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High dose radiolysis of aqueous solutions of chloromethanes: Importance in the storage of radioactive organic wastes

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Abstract

The radiolysis of aqueous solutions of chloromethanes (dichloromethane, CH_2Cl_2; chloroform, $CHCl_3$; and carbon tetrachloride, CCl_4) was performed with γ-rays to doses sufficient to completely decompose the solute in order to estimate the effects of radiation on the long-term storage of mixed waste in enclosed containers. One of the main relevant products was the inorganic chloride anion, which increased in concentration with increasing radiation dose due to the reactions of radiolytic decomposition products of water with the chloromethane. The pH of the solutions was observed to decrease with irradiation due to the formation of H_3O^+ as the counter ion to Cl^-, i.e. the main radiolytic decomposition product is hydrochloric acid. Polymer formation was observed in aerated solutions as a precipitate while deaerated solutions exhibited a slight turbidity.

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1. Introduction

Radioactive wastes from nuclear facilities containing mixtures of radionuclides, metals, and volatile organic chemicals are undergoing changes due to self-radiolysis that may lead to long-term management problems. About 2% of the confined transuranic, TRU, and mixed waste from waste treatment processes contains chlorinated organic compounds like carbon tetrachloride, chloroform, methylene chloride, as well as di-, tri-, and per-chloroethylene and this material makes up almost a third of the US Department of Energy stored waste [1]. Decomposition of chlorinated organic polymers like seals and pump oils can also generate organic chloride solutions. The self-irradiation of these

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chloro-carbon materials affects the redox speciation and partitioning of these contaminants in the aqueous and gas phase and the overall pH, which creates potential uncertainties in their future handling and long-term storage. The presence of water, which can come from the atmospheric humidity, waste treatment processes or even ground water in the case of buried waste, will significantly alter the chemistry of the radiolytic processes. The movement of these solutions and their interactions with subsurface media are poorly understood. The generation, nature, and transport of colloids or polymers by extreme pH fluids are also of interest. Some effects of pH and chloride ion on corrosion [2] and stochastic models of pitting corrosion [3] in radioactive waste tanks have been reported earlier. However, much more work needs to be done. A better understanding of the chemical fate of contamination in these complex mixed waste systems is required to address risk assessment and develop remediation methods to such contaminated sites.

The radiation chemistry of aqueous chloromethane solutions is important from a fundamental point of view for gaining insight into the effect of non-polar reactants in a polar medium like water. Initial product yields have been reported in the radiation induced decomposition of chloromethanes in both aerated and deaerated conditions, at various pH, and in the presence of radical scavengers like formate or *t*-butanol [4–16]. Because of their high electron affinity, the primary step in the reduction of chloromethanes is reaction with the hydrated electron by a dissociative electron capture mechanism to release the chloride anion, Cl^-. The residual carbon centered radical can form peroxy radicals in the presence of trace amounts of oxygen with a diffusion controlled rate [17–20]. Subsequent hydrolysis gives more Cl^-. The stoichiometric relationship $Cl^-/e^-_{aq} = 1$ is observed only in the low dose radiolysis of oxygen free solutions of $CHCl_3$ and CCl_4, and the ratio increases considerably with traces of oxygen [4,5,21–23]. The superoxide radical anion formed by the reaction of the hydrated electron with oxygen does not react with CCl_4 [16]. In all these studies, there are no results on the extent of solute mineralization and the final Cl^- yield at very high radiation doses.

This work presents the results of the γ-radiolysis of aqueous solutions of dichloromethane (CH_2Cl_2), chloroform ($CHCl_3$), and carbon tetrachloride (CCl_4). The concentrations of the solutes were measured accurately from the decay trace of the hydrated electron and the rate constants for that reaction with the respective chloromethanes using pulse radiolysis techniques. The production of Cl^- and H_3O^+ (HCl) was determined at high doses in the radiolysis of aerated and deaerated solutions. Post-irradiated solutions were also analyzed for Cl_2, ClOH and other anionic species. Polymers formed in the radiolysis of aerated solutions were characterized for their mass, functional groups and elemental composition.

2. Experimental section

High purity dichloromethane (CH_2Cl_2) and chloroform ($CHCl_3$) (99.5% purity, without stabilizer from ChemService) and carbon tetrachloride (CCl_4) (99.9% purity HPLC grade without stabilizer from Sigma–Aldrich) were used as received without further purification. Purified water (resistivity 18.7 MΩ/cm) from an in-house H_2Only system (consisting of a UV lamp and several microporous ultrafilters) was used to prepare all solutions. Chloromethanes are difficult to solubilize in water [24] due to the large differences in polarity. They are highly volatile and evaporate from normal ground stoppered volumetric flasks. Standard solutions of the liquid chloromethanes were prepared by placing measured volumes of the solute in vacuum stoppered volumetric flasks containing water. The solutions were stirred for at least 48 h to completely solubilize the chloromethanes. Dichloromethane dissolves comparatively quickly whereas ~72 h of stirring was required for preparing 5 mM CCl_4 solution. Deaerated solutions are prepared by using a freeze-pump-thaw technique on a vacuum line to avoid purging the solute by bubbling with an inert gas.

Irradiations with γ-rays were performed with a Shepherd 109 ^{60}Co source at a dose rate of about 106 Gy min^{-1} (10.6 krad min^{-1}) as determined by the Fricke dosimeter. Pyrex tubes of 10 mm diameter sealed with rubber septa were used since flame sealing had a strong effect on the concentration of the solute. The head space of the tube was kept as small as possible to minimize solute loss due to equilibration of solute between the aqueous and the gas phase.

Pulse radiolysis experiments were performed using 3 ns pulses of 8 MeV electrons from the linear accelerator (linac) of the Notre Dame Radiation Laboratory (TB-8/16-1S linac). The linac, the spectrophotometric detection setup, and the computer-controlled data acquisition and detection systems are described in detail elsewhere [25]. The concentration of radicals generated was approximately 4 μM per pulse with a dose of about 7 Gy (0.7 krads) per pulse as determined by the thiocyanate dosimeter. The rate coefficient measurements were performed with aerated solutions to avoid the uncertainty in concentration of solutes after purging with inert gas or using a freeze-pump-thaw technique. Competition of oxygen with the solutes for the hydrated electron ($k_\phi = 1.9 \times 10^{10}$ dm^3 mol^{-1} s^{-1} [26] $\times 0.25 \times 10^{-3}$ mol dm$^{-3} = 5 \times 10^6$ s^{-1}) was kept to a minimum by adjusting the solute concentration. The detection limit is sufficiently fast (∼10 ns) to limit contributions due to hydrated electron reaction with oxygen on the time scale of the observations.

The Cl$^-$ concentrations were measured using an ion chromatograph (model Dionex 500) having a 25 μl sample loop, IonPac AS11 (4 mm × 250 mm) analytical column, IonPac AG11 guard column (4 mm × 50 mm), Anion Self-Regenerating Suppressor (ASRS ULTRA), suppressed conductivity detector CD25, and a Dionex AS40 automated sampler. Remote operation of the instrument and data analysis was carried out using commercial software (Chromeleon Version: 6.50). The eluent was a 12 mM NaOH solution at a flow rate of 1.5 ml/min. A suppressor current of 45 mA was applied to the auto suppressor. Under these conditions the retention time was ∼1.27 min for Cl$^-$ detection. Following irradiation, but prior to ion chromatographic analysis, irradiated and unirradiated samples were purged with nitrogen to remove the undecomposed chloromethane, which may hydrolyse on the analytical column resulting in high Cl$^-$ concentrations. The Cl$^-$ concentrations in unirradiated solutions (due to hydrolysis of solute) were measured and subtracted from the irradiated solutions. The rate of hydrolysis increases with increasing solute concentration, but the maximum corrections for hydrolysis were for the lowest solute concentrations. In no experiment did hydrolysis account for more than 3% of the chloromethane decomposition. Typical corrections due to hydrolysis were much smaller than the maximum and only about 0.3%.

The pHs of the solutions were measured using a bench-top pH meter by Orion (model 420A). Analysis of Cl_2 and ClOH was done using a CHEMetrics 2 SAM (Single Analyte Meters) kit with self-filling vacu-vial ampoules. The vacu-vials contain 2 ml of *N*,*N*-diethyl-*p*-phenylenediamine reagent in vacuum sealed ampoules that turn pink colored within one minute by oxidation with Cl_2 and ClOH. The instrument was calibrated with standard solutions.

The polymer mass was analyzed by gel permeation chromatography (GPC) using a Waters 515 HPLC pump, 50 μl sample loop injector, an Eppendorf TC-50 temperature controller, Eppendorf CH-430 column oven, Phenomenex columns, Shodex SE-61 refractive index detector, SRI module 203 A/D converter, and Pentium processor with Peak Simple software. The polymer was characterized by GPC at 40 °C with two 300 mm × 7.8 mm Phenomenex Phenogel columns (5 μm particle size and 50 Å porosity) using THF as eluant at a flow rate of 0.6 ml/min. The equipment was calibrated with polystyrene standards before the analysis of the polymer.

The change in polymer production with dose was examined by irradiating equal volumes (4 ml) of known concentration chloromethane in Pyrex tubes. After the irradiation, the liquid phase was removed by heating in a sand bath and the residue subsequently dried in a vacuum oven. The weights of the dry residues after irradiation was used to determine the variation in polymer yield with dose.

FTIR spectra were recorded on a Bruker Vertex 70 FTIR spectrometer with resolution of 4 cm^{-1}, 256 scans in the range 400–4000 cm^{-1}. The crystalline solid polymer weighed only a few milligrams and was measured in an ATR attachment. Elemental analysis of the polymer for C, H, O and Cl was performed by a commercial laboratory, Midwest Microlab, Indianapolis, IN.

3. Results and discussion

Evaluation of the total production of final products requires knowledge of the concentration of the initial chloromethane. Deaeration of the sample unavoidably resulted in loss of solute. A variety of irradiation cells and techniques were used so the initial concentration of the chloromethanes needed to be determined accurately. Pulse radiolysis techniques were used to measure the decay rate of the hydrated electron. The decay rate was used in conjunction with the rate coefficients of Table 1 to determine chloromethane concentration. This technique for determining chloromethane concentration allows for self-consistency in all of the experiments involving product determination. Other more conventional techniques for measurement of chloromethanes such as gas chromatography and FTIR are

Table 1
Rate coefficients of chloromethanes with the hydrated electron

Compound	$e_{aq}^- \times 10^{-10}$ ($M^{-1}\,s^{-1}$)	References
Carbon tetrachloride	1.5	This work
	1.3	Afanassiev et al. [27]
	1.9	Meisel et al. [28]
	2.4	Micic and Cercek [29]
Chloroform	1.1	This work
	3.0	Hart et al. [30]
Dichloromethane	0.38	This work
	0.6	Balkas [6]
Chloromethane	0.047	Schmidt et al. [31]

problematical because of loss of solute in sampling and because of the relatively large amount of water compared to solute, respectively.

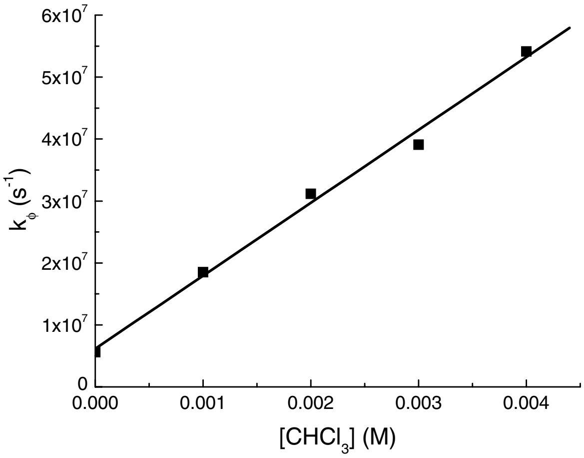

Fig. 1. Pseudo-first order rate coefficients for the hydrated electron decay as a function of $CHCl_3$ concentration. The slope of the fitted line gives a second order rate coefficient of $1.1 \times 10^{10}\,M^{-1}\,s^{-1}$. The intercept is due to the reaction of the hydrated electron with O_2.

The hydrated electron has a strong absorption with a maximum at about 720 nm [26]. Variation in the decay of the hydrated electron optical absorption with an added solute offers a simple method for determining the associated rate coefficient. In the case of the chloromethanes, the reaction is

$$e_{aq}^- + \text{chloromethane} \rightarrow Cl^- + (\text{chloromethane-Cl})^\bullet \qquad (1)$$

where (chloromethane-Cl)$^\bullet$ is the chloride ion elimination product. A great effort was made to maintain a constant solute concentration throughout the course of the pulse radiolysis experiments. Maximum solubilities are 236, 68, and 5 mM for CH_2Cl_2, $CHCl_3$, and CCl_4, respectively [24]. Rate coefficients for hydrated electron reactions with the three chloromethanes were obtained from simple exponential fits to the kinetic traces at different solute concentrations. Typical results for the pseudo-first order rate coefficients are shown in Fig. 1 as a function of $CHCl_3$ concentration. The slope of the line gives the rate coefficient for the reaction of the hydrated electron with $CHCl_3$ and the intercept gives the rate coefficient for the reaction of the hydrated electron with O_2. The rate coefficient for reaction of the hydrated electron with O_2 is found to be $2.5 \times 10^{10}\,dm^3\,mol^{-1}\,s^{-1}$ in reasonable agreement with published values [26]. Rate coefficients are tabulated in Table 1 with literature values for all of the chloromethanes [6,27–31]. The agreement of the present measurement for CCl_4 with the literature values is good, but lower results are observed in this work for $CHCl_3$ and CH_2Cl_2. The low concentrations of chloromethanes used in this work should avoid complications due to solute association. A significant increase in rate coefficients is observed with increasing number of chlorine atoms. The variation is almost a factor of 30 from CH_3Cl to CCl_4. The dependence of the rate coefficients with the number of chlorine atoms on the chloromethane is shown in Fig. 2. The data show that the rate coefficients are proportional to the number of chlorine

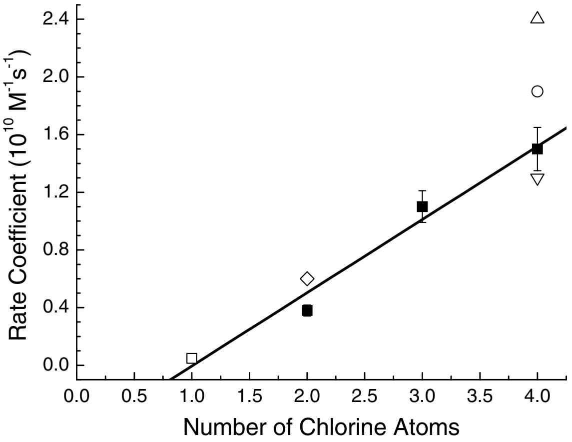

Fig. 2. Rate coefficients for the hydrated electron with the various chloromethanes as a function of the number of chlorine atoms: (■) this work; (▽) Ref. [27]; (○) Ref. [28]; (△) Ref. [29]; (◇) Ref. [6]; (▽) Ref. [31].

atoms and the agreement within the present results is good.

Irradiation of aqueous solution of chloromethanes produces Cl^- as a radiolytic product in reaction 1. The reactions of the H atom and OH radical are

$$^{\bullet}H + \text{chloromethane} \rightarrow HCl + (\text{chloromethane-Cl})^{\bullet} \tag{2}$$

$$^{\bullet}OH + \text{chloromethane} \rightarrow H_2O + (\text{chloromethane-H})^{\bullet} \tag{3}$$

where $(\text{chloromethane-H})^{\bullet}$ is a carbon centered radical derived from the H atom abstraction reaction from the parent chloromethane. The products of reaction (2) are based on experiments with chloroethanes [32] and further work is in progress to determine the exact mechanism of H atom reactions in chloromethanes. Reactions of the carbon centered radicals with other water radiolysis products, with each other, and with the parent compound are expected to occur. Chlorine elimination reactions and hydrolysis lead to the production of Cl^-. The Cl^- production increases with increase in dose and reaches a plateau due to complete depletion of the solute. The ratio of the Cl^- concentration to original chloromethane concentration is given as a function of dose in Fig. 3 for aerated and deaerated solutions of each chloromethane. This ratio gives the equivalent number of Cl^- ions produced by radiolytic decomposition of the parent compound. After a dose of ~50 kGy, complete decomposition of the chloromethanes was observed in deaerated solutions as evidenced by the equivalents of Cl^- produced about 4, 3 and 2 for CCl_4, $CHCl_3$ and CH_2Cl_2, respectively. On the other hand, in aerated solutions the equivalents of Cl^- were found to be about 3, 2 and 1 for CCl_4, $CHCl_3$ and CH_2Cl_2, respectively. In all cases, almost one Cl^- equivalent less was found in aerated solutions compared to the respective deaerated solutions. Incomplete mass balances were reported in the photolysis of 1,1,1-trichloroethane and tetrachloroethylene [33,34].

Solution pH was determined as a function of dose in order to establish the counter cation to Cl^- production. The proton concentrations calculated from the pH values of the solutions show excellent agreement with the Cl^- concentration suggesting no other ionic species are made in the radiolysis. Fig. 4 shows a typical comparison of H_3O^+ and Cl^- concentrations in γ-irradiated aqueous solutions of aerated (4 mM) and deaerated (2 mM) CCl_4.

The difference in Cl^- production between aerated and deaerated solutions suggests that one chlorine atom equivalent is not converted to Cl^- in aerated solutions. No extra anion peak was observed in the ion chromatography suggesting that the formation of chlorine–oxygen anions does not occur. A specific test for residual Cl_2 or ClOH found neither of these two compounds. The results suggest that a neutral chlorine atom remains attached to a carbon compound.

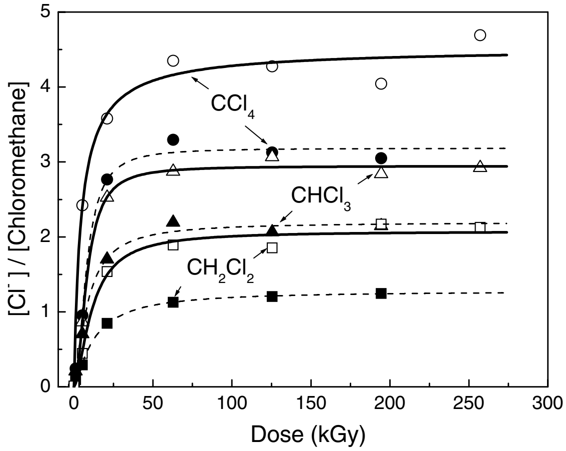

Fig. 3. Normalized Cl^- concentration in aerated (●) 3.98 mM CCl_4, (▲) 5.15 mM $CHCl_3$, (■) 6.75 mM CH_2Cl_2, deaerated (○) 2.04 mM CCl_4, (△) 1.83 mM $CHCl_3$ and (□) 3.78 mM CH_2Cl_2 solutions.

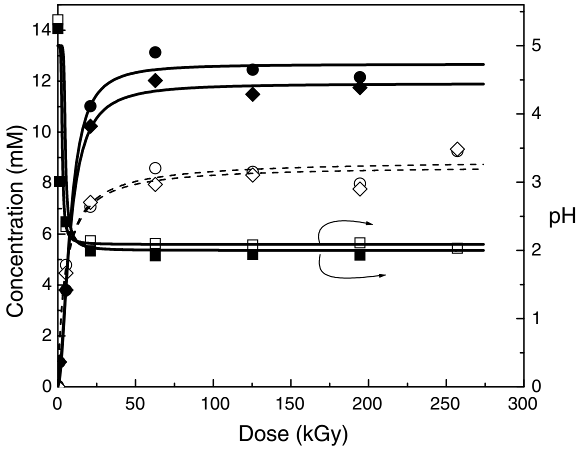

Fig. 4. Variation of Cl^- concentration (●), pH (■) and the corresponding proton concentration (◆) in aerated 3.98 mM CCl_4 solutions and deaerated 2.04 mM CCl_4 solutions (closed and open symbols, respectively).

In aerated solutions of CH_2Cl_2 and $CHCl_3$, a cream-white sticky precipitate was observed at high doses (20 kGy dose in 6.7 mM CH_2Cl_2 solution). The precipitate is formed in all the chloromethane solutions, but it is readily observable in CH_2Cl_2 solutions because this compound has the highest solubility and thereby more precipitate is formed per unit volume of solution. Extraction of the polymer using ethyl acetate showed it to be a mixture of two phases: a brown colored gel and a white colored solid. The former was soluble in most solvents such as $CHCl_3$, THF, CH_2Cl_2, acetone and methanol, but insoluble in non-polar solvents such as hexane and toluene whereas the latter compound was found to be soluble only in methanol. The amount of polymer produced was dependent on the initial concentration of the solute and volume of irradiated sample. The polymer yield was less than 0.1 mg when 4 ml of 10 mM CH_2Cl_2 aerated solution was irradiated in a dose range of 57 kGy–4 MGy and could not be weighed by a normal electronic balance. About 4 ml of 100 mM CH_2Cl_2 solution was irradiated to complete solute depletion and the precipitate weight was found to be ~1.2 mg which corresponds to ~4% of the total solute weight. A GPC analysis of the polymer fraction that dissolves in THF is shown in Fig. 5. The plot shows a broad peak with an onset retention time of 19 min and a peak at 22 min. This elution time corresponds to a polymer with an average molecular weight of ~700 Da as seen in the upper scale of Fig. 5. The broad peak clearly indicates the existence of a mixture of polymers with different chain lengths. The molecular weights calculated from the retention times cover a range of 200–2000 Da.

The FTIR spectra of the polymer gel and solid are given in Fig. 6 and can be seen to be different in the lower wave number region. The broad band above 3000 cm^{-1} is due to hydrogen bonded hydroxyl groups in both the components, the peak at 2970 cm^{-1} is assigned to the alkyl C–H bond stretching and the peak at 1770–1720 cm^{-1} is assigned to C=O stretching. Peaks below 1500 cm^{-1} are too complex to assign due to stretching from a variety of single bonds.

Elemental analysis of the polymer mixture formed in aerated solutions for C, H, O, and Cl atoms gave relative amounts of 37.87%, 4.14%, 18.59%, and 37.67%, respectively. These values correspond to a monomer with approximate C_3H_3OCl stoichiometry. Since the average molecular weight of the polymer is about 700 Da, an average polymer contains about eight monomer units. Obviously, wide variations in the number of monomer units are possible and mixed polymer formation, i.e. polymers composed of different monomer units, is possible.

Chloromethanes react with the hydrated electron at the rates listed in Table 1 to produce Cl^- and carbon centered radicals as given in Eq. (1). Carbon centered radicals are also produced by the abstraction reactions of H atoms and OH radicals, Eqs.

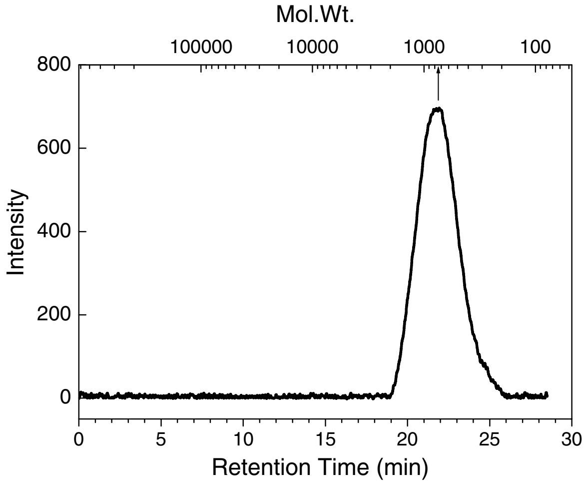

Fig. 5. Gel permeation chromatograph of the polymer (2% W/V in THF) formed by irradiation of 150 mM aerated CH_2Cl_2 solution up to a dose of 0.3 MGy. The mass corresponding to a given retention time is given on the top scale. The retention time of 22 min corresponds to a mass of 700 Da.

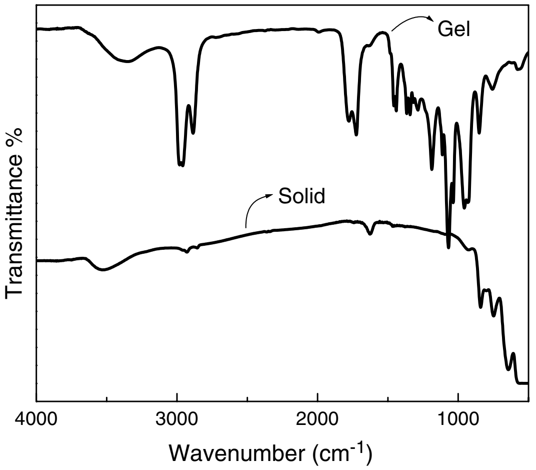

Fig. 6. FTIR spectrum of the polymers formed from the radiolysis of 150 mM aerated CH_2Cl_2 solution up to a dose of 0.3 MGy.

(2) and (3). Beyond this point the chemistry becomes uncertain. A carbon centered radical subsequently reacts with oxygen in aerated solutions forming peroxyl radicals, which can participate in a number of other reactions including chain reactions to form stable products [17,18,20]. Carbon centered radicals can dimerize or combine with each other to give chloroethanes and higher order molecules. Products like C_2Cl_6, $C_2H_2Cl_4$, and CH_2Cl_2 are detected in the radiolysis of chloromethanes [9,14]. Reaction of the chloromethane radicals with hydrated electrons can generate carbene radicals, which can dimerize to produce unsaturated aliphatic compounds. However the probability of such a process is very small. An unsaturated compound is a good radical trap and may act as a seed for the initiation of polymer formation with any other carbon centered radical. Carbene radicals are reported to be an intermediate product in CCl_4–water (ice) films [35] and in heme/TiO_2 [36], but their existence in aqueous solutions is unknown. Other oxygen containing products like HCHO, HCOOH, CO and CO_2 are also reported in the radiolysis of chloromethanes [8,9,13].

Solution pH decreases with increasing chloroform degradation due to formation of H_3O^+ as the counter ion to Cl^-. Essentially, the radiolysis is making hydrochloric acid. Several investigators have noticed that product yields depend on pH. Choi and Hoffman [37,38] have reported that in the degradation of CCl_4 at pH 2.7 they observe formation of $CHCl_3$, C_2Cl_4, and C_2Cl_6, whereas these products are not observed at pH 12.4 due to base catalyzed hydrolysis. Similarly, Getoff [8] reported the yields of Cl^- from $CHCl_3$ to be the highest at pH 6.5 (14.2 molecule/100 eV) and lower at pH 3 (12.0 molecule/100 eV) and pH 11.2 (10.2 molecule/100 eV).

Complete decomposition of aqueous chloromethane solutions to Cl^- and H_3O^+ by 20 kGy doses of γ-rays is possible only in deaerated conditions. In aerated solutions, approximately one chlorine atom equivalent is apparently contained in a polymer. Complete mineralization of the chloromethanes to CO_2, Cl^- and H_3O^+ does not occur at doses on the order of 20 kGy. Polymer formation in aerated solutions may cause practical problems such as the plugging of pores or membranes used in remediation applications. Of course, radiolytic degradation of the polymer may occur at much higher doses to give complete mineralization of the chloromethane. The results show that radiation can readily decompose aqueous solutions of chloromethanes, especially when deaerated. However, the hydrochloric acid composed of the Cl^- and H_3O^+ products is highly corrosive and may pose waste management or other environmental concerns with enclosed metal containers.

4. Conclusions

The radiolysis of aqueous solutions of chloromethanes (dichloromethane, CH_2Cl_2; chloroform, $CHCl_3$; and carbon tetrachloride, CCl_4) was performed with γ-rays to doses sufficient to completely decompose the solute in order to estimate the effects of radiation on the long-term storage of mixed waste in enclosed containers. One of the main relevant products was the inorganic chloride anion, which increased in concentration with increasing radiation dose due to the reactions of radiolytic decomposition products of water with the chloromethane. The pH of the solutions was observed to decrease with irradiation due to the formation of H_3O^+ as the counter ion to Cl^-, i.e. the main radiolytic decomposition product is hydrochloric acid. The radiolysis of deaerated solutions to very high doses gave complete decomposition of the chloromethane to an equivalent concentration of Cl^- (1 mM $CH_{4-n}Cl_n$ gave n mM Cl^- at a dose of 50 kGy). In aerated solutions irradiated to same dose, the final Cl^- concentration was always about one unit equivalent less than the predicted maximum available (1 mM $CH_{4-n}Cl_n$ gave $(n-1)$ mM Cl^- at a dose of 50 kGy). The H_3O^+ concentration exactly matched that of the Cl^- concentration in both aerated and deaerated solutions indicating existence of one neutral chlorine atom equivalent in aerated solutions. No residual Cl_2 or ClOH or anions other than Cl^- were found in the irradiated solutions. Polymer formation was observed in aerated solutions as a precipitate while deaerated solutions exhibited a slight turbidity. The residual neutral chlorine atom equivalent in aerated solutions is found to be part of a polymer chain. Analysis of the polymer with gel permeation chromatography suggests an average molecular mass of ~700 Da. FTIR and elemental analysis suggest a polymer unit of C_3H_3OCl with a C=O functional group.

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