[CONTRIBUTION FROM THE LOS ALAMOS SCIENTIFIC LABORATORY]

Chemical Effects Produced in Chloroform by γ-Rays[1]

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A detailed study of the chemical effects produced in a chloroform–oxygen system by the radiation from a Co^{60} source is presented. Temperature, time of irradiation and oxygen concentration have been shown to alter materially the types and quantities of products found. Data obtained in this work may clarify some of the problems in connection with photochemical studies.

Introduction

A number of investigators have reported the rapid decomposition of chloroform in the presence of air or oxygen when exposed to light over a wide spectral region. A comprehensive review of this subject was made by Baskerville in 1912.[2] The decomposition products reported have included such substances as chlorine, hydrogen chloride, phosgene, water, carbon dioxide, hexachloroethane, hypochlorous acid and various peroxides.[3-6] Phosgene is the only product agreed upon by the majority of workers in this field. In recent years studies have been made with chloroform using X-rays and γ-rays as the energy source for decomposition.[7-13]

It has been the purpose of this investigation to study more completely the effect of γ-radiation upon the decomposition of pure dry chloroform in an atmosphere of oxygen.

Reproducible data have been obtained by using specially purified chloroform. A striking change in the chemistry and quantities of decomposition products is observed when oxygen is present during irradiation. The growth of "total chloride," "total acid" and "total oxidizing agent" has been followed with time at constant dosage rate. Chlorine and an organic peroxide have been shown to be components of the "oxidizing agents." Attempts have been made to characterize this peroxide further.

I. Experimental

A. **Purification of $CHCl_3$.**—Various research workers in this field have frequently encountered difficulty in obtaining reproducible chloroform.[8] Different manufacturers add alcohol to $CHCl_3$, usually from 0.5–1%, as a stabilizer. Treatment with 98% sulfuric acid, chlorine dioxide or water[9] have all been used in attempts to remove the stabilizer and impurities.

Purification of chloroform with fuming sulfuric acid effectively removes such materials as alcohol, aldehydes, ketones, etc. The results obtained with chloroform given this treatment agree within ±4%. Since extreme care is required to achieve this reproducibility, the methods of purification, sample preparation and analysis are given below.

Batches of 500 cc. of $CHCl_3$ were prepared by successive 30 min. washes with the following reagents: two times with 500 cc. of fuming H_2SO_4, 500 cc. of distilled H_2O, 500 cc. of saturated $NaHCO_3$ and two more times with 500 cc. of H_2O. The mixtures were stirred with a "turbo stirrer" which sucks up the heavier layer and disperses it through the upper phase in fine droplets. The $CHCl_3$ was drained into a low-actinic erlenmeyer flask containing about 20 g. of Drierite and equipped with stopcock and standard taper joints for connection to a vacuum line.

Samples for evaluating the purification methods were prepared in the following way. The flask containing the dried $CHCl_3$ was frozen in liquid N_2, connected to the vacuum line and the air removed in the conventional manner. The $CHCl_3$ was allowed to come to room temperature, and samples were prepared by chilling with liquid N_2 an ampoule connected to the evacuated manifold by a standard taper joint. The desired quantity of $CHCl_3$ was condensed in the sample container. Oxygen was admitted to a pressure of 500 mm., and the $CHCl_3$ was held at the temperature of Dry Ice for 5 minutes before the ampoules were flame sealed. The quantity of $CHCl_3$ taken was determined by weighing previously tared tubes (10 mm. o.d.). In each case between 0.9 and 1.1 cc. of $CHCl_3$ was used; the O_2 varied from 0.014 to 0.015 millimole (about 3.3 cc. at Dry Ice temperature).

The tubes were placed 2.5 inches from the 15 curie Co^{60} source and irradiated for 21 hours at 4,720 r./hr. Analysis for total chloride ion was performed as outlined in the section on Analysis of Products. The chloride originates from such compounds as HCl, Cl_2, $COCl_2$ and presumably a species such as CCl_3OOH.

Baker and Mallinckrodt chloroform, which contain 1.0% and 0.5% of ethyl alcohol, respectively, as stabilizers, were used in this study. The necessity for giving the chloroform a rigorous chemical treatment can be seen in the following results which are expressed in meq. $Cl^-/10^3$ r./cc. $CHCl_3$: with no treatment values of 1.22×10^{-5} and 7.16×10^{-5} were obtained for Baker and Mallinckrodt $CHCl_3$, respectively; treatment by successive water washes or with concd. H_2SO_4 increased the sensitivity of the $CHCl_3$ somewhat, but the desired degree of reproducibility was not attained. Purification by the method described above yielded values of $4.47 \times 10^{-4} \pm 4\%$ for five different lots of $CHCl_3$ including one of Mallinckrodt Technical Grade.

In addition to the methods listed above, unsuccessful attempts were made to purify $CHCl_3$ by: fractional distillation, refluxing in the presence of metallic sodium, washing with $NaHSO_3$ and $K_2S_2O_3$. Treatment with fuming H_2SO_4, as described above, has been the only successful method found for preparing reproducible $CHCl_3$. The $CHCl_3$ used throughout this study was prepared by the fuming H_2SO_4 method.

B. **Source of γ-Rays.**—Two Co^{60} sources, 15 and 50 curies, were employed in the irradiation. Samples were irradiated at a distance of 2.5 inches from the 15 curie source (4,720 r./hr.) and 2 inches from the 50 curie source (18,700 r./hr.). The Co sources were positioned accurately by the use of a remote control pulley system.

Dosage rates were measured with a 2500 r. chamber and meter manufactured by the Victoreen Company of Cleveland, Ohio.

C. **Analysis of Products.** (1) **Total Chloride.**—The sealed ampoule was broken in a glass stoppered graduate containing 5 cc. of 0.1 *N* NaOH and 0.1 cc. of 30% H_2O_2 (to convert NaOCl to NaCl). After several minutes' shaking, the contents were rinsed into a 25-cc. volumetric flask and diluted. The Cl^- was determined potentiometrically with 0.010 *N* $AgNO_3$. Blanks were determined with each sample in the usual manner.

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[1] This document is based on work performed for the Atomic Energy Commission at Los Alamos Scientific Laboratory.

[2] C. Baskerville, *Ind. Eng. Chem.*, **4**, 281, 362 (1912).

[3] A. M. Clover, THIS JOURNAL, **45**, 3133 (1923).

[4] D. G. Hill, *ibid.*, **54**, 32 (1932).

[5] A. T. Chapman, *ibid.*, **57**, 419 (1935).

[6] A. T. Chapman, *ibid.*, **56**, 818 (1934).

[7] P. Gunther, H. D. Von der Horst and G. Cronheim, *Z. Elektrochem.*, **34**, 616 (1928).

[8] W. B. S. Bishop, *J. Proc. Sydney Tech. Coll. Chem. Soc.*, **5**, 66 (1933).

[9] G. V. Taplin and C. H. Douglas, UCLA-58.

[10] G. V. Taplin, C. H. Douglas and P. Sanchez, UCLA-118.

[11] G. V. Taplin, C. H. Douglas and S. C. Sigaloff, UCLA-192.

[12] G. Harker, *Nature*, **133**, 378 (1934).

[13] W. Minder and H. Heydrich, *Trans. Faraday Soc.*, Preprint, Spring Meeting, 1952.

(2) **Total Acid.**—This product represents all species reacting with NaOH which was added in excess. Under the analytical conditions employed here CO_2 does not act as an acid. Aliquots of the solution prepared for the total Cl^- determination were used in this analysis. Back titration with 0.010 *N* HCl was carried out to a *p*H of 5. In addition to neutralization of the free HCl the following reactions apparently take place in this determination

$$Cl_2 + H_2O_2 \longrightarrow 2Cl^- + 2H^+ + O_2$$

$$COCl_2 + H_2O \longrightarrow 2Cl^- + 2H^+ + CO_2$$

$$CCl_3OOH + H_2O \longrightarrow 3Cl^- + 3H^+ + {}^1/_2O_2$$

(3) **Total Oxidizing Agent.**—Sealed samples were broken in a glass stoppered graduate containing 5–10 ml. of 0.6 *M* KI. (HCl was added only to special samples the acid concentration of which was known to be low. Experiments indicated enough HCl was present in the irradiated $CHCl_3$ samples that the addition of more acid did not affect the results.) After thorough shaking, the contents were rinsed into an erlenmeyer flask, and the liberated iodine was titrated with 0.010 *N* $Na_2S_2O_3$ using starch as an indicator.

Samples which were stored as long as 18 hours showed no change in quantity of oxidizing agent from those which were analyzed immediately after irradiation.

(4) **Peroxide.**—The quantitative determination of peroxide was carried out by breaking the glass ampoule in a glass stoppered graduate containing 10 ml. of $Ti(SO_4)_2$ reagent.[14] After allowing 5 minutes for color development the solutions were diluted to 50 ml. and absorption measurements made at 410 mμ and 0.1 mm. slit width using a Beckman quartz DU spectrophotometer. The results were then compared to a standard curve prepared by using known amounts of H_2O_2. Although high concentrations of Cl_2 decompose the titanium peroxy complex, this was not a significant factor during this study.

An independent method[15] based on the oxidation of Fe^{++} to Fe^{+++} in alcohol gave results identical to those obtained with the $Ti(SO_4)_2$ reagent.

(5) **Chlorine.**—Since the unknown peroxide also reacts readily with KI solution, chlorine was determined spectrophotometrically by measuring the absorption at 330 mμ and comparing to a standard curve for Cl_2 dissolved in CCl_4. The absorption spectrum for irradiated $CHCl_3$ shows only the single peak between 290 and 400 mμ. It was concluded that other oxidizing agents such as ClO_2 (360 mμ) and HOCl (320 mμ) cannot be present in large quantities.

(6) **Phosgene.**—A Perkin–Elmer double beam spectrophotometer was used in determining the absorption at 5.54 μ. Quantitative data were obtained by referring to a standard curve prepared from known amounts of $COCl_2$ in $CHCl_3$.

(7) **Hexachloroethane.**—Slow evaporation of irradiated $CHCl_3$ yields a small quantity of crystals. Determinations of solubility, total chloride ion, melting point and crystal pattern indicated these crystals were hexachloroethane.

A 100-cc. sample of irradiated $CHCl_3$ containing 2.17 millimoles of peroxide was fractionally distilled to maintain the C_2Cl_6 in the residue. Only 0.07 millimole of C_2Cl_6 was found; thus only about 3% of the chloroform decomposition proceeds through the mechanism which yields hexachloroethane as a final product.

II. Results

A. Effect of Oxygen on Decomposition of $CHCl_3$.—Various studies[2,3] have shown that the decomposition of $CHCl_3$ by irradiation is greatly increased when oxygen or air is present. This conclusion has been confirmed for the conditions described in this report.

Samples containing no oxygen and irradiated with as high as 10^7 r. showed no detectable oxidizing agent and only trace quantities of chloride ion. Milligram quantities of hexachloroethane were produced, however. When oxygen was present during the irradiation, measurable amounts of Cl_2, HCl, $COCl_2$ and peroxide were obtained. The quantitative aspects of this relationship can be seen in Fig. 1. Determination of chloride ion served as a very accurate method for evaluating decomposition since it represents the sum of all the chlorine species susceptible to hydrolysis: *viz.*, HCl, Cl_2, $COCl_2$ and the peroxide.

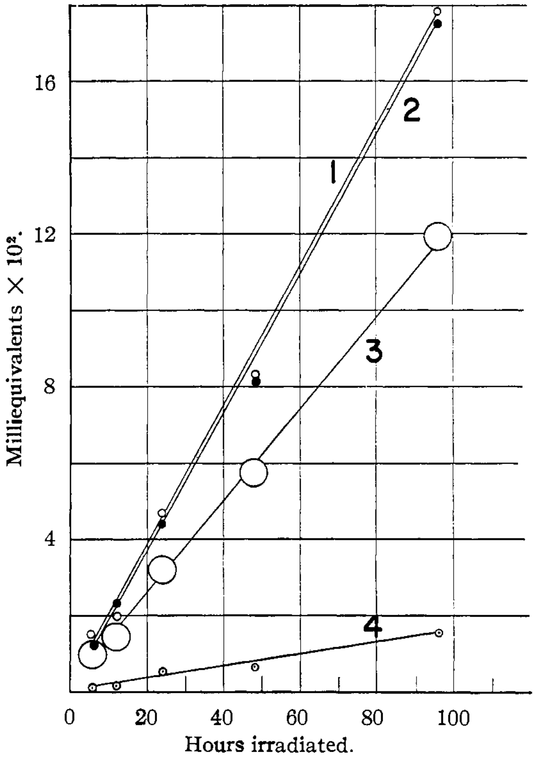

Fig. 1.—Determination of products in an irradiated $CHCl_3$–O_2 system: 1, total Cl^-; 2, total H^+; 3, oxidizing agent and peroxide; 4, phosgene. All irradiations at 4720 r./hr. and initial oxygen pressure at 580 mm.

In Fig. 1 can also be seen the linear increase of "total H^+" and "total Cl^-" with time. The parallel growth of these two components suggests that the chloride species found among the decomposition products act as acids when treated with NaOH and H_2O_2 (see analysis for "total Cl^-"). Phosgene which forms quite slowly eventually becomes one of the major constituents. During this time of irradiation the peroxide and total oxidizing agent are nearly equal and are plotted as one component. Samples taken after longer irradiation times from sealed cells (see Table II) indicate that the total oxidizing agent exceeds the sum of the peroxide and chlorine. This discrepancy increases with increasing chlorine concentration.

Figures 2 and 3 illustrate quantitatively the growth and decay of total oxidizing agent and peroxide when $CHCl_3$ samples were exposed to different quantities of oxygen during irradiation. The initial rate of formation of these products appears to be independent of oxygen concentration.

In a series of experiments samples of chloroform containing varying amounts of oxygen were irradiated for a fixed time. It was observed that the total Cl^-(or H^+) found after irradiation increased

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[14] Snell and Snell, "Colorimetric Methods of Analysis," Third Edition, Vol. II, D. Van Nostrand Co., Inc., New York, N. Y., 1949, p. 882.

[15] *Ibid.*, pp. 883–885. (All solutions made up in 95% alcohol.)

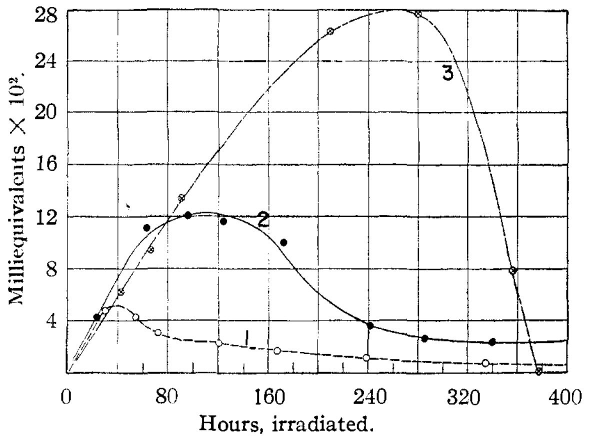

Fig. 2.—Oxidizing products found at various initial oxygen pressures: 1, 100 mm.; 2, 248 mm.; 3, 500 mm. All irradiations at 4720 r./hr.

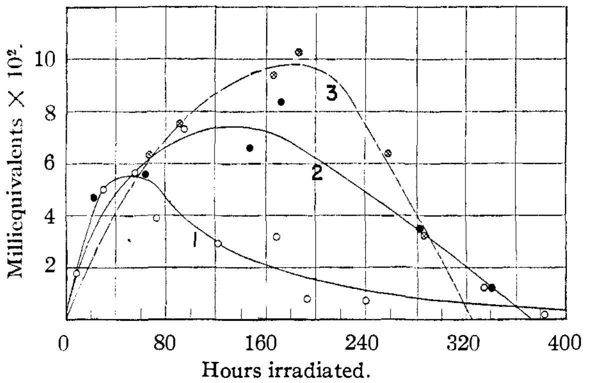

Fig. 3.—Peroxide found at various initial oxygen pressures: 1, 100 mm.; 2, 248 mm.; 3, 500 mm. All irradiations at 4720 r./hr.

with increasing oxygen concentrations up to a point where the products found were independent of initial oxygen concentration.

In Fig. 4 the growth and decay of chlorine (absorption peak at 330 mμ) are shown with time. When the oxygen was replenished in the sealed silica cell at the end of 48 hours, the chlorine again became evident only to disappear with further irradiation. When one plots the optical densities at 330 mμ (obtained during the run with the initial charge of oxygen, Fig. 4) against time, a straight line going through the origin is obtained. Although the chlorine is not a major constituent of the decomposition products initially, its growth is nevertheless linear which suggests that a fraction of it might originate from a primary act.

B. Influence of Temperature on the $CHCl_3$–O_2 System.—Samples containing 1 cc. of $CHCl_3$ and about 3 cc. of O_2 at 500 mm. were irradiated under identical conditions except for temperature. At the end of the irradiation period an analysis for total Cl^- was made as described above. The results obtained are given in Table I.

TABLE I

INFLUENCE OF TEMPERATURE ON DECOMPOSITION

Temp., °C.	−80	−43	0	19	21	37
Cl^-/cc. $CHCl_3$ × 10^2 meq.[a]	0.30(s)	0.25	1.25	2.48	2.56	3.54

[a] Average of three determinations.

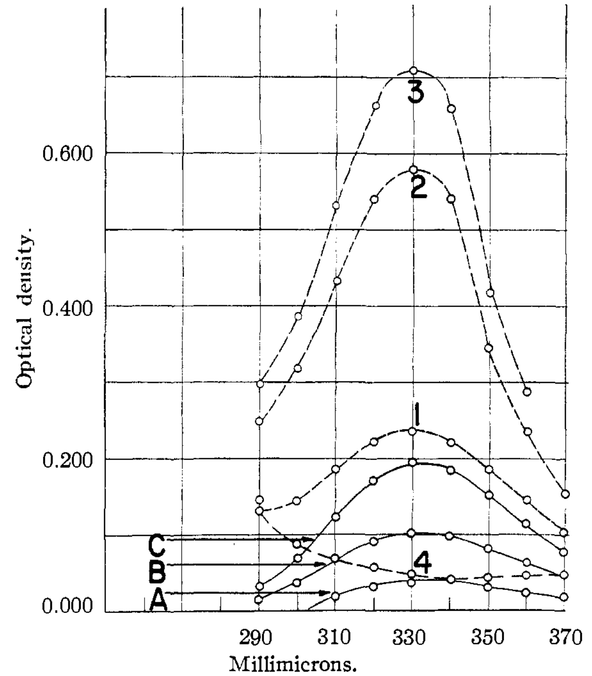

Fig. 4.—Spectrophotometric analysis of sample in sealed cell: —, first irradiation (in hr.), A = 8, B = 18, C = 33; -----, irradiation after replenishing oxygen (in hr.) 1 = 26, 2 = 56, 3 = 69, 4 = 96. All irradiations at 18,700 r./hr. and initial oxygen pressures of *ca.* 580 mm.

From these data it is apparent that the temperature at which samples are irradiated, controls to some extent the quantity of $CHCl_3$ decomposed. Consequently, the other experiments described in this paper were carried out at 22 ± 2°.

C. Composition of "Total Oxidizing Agent."—Although the proportions of Cl_2 and peroxide may vary during an irradiation, Table II indicates that the oxidizing agent is primarily peroxide and chlorine. Samples of $CHCl_3$ in O_2 were irradiated for various times in sealed bulbs attached to absorption cells. At the end of the irradiation period the absorption at 330 mμ was determined. The cells were then opened, and the solutions were assayed for "total oxidizing agent" and the unidentified "peroxide." All results are based on 1 cc. of $CHCl_3$.

TABLE II

COMPOSITION OF OXIDIZING AGENT

Sample	Total oxid. agent, meq.	Peroxide, meq.	Oxid. agent minus peroxide, meq.	Cl_2 by absorption at 330 mμ, meq.	Oxid. agent unaccounted for, meq.
1	0.0789	0.0764	0.0025	0.0025	None
2	.0864	.0815	.0049	.0057	−0.0008
3	.1258	.1070	.0188	.0035	+ .0153
4	.1400	.1060	.0340	.0071	+ .0269

D. Effect of H_2O on Decomposition of $CHCl_3$.—In an attempt to increase the sensitivity of the system, samples were prepared by condensing 0.5 cc. of H_2O over the $CHCl_3$ layer. Irradiations were carried out as described earlier. Erratic results were obtained in these experiments. In contrast to the work of Gunther[7] and of Clover,[3] it was found that the addition of water actually decreased the quantity of decomposition products as determined by an analysis for total Cl^-. The data in Table III are presented to show this effect; samples received 2 × 10^5 r. Results are based on 1 cc. of $CHCl_3$.

TABLE III

INHIBITING EFFECTS OF WATER

System	Approximate no. of observations	Meq. $Cl^-/10^3$ r.
$CHCl_3$-vacuum	20	0.00
$CHCl_3$-H_2O-vacuum	20	0.00
$CHCl_3$-O_2	500	4.4×10^{-4}
$CHCl_3$-H_2O-O_2	20	1.5×10^{-4}

E. Attempts at Identification of Peroxide.—Considerable difficulty was encountered by Clover[3] and Chapman[5] in attempts to isolate and identify the peroxide formed in their experiments. The peroxide encountered in this study behaves qualitatively in the same manner as does that which is formed when radiation of longer wave length is used to initiate the decomposition reaction. The two peroxides are presumably the same material.

By using a low temperature distillation procedure it has been possible to concentrate the peroxide and to effect a separation from the more volatile decomposition products. This separation permitted a partial analysis of this unidentified peroxide.

In the preparation of samples for distillation an annular bottle containing 100 cc. of $CHCl_3$ was connected to a 5-liter flask of O_2 and irradiated until the peroxide content reached a maximum, usually about 0.12 meq. per cc. Concentration was then effected by using a Snider column with a partial condensation type distillation head.[16] This type of column allows distillation to take place at a relatively low temperature, thus retarding the thermal decomposition of the peroxide. A concentration of 2.5 meq. of peroxide per cc. of $CHCl_3$ was obtained in this manner. Attempts to concentrate this further resulted in decomposition of the peroxide into $COCl_2$, Cl_2 and possibly HCl.

The following observations (Table IV) have been made showing that the peroxide is not H_2O_2.

TABLE IV

COMPARISON OF H_2O_2 WITH ORGANIC "PEROXIDE"

Material tested	Rate of reaction with $Ti(SO_4)_2$	Rate of reaction with KI
H_2O_2	Fast	Slow
Irrad. $CHCl_3$	Slow	Fast
Irrad. $CHCl_3$ distilled to remove volatile chlorine species	Slow	Fast
Irrad. $CHCl_3$ distilled to remove volatile chlorine species and then treated with H_2O	Fast	Slow

In addition to the information in Table IV other evidence exists indicating the peroxide formed in this system is not H_2O_2. It is possible, however, to convert this peroxide to H_2O_2 under special conditions.

When a sample of irradiated $CHCl_3$, containing 0.012 meq. of peroxide, was shaken with an equal volume of H_2O, the total peroxide decreased to 20% of its original concentration with only 6.5% of this being found in the aqueous phase. However, when the more volatile decomposition products were removed by distillation, and the resulting $CHCl_3$, containing 0.079 meq. of peroxide, was shaken with an equal volume of H_2O, a decrease to only 76% of the original peroxide was observed. In this instance all of the peroxide was found in the water phase.

These results indicate that the peroxide is more susceptible to decomposition by water in the presence of the other reaction products, and since in the first experiment the total remaining peroxide was found primarily in the chloroform phase very little conversion to H_2O_2 has taken place. In the second experiment where the decomposition products were removed prior to the addition of water, one finds only a comparatively small loss in total peroxide. In this reaction all of the remaining peroxide must be H_2O_2 since it is found in the aqueous phase which exhibits, as described earlier, reactions similar to those of H_2O_2 solutions.

Because of the decomposition at higher concentrations (2.5 meq./cc.), it was decided to determine the composition of the peroxide by other means. Samples of irradiated $CHCl_3$ were therefore distilled until no test for Cl^- was obtained in the distillate (the volatile chlorine species are usually removed in the first 30 cc. of a 100-cc. sample). Samples of the $CHCl_3$ in the distillation flask were then analyzed immediately for chloride ion and peroxide. Assuming all of the chlorine in the peroxide molecule is hydrolyzed and that there are two equivalents per mole of peroxide the results of six determinations indicate that there are 2.91 ± 0.35 atoms of chlorine per molecule of peroxide.

Both CH_2Cl_2 and $CHCl_3$ yield peroxide when irradiated in the presence of O_2. However, when CCl_4 and C_2Cl_4 are irradiated in the presence of O_2, no peroxide is formed even though $COCl_2$ and Cl_2 are found in substantial quantities. This seemed to indicate that hydrogen is important to the mechanism and might be present in the peroxide molecule.

A strong absorption band due to O–H stretching is found at 2.9 μ in the infrared. This absorption peak is present only when appreciable amounts of peroxide are found in $CHCl_3$ by the $Ti(SO_4)_2$ test. It was thought that by irradiating deutero-chloroform ($CHCl_3$-*d*), one would be able to observe a shift from the O–H to the O–D stretching bond.

Chloroform prepared by the reaction of chloral hydrate ($CCl_3CH(OH)_2$) and NaOH, treated with fuming H_2SO_4 and then distilled, exhibited the same characteristics as purified commercial $CHCl_3$. However, when $CHCl_3$-*d* was prepared[17] and irradiated in the same manner, a much greater resistance to decomposition was observed. Samples irradiated up to 7.5 × 10^6 r., although giving slight colorimetric tests for peroxide, showed no absorp-

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[16] H. S. Booth and A. R. Bozarth, THIS JOURNAL, **61**, 2927 (1939).

[17] F. W. Breuer, *ibid.*, **57**, 2236 (1935).

tion in the 2.9 to 4.0 μ region (in H_2O_2 and D_2O_2 the O–H and O–D stretching bonds are found at 2.93 and 3.99 μ, respectively). Purified commercial $CHCl_3$ under similar conditions has shown an appreciable absorption at 2.9 μ with much less exposure. There is a possibility that some impurities in the $CHCl_3$-*d* inhibited the decomposition reaction or that this may be a real isotope effect on rates.

An additional experiment was attempted to determine the existence of hydrogen in the peroxide molecule. Samples of irradiated $CHCl_3$ were distilled to remove the more volatile products and then shaken with gaseous DCl at temperatures of from 10 to 20° for periods of about 3 hours. Only small quantities of peroxide were found in the resulting solutions which were tested with $Ti(SO_4)_2$ reagent. In the infrared absorption spectra of these samples no peak was observed at 2.93 μ (O–H). However, there was considerable absorption at 4.9 μ (unknown) and a very slight absorption at 3.95 μ (O–D).

Although no conclusive proof exists at this time as to the exact structure of this peroxide molecule, the preceding experiments indicate the formula to be CCl_3OOH.

F. Reaction at High Dosages.—Figure 5 is presented to show the extent of linearity when $CHCl_3$ is irradiated in about 3 cc. of O_2 at 250 mm. pressure. It is apparent that some Cl^- is formed even after the oxidizing agent begins to disappear. When the oxidizing agent is completely gone, the Cl^- levels off and begins to decrease at about 800 hours (3.8×10^6 r.).

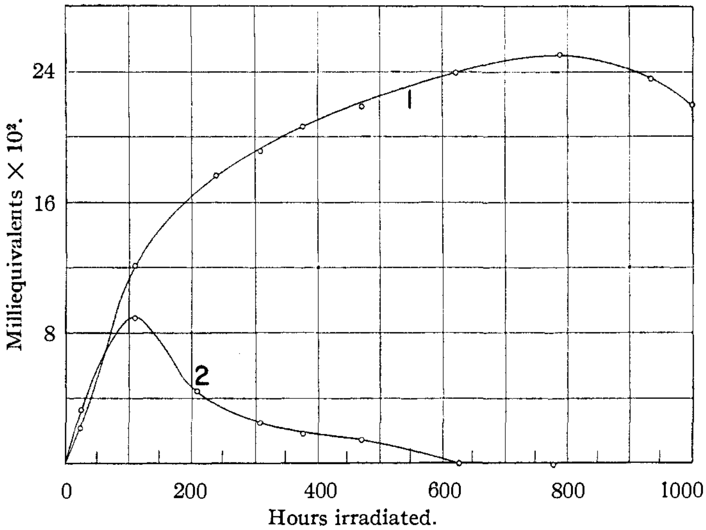

Fig. 5.—Chloride ion found after long exposures: 1, total chloride ion; 2, total oxidizing agent. All irradiations at 4720 r./hr. and initial oxygen pressures of 250 mm.

In duplicate samples taken at 1000 hours (Fig. 5) and analyzed for $COCl_2$ and "total Cl^-" the molar ratio of HCl to $COCl_2$ was 6.3:1. Ratios of 6.7, 7.7 and 8.3 were obtained with previous samples.

Assuming that after the disappearance of oxidizing agents, $COCl_2$ and HCl are the only chlorine species which would yield Cl^- when treated with NaOH and H_2O_2 as described earlier, then the over-all decomposition reaction yields about 6 to 8 moles of HCl for every mole of $COCl_2$.

G. Calculation of Yield.—The current method for reporting yields in the field of radiation chemistry is based upon atoms formed per 100 electron volts absorbed energy. Since the results presented thus far are expressed in terms of roentgens, calculations are given below to convert these results to the "*G* values" (atoms/100 e.v.).

In Fig. 1 at 80 hours it is observed that 0.142 meq. Cl^- or 8.51×10^{19} atoms are produced in 1 cc. of $CHCl_3$ by 3.78×10^4 r. This quantity of radiation is equivalent to 2.93×10^{19} e.v. if one uses the following constants: 1.61×10^{12} ion pairs/g. of air/r., 32.5 e.v./ion pair and 1.48 as the density of $CHCl_3$.

Thus there are 290 atoms of Cl^- formed for every 100 e.v. absorbed. Assuming the decomposition of $CHCl_3$ proceeds largely to give chlorine species susceptible to hydrolysis, then each molecule of $CHCl_3$ decomposed yields three atoms of Cl^-. Therefore, 97 $CHCl_3$ molecules are decomposed per 100 e.v. absorbed.

Hardwick[18] and Hochanadel[19] list for the Fe^{++} to Fe^{+++} system *G* values of 20.8 and 15.5, respectively. The decomposition of $CHCl_3$ in O_2 obviously proceeds by a chain reaction.

III. Discussion

This investigation has shown that the decomposition of $CHCl_3$ in the presence of O_2 proceeds by a chain reaction when the system is irradiated with γ-rays. The types and quantities of decomposition products existing at any one time depend on the oxygen concentration and the length of irradiation. These factors have undoubtedly accounted for the disagreement by various investigators in this field. During irradiation many reactions probably occur simultaneously. The over-all reaction may be considered as consisting of two phases. In the first phase the peroxide, whose rate of formation is not markedly affected by the oxygen concentration, is initially the major component of the oxidizing agent. On the basis of the data obtained, the peroxide found in irradiated $CHCl_3$ consists mainly of the species CCl_3OOH. Chapman[5,6] postulates the existence of two species, *viz.*, CCl_3OOH and CCl_2OO. Since six separate experiments gave an average value of 2.91 ± 0.35 chlorine atoms/molecule of peroxide, it is unlikely that a peroxide compound containing fewer chlorine atoms exists to any appreciable extent. The evidence for the existence of an O–H band at 2.93 μ indicates the presence of a hydrogen atom in the molecule, and the experiment with DCl in which the hydrogen atom was exchangeable with D in DCl substantiates this point. If the peroxide is accepted as being CCl_3OOH, then the formation of this compound is the principal reaction during this phase since it largely accounts for the total H^+ and Cl^-.

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(18) T. J. Hardwick, *Can. J. Chem.*, **30**, 17 (1952).

(19) C. J. Hochanadel, Abstract Cleveland Meeting A.C.S., 1951, p. 42-P.

Among the first reactions is also the linear growth of small amounts of Cl_2 and $COCl_2$. As the reaction progresses the formation of chlorine (difference between oxidizing products and peroxide) continues at an accelerated rate at higher oxygen concentrations (see Figs. 2 and 3).

As the reaction progresses, it enters a second phase in which the peroxide and chlorine disappear to yield $COCl_2$, HCl and other products. The disappearance of chlorine can probably be accounted for by the chlorination of $CHCl_3$ to yield CCl_4 and HCl. Several features of the second stage seem of considerable interest. One is that the ratio of $HCl/COCl_2$ after long irradiation periods is much in excess of that corresponding to the net change

$$CHCl_3 + {}^1/_2O_2 \longrightarrow COCl_2 + HCl$$

Departures from this stoichiometry in the observed direction could be accounted for by the formation of other oxygen-containing products (*e.g.*, CO or CO_2) or some carbon–chlorine compounds which were not detected in this study. It should be noted that water has never been observed in the reaction products. A second point of interest is that oxygen remains in the system even during the second phase. Apparently the accumulation of some product explains the differing reactions in the first and second phases.

A. **Mechanism.**—One may regard the decomposition of chloroform by oxygen as proceeding mainly through intermediates which ultimately decompose to yield HCl, $COCl_2$ and chlorinated hydrocarbons. Of primary importance in this study was the formation of a peroxide, presumably CCl_3OOH. The net reaction for the production of this component can be considered as

$$CHCl_3 + O_2 \longrightarrow CCl_3OOH$$

No definite conclusions about complete mechanisms can be drawn from these studies. The radicals resulting from the interaction of the radiation and chloroform presumably generate a chain reaction for the combination of oxygen and chloroform. Since mass spectrograph studies of $CHCl_3$ give $CHCl_2^+$ and $CHCl_2^{++}$ as the most abundant fragments resulting from electron impact on $CHCl_3$ gas, it is not unreasonable that these same fragments would result in liquid $CHCl_3$ bombarded by gamma rays. The primary act in the production of the peroxide compound would therefore probably be

$$CHCl_3 \xrightarrow{\gamma\text{-rays}} CHCl_2 + Cl$$

The data indicate that of the products studied, the peroxide is the only compound produced by a chain reaction in the initial stages; chlorine, phosgene, hexachloroethane and hydrogen chloride apparently result principally from reactions generating the chain-carrying species or reactions which result in the net destruction of radicals.

B. **Application to Dosimetry.**—The excellent agreement obtained with Cl^- determinations suggests the use of the $CHCl_3$–O_2 system as a dosimeter for higher dosages. The analysis for total oxidizing agent can also be performed conveniently. However, it should be pointed out that even though the decomposition of $CHCl_3$ is a chain reaction, the quantities of products involved are still quite small. Consequently, for dosages less than 1000 r., micro-techniques would have to be employed even to determine Cl^- which represents not only the HCl and $COCl_2$ produced but also Cl_2 and CCl_3OOH. By irradiating 1 cc. of $CHCl_3$ in 0.014 millimole of O_2 one would expect only 4.5×10^{-4} meq. Cl^- to be produced by 10^3 r.

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Physical Properties of Organosilicon Compounds. I. Hexamethylcyclotrisiloxane and Octamethylcyclotetrasiloxane

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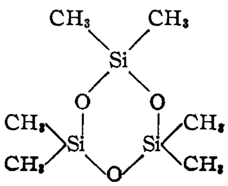
The vapor pressure of hexamethylcyclotrisiloxane as a function of temperature has been determined. The enthalpies of vaporization, fusion and sublimation are 9.5, 3.7 and 13.2 kcal./mole, respectively. For octamethylcyclotetrasiloxane the enthalpy of fusion is 4.4 kcal./mole. Octamethylcyclotetrasiloxane is well suited as a cryoscopic solvent.

Introduction

Hexamethylcyclotrisiloxane (I) is unique among cyclic dimethylsiloxanes because it possesses a planar, strained ring structure[1,2] and unusual physical properties, *e.g.*, a comparatively high melting point and short liquid range.[3] Thus it was of interest to determine its vapor pressure as a function of temperature, and its enthalpies of vaporization, sublimation and fusion. In order to compare the properties of I with those of a typical non-planar homolog, the enthalpy of fusion of octamethylcyclotetrasiloxane (II) was deter-



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