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# The Radiolysis of Aqueous Solutions of Dichloromethane

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THE RADIOLYSIS OF AQUEOUS SOLUTIONS OF DICHLOROMETHANE

by

Steven Michael Odre

UC 1971

Senior Thesis Submitted  
in Partial Fulfillment  
Of the Requirements of Graduation

Department of Chemistry  
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June 5, 1971

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This Thesis

Submitted by

Steven M. Odie

to the

Department of Chemistry of Union College

in partial fulfillment of the requirements of the degree of

Bachelor of Science with a Major in Chemistry

is approved by

John L. Feata



ABSTRACT

Aqueous solutions of dichloromethane have been irradiated with a cobalt-60 gamma source. Products of the radiolysis have been determined in order to formulate the mechanism of the radiation induced decomposition. Chemical studies have shown that hydrochloric acid and hydrogen peroxide are two of the major products of the radiolysis. Traces of formaldehyde have also been found.

The effect of oxygen and dichloromethane concentrations on product yields was determined. It has been found that the product yields are independent of dose rate.

The proposed mechanism is initiated by the hydrated electron and the hydroxyl radical - both products of the radiolysis of water.



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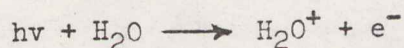
## INTRODUCTION

Radiation chemistry can be defined as the study of the chemical effects produced by the absorption of high energy radiation. This radiation causes both ionization and excitation. Since a large amount of energy is needed, high energy sources are used - either X-rays or gamma rays. But since X-ray sources are fairly expensive, reliable gamma ray sources are used.

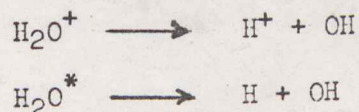
### A. Radiolysis of Water

The basic observation in the irradiation of dilute aqueous solutions is that the major chemical change occurs in the dissolved material while the water undergoes virtually little or no decomposition. But since water is the major component of the system, it must originally absorb practically all of the energy of the radiation.

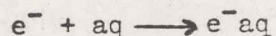
When a  $\gamma$ -ray photon interacts with water, it produces a charged water molecule and a high speed electron:



This high speed electron will then interact with other water molecules causing further ionizations and excitations. The ionized and excited water molecules can then dissociate into radical products:



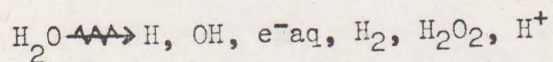
Every time this moving electron interacts with a water molecule it will lose some energy - due to this loss in energy, the electron will gradually be slowed down - thereby increasing the probability of interaction with other water molecules. Once this electron has reached thermal energy it will become solvated.



While the greater portion of these ions and radicals recombine to form water, some combine to form other molecular products.



Therefore, the primary products formed from the irradiation of water by high energy photons consists of both radicals and molecular products.



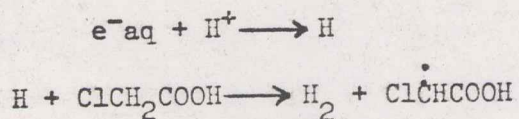
#### B. Existence of the Solvated Electron

Chemical and physical studies have conclusively demonstrated the existence of the solvated electron. Chemical evidence has been shown thru the radiolysis of chloroacetic acid.<sup>1</sup> In "neutral" solution the major product is chloride ion. But in acidic solution, the major product is molecular hydrogen. This is due to the fact that in a neutral solution the solvated electron produces a chloride from the chloracetic acid.





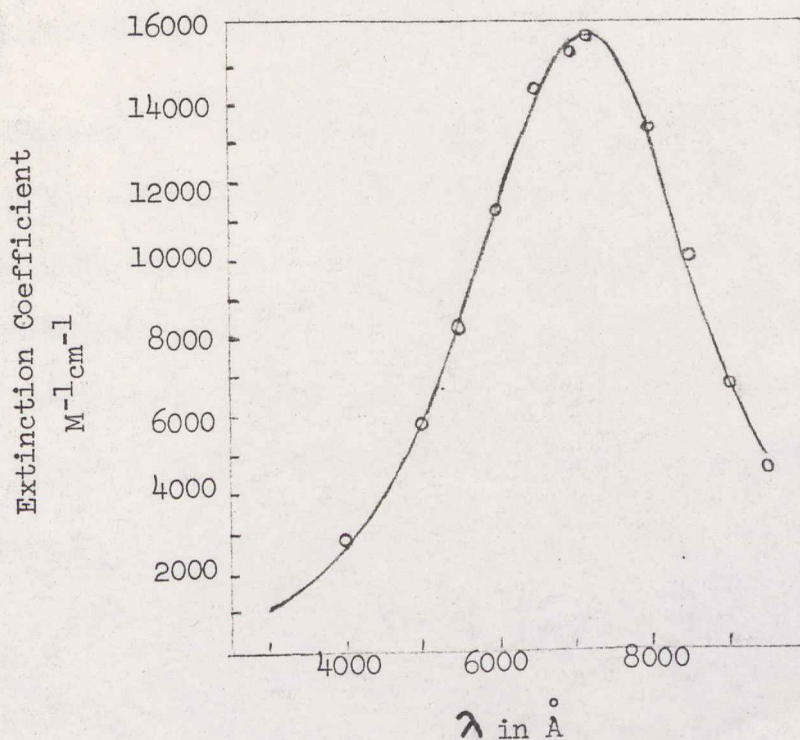
But in acidic solutions, the solvated electron is converted into a hydrogen radical which subsequently abstracts a hydrogen atom from the chloroacetic acid to form molecular hydrogen.



Yields of molecular hydrogen are increased as the pH is decreased.

Hart<sup>2</sup> through pulse radiolysis and absorption spectroscopy (see figure 1) has proven the existence of the solvated electron.

FIGURE 1 - ABSORPTION SPECTRUM OF THE SOLVATED ELECTRON





### C. G-Values

Yields of the primary radicals and molecular products are determined quantitatively versus the amount of energy received by the solution. These yields are expressed in terms of the G value which is defined as the number of molecules (or ions) formed or destroyed per 100 e.v. of energy absorbed by the solution. The yields of the primary products in neutral aqueous solutions, extrapolated to zero concentration of solute, are:

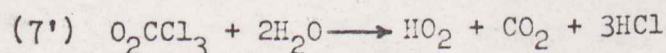
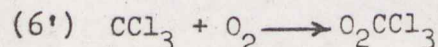
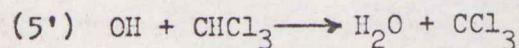
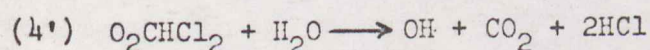
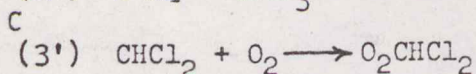
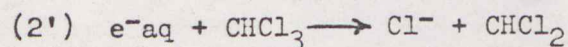
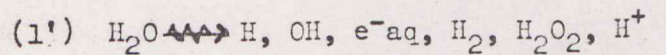
$$G_{e^{-}aq} = 2.85; G_{OH} = 2.25; G_{H_2O_2} = 0.7; G_H = 0.55^3$$

These G values are obtained thru scavenger studies on known systems.

### D. Radiolysis of Aqueous Chloroform Solutions

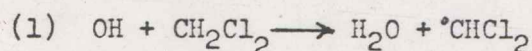
Radiolysis of dilute aqueous solutions of organic compounds containing halogen results in the formation of the halide ion.

In 1969, Rezanoff, McCallum and Woods<sup>4</sup> proposed a mechanism for the radiolysis of aqueous chloroform. The major products are hydrochloric acid and hydrogen peroxide and the proposed mechanism does not involve a chain. Their mechanism includes the following reactions.

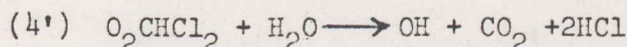
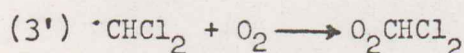


From this series of reactions the following observations can be made: 1. the initial attack by the primary radical produces a second radical; 2. this second radical is scavenged by  $O_2$  producing a peroxy-radical; 3. this peroxy-radical can then be hydrolyzed.

Using these steps we can propose some possible reactions for the radiolysis of aqueous dichloromethane. First the abstraction of hydrogen from dichloromethane produces a  $\cdot CHCl_2$  radical



This  $\cdot CHCl_2$  radical is identical with the one produced in reaction (2'). Assuming the reactions in Wood's mechanism to be valid the following reactions should occur:



But reactions (1), (3') and (4') constitute a chain.

There are two main characteristics of a chain mechanism :

1. a chain is usually reflected by a dose rate dependence; 2. the product yields will be much greater than that of the primary products.

Woods and Spinks<sup>5</sup> did an extensive study of the radiolysis of aqueous solutions of organic compounds containing halogens. TABLE I lists some of the compounds investigated and the corresponding G values for the production of halide ion at three different dose rates



TABLE I - Yield of Halide Ion from Irradiated Aqueous Solutions of Organic Halogen Compounds (5)

Compound	G(Halide Ion)		
	dose rate (rads/min.)		
	1020	450	17
$\text{Br}_3\text{CCH}(\text{OH})_2$	69	98	360
$\text{Cl}_3\text{CCH}(\text{OH})_2$	43	50	112
$\text{Cl}_3\text{CCOOH}$	16		15.5
$\text{Cl}_3\text{CH}$	27		27

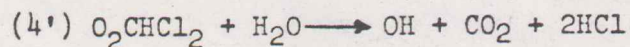
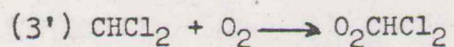
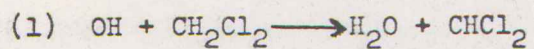


From TABLE I it is apparent that the radiolysis of aqueous  $\text{Br}_3\text{CCH}(\text{OH})_2$  involves a chain mechanism.  $G(\text{Br}\cdot)$  is increased from 69 to 360 as the dose rate was decreased from 1020 rads/min to 1 rads/min. Woods, et.al., recognized that a dose rate dependence would exist at "lower" dose rates, but felt that at "higher" dose rates, the concentrations of radicals would be sufficient such that the chain length would approach unity and the yield would become independent of the dose rate. This is what happens in the radiolysis of aqueous  $\text{Br}_3\text{CCH}(\text{OH})_2$ . This relationship between dose rate and G value is not so apparent for the radiolysis of aqueous  $\text{Cl}_3\text{COOH}$  or  $\text{Cl}_3\text{CH}$ . From TABLE I the value of  $G(\text{Cl}\cdot)$  does not change as the dose rate is decreased from 1020 rads/min to 1 rads/min. This does not preclude a chain mechanism which, if it exists, would be apparent only at extremely low dose rates, but does indicate that a chain mechanism could play only a very minor or non-existent part in the mechanism at dose rates above 1 rads/min.

#### E. Purpose of the Investigation.

The purpose of this investigation into the radiolysis of aqueous dichloromethane is to complement the previous investigation of the radiolysis of aqueous chloroform through the usage of a similar related compound.

Of primary concern was whether any dose rate dependence existed for dichloromethane as suggested by the chain



Also information was obtained concerning the concentration dependence of dichloromethane and oxygen. A study for the detection and measurement of formaldehyde yields were carried out.

With this information a reasonable mechanism for the radiolysis of aqueous dichloromethane can be proposed.



## EXPERIMENTAL

### A. Materials

The water to be used in preparing solutions and for final rinsing of containers which would be in contact with the solutions prior to irradiation was purified by taking ordinary distilled water and redistilling it from alkaline permanganate. The purified water was stored in a closed pyrex bottle.

Water to be used in the analysis for chloride ion was prepared by passing it through a Barnstead demineralizer.

Matheson, Coleman, and Bell, Spectroquality dichloromethane was used as supplied.

Matheson purified oxygen was further purified by passing it through potassium hydroxide solution and a water scrubber.

Matheson purified nitrogen was further purified by passing it over hot copper and through a water cooled condensor.

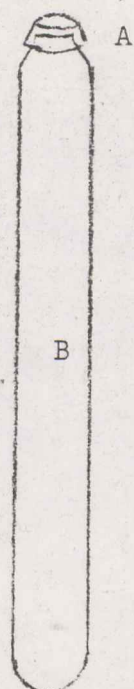
All other chemicals were reagent grade and were used as directed by authors of analytical techniques.

The radiation ampoules, Figure 2-A, were fabricated from twelve millimeter pyrex tubing. One end was closed and rounded while the other end was drawn to produce an opening which could be sealed with a serum cap. The overall length of the ampoule was about six inches and could hold ten milliliters of liquid.

### B. Preparation of Samples

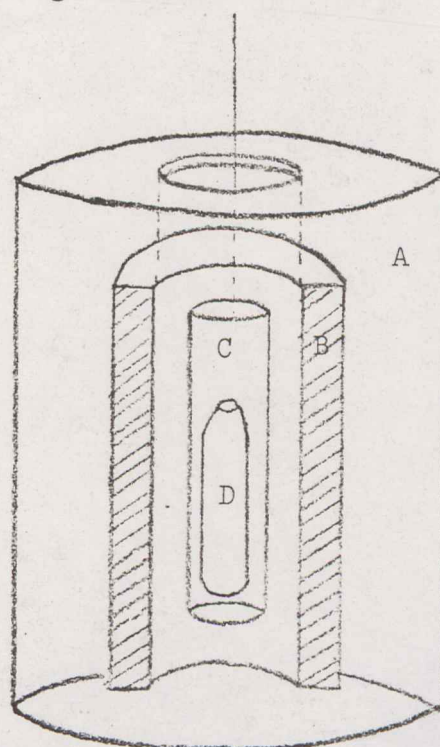
A saturated aqueous solution of dichloromethane was prepared by shaking an excess of dichloromethane with doubly-distilled water.





- A - Serum C p  
B - 6" Pyrex Tube

Fig. 2-A RADIATION VESSEL



- A - Source Shielding  
B - Colbalt 60 Source  
C - Vessel Holder  
D - Vessel

Fig. 2-B COLBALT 60 SOURCE

Fig. 2 RADIATION VESSEL AND COLBALT 60 SOURCE

The concentration of the solution at room temperature was approximately  $2.3 \times 10^{-1}M$  dichloromethane. Less concentrated solutions were prepared by diluting the saturated solution with doubly-distilled water.

#### Oxygenation of Samples

The purified oxygen was saturated with aqueous dichloromethane before introduction into the samples by passing it through the interface of doubly-distilled water and dichloromethane. The saturated oxygen was introduced into the samples through the serum cap using a hypodermic needle. The ampoule was exhaust vented using a second hypodermic needle which just pierced the serum cap. The samples were oxygenated for 35-40 minutes with the rate of flow such that a nearly continuous stream of gas bubbles were passing through the sample. The exhaust needle was removed just prior to the inlet needle to insure a slight positive pressure in the ampoule.

#### Deaeration of Samples

Solutions were deaerated by bubbling pure nitrogen through them using the same technique as was utilized for oxygenation. Forty-five minutes were required to insure complete deaeration.

#### Air Saturation of Samples

Air saturated solutions were prepared by drawing washed and saturated with aqueous dichloromethane air through the solutions.

#### Irradiation Procedure

Figure 2-B is a sketch of the cobalt-60 gamma source used to irradiate the solutions. The ampoule containing the solution was placed in an aluminum tube. The tube was then lowered into the source for a definite period of time. The cobalt-60 completely surrounds



the aluminum tube, thus insuring a uniform dose rate. Dose rates were determined using the Fricke ferrous sulfate dosimeter. Utilizing a value of  $G(\text{Fe}^{+3}) = 15.5$ , the dose rate was determined to be  $7.5 \times 10^{16}$  e.v.g<sup>-1</sup> min<sup>-1</sup>.

### C. Analysis

#### Chloride Ion Determination

The chloride ion content of the irradiated samples was determined colorimetrically using an adaptation of the method described by Bergman and Sanik<sup>6</sup>. The method is based upon the displacement by chloride ion of the thiocyanate ion from mercury thiocyanate in the presence of  $\text{Fe}^{+3}$ . The absorption of the iron-thiocyanate complex formed is measured at 450 nm using a Beckman Model Du spectrophotometer and a 1 cm. cell.

The analysis is conducted by using a 4 ml aliquot of sample in a 10 ml flask. To this was added 1 ml of the ferric ion solution and mixing well. Then is added 1 ml of ethanol saturated with the mercuric thiocyanide. After mixing well, the solution is diluted to the mark. At ten minutes after the addition of the mercuric thiocyanide, the color is measured. Because of the possibility of very slight amounts of chloride ion being present in the water used for sample dilution, reagent blanks were necessary every time a new "batch" of demineralized water was prepared.

A calibration curve was used to convert the optical density readings to chloride ion concentration. This calibration curve, shown as Figure 8, is included in the appendix.



### Hydrogen Peroxide Determination

Hydrogen peroxide content of the irradiated samples was determined colormetrically using the method described by Allen, Hochanadel, Ghormley and Davis<sup>7</sup>. The method is based upon the oxidation of iodide by the hydrogen peroxide. The absorption of the  $I_3^-$  complex formed is measured at 350m $\mu$  using a Cary Model spectrophotometer.

The analysis is conducted by using a 4ml aliquot of sample in a 10ml flask. To this was added equal volumes (2.5ml) of the test reagents. The test reagents consist of: (1) a solution containing 1g. of NaOH, 33g. of potassium iodide and 0.1g. of  $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$  dissolved in 500ml of distilled water; (2) 10g. of potassium acid phthalate in 500ml of distilled water. The alkaline iodide solution is stable but the iodide reacts rapidly with peroxide in the presence of the molybdate catalyst at the pH of the mixture.

A calibration curve was used to convert the optical density readings to hydrogen peroxide concentration. This calibration curve is included in the appendix.

### Formaldehyde Determination

Formaldehyde content of the irradiated samples was determined colormetrically using the method described by Bricker and Johnson<sup>8</sup>. The method is based upon the condensation of formaldehyde with chromotropic acid.

The analysis is conducted by using 0.9ml aliquot of sample in a test tube. To this 0.5ml of chromotropic acid reagent (10% in water solution) is added, followed by 5ml of concentrated sulfuric acid. The mixture is heated on a boiling water bath for 30 minutes, cooled, and made up to exactly 50ml by dilution with water. The absorbance



of the resulting solution is measured at 570mu using a Cary Model spectrophotometer. The amount of formaldehyde is determined from a calibration curve. The calibration graph is included in the appendix.

## RESULTS

### A. Dose Rate Dependence

TABLE II shows the production of chloride ion for aqueous  $5.75 \times 10^{-2} \text{M}$  dichloromethane as the dose rate was increased from 13.7 rads/min. to 1244 rads/min. Since the  $G(\text{Cl}^-)$  value remains essentially constant, it can be assumed that there is no dose rate dependence thereby making it very unlikely that a chain occurs in the radiolysis of dichloromethane.

### B. Oxygen Concentration Dependence

TABLE III illustrates the effect of varying the concentration of oxygen in the sample. The values of  $G(\text{Cl}^-)$  for air and oxygen saturated solutions of aqueous  $5.75 \times 10^{-2} \text{M}$  dichloromethane are 14.9 and 12.9 respectively. The values of  $G(\text{H}_2\text{O}_2)$  for air and oxygen saturated solutions are 2.99 and 2.95 respectively. The concentration of oxygen is approximately  $2.5 \times 10^{-4} \text{M}$  in air saturated solution and  $1 \times 10^{-3} \text{M}$  in oxygen saturated solutions. Thus, a decrease in chloride ion concentration occurs with an increase in oxygen concentration and the hydrogen peroxide concentration remains fairly constant.

### C. Dichloromethane Concentration Dependence

The values of  $G(\text{Cl}^-)$  in oxygen saturated solutions increases from 11.5 to 16.3 while the concentration of dichloromethane increases from  $2.30 \times 10^{-2} \text{M}$  to  $2.30 \times 10^{-1} \text{M}$ . The values of  $G(\text{H}_2\text{O}_2)$  in oxygen saturated solutions show virtually no change while the dichloromethane concentration was varied over the same range. TABLE IV shows that the  $G(\text{Cl}^-)$  value increases with increasing dichloromethane concentration and the  $G(\text{H}_2\text{O}_2)$  values remain fairly constant.



TABLE II -  $G(\text{Cl}^-)$  Value at Various Dose Rates

Dose Rate (rads/min.)	$G(\text{Cl}^-)$
13.7	15.0
124.	14.8
434.	14.6
1244.	14.9

$\text{CH}_2\text{Cl}_2$  conc. =  $5.75 \times 10^{-2}\text{M}$

air saturated samples

TABLE III -  $G(\text{Cl}^-)$  and  $G(\text{H}_2\text{O}_2)$  Values Obtained from the Radiolysis of Dichloromethane varying the Oxygen Concentration

Atmosphere (saturated)	$G(\text{Cl}^-)$	$G(\text{H}_2\text{O}_2)$
air	14.9	2.99
oxygen	12.9	2.95

$\text{CH}_2\text{Cl}_2$  conc. =  $5.75 \times 10^{-2}\text{M}$



TABLE IV -  $G(\text{Cl}^-)$  and  $G(\text{H}_2\text{O}_2)$  Values Obtained when Varying the  
Dichloromethane Concentration in Oxygen Saturated Solutions

Concentration of Dichloromethane (saturated)	$G(\text{Cl}^-)$	$G(\text{H}_2\text{O}_2)$
$2.30 \times 10^{-1}\text{M}$	16.3	2.84
$1.73 \times 10^{-1}\text{M}$	15.1	
$1.15 \times 10^{-1}\text{M}$	13.8	3.00
$5.75 \times 10^{-2}\text{M}$	12.9	2.95
$2.30 \times 10^{-2}\text{M}$	11.5	

#### D. Scavenger Studies for the Solvated Electron

TABLE V shows the dependence of  $G(\text{Cl}^-)$  and  $G(\text{H}_2\text{O}_2)$  upon the concentration of nitrate ion, an efficient electron scavenger. As the nitrate concentration was increased from 0.0 to 0.05113 moles/liter, the values of  $G(\text{Cl}^-)$  decreased from 14.9 to 10.2 and the  $G(\text{H}_2\text{O}_2)$  values decreased from 2.99 to 1.38 in air saturated solutions of aqueous  $5.75 \times 10^{-2}\text{M}$  dichloromethane.

#### E. Formaldehyde Detection

Present work has noted the existence of formaldehyde as only a minor product of the radiolysis. A calibration curve for the colorimetric determination of formaldehyde has been obtained, but a precise value of  $G(\text{HCHO})$  has not yet been determined.



TABLE V -  $G(\text{Cl}^-)$  and  $G(\text{H}_2\text{O}_2)$  Values Obtained in Scavenger Studies  
for the Solvated Electron

Concentration of Nitrate	$G(\text{Cl}^-)$	$G(\text{H}_2\text{O}_2)$
0.0 moles/l.	14.9	2.99
0.00498 moles/l.	12.6	2.26
0.00996 moles/l.	12.5	1.83
0.05113 moles/l.	10.2	1.38

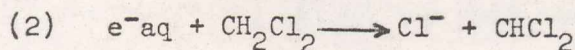
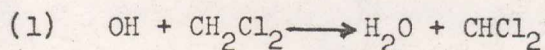
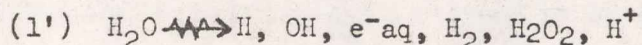
$\text{CH}_2\text{Cl}_2$  conc. =  $5.75 \times 10^{-2}\text{M}$

air saturated samples

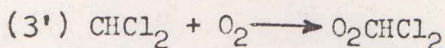
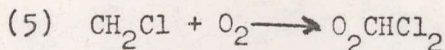
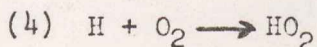
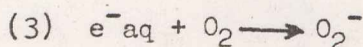
## DISCUSSION

The reactive species produced in water by gamma radiation are the solvated electron, hydrogen radicals, and hydroxyl radicals. Molecular hydrogen and hydrogen peroxide are also produced and are probably protected from radical attack by the relatively high concentrations of dichloromethane.

The reactions of the reactive species in aqueous dichloromethane are:



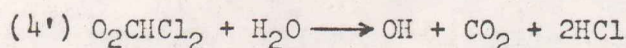
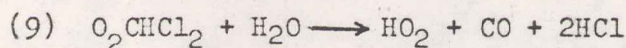
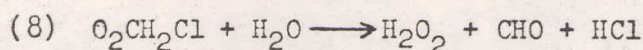
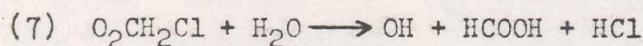
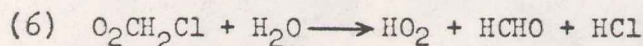
Since oxygen is a very efficient radical scavenger, the following additional reactions are expected to occur when solutions of aqueous dichloromethane are irradiated in the presence of oxygen



The experimental yield of chloride in the presence of oxygen was found to be much greater than the yields of primary radicals from the radiolysis of water. Absence of a dose rate effect implies that the large chloride yield is not the result of a chain reaction. But it is a well recognized fact that halo-organic peroxides undergo hydrolysis

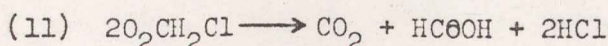
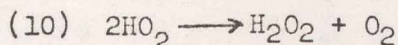


readily. Listed below are plausible hydrolytic reactions of the peroxy radicals formed in reactions (5) and (3'). Only those reactions in which hydrochloric acid is formed as a product have been considered.

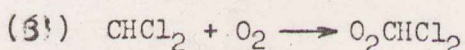
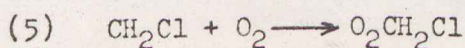
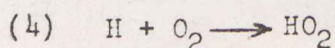
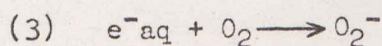
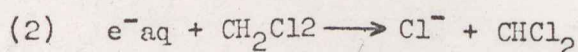
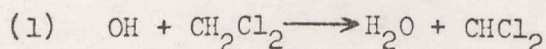
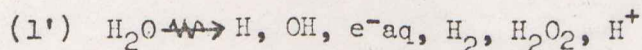


Reactions (8) and (4') are considered to be invalid due to the lack of a dose rate dependence. Reaction (6) is considered only a minor part of the mechanism due to the fact that only small amounts of formaldehyde have been detected in the irradiated solutions.

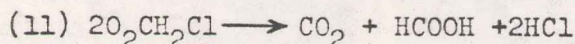
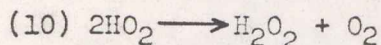
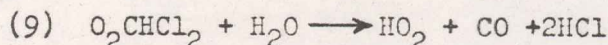
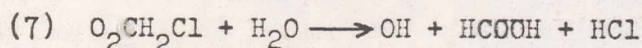
Peroxy radicals can also undergo disproportionation and the following reactions must be considered in the development of the radiolysis mechanism



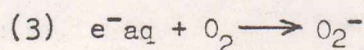
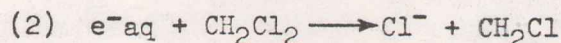
Using the above reactions a mechanism for the radiolysis of aqueous dichloromethane in the presence of oxygen can be proposed







The dependence of  $G(\text{Cl}^-)$  and  $G(\text{H}_2\text{O}_2)$  on oxygen concentration and dichloromethane concentration can be explained in terms of the competition between reactions (2) and (3) for the solvated electron



If the oxygen concentration increases while the dichloromethane concentration remains constant, the value of  $G(\text{Cl}^-)$  should decrease.

If the dichloromethane concentration increases while the oxygen concentration remains constant, the value of  $G(\text{Cl}^-)$  should increase.

The hydrogen peroxide yields should be essentially independent of either oxygen or dichloromethane concentration. These predicted changes in the value of  $G(\text{Cl}^-)$  and  $G(\text{H}_2\text{O}_2)$  are consistent with the results shown in TABLES III and IV.

Calculations from a proposed mechanism should result in  $G$  values which are the same as those experimentally observed. These calculations are based upon the general equation

$$G(P) = aG_{e^-_{\text{aq}}} + bG_{\text{OH}} + cG_{\text{H}} + dG_{\text{H}_2\text{O}_2}$$

wherein

$a$  = a number of molecules of product formed per solvated electron

$b$  = number of molecules of product formed per hydroxyl radical

$c$  = number of molecules of product formed per hydrogen radical



$d$  = number of molecules of product formed per molecule of hydrogen peroxide.

It is possible to estimate the theoretical maximum or minimum  $G(\text{Cl}^-)$  values allowed by the proposed mechanism. If the peroxy radical  $\text{O}_2\text{CH}_2\text{Cl}$  undergoes hydrolysis, reaction (7), to the exclusion of disproportionation reaction (11), the  $G(\text{Cl}^-)$  would be

$$G(\text{Cl}^-) = 4G_{\text{e-aq}} + 2G_{\text{OH}} = 17.8$$

If the peroxy radical  $\text{O}_2\text{CH}_2\text{Cl}$  undergoes disproportionation, reaction (11), to the exclusion of hydrolysis, reaction (7), the  $G(\text{Cl}^-)$  value would be

$$G(\text{Cl}^-) = 2G_{\text{e-aq}} + 2G_{\text{OH}} = 11.8$$

If both reactions (7) and (11) occur, the  $G(\text{Cl}^-)$  should be between 11.8 and 17.8. The observed value of 14.9 in air saturated  $-5.75 \times 10^{-2} \text{M}$  dichloromethane does lie within this range.

For these calculations values for air-saturated solutions must be used. Since in the air saturated solution the concentration of dichloromethane is 600 times that of oxygen, the competition between reactions (2) and (3) is rather insignificant.

From the experimental value of  $G_{\text{H}_2\text{O}_2}$  it is possible to estimate the value of  $G(\text{Cl}^-)$ . From the proposed mechanism one can write:

$$G(\text{Cl}^-) = (2) + (7) + 2(11) + 2(9) \quad (\text{a})$$

This equation is interpreted as follows:

The number of chloride ions formed per 100ev. is equal to the number of times reaction (2) occurs per 100ev. plus the number of times reaction (7) occurs per 100ev. plus twice the number of times

reaction (11) occurs per 100ev. plus twice the number of times reaction (9) occurs per 100ev.

In addition, from the proposed mechanism the following relationships exist:

$$(2) = G_{e^{-aq}} \quad (b)$$

$$(7) + 2(11) = G_{e^{-aq}} \quad (c)$$

$$G_{OH} + (7) = (9) \quad (d)$$

$$G_{H_2O_2} = 1/2 G_H + 1/2(9) + 1/2(7) \quad (e)$$

Now from (d) and (e)

$$(9) = G_{H_2O_2} + 1/2 G_{OH} - 1/2 G_H$$

Now making the appropriate substitutions into (a) one obtains

$$G(Cl^-) = 2G_{e^{-aq}} + 2G_{H_2O_2} + G_{OH} - G_H$$

Using the experimentally determined  $G_{H_2O_2} = 2.99$ ,

$G(Cl^-) = 14.4$  as compared to the  $G_{(Cl^-)} = 14.9$ , experimentally determined for air saturated aqueous  $5.75 \times 10^{-2} M$  dichloromethane.



BIBLIOGRAPHY

- (1) E. Hayon and J. Weiss, J. Chem. Soc. 1969, 5091
- (2) Hart, E.J., Ann. Rev. of Nucl. Science 15, (1965)
- (3) Daniels, M., and Wigg, E.E., J. Phys. Chem. 71, 1024, (1967)
- (4) Rezansoff, B.J., McCallum, K.J., and Woods, R.J., Can. J. Chem. 48, 271 (1970)
- (5) Woods, R.J., and Spinles, J. W. T., Can. J. Chem. 38, 77, (1960)
- (6) Bergman, J.G. and Sanik, J.Jr., Anal. Chem. 29, 241 (1957)
- (7) Allen, A.O., Hochanadel, C.J., Ghormley, J. A. and Davis, T.W. J. Phys. Chem. 56, 585 (1952)
- (8) Bricker, C.E. and Johnson, H.R., Ind. Eng. Chem., Anal. Ed., 17 400-2 (1945)

APPENDIX

Plot of Optical Density versus Irradiation Time for Fricke

Dosimeter .....	A - 1
Calibration Curve for Determination of Chloride Ion .....	A - 2
Calibration Curve for Determination of Hydrogen Peroxide..	A - 3
Calibration Curve for Determination of Formaldehyde .....	A - 4
Dose Rate Calculation .....	A - 5
Sample Calculation of $G(\text{Cl}^-)$ .....	A - 6



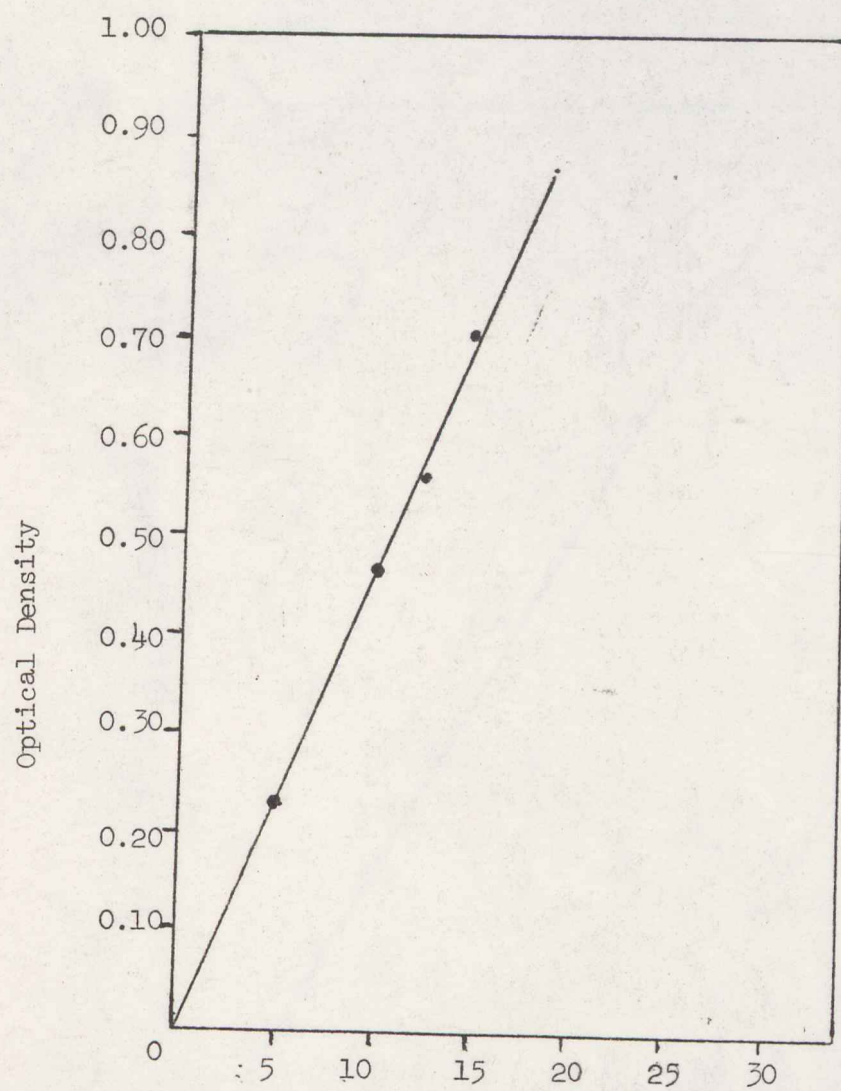


Fig. 3 - Plot of Optical Density versus  
Irradiation Time for Fricke Dosimeter

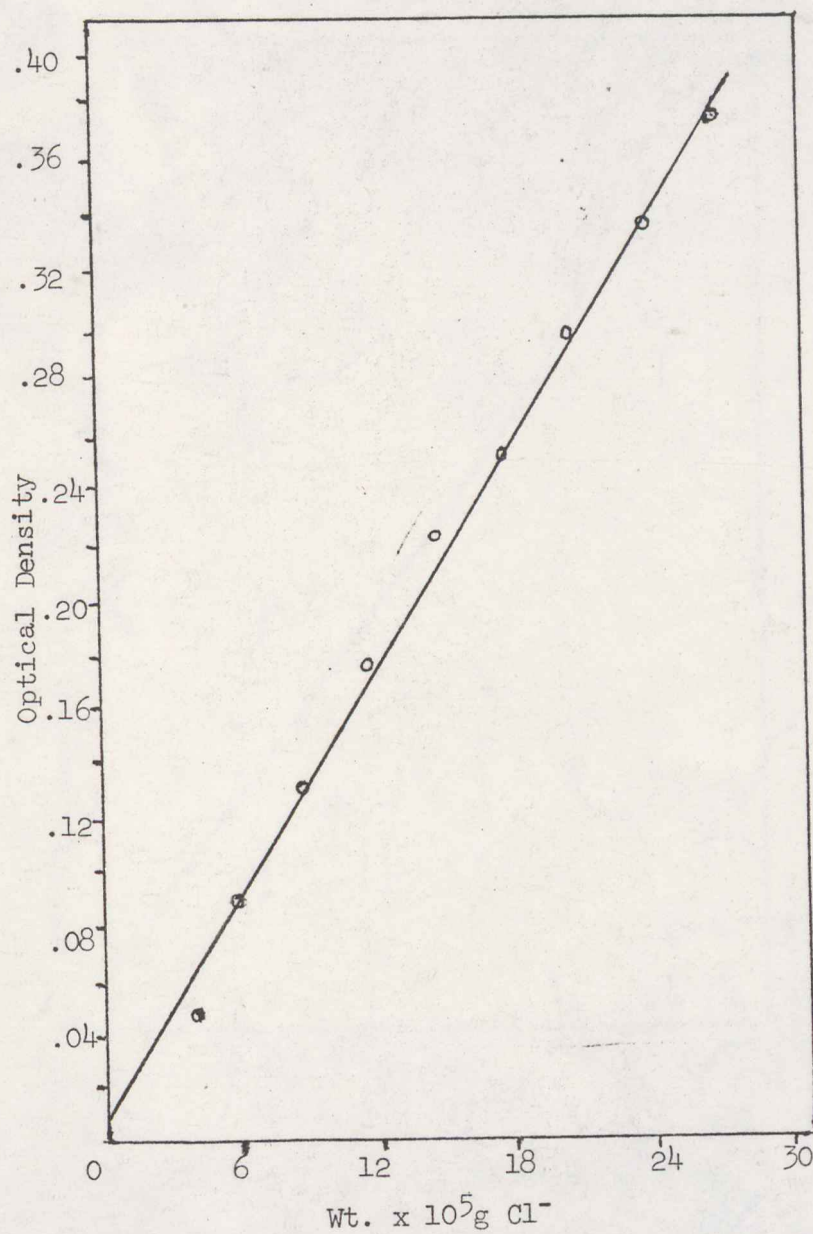


Fig. 4 - Calibration Curve for Determination of Chloride Ion



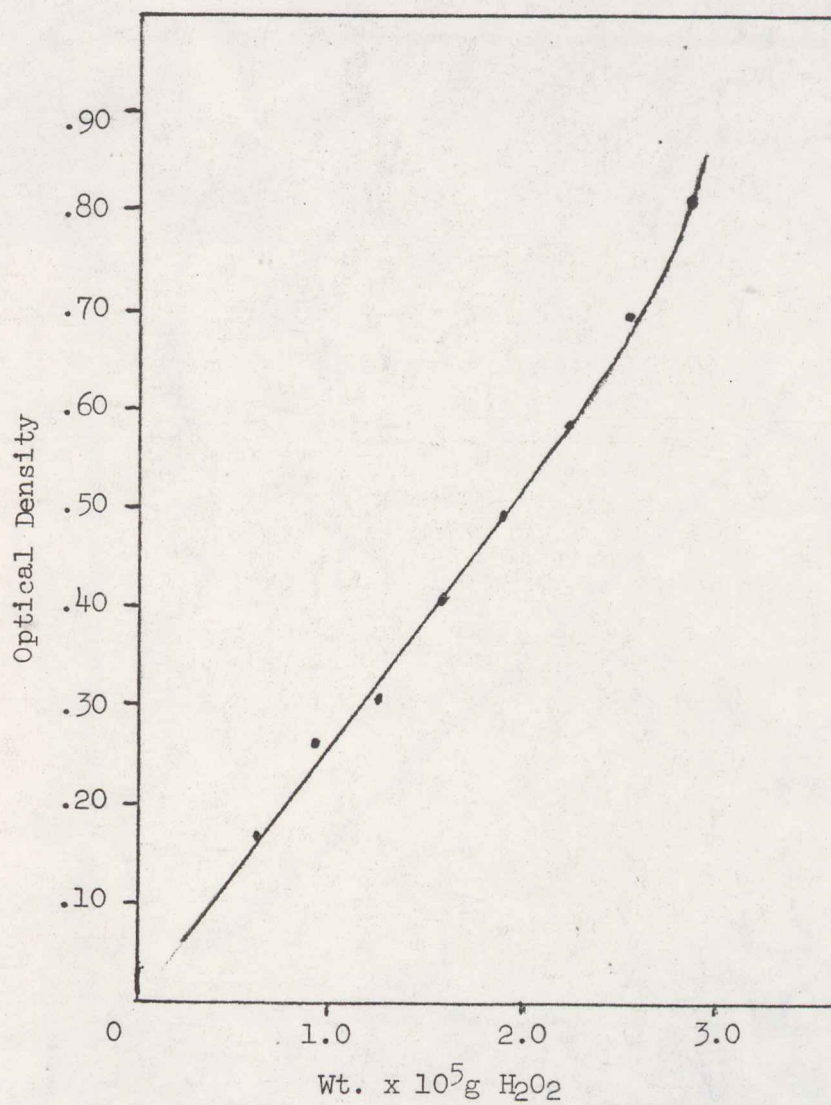


Fig. 5 - Calibration Curve for Determination of Hydrogen Peroxide

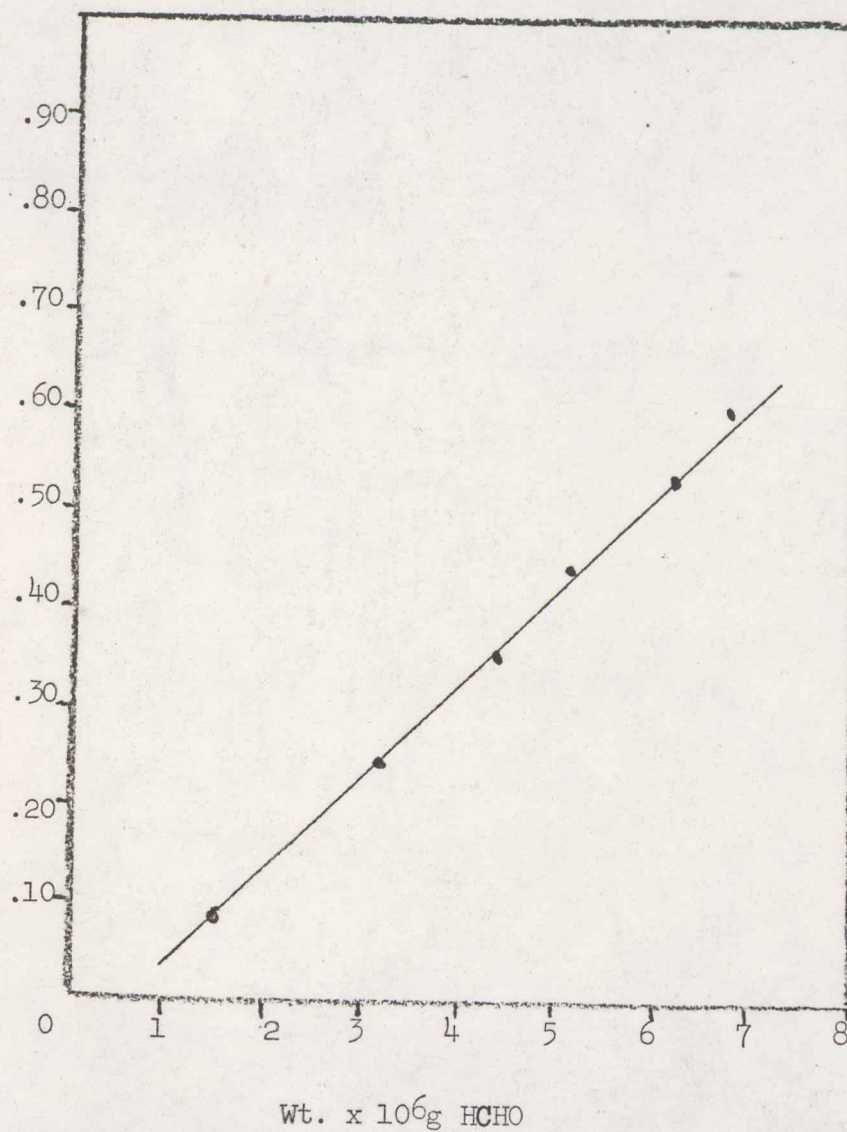


Fig. 5 - Calibration Curve for Determination of Formaldehyde



## SAMPLE DOSE RATE CALCULATION

Dose rate calculations are based upon the data obtained from the optical density of the Fricke dosimeters versus the length of the irradiation time and the following equation:

$$\text{Dose Rate } \frac{\text{e.v.}}{\text{g min}} = \frac{\Delta \text{ O.D.}}{\Delta T} \times \frac{N}{\epsilon d \rho} \times \frac{100 \text{ e.v.}}{G(\text{Fe}^{+3})}$$

$$\text{given } \frac{\Delta \text{ O.D.}}{\Delta T} = \text{from Figure 7, } \left( \frac{.45 - .23}{15 - 5} \right) = \frac{.044}{\text{min}}$$

$$\epsilon = 2178 \text{ at } 23.5^\circ\text{C}$$

$$d = 1 \text{ cm}$$

$$\rho = 1.024 \times 10^3 \text{ g l}^{-1} \text{ for } 0.8\text{N H}_2\text{SO}_4$$

$$N = 6.023 \times 10^{23}$$

$$G(\text{Fe}^{+3}) = 15.5$$

$$\text{Dose Rate} = \frac{.044 \times 6.023 \times 10^{23} \times 10^2}{2178 \times 1 \times 1.024 \times 10^3 \times 15.5}$$

$$= 7.62 \times 10^{16} \text{ e.v. g}^{-1} \text{ m}^{-1}$$

# SAMPLE CALCULATION OF G(Cl<sup>-</sup>)

A - 6

The calculation of G(Cl<sup>-</sup>) is based upon the initial slope data from the yield-dose curve and the following equations:

$$\frac{\text{molecules formed}}{\text{min}} = \frac{\Delta \text{Cl}^-}{\Delta T} \times \frac{N}{\text{M.W}}$$

$$\frac{\Delta \text{Cl}^-}{\Delta T} = \text{from Figure 3, } \frac{6.71 \times 10^{-5} \text{ g}}{10 \text{ min}}$$

$$N = 6.023 \times 10^{23}$$

$$\text{M.W} = 35.45.$$

$$\frac{\text{molecules formed}}{\text{min}} = \frac{6.71 \times 10^{-6} \times 6.023 \times 10^{23}}{35.45}$$

$$= 1.14 \times 10^{17}$$

$$\frac{\text{dose}}{\text{min}} = D_R \times \rho \times v$$

$$D_R = 7.56 \times 10^{16} \text{ e.v. g}^{-1} \text{ min}^{-1}$$

$$\rho = 1.01 \text{ g ml}^{-1}$$

$$v = 10 \text{ ml}$$

$$\frac{\text{dose}}{\text{min}} = 7.56 \times 10^{16} \times 1.01 \times 10$$

$$= 7.635 \times 10^{17} \text{ ev min}^{-1}$$



$$\frac{\text{molecules}}{\text{dose}} = \frac{\text{molecules formed min}^{-1}}{\text{dose min}^{-1}}$$

$$= \frac{1.14 \times 10^{17}}{7.635 \times 10^{17}}$$

$$= .1492 \text{ molecules ev}^{-1}$$

$$\text{note } G(P) = \frac{\text{molecules}}{100\text{ev}}$$

$$G(\text{Cl}^-) = 14.92$$