UNION COLLEGE - GRADUATE STUDIES

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A STUDY OF THE RADIOLYSIS OF AQUEOUS DICHLOROMETHANE

A thesis presented to the Committee on Graduate Studies and the Department of Chemistry of Union College, Schenectady, New York in partial fulfillment of the requirements for the degree of Master of Science.

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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 analysis of irradiated solutions has shown that hydrochloric acid and formic acid are among the products of the decomposition.

The effect of oxygen and dichloromethane concentrations on the production and yield of chloride ion has been determined.

From the results, a mechanism for the radiolysis of aqueous dichloromethane in the presence of oxygen has been deduced.

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INTRODUCTION

The radiolysis of aqueous solutions of organic compounds containing halogens became of interest because of the possible use of such systems as chemical dosimeters. However a greater interest developed in the actual reactions occurring between the solute and the intermediate radicals which are formed by the irradiation of water.

A. Radiolysis of Water

The initial studies to determine the principal products formed when water has been irradiated with energetic photons concluded that radical and molecular species were formed

$$H_2O \rightsquigarrow H,\ OH,\ H_2O_2,\ H_2,\ H^+$$

However there was not much known about the actual processes that could give rise to these products. Later studies concluded that the energetic photons liberate high energy electrons from solvent molecules. These electrons then interact with other solvent molecules causing ionization and disassociation

$$H_2O \rightsquigarrow H_2O^+ + e^-$$

$$H_2O^+ \rightarrow H^+ + OH$$

$$H_2O \rightarrow H + OH$$

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

$$H + H \rightarrow H_2$$

$$OH + OH \rightarrow H_2O_2$$

In 1952, Allen, Hochanadel, Ghormley, and Davis(1) being concerned with the decomposition of water in a nuclear reactor, performed studies of the radiolysis of water with various concentrations of added hydrogen, oxygen, and hydrogen peroxide. The expected reactions were

(1") $OH + H_2 \rightarrow H_2O + H$

(2") $H + H_2O_2 \rightarrow H_2O + OH$

(3") $H + O_2 \rightarrow HO_2$

(4") $2HO_2 \rightarrow H_2O_2 + O_2$

The studies however lead to results that could not be fully explained in terms of these reactions.

In 1953 Platzman(2) mathematically concluded that some of the secondary electrons produced by the interaction of the high speed electrons with water molecules would escape the electrostatic attraction of the parent ion and would become solvated.

In 1959 Barr and Allen(3) continued the 1952 studies and were forced to conclude that the "hydrogen atom" produced by the oxidation of molecular hydrogen with hydroxyl radical in reaction (1") was not the same as the "hydrogen atom" formed in the radiolysis of water.

Other evidence mounted that Barr and Allen's strange "hydrogen atom" from water radiolysis was Platzman's solvated electron. In 1965, Hart(4) through pulse radiolysis and absorption spectrum studies conclusively demonstrated the existence of the solvated electron. Thus it is now believed that the primary products of the radiolysis are

$$H \rightsquigarrow H,\ OH,\ e^-_{aq},\ H_2,\ H_2O_2,\ H^+$$

The yields of these primary radicals and molecular products are determined quantitatively versus the amount of energy received by the aqueous solution. These yields are expressed in terms of the G value which is defined as the number of particles produced per one hundred e.v. of energy absorbed by the solution. The yields of these primary products in neutral aqueous solutions, extrapolated to zero concentration of solute, are:

$G_{e^-_{aq}} = 2.85$, $G_{OH} = 2.25$, $G_{H_2O_2} = 0.7$, and $G_H = 0.55$(5).

B. Radiolysis of Aqueous Solutions

In the radiolysis of aqueous solutions the energetic photon will react with molecules of either the solvent or the solute which are in its path. The reactions of the photon with the solute are inconsequential when the concentration is 1×10^{-1}M or less. In these dilute solutions the effects of interest are the reactions between the species from the radiolysis of the water and the solute.

C. Radiolysis of Aqueous Organic Halogen Compounds

Upon radiolysis, aqueous solutions of some organic compounds containing halogens produce yields of halide ion which are in many cases much larger than the yields of the primary radicals produced from the radiolysis of water. For the radiolysis of aqueous chloroform in the presence of oxygen, Teply and Bednar(6) in 1958 obtained a value of $G(Cl^-) = 25.8 \pm 1.3$. They proposed a chain mechanism to account for the yield of halide ion. Their proposed mechanism includes the following reactions

(0') $H_2O \rightsquigarrow H, OH, H_2, H_2O_2, H^+$

(1') $OH + CHCl_3 \rightarrow H_2O + CCl_3$

(2') $CCl_3 + O_2 \rightarrow ClO + COCl_2$

(3') $ClO + CHCl_3 \rightarrow HCl + COCl_2 + Cl$

(4') $Cl + CHCl_3 \rightarrow HCl + CCl_3$

Reactions (2'), (3'), and (4') are the chain propogating steps. The radical CCl_3 is consumed in reaction (2') and is regenerated in reaction (4'). The work by Teply and Bednar was done prior to actual discovery of the hydrated electron, therefore the hydrated electron played no part in their mechanism.

Woods and Spinks(7) 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(7)

Compound	G(halide ion)		
	dose rate		
	1020 rads/min	450 rads/min	17 rads/min
$Br_3C-CH(OH)_2$	69	98	360
$Cl_3C-CH(OH)_2$	43	50	112
Br_3C-CH_2OH	31	32	89
Cl_3C-CH_2OH	24.5		27
Cl_3CH	27		27
$Br_3C-COOH$	41	38	39
$Cl_3C-COOH$	16		15.5

A chain reaction terminated by recombination of chain propogating radicals will be reflected by a dose rate dependence. In Table I, this relationship is very apparent for the radiolysis of $Br_3C-CH(OH)_2$. The $G(Br^-)$ value increased from 69 to 360 as the dose rate decreased from 1020 rads/min to 17 rads/min. Woods, et al, recognized that a dose rate dependence could 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 apparently what happens in the radiolysis of aqueous Br_3C-CH_2OH. From Table I it can be seen that there is no real change in $G(Br^-)$ until the dose rate becomes less than 450 rads/min. This relationship is not so apparent for the radiolysis of aqueous chloroform. From Table I the value of $G(Cl^-)$ does not change as the dose rate is decreased from 1020 rads/min to 17 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-existant part in the mechanism at dose rates above 17 rads/min.

In 1969, Rezansoff, McCallum, and Woods(8) did additional studies to clarify the mechanism of the radiolysis of aqueous chloroform. They reported a value of $G(Cl^-) = 28.4 \pm 1.0$. The mechanism which they propose for the radiolysis of chloroform does not involve a chain and includes the following reactions

(5') $H_2O \rightsquigarrow H, OH, e^-_{aq}, H_2, H_2O_2, H^+$

(6') $e^-_{aq} + CHCl_3 \rightarrow Cl^- + CHCl_2$

(7') $CHCl_2 + O_2 \rightarrow O_2CHCl_2$

(8') $O_2CHCl_2 + H_2O \rightarrow OH + CO_2 + 2HCl$

(9') $OH + CHCl_3 \rightarrow H_2O + CCl_3$

(10') $CCl_3 + O_2 \rightarrow O_2CCl_3$

(11') $O_2CCl_3 + 2H_2O \rightarrow HO_2 + CO_2 + 3HCl$

(12') $CHCl_2 + H_2O \rightarrow CHO + 2HCl$

(13') $CHO + CHCl_3 + H_2O$

$\rightarrow CHCl_2 + HCOOH + HCl$

(14') $H + O_2 \rightarrow HO_2$

(15') $2HO_2 \rightarrow H_2O_2 + O_2$

Based upon their proposed mechanism, the following relationships exist between the calculated and the observed values for $G(Cl^-)$ and $G(H_2O_2)$

$$G(Cl^-) = 6\ G_{e^-_{aq}} + 3\ G_{OH} + 3\ G(HCOOH)$$

$$= 28.77$$

Found 28.4 ± 1.0

$$G(H_2O_2) = G_{H_2O_2} + 0.5\ 6_H + 0.5 G_{e^-_{aq}} + 0.5\ 6_{OH}$$

$$= 3.89$$

Found 2.3 ± 0.1

The calculated and experimentally obtained values for $G(Cl^-)$ are in close agreement. However the differences between the calculated and observed values for $G(H_2O_2)$ leaves some doubt as to the correctness of the proposed mechanism.

D. Purpose of Investigation

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

Previous investigations by Festa and Odre(9) have produced for air saturated samples of aqueous dichloromethane ($5.7 \times 10^{-2}M$) values of $G(Cl^-) = 15.3$ and $G(H_2O_2) = 3.0$. It was also found that the product yield is independent of dose rate in the range studied 13.7 to 1237 $rads/min^{-1}$. From this it has been determined that the mechanism is probably not a chain mechanism and definitely is not one which is terminated by a recombination of chain propogating radicals.

In the present effort, the effect of oxygen concentration and dichloromethane concentration on the product yield has been determined. In addition formic acid has been detected as one of the products of the radiolysis. With this information a reasonable mechanism has been proposed for the radiolysis of aqueous dichloromethane in the presence of oxygen.

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 permangamate. 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 condenser.

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

The radiation ampoules, Figure 1-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. The

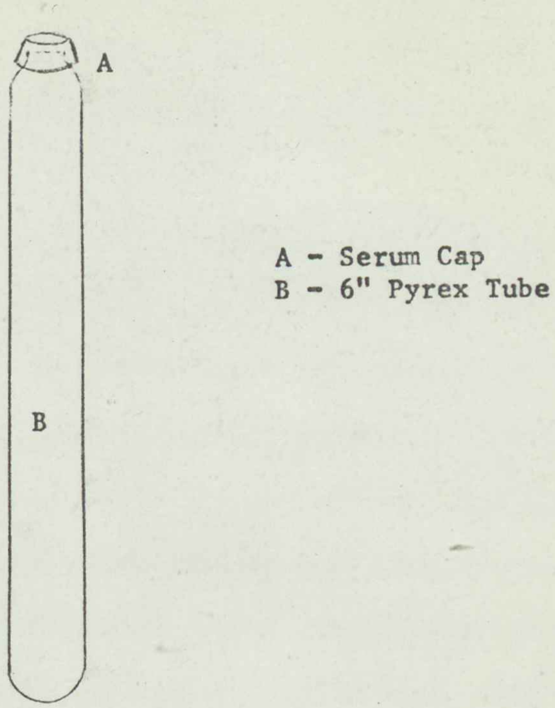


Fig. 1-A RADIATION VESSEL

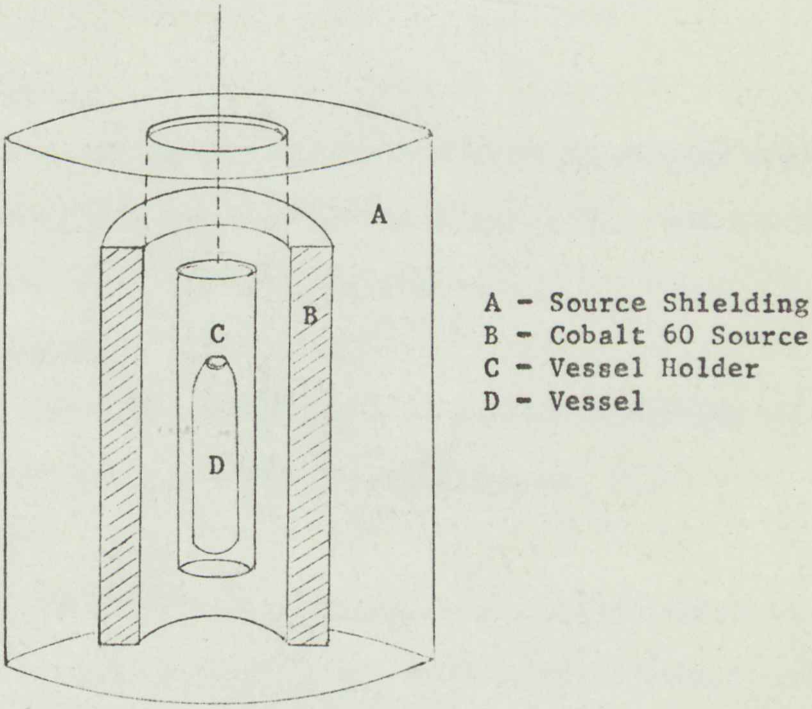


Fig. 1-B COBALT 60 SOURCE

Fig. 1 RADIATION VESSEL AND COBALT 60 SOURCE concentration of the solution at room temperature was approximately 2.3×10^{-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 1-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(10). Utilizing a value of $G(Fe^{+3}) = 15.5$, the dose rate was determined to be 7.5×10^{16} e.v.g^{-1} min^{-1}.

C. Analysis

Chloride Ion Determination

The chloride ion content of the irradiated samples was determined colormetrically using an adaptation of the method described by Bergman and Sanik(11). The method is based upon the displacement by chloride ion of the thiocyanate ion from mercury thiocyanate in the presence of Fe^{+3}. The absorption of the iron-thiocyanate complex formed is measured at 450 nm using a Beckman Model Du spectrophotomer 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 thiocyanate. After mixing well, the solution is diluted to the mark. At ten minutes after the addition of the mercuric thiocyanate, 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 Ion Determination

The hydrogen ion content was determined by measuring the pH of the irradiated solution using a Beckman, Century SS, expanded scale, pH meter and a Beckman combination electrode. The hydrogen ion concentrations were corrected for activities using a table of standard activity coefficients for hydrochloric acid.

Formic Acid Determination

Most analytical procedures found in the literature for the determination of micro amounts of formic acid require the acid to be determined indirectly either by the measurement of formaldehyde after reduction of the acid or by the measurement of carbon dioxide after oxidation of the acid. Because of the possibility that minute amounts of formaldehyde could be a product of the radiolysis, and that carbon dioxide is a probable product of the radiolysis, a direct method for the determination of formic acid was deemed necessary to insure accurate results.

The isotopic dilution method used by Rezansoff, et al, was explored, but was found to be prohibitively expensive.

The colormetric method described by Draganic(12) was investigated but it was determined that hydrochloric acid interferes with the reaction.

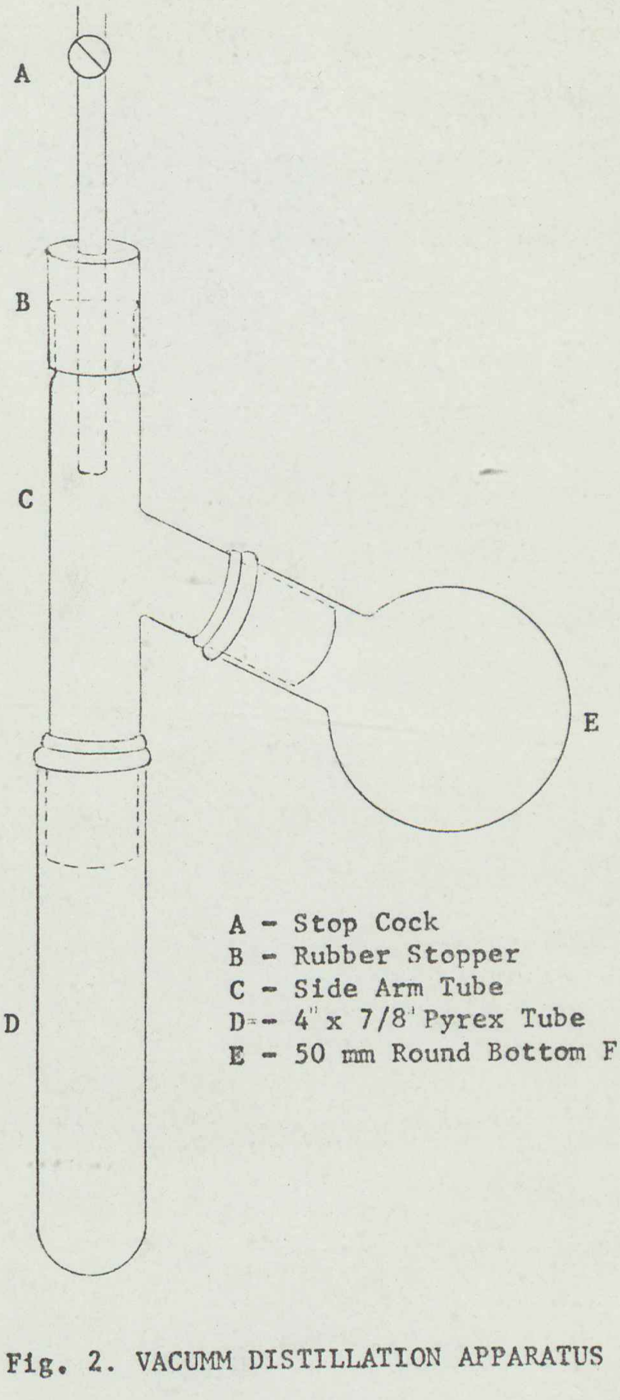
Recognizing the futility of the search for an acceptable direct method, an adaptation of a method described by Grant(13) was used to detect formic acid. The method is the reduction of the formic acid to formaldehyde using hydrochloric acid and magnesium

$$HCOOH + Mg + HCl \rightarrow HCHO + MgCl_2 + H_2O.$$

The formaldehyde is then reacted with chromotropic acid (1, 3-dehydroxy napthalene, 6, 8-disulfonic acid) producing a violet colored complex whose optical density is measured at 570 nm.

Formaldehyde is formed in the radiolysis of aqueous dichloromethane. Since the primary purpose was to detect formic acid, the formaldehyde was removed by a distillation technique suggested by Grant. The distillation apparatus used is shown in Figure 2.

The analysis of the irradiated sample was conducted by carefully placing about 16 mg of phenylhydrazine hydrochloride in the bottom of the 50 ml side arm flask. To this was slowly added 2 ml of the irradiated solution. The phenylhydrazine reaction was allowed to proceed at room temperature for about 10 minutes, or until all of the phenylhydrazine had become wet by the liquid. The distillation flask was assembled carefully, insuring that the liquid remained in the side flask. The contents of the side flask were frozen in a dry ice-acetone mixture. With the side flask being maintained at the freezing temperature, the apparatus was evacuated to about 0.1 mm of mercury.The position of the evacuated apparatus was then adjusted so that the receiver tube was immersed about one inch in a dry ice-acetone mixture and distillation to dryness was allowed to proceed at room temperature. About three hours were required for the distillation. A 0.5ml aliquot of the distillate was placed carefully in the bottom of a test tube immersed in a 0°C bath. To this was added a tightly coiled strip of magnesium which was 10 cm long by 3 mm wide and weighed approximately 80 mg. The strip had been burnished to brightness using steel wool, and then stored in a desicator over sodium hydroxide to protect it from atmospheric attack. To this was added 0.5 ml of concentrated hydrochloric acid in portions of 0.05 ml at intervals of not less than one minute. At one minute after the last portion of hydrochloride had been added, 1.5 ml of the chromotropic acid reagent was added and the tube was immersed in boiling water for a period of thirty minutes. The precautions against absorption of water vapor or uneven illumination suggested



A - Stop Cock
B - Rubber Stopper
C - Side Arm Tube
D - 4" x 7/8" Pyrex Tube
E - 50 mm Round Bottom Flask

Fig. 2. VACUMM DISTILLATION APPARATUS

period of thirty minutes. The precautions against absorption of water vapor or uneven illumination suggested by MacFayden(14) were observed. When the solution was removed from the boiling water bath, it was diluted with 3 ml of water stirred well. The precipitate of $MgCl_2$ was allowed to settle. After about five minutes the optical density of the supernatant liquid was measured using a Cary Model 14 Spectrophotometer and a 1 cm cell.

RESULTS

A. Chloride Ion Production

Figure 3 shows the production of chloride ion as a function of dose for aqueous 5.75 x 10^{-2}M dichloromethane in oxygen, air and nitrogen saturated solutions. Figure 4 shows this same relationship for aqueous 2.3 x 10^{-1}M dichloromethane in oxygen saturated solutions. The product yield (G value) is determined from the initial slope data of the plot.

The curves are fairly linear over the dose range under consideration with the exception of the curve for air saturated solutions which has an abrupt change of slope at about a dose of 13 x 10^{15} e.v.g^{-1}. This abrupt change is due to oxygen depletion in the solution. Similar results were obtained by Teply and Bednar in the radiolysis of air saturated aqueous 7 x 10^{-2}M chloroform solutions.

In Figure 3, the slope in the upper portion of the curve of air saturated solutions corresponds to a $G(Cl^-) = 4.37$. The slope for the curve for nitrogen saturated solutions corresponds to a $G(Cl^-) = 5.07$. This confirms that the change of slope is due to a depletion of oxygen in the system.

The values of $G(Cl^-)$ for air and oxygen saturated solutions of aqueous 5.75 x 10^{-2}M dichloromethane are 14.9 and 12.79, respectively. The concentration of oxygen is approximately 2.5 x 10^{-4}M in air saturated solution and 1 x 10^{-3}M in oxygen saturated solutions. Thus, a decrease of chloride ion production occurs with an increase in concentration of oxygen.

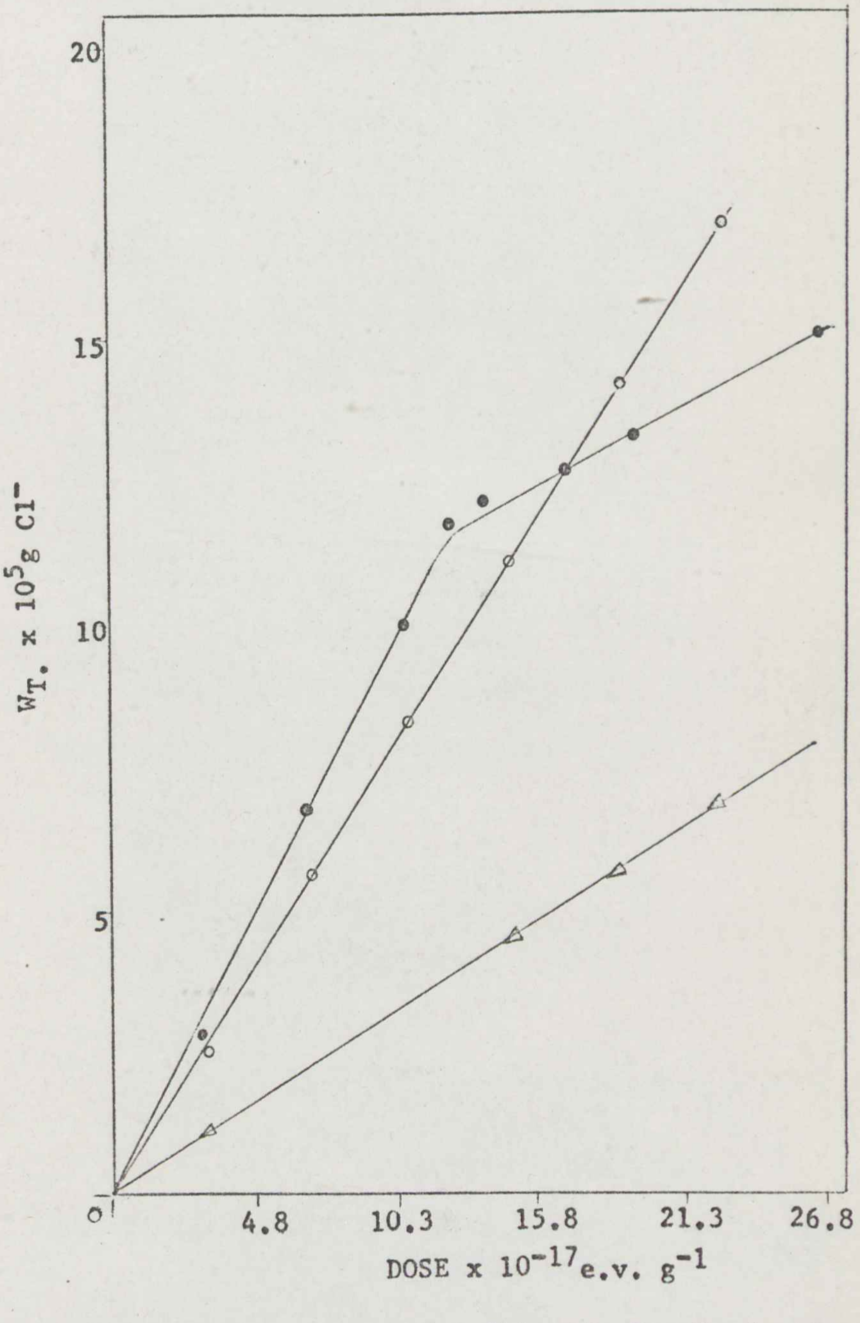


Fig. 3. Yield-Dose Curves for Chloride Ion Production in Irradiated Aqueous 5.75×10^{-2}M Dichloromethane, (o) Oxygen Saturated, (•) Air Saturated, (△) Nitrogen Saturated

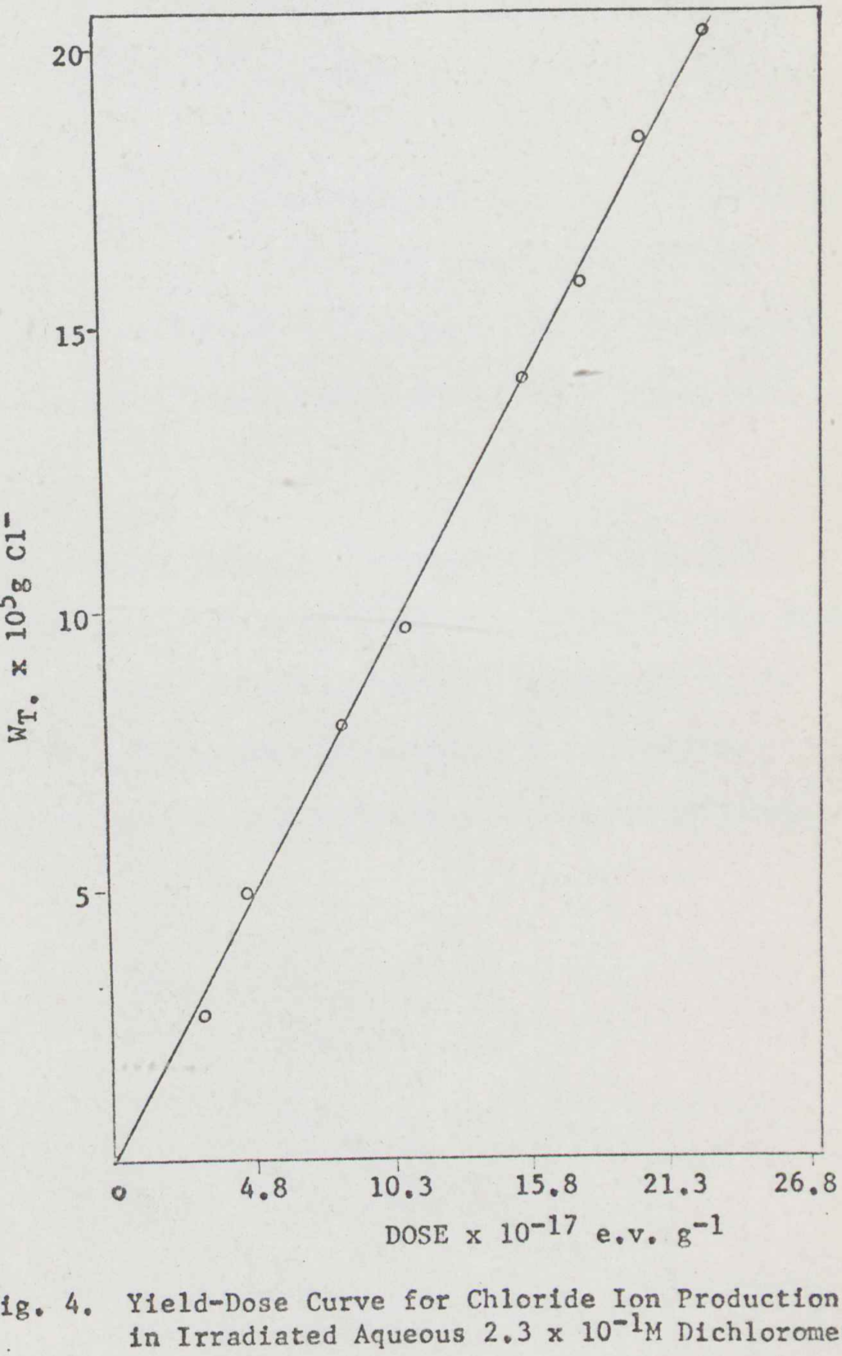


Fig. 4. Yield-Dose Curve for Chloride Ion Production in Irradiated Aqueous 2.3×10^{-1}M Dichloromethane

A comparison of the G(Cl^-) values in Table II for the different concentrations of dichloromethane in oxygenated solutions shows that an increase of chloride ion production occurs with an increase in concentration of dichloromethane. The G(Cl^-) values for the 2.3 x 10^{-1}M and the 5.75 x 10^{-2}M dichloromethane solutions are 12.8 and 15.2 respectively.

B. Hydrogen Ion Production

Figure 5 shows the production of hydrogen ion as a function of dose. From the slope data, G(H^+) = 12.3. This yield, within experimental error, is about the same as the G(Cl^-) = 12.8 value from these solutions. Therefore the principal product of the radiolysis is hydrochloric acid.

C. Formic Acid Detection

Figure 6 shows the results from the chromotropic acid test for formic acid upon irradiation of 5.75 x 10^{-2}M aqueous dichloromethane (oxygen saturated) solutions. The results clearly indicate an increase in the production of formic acid with an increase in dose. No calibration curve was prepared and thus a G value for formic acid was not obtained.

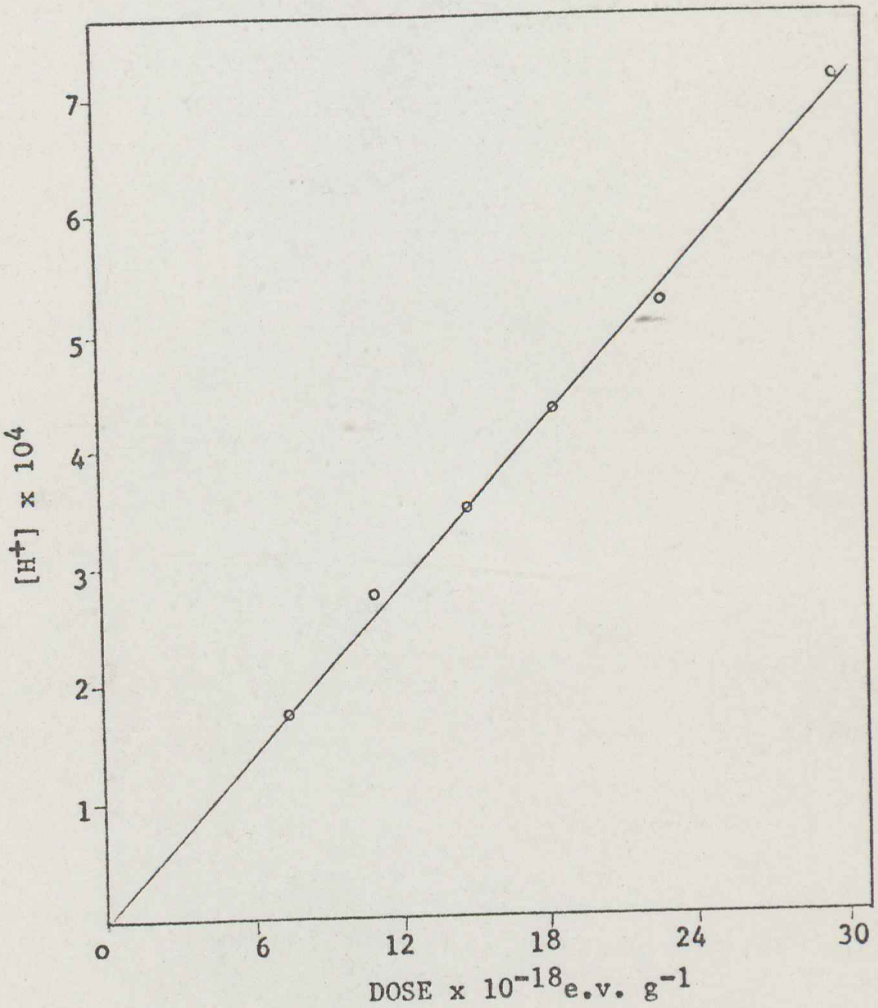


Fig. 5. Yield-Dose Curve for Hydrogen Ion Production in Irradiated Aqueous 5.75×10^{-2}M Dichloromethane

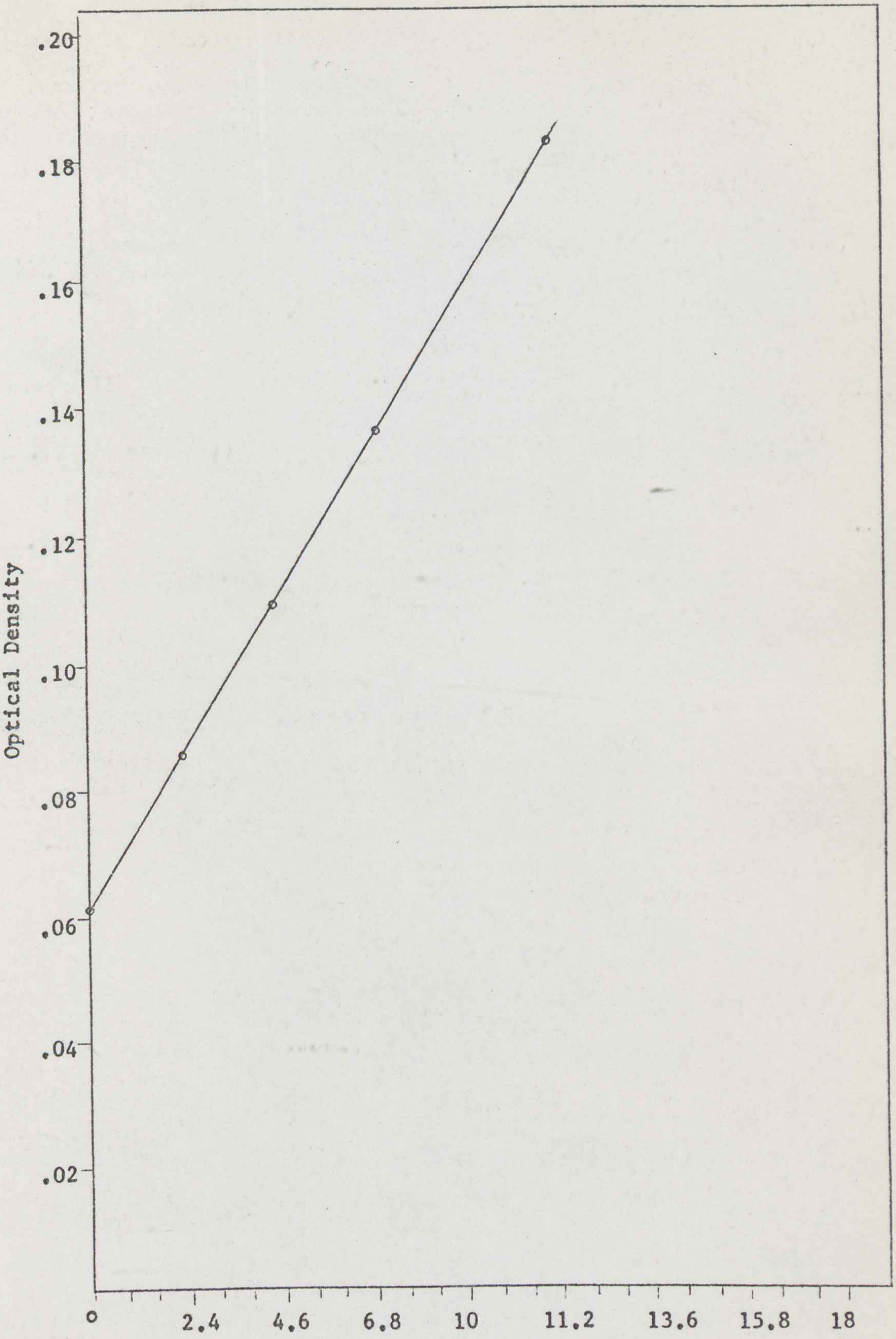


Fig. 6. Optical Density-Dose Curve for Formic Acid Produced in Irradiated Aqueous 5.75 x 10^{-2}M Dichloromethane

TABLE II

G Values Obtained from Gamma Irradiated

Aqueous Dichloromethane

CH_2Cl_2 Concentration	Atmosphere	$G(Cl^-)$	$G(H^+)$	G(HCOOH)
5.75×10^{-2}	O_2	12.8	12.3	Present
	Air	14.9 (4.37)		
	N_2	5.07		
2.3×10^{-1}	O_2	15.2		

(4.37) Value after dose of 13×10^{15} e.v.g^{-1}

DISCUSSION

The reactive species produced in the radiolysis of water are hydrated electrons, hydrogen radicals, and hydroxyl radicals. 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:

(0) $H_2O \rightsquigarrow H, OH, e^-_{aq}, H_2, H_2O_2, H^+$

(1) $e^-_{aq} + CH_2Cl_2 \rightarrow Cl^- + CH_2Cl$

(2) $OH + CH_2Cl_2 \rightarrow H_2O + CHCl_2$

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.

(3) $e^-_{aq} + O_2 \rightarrow O_2^-$

(4) $H + O_2 \rightarrow HO_2$

(5) $CH_2Cl + O_2 \rightarrow O_2CH_2Cl$

(6) $CHCl_2 + O_2 \rightarrow O_2CHCl_2$

The yields of chloride ion were found to be much higher than the yields of the primary radicals from the radiolysis of water. The absence of a dose rate dependence gives a very low probability that a chain mechanism occurs.

It is well recognized that halo-organic peroxides undergo hydrolysis readily. Listed below are plausible hydrolytic reactions of the peroxy radicals formed in reactions (5) and (6). Only those reactions in which hydrochloric acid is formed as a product have been considered.

(7) $O_2CH_2Cl + H_2O \rightarrow HO_2 + HCHO + HCl$

(8) $O_2CH_2Cl + H_2O \rightarrow OH + HCOOH + HCl$

(9) $O_2CH_2Cl + H_2O \rightarrow H_2O_2 + CHO + HCl$

(10) $O_2CHCl_2 + H_2O \rightarrow OH + CO_2 + 2HCl$

(11) $O_2CHCl_2 + H_2O \rightarrow HO_2 + CO + 2HCl$

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

(12) $2HO_2 \rightarrow H_2O_2 + O_2$

(13) $2O_2CH_2Cl \rightarrow CO_2 + HCOOH + 2HCl$

The proposed mechanism for the radiolysis of aqueous dichloromethane in the presence of oxygen is:

(0) $H_2O \rightsquigarrow H, OH, e^-_{aq}, H_2, H_2O_2, H^+$

(3) $e^-_{aq} + O_2 \rightarrow O_2^-$

(1) $e^-_{aq} + CH_2Cl_2 \rightarrow Cl^- + CH_2Cl$

(2) $OH + CH_2Cl_2 \rightarrow H_2O + CHCl_2$

(4) $H + O_2 \rightarrow HO_2$

(5) $CH_2Cl + O_2 \rightarrow O_2CH_2Cl$

(6) $CHCl_2 + O_2 \rightarrow O_2CHCl_2$

(8) $O_2CH_2Cl + H_2O \rightarrow OH + HCOOH + HCl$

(13) $2\ O_2CH_2Cl \rightarrow CO_2 + HCOOH + 2HCl$

(11) $O_2CHCl_2 + H_2O \rightarrow HO_2 + CO + 2HCl$

(12) $2HO_2 \rightarrow H_2O_2 + O_2$

Since formaldehyde is only a minor product of the radiolysis, a reaction for its formation has not been included in the above mechanism. Small amounts of formaldehyde may be formed via reaction (7).

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

$$G(P) = aG_{e^-_{aq}} + bG_{OH} + cG_H + dG_{H_2O_2}$$

wherein

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

Not knowing the rate constants for all of the competing reactions, a $G(Cl^-)$ value based upon the proposed mechanism can not be determined. However we can estimate the theoretical maximum or minimum $G(Cl^-)$ values allowed by the proposed mechanism. If the peroxy radical O_2CH_2Cl undergoes hydrolysis, reaction (8), to the exclusion of disproportionation, reaction (13), then $G(Cl^-)$ would be

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

If the peroxyl radical O_2CH_2Cl undergoes disproportionation, reaction (13), to the exclusion of hydrolysis, reaction (8), the $G(Cl^-)$ value would be

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

If both reactions (8) and (13) occur, then $G(Cl^-)$ should be between 11.8 and 17.8. The observed value of 14.9 does lie within this range.

Using this same argument, the observed value of $G(H_2O_2)$ should lie within the range

$$0.5G_{OH} + 0.5G_H + G_{H_2O_2} < G(H_2O_2)_{obs} < 0.5G_{e^-_{aq}} + 0.5G_{OH} + 0.5G_H + G_{H_2O_2}$$

Substituting the values for the primary yield, one obtains

$$2.4 < G(H_2O_2)_{obs} < 3.9$$

The observed value for $G(H_2O_2)_{obs}$ is 3.0. (15)

The dependence of $G(Cl^-)$ on oxygen concentration and dichloromethane concentration can be explained in terms of the competition between reaction (3) and reaction (1) for the solvated electron.

$$(3) \qquad e^-_{aq} + O_2 \rightarrow O_2^-$$

$$(1) \qquad e^-_{aq} + CH_2Cl_2 \rightarrow Cl^- + CH_2Cl$$

If the oxygen concentration increases while the dichloromethane concentration remains constant, the value of $G(Cl^-)$ should decrease. If the dichloromethane concentration increases while the oxygen concentration remains constant, the value of $G(Cl^-)$ should increase. These predicted changes in the value of $G(Cl^-)$ are consistent with the results shown in Table II.

The proposed mechanism for the radiolysis of aqueous dichloromethane in the presence of oxygen presupposes that formic acid is one of the major products. Assuming that formic acid is formed in reactions (8) and (13), the value of G(HCOOH) should lie between 1.5 and 3.0.

Once the value of G(HCOOH) has been obtained it is possible to estimate the theoretical value of $G(Cl^-)$. From the proposed mechanism we can write

$$G(Cl^-) = (1) + (8) + 2(13) + 2(11) \qquad (a)$$

This equation is interpreted as follows:

> The number of chloride ions formed per 100 e.v. is equal to the number of times reaction (1) occurs per 100 e.v. plus the number of times reaction (8) occurs per 100 e.v. plus twice the number of times reaction (13) occurs per 100 e.v. plus twice the number of times reaction (11) occurs per 100 e.v.

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

$$(1) = G_{e^-_{aq}} \qquad (b)$$

$$(8) + 2\ (13) = G_{e^-_{aq}} \qquad (c)$$

and also

$$G_{OH} + (8) = (11) \qquad (d)$$

$$(8) + (13) = G(HCOOH) \qquad (e)$$

Now from (b), (c) and (d)

$$(11) = G_{OH} + 2G(HCOOH) - G_{e^-_{aq}}$$

Now making the appropriate substitutions into (a) we obtain

$$G(Cl^-) = 4G(HCOOH) + 2G_{OH}$$

Based upon the value of $G(Cl^-) = 14.9$ for air saturated aqueous 5.75×10^{-2}M dichloromethane, the relationship predicts that the value of G(HCOOH) should be about 2.3.

Future work should include an accurate determination of G(HCOOH) to see if the derived relationship holds.

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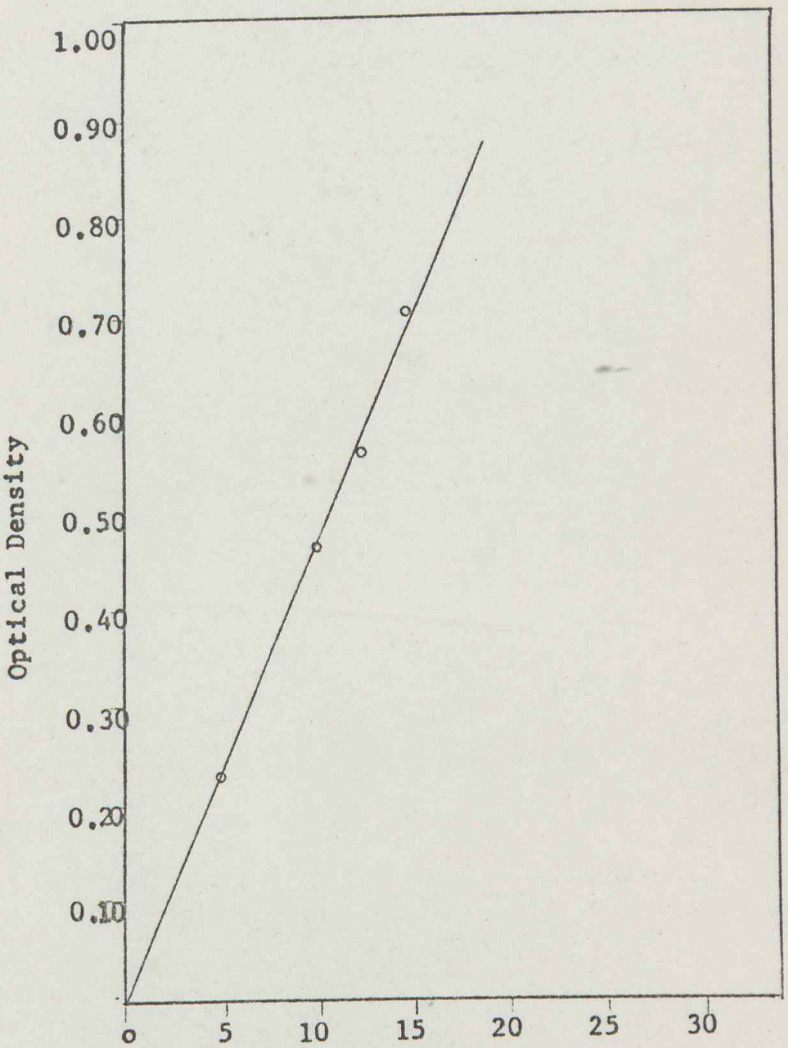

Fig. 7. Plot of Optical Density versus Irradiation Time for Fricke Dosimeters

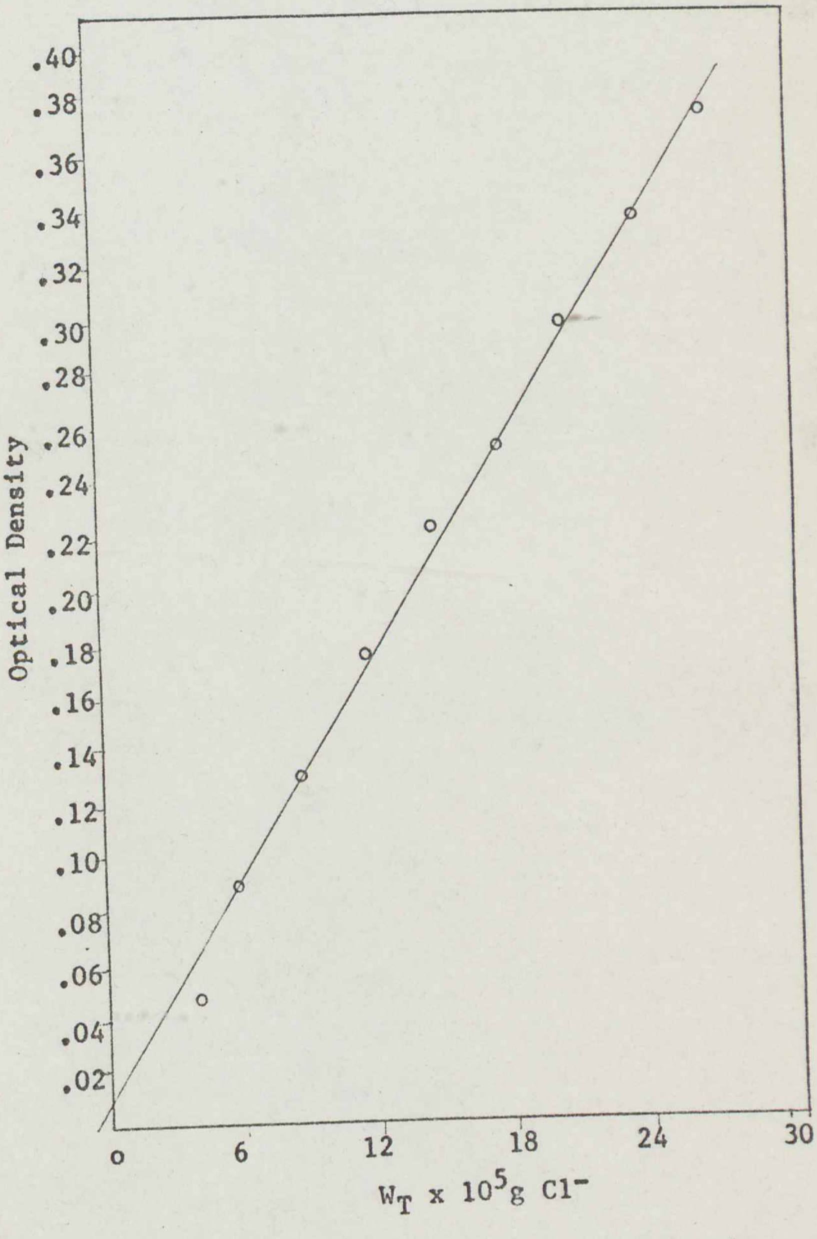

Fig. 8. Calibration Curve for Determination of Chloride Ion

A-3 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:

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

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

ε = 2178 at 23.5°C

d = 1 cm

ρ = 1.024×10^3 g l^{-1} for 0.8N H_2SO_4

N = 6.023×10^{23}

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

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

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

A-4 SAMPLE CALCULATION OF G(Cl^-)

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

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

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

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

$$M.W = 35.45.$$

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

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

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

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

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

$$v = 10\ ml$$

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

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

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

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

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

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

$G(Cl^-) = 14.92$