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	Mole × 10^3 Acid$_a$ b	$(I_{\text{abs.}}/I_0)_r$ c	$(I_{\text{abs.}}/I_0')_a$ d	Q. Y. equiv. acid/einstein $1.70 \times 0.635\ ad(1 - c)/bc$
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
					Av. 301

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.

[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 438]

The Peroxidation of Chloroform

BY ALAN T. CHAPMAN[1]

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.

of the thermal oxidation. Care was taken that no direct sunlight fell on any of the bottles during the day. The bottles were shaken frequently to saturate the chloroform with air.

Analysis was carried out by pipetting a 1-cc. sample from a bottle and introducing it immediately into an iodine flask containing aqueous potassium iodide solution. The iodine liberated was titrated with dilute (0.01–0.05 *N*) sodium thiosulfate solution using the purple starch color as the end-point. This titration gave the total oxidizing strength of the solution, *i. e.*, the chlorine content plus the peroxide content. The solution was boiled in order to remove the carbon dioxide resulting from the hydrolysis of the phosgene, cooled, and then potassium iodate was added. The acid content was determined by the titration of the additional iodine liberated.

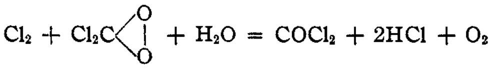
For a more complete analysis another 1-cc. sample was pipetted into a separate flask containing an excess of 0.01 *N* potassium permanganate solution acidified with dilute sulfuric acid. After shaking thoroughly, the excess permanganate was treated with potassium iodide solution and the iodine titrated as before. This enabled, therefore, the calculation by difference of the fraction of the total oxidizing strength which was peroxide.

Products of the Reaction.—The characteristic odor disclosed the presence of phosgene.

The most satisfactory test for a peroxide in the presence of chlorine consists in treating the chloroform sample with two drops of a 10% solution of titanium sulfate in dilute sulfuric acid.[6] A positive peroxide test was obtained with all samples of purified chloroform within one to two weeks after placing them in bottles.

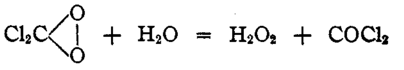
That the peroxide is not hydrogen peroxide is evidenced by the fact that the former reacts rapidly with aqueous potassium iodide solution. To explain this phenomenon Clover[7] suggested that the compound formed was dichloro-carbon peroxide, CO_2Cl_2.

A peroxide sample which has been agitated thoroughly in water, liberates iodine slowly upon the addition of potassium iodide. Under these conditions the chlorine present oxidizes the peroxide, liberating acid at the expense of the oxidizing strength according to the reaction



$$Cl_2 + Cl_2C\langle{}^{O}_{O}| + H_2O = COCl_2 + 2HCl + O_2 \quad (1)$$

The excess peroxide is converted to hydrogen peroxide



$$Cl_2C\langle{}^{O}_{O}| + H_2O = H_2O_2 + COCl_2 \quad (2)$$

Table I gives the results of having potassium iodide present initially in solution, and of adding it after the sample has been treated with water. The total number of equivalents in either case should be the same.

TABLE I

EFFECT OF WATER ON THE PEROXIDE

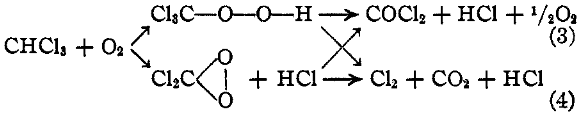
Concentrations in equivalents per liter

	KI present initially		KI added later	
Oxid. str.	0.1756	0.1310	0.0225	0.1134
Acidity	.1032	.0656	.2552	.0816
Total	.2788	.1966	.2777	.1950

In contradistinction to the evidence of the peroxide formation, the results of Chatterji and Dhar[8] on the oxidation of chloroform in tropical sunlight show the presence of chlorine among the decomposition products.

A very sensitive qualitative test for chlorine in the presence of a peroxide consists in using tetramethyl base paper.[9] Positive free chlorine tests of this nature were obtained *simultaneously* with positive peroxide tests. This evidence proves the coexistence of both chlorine and peroxide in chloroform solution.

In view of these facts the reaction scheme



is proposed. Since isolation[10] of the compound was unsuccessful no direct analysis was secured. It is not unreasonable to assume that both peroxides are formed during the oxidation process and that one leads to the final products of Eq. 3 and the other to those of Eq. 4.

Thermal Reaction.—In Fig. 1 the peroxide, chlorine, and acid concentrations expressed in equivalents per liter are plotted as ordinates against the exposure time in days as abscissas. The pronounced feature of this and succeeding figures is the gradual increase of the oxidizing strength (composed of the sum of the chlorine and peroxide concentrations) to a certain maximum value from which it decreases rapidly to a negligible value. As two or three months are often required for this maximum to be reached, the exact peak could not in general be determined without exhausting the solution by continual sampling. This rapid decomposition of the peroxide

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[6] Treadwell-Hall, "Analytical Chemistry," John Wiley and Sons, N. Y., 1927, Vol. I, pp. 89 and 168.

[7] Clover, THIS JOURNAL, **45**, 3133 (1923).

[8] Chatterji and Dhar, *Z. anorg. allgem. Chem.*, **191**, 155 (1930).

[9] This paper was made by dipping strips of filter paper in a dilute alcoholic solution of tetramethyl-di-*p*-diaminodiphenylmethane. Mellor, "Comprehensive Treatise on Inorganic and Physical Chemistry," Longmans, Green and Co., London, 1922, Vol. I, p. 950.

[10] Distillation increases the strength of the peroxide about twofold but caused decomposition on further concentration.

certainly takes less than a day to reach completion. The decomposition produces a large amount of phosgene and hydrogen chloride, occasionally forcing the stopper from the bottle. If the solution is then replenished with oxygen, further significant oxidation does not occur.

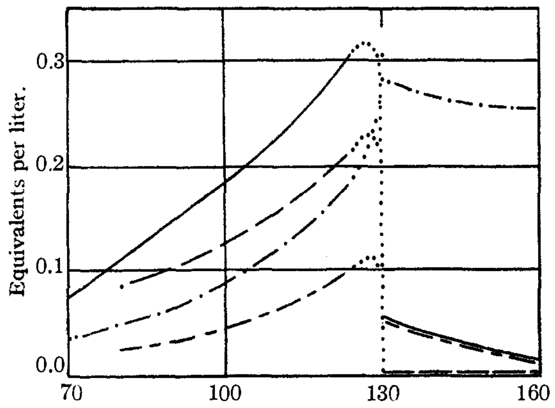

Fig. 1.—Thermal oxidation of chloroform: ——— total oxidizing strength, — — — peroxide concentration, —·—· acid concentration, ———— chlorine concentration, ······· unanalyzed portion.

The chlorine produced by this thermal reaction does not disappear as rapidly as the peroxide, but it slowly chlorinates the chloroform.

Figure 2 summarizes the data on a number of thermal reaction experiments. If reaction (3) or (4) proceeded only to the intermediate peroxide stage, the ratio of the total oxidizing strength to the acidity should be 2.00.[11] The data indicate a considerable amount of oxidizing strength in addition to that attributable to peroxide, which must come from a substantial fraction of the reaction yielding chlorine by Eq. 4. Later in the course of the peroxidation this ratio generally falls below 2.00 before the sudden decomposition takes place. The increasing predominance of Eq. 3 yielding acid in the form of phosgene and hydrogen chloride explains this behavior.

Light Reaction.—Experiments in which both the liquid and the gas phase were subjected to a source of diffuse light, differ from the thermal experiments primarily in that the maximum oxidizing strength is about half as great and is reached in about half the time. The accelerated rate is accounted for by the light absorption of the chlorine produced in the initial thermal reaction. The ratio of the oxidizing strength to the acidity follows the same general course as before. Upon the completion of the reaction, the chlorine disappears rapidly.

The solution develops a greenish-yellow color which disappears at the time of the sudden decomposition. Photometric analysis to ascertain whether this color was attributable to the chlorine or to the peroxide, failed as the color vanished on exposure to an intense source of light.

By covering one-half of the bottle, the effect of the light on the liquid or the gaseous chloroform could be determined independently. The data showed that for the same period of illumination nearly twice the concentration of peroxide can be obtained by exposure of the gas phase instead of the liquid phase.

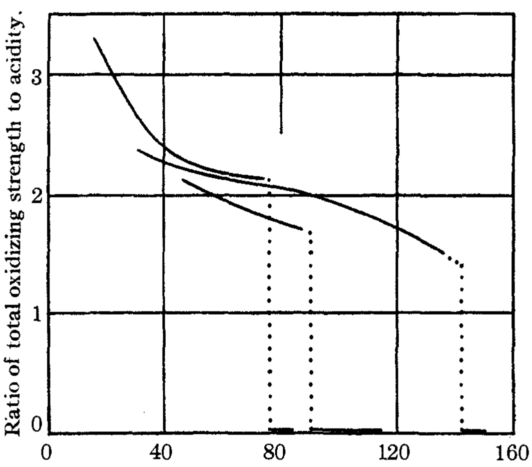

Fig. 2.—Peroxide concentration in thermal reaction. Each curve represents a separate experiment.

Effect of Oxygen, Phosgene, Chlorine and Carbon Tetrachloride.—A sample in which the chloroform was saturated with oxygen instead of air and then was exposed to diffuse light displayed the usual behavior.

An experiment (25 cc. of $CHCl_3$, 25 cc. of CCl_4 containing 0.1402 g. of $COCl_2$) was prepared. The results show, on account of the added phosgene, a high initial acidity which is exceeded after 25 days by the oxidizing strength. The latter reached a maximum value of 0.22 *N* at sixty days.

The effect of added chlorine is more pronounced. Figure 3 gives an experiment in which chlorine in carbon tetrachloride solution was added to chloroform which was already partially oxidized. This case shows unmistakable evidence that about one-half of the decomposition proceeds according

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(11) This statement depends on the assumption that the peroxide reacts with potassium iodide according to the equation

$$Cl_3C—O—O—H + 2KI = I_2 + 2KCl + HCl + CO_2$$

to Eq. 3 and the other half to Eq. 4. In addition it is surprising that the small amount of peroxide remaining, completely inhibits the chlorination. The sample was exhausted before any further change was observed.

A solution 50% chloroform and 50% carbon tetrachloride followed a course similar to other "light" experiments. The maximum oxidizing strength of 0.29 N was reached in ninety days.

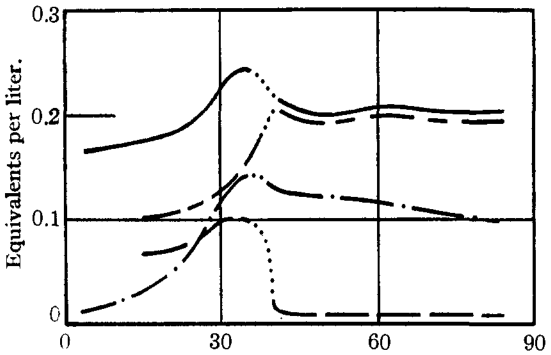

Fig. 3.—Effect of added chlorine: ——— total oxidizing strength, — — — peroxide concentration, — · — · acid concentration, — – – – chlorine concentration, · · · · · · · unanalyzed portion.

Effect of Alcohol and Hydrogen Peroxide Preservatives.—Alcohol is a common preservative[12] for chloroform. A sample containing 0.5% of alcohol was placed in a bottle beside the various other experiments. From portions extracted at infrequent intervals no sign of oxidation or decomposition whatsoever was observed in nearly two years.

The particular objective here consisted in finding a preservative which would stabilize the peroxide, in order to permit subsequent analysis. Glycerol, acetanilide and salicylic acid were selected. If 0.5 g. or less of one of these, or alcohol, was added to 50 cc. of chloroform whose oxidizing strength had reached at least 0.05 N, the destruction was rapid and complete, requiring the greatest length of time with salicylic acid (six days). On the other hand, if these preservatives were added initially to pure chloroform, no oxidation took place except with the case of salicylic acid, in which the customary reactions took place although somewhat more slowly. Hydrogen peroxide preservatives not only fail to stabilize the chloroform peroxide but also destroy it.

Peroxidation Catalysts.—On account of the length of time required for the oxidation, various substances were added to chloroform with the hope of accelerating the reaction in order that a more precise study could be made under more reproducible conditions. Limited space necessitates the elimination of the majority of these data. Some measure of success was attained with a chloroform sample in which a small crystal of trichloroacetic acid had been added. In this case the oxidizing strength was increased to a two-fold larger maximum value in an appreciably shorter time than a corresponding "light" experiment, without modifying the general characteristics. A small amount of added glacial acetic acid has a similar but less pronounced effect.

Oxidation in Sunlight.—A sample of chloroform exposed to direct sunlight for two eight hour periods on consecutive days showed an oxidizing strength of 0.02 N which disappeared on further exposure. The sample was then allowed to stand in diffuse light for two months. Analyses showed no further oxidation or decomposition to occur. One is drawn to the conclusion in this case as in others that some product as yet undetermined exists at the end of the reaction which inhibits further peroxidation. Inconsistency with the original objectives restrains further conjectures.

The author is indebted to the National Research Council and the Gates Chemical Laboratory for providing the facilities with which to study the photo-sensitized oxidation and the peroxidation of chloroform.

Summary

The thermal oxidation of chloroform in the presence of air produces an intermediate peroxide which yields initially chlorine and finally phosgene and hydrogen chloride as the products. The photo-reaction displays a similar behavior differing only in an accelerated rate and a smaller yield of peroxide.

A reaction scheme which correlates the present data is proposed.

The effect of a considerable number of reagents and conditions on this peroxide is given.

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[12] Considerable work on preservatives has been treated by Clover, Ref. 7, p. 3136.