the exposure of the reacting gases to any material other than glass, an apparatus diagrammed in Fig. 1 was constructed. The cylindrical reaction vessel G was 40 cm. in length and 3.7 cm. in diameter. Later measurements on the effect of light intensity were made with a 500-cc. spherical Pyrex flask. A mercury vapor pump evacuated the system. The chloroform and chlorine bulbs (R and S) were broken by magnetically operated glass enclosed hammers, the gases immediately condensing in the liquid air trap T. Oxygen was introduced through stopcocks O and B. The system was isolated by sealing the constriction at C. The pressure of oxygen was noted, the liquid air trap removed, and then, when thermal equilibrium was attained, the total pressure of oxygen, chloroform and chlorine was observed.

Circulation of the gas was accomplished by means of the all-glass stirring device F which will be described in detail elsewhere.[3] Briefly it operated on the principle of a three-phase induction motor employing a "squirrel-cage" armature enclosed in glass. Temperature control was secured by means of an air thermostat indicated by the dotted line in Fig. 1.

Pressure measurements were made with the aid of a glass diaphragm clicker gage H used in conjunction with a mercury manometer. The precision was of the order of ±0.1 mm.

The thermostat was provided with a window admitting radiation from either a 500-watt incandescent projection lamp, or an upright-type Pyrex mercury arc. A 6% aqueous solution of copper sulfate, and in addition with the arc, Corning glasses "Noviol A" and "blue-purple ultra" immersed in a water trough served as light filters. In all cases the light was well collimated.

After the reaction, the final oxygen pressure was recorded by replacing liquid air on trap T. The system was then flushed out with dry nitrogen through tips D and E into wash bottles containing successively potassium iodide solution, hot water, and two additional potassium iodide solutions. The method of analysis has already been described.[4]

A 500-cc. spherical Pyrex flask with all the necessary accoutrement except the stirrer and manometer proved useful in carrying out experiments in sunlight or in darkness.

Inhibition of Chlorination; Thermal Oxidation.—Preliminary experiments in which the gases stood for two to four hours in darkness showed no pressure increase—evidence for the exclusion of appreciable thermal oxidation.

The chlorination reaction, however, was not excluded, since this is accompanied by no pressure change. After standing for four hours in darkness, in no case was acid discernible in excess of that attributable to a small experimental error.

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(1) National Research Fellow in Chemistry.

(2) A. T. Chapman, THIS JOURNAL, 56, 818 (1934).

(3) A. T. Chapman, *Rev. Sci. Inst.*, not yet published.

(4) Ref. 2, p. 819.

The close agreement between the moles of chlorine determined by analysis and that originally introduced into the vessel substantiated the fact that an appreciable thermal chlorination reaction did not occur, and that the photochlorination process was inhibited completely. No correction was made, therefore, in later experiments for either a chlorination or a thermal oxidation reaction.

Chloroform Oxidation with White Light.—In Fig. 2 the pressure increase in millimeters of mercury is plotted as ordinates against exposure time in minutes as abscissas. Since an excess of oxygen was present, the total pressure increase and likewise the oxygen pressure decrease should be equal to one-half the initial chloroform pressure according to the reaction

$$CHCl_3 + {}^1/_2O_2 = HCl + COCl_2 \qquad (1)$$

Table I summarizes the data of a number of experiments in which the projection lamp served as the light source.

TABLE I

COMPLETE OXIDATION OF CHLOROFORM WITH WHITE LIGHT, T = 25.0°

A. Analytical Measurements

Expt.	Mole × 10^3 CHCl$_3$	Cl$_2$	Oxid. yield	Acid yield	Moles acid/ moles CHCl$_3$	Exposure time, min.
10	0.898	2.46	2.44	2.60	2.89	191
11	.987	2.46	2.40	2.84	2.88	530
13	1.05	2.12	2.08	2.90	2.76	287
14	1.33	2.63	2.49	3.88	2.92	391
15	1.69	3.78	3.62	4.48	2.66	306
16[a]	1.13	2.55	2.34	0.03	..	142
17	1.85	4.50	4.39	5.33	2.88	292

B. Pressure Measurements

Expt.	Initial pressure, cm. p_{CHCl_3}	p_{Cl_2}	p_{O_2}	p_t	$\Delta p_t/p_{CHCl_3}$	$\Delta p_{O_2}/p_{CHCl_3}$
10	2.43	6.73	10.56	19.72	0.482	0.463
11	2.71	6.78	5.50	14.99	.483	.493
13	2.86	5.73	5.63	14.22	.487	.497
14	3.67	7.13	5.82	16.62	.487	.477
15	3.80	8.64	7.74	20.18	.461	.500
16[a]	2.58	5.88	7.75	16.21	.000	.000
17	4.23	10.45	8.97	23.65	.475	.478

[a] Carbon tetrachloride instead of chloroform.

Columns 4A and 5A give the oxidizing strength and the acidity as determined by analysis. According to Eq. 1 complete oxidation of chloroform should produce three equivalents of acid per mole of chloroform.

Chloroform Oxidation with Sunlight.—The fact that the theoretical value of 0.5 for the $\Delta p_t/p_{CHCl_3}$ and the $-\Delta p_{O_2}/p_{CHCl_3}$ ratios and of 3.00 for the ratio M_{Acid}/M_{CHCl_3} were never quite attained, suggested that the exposure times were insufficient. Fifteen experiments were performed in sunlight for one to five days with the simplified reaction vessel.

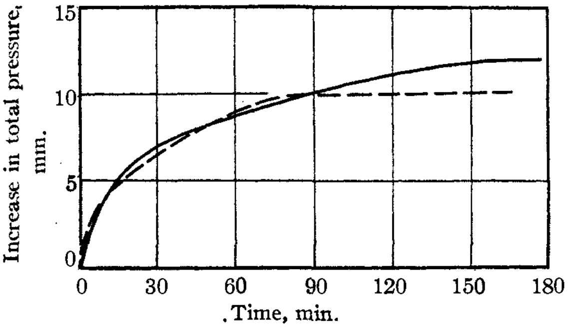
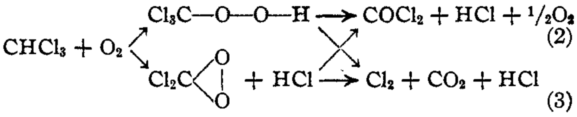


Fig. 2.—Broken line, Expt. 10; continuous line, Expt. 11.

The results of these experiments differed from those given in Table I in the appearance of an oxidizing strength in excess of that of the chlorine originally introduced, and a corresponding loss in total acidity compatible with the equations



No positive peroxide tests were obtained. Neither phosgene nor carbon tetrachloride was oxidized under the same conditions.

In a few examples at least 50% of the oxidation appeared to proceed by reaction (3). The cause of such behavior particularly in contrast to the "white light" experiments will be determined by a complete study of the sensitized oxidation of chloroform with sunlight under more critical conditions. The possibility of the intermediate peroxide as a new light absorbing constituent should be considered.

Kinetics of the Reaction.—Table II summarizes the effect of the various factors on the rate of oxidation. Experiments marked (*b*), (*c*), etc., give partial pressures of chloroform and oxygen computed from the initial partial pressures (*a*) on the basis that the reaction proceeds entirely to phosgene and hydrogen chloride.

Chloroform Concentration.—The partial pressure of chloroform was varied six-fold. The rate constants show no direct dependence on this concentration until the partial pressure of chloroform fell to the lowest values studied. At low pressures the rate of oxidation approaches a dependence on the half power of the chloroform concen-

TABLE II

RATE OF CHLOROFORM OXIDATION WITH λ4358 Å.; T, 25°

Expt.	$p_{\mathrm{CHCl_3}}$, mm.	$p_{\mathrm{Cl_2}}$, mm.	$p_{\mathrm{O_2}}$, mm.	p_{t}	dp/dt mm. × min.$^{-1}$ a	I_x/I_0 trans. of screen b	$I_{\mathrm{abs.}}/I_x$ c	k a/bc	k' $k/(p_{\mathrm{CHCl_3}})^{1/2}$
18 (a)	47.7	101.8	83.2	232.7	8.54	1.000	0.184	4.64	6.72
(b)	41.0		79.9	236.0	5.17	0.459		6.14	9.60
(c)	37.4		78.1	237.8	2.58	.2395		5.87	9.59
(d)	35.8		77.3	238.6	0.820	.1032		4.27	7.12
(e)	30.7		74.8	241.1	8.43	1.000		4.58	8.28
19 (a)	72.9	92.1	97.7	262.7	12.9	1.000	.167	7.72	9.04
(b)	65.3		93.9	266.5	5.12	0.459		6.64	8.21
(c)	59.4		90.9	269.5	2.35	.2395		5.87	7.61
(d)	55.7		89.0	271.4	0.883	.1032		5.12	6.87
(e)	53.6		87.9	272.5	12.3	1.000		7.37	10.1
20 (a)	24.4	97.8	87.7	209.9	10.2		.178	5.73	11.6
(b)	17.0		84.0	213.6	6.82			3.83	9.32
(c)	12.0		81.5	216.1	5.74			3.22	9.32
21 (a)	49.2	56.0	87.0	192.2	7.71		.106	7.27	10.4
(b)	42.4		83.6	195.6	10.7			10.2*	15.7
(c)	36.6		80.7	198.5	5.13			4.84	8.00
23 (a)	63.8	57.2	155.0	276.0	7.53		.107	7.03	8.78
(b)	52.0		149.0	281.9	11.0			10.3*	14.3
(c)	44.3		145.2	285.8	7.52			7.03	10.5
24 (a)	19.6	36.6	41.0	97.2	4.00		.070	5.72	12.9
(b)	15.6		39.0	99.2	3.88			5.53	14.0
25 (a)	63.3	61.5	59.6	184.4	14.8		.117	12.7*	16.0
(b)	50.3		53.1	190.9	10.2			8.72	12.3
26 (a)	22.7	109.9	85.0	217.6	12.2		.196	6.22	13.0

Expts. marked with asterisk, $T = 35.0°$; both constants k and k' contain the constant I_0, the intensity of radiation at the screen.

tration.[5] The constants, k', have been computed on this basis.

Oxygen Concentration.—When oxygen in excess of that necessary for the reaction was present, no evidence whatsoever was observed to show any dependence on this factor. With a limited amount of oxygen Schumacher and Wolff[6] have found the chlorination of chloroform to be inhibited. After the oxygen has been consumed, the reaction proceeds without further change in pressure.

Chlorine Concentration.—The chlorine concentration has been varied three-fold. The rate of oxidation is directly proportional to the first power of the chlorine concentration. The chlorine acts solely as the light absorbing agent. The absorption was maintained below 20% in all cases and was computed using the value of 1.64[7] as the molal absorption coefficient of gaseous chlorine.

Light Intensity.—The effect of light intensity on the oxidation rate was determined by inserting calibrated screens. Every reasonable precaution was taken to keep the mercury arc constant. The coherence of the rate constants for Expts. 18 and 19 in which the relative light intensity, I_x/I_0, was varied nearly ten-fold, shows that the rate of oxidation is directly proportional to the first power of the intensity of the incident light.

Temperature.—In Expts. 21, 23 and 25 the temperature was varied during the course of the reaction. The average of the temperature coefficient, $(k_{\mathrm{t}+10})/k_{\mathrm{t}}$, was found to be 1.44.

Quantum Yield.—The general reproducibility of the quantum yield for the liquid phase chlorine-sensitized oxidation of chloroform suggested the use of this reaction as a suitable actinometer. The mercury arc was used as the radiation source. Corrections were applied for reflection losses, temperature coefficients and for the interposition of calibrated screens in the first two experiments. The absorption of light by chlorine in carbon tetrachloride solution was computed using the value 2.26[8] as the molal absorption coefficient. The results are given in Table III.

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[5] Recently Schumacher and Wolff (*Z. physik. Chem.*, **B26**, 453 (1934)) have studied this reaction and find the rate to depend on $(\mathrm{CHCl_3})^{1/2}$ at all pressures.

[6] Schumacher and Wolff, *ibid.*, **B25**, 170 (1934).

[7] Von Halban and Siedentopf, *ibid.*, **103**, 81 (1922).

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

TABLE III

QUANTUM YIELDS WITH λ 4358 Å.; T, 25.0°

Q. Y. for Actinometer = 1.70 equiv. acid/einstein

Expt.	Mole × 10^3 Acid$_r$ a	Acid$_a$ b	$(I_{abs.}/I_0)_r$ c	$(I_{abs.}/I'_0)_a$ d	Q. Y. equiv. acid/einstein 1.70×0.635 $ad(1-c)/bc$
18	3.08	3.82	0.184	0.867	334
19	5.18	10.1	.167	.850	235
20	3.80	5.61	.178	.849	286
21	2.68	4.98	.106	.833	408
22	2.05	6.34	.141	.820	175
23	2.93	4.95	.107	.844	452
25	2.85	9.03	.117	.840	216
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Area$_a$/area$_r$ = 0.635; subscripts "r" and "a" refer to gaseous reaction and actinometer, respectively; I_0 and I'_0 are the incident light intensities at the reaction vessel and at the actinometer.

The variations in quantum yields of about a three-fold magnitude cannot be correlated. The average value is approximately 300 moles of acid formed, or 100 moles of chloroform oxidized per einstein of absorbed radiation.

Discussion and Mechanism.—The relatively high quantum yield leaves no doubt that the oxidation proceeds by a chain mechanism. As in the case of the liquid phase reaction, both the rates and the quantum yield are somewhat smaller than those for the tetrachloroethylene oxidation.[9]

A unique solution to the problem of a mechanism for the oxidation of chloroform has not as yet been found. The chain may be started with either ClO_2 or CCl_3 formed in the second step. Since the oxidation rate varies with intensity in a manner different from the chlorination[10] the chain breaking step is supposedly somewhat different.

The author wishes to express his appreciation to Professor R. G. Dickinson for the interest which he has taken in this study and for the frequent helpful suggestions.

Summary

The oxidation of chloroform with chlorine as the photosensitizer proceeds without accompanying thermal or chlorination reactions; the products formed are phosgene and hydrogen chloride.

The rate of oxidation for small light absorptions is found to be proportional to the first power of the light intensity, the first power of the chlorine concentration, and independent of the concentrations of chloroform and oxygen. At low concentrations of chloroform a dependence on the half power is observed.

The temperature coefficient has been determined. The quantum yield is approximately 100 moles of chloroform oxidized per einstein of radiation absorbed.

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[9] Dickinson and Leermakers, THIS JOURNAL, **54**, 3852 (1932); Dickinson and Carrico, *ibid.*, **56**, 1473 (1934).

[10] Ref. 6, p. 169.

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The Peroxidation of Chloroform

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In 1848 Morson[2] observed that "pure" chloroform underwent a decomposition in the presence of light and air with the production of chlorine, hydrochloric acid and probably other "chlorine compounds."[3] The presence of phosgene as one of the principal products leaves no doubt that the reaction is one of oxidation.

The study of the oxidation of chloroform has a two-fold objective—(1) to determine by careful analysis the reactions involved, and (2) to apply the results in a more complete understanding of the kinetics and mechanism of the photo-sensitized oxidation of chloroform.[4] Since the results of the latter objective have already been treated this paper will be concerned in particular with the former.

Reagents.—Chloroform was purified according to methods previously described.[5] All other reagents used were of C. P. quality.

Procedure.—The procedure followed in order to eliminate a large amount of complicated apparatus, consisted in filling glass-stoppered bottles one-third to one-half full of chloroform, and placing them in a source of diffuse light. Bottles which were lacquered black were used in the study

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[1] National Research Fellow in Chemistry.

[2] Morson, *Pharm. J.*, **8**, 69 (1848).

[3] For summary of the earlier work see Baskerville and Hamor, *J. Ind. Eng. Chem.*, **4**, 212, 278, 362, 422, 499, 571 (1912).

[4] Chapman, THIS JOURNAL, (a) **56**, 818 (1934); (b) **57**, 416 (1935).

[5] Ref. 4b, p. 416.