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Radiolytic Degradation of Chlorinated Hydrocarbons in Water

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Radiolytic degradation of chlorinated hydrocarbons (chloroform, trichloroethylene, and tetrachloroethylene) in water was carried out. Water solutions of the chlorinated hydrocarbons with different concentrations were irradiated with γ rays. Concentrations of methane, ethane, CO, CO_2, H_2, and O_2 after the irradiation were determined by gas chromatography. Concentration of chloride ion in the irradiated sample was determined by ion chromatography. Experimental results show that radiolytic degradation of the chlorinated hydrocarbon increased with the radiation dose. Methane, ethane, CO_2, H_2, and Cl^- concentrations increased with the radiation dose and the sample concentration. On the other hand, O_2 concentration decreased with the radiation dose and the sample concentration. When sample concentration was high, dissolved oxygen might be not enough for converting most of the C atoms in the sample into CO_2. This resulted in a low decomposition ratio. Addition of H_2O_2 as an oxygen resource could increase the decomposition ratio greatly. Furthermore, gas chromatography-mass spectroscopy was applied to identify some intermediates of the radiolytic dehalogenation. Radiolytic degradation mechanisms are also discussed.

Concerns about contamination of groundwater and surface water by chlorinated organic compounds have increased since degradation of the chlorinated organics is hard to achieve by common biological methods. Although they can be removed by adsorption on activated carbon, the adsorption can not ultimately resolve the hazardous problem of the chlorinated organics. It just transfers the hazardous chlorinated organics from water to the activated carbon.[1] Various methods have been tried for decomposing the chlorinated organic compounds in water. For example, zero-valent iron has been used for study of destruction of chlorinated solvents.[2–4] Photocatalytic degradations using TiO_2 and the photo-fenton reaction have been investigated for decomposing the chlorinated organics.[5–6]

Ionizing radiation is known to often stimulate chemical reactions.[7–8] Ionizing radiation-induced decomposition of organic compounds has been studied well. It is well known that chemical bonds of C–H, C–C, and C–O in organic compounds can be easily broken by irradiation of γ rays. On the other hand, the decomposition mechanism is rather different when the organic compounds are distributed in water since radiolysis of water and its active products such as OH radical and hydrated electron would play important roles. Because of the strong decomposition effect, ionizing irradiation-induced decomposition is expected to be an important method for treatment of water pollutants, especially for those pollutants that are not easily degraded by other methods. So far, many works have been directed towards the radiolytic dehalogenation of chlorinated organic compounds by γ rays. For example, radiolytic dehalogenations of chloroform,[9] 1,2-dichloroethane,[10] chlorobenzene,[11] and chlorophenols[11–14] in water have been reported. Radiolytic dehalogenations of 1,1,2-trichloro-1,2,2-trifluoroethane (CFC-113) and trichloroethylene adsorbed on molecular sieve have been investigated.[15–16] Radiolytic decomposition of polychlorinated biphenyl (PCB) in 2-propanol has been studied too.[17] Mechanisms of the radiolytic dehalogenation process of chloro-organics such as dichloroethene[18–19] and chlorophenol solution[20] have also been discussed. However, only concentrations of chloride ion and chloro-organic compounds are determined and analyzed in these studies. Most of the intermediates produced in the radiolytic decomposition process have not been confirmed. Therefore, not all details of the dehalogenation process have been understood. For example, formations of methane and ethane from the radiolytic degradation of chlorinated organic compounds in water have neither been reported nor expected in these radiolytic decomposition researches, although ethane has been found in irradiation of pure chloroform by γ rays.[21]

Ionizing radiation from spent nuclear fuels as well as from radioactive wastes is now or will soon be a severe environmental problem. If the ionizing radiation from spent nuclear fuels as well as radioactive wastes could be utilized for decomposing organic pollutants in water, this would be eminently meaningful to mankind. In order to explore the potential applications of radiolytic degradation in water treatment and its mechanism, radiolytic degradations of chlorinated hydrocarbons such as chloroform, trichloroethylene, and tetrachloroethylene in water are carried out in this work. In addition to examinations of the concentration changes of chlorinated hydrocarbon and chloride ion before and after irradiation of γ rays, methane, ethane, CO, CO_2, H_2, and O_2 are also determined by gas chromatography. Furthermore, gas chromatography-mass spectroscopy (GC-MS) is applied to identify some intermediates of the radiolytic dehalogenation. Radiolytic degradation mechanisms are also discussed.

Experimental

Sample Preparation: Two ml of a chlorinated hydrocarbon (chloroform, trichloroethylene, or tetrachloroethylene) was added to 100 mL water. The chlorinated hydrocarbon -water mixture was stirred completely at room temperature. The mixture was stored in a dark place for 1 week so that the water phase became saturated with the solvent. The water phase was used as a sample solution with saturated chlorinated hydrocarbon. The saturated concentrations of chloroform, trichloroethylene, and tetrachloroethylene were calculated from their dissolubility to be about 8000, 1100, 150 ppm, respectively. The saturated sample solutions were further diluted with water for 10 or 100 times so that 1/10 or 1/100 saturated solutions of chlorinated hydrocarbons were obtained.

Irradiation with γRays: A fifty ml sample solution of each chlorinated hydrocarbon with desirable concentration was added into a 70 mL glass vial. Then the glass vial was sealed with a corker. The glass vial was placed around a γ ray source (^{60}Co, Japan Radioisotope Association Koka Laboratory) for a certain radiation dose (10, 30, 60, 100 kGy).

Gas Chromatorgaphic Determination: In determinations of CO, CO_2, CH_4, and C_2H_6, 0.5 mL gas sample from gaseous phase in the irradiated glass vial was injected into a gas chromatograph (Hitachi, GC-3900) with an FID detector and a methanizer (350 °C) that converted CO and CO_2 into CH_4. The separation column was an active carbon (60–80 mesh) column (3 mm i.d. × 2 m), and the carrier gas was N_2 (flow rate: 50 mL/min). The column was first kept at 80 °C for 5 min, then the temperature was raised to 150 °C at a rising rate of 20 °C/min. In determinations of H_2 and O_2, a TCD detector (100 °C) was used in the gas chromatograph. The gas oven was kept at 60 °C. The electric current of the TCD detector was 50 mA.

In determinations of chloroform, trichloroethylene, and tetrachloroethylene, 0.5 mL gas sample from the gaseous phase of the irradiated glass vial was injected into a gas chromatograph (Perkin Elmer, Auto System XL) with a capillary column (supelcowax 10, 60 m × 0.53 mm i.d.) and a FID detector. The carrier gas was He, and flow rate was 50 mL/min. The gas oven was kept at 60 °C for 5 min and then the temperature was raised to 95 °C at a rising rate of 5 °C/min.

Ion Chromatographic Determination: An ion chromatograph (Tosoh CO8020) with a conductivity detector was used for determination of chloride ions in the irradiated sample solution. The column was TSK-gel IC-Anion-PW (Tosoh), and the mobile phase was borate buffer (pH 7.85) containing 12% CH_3CN and 0.4% butanol. The flow rate of the mobile phase was 1.0 mL/min, and the sample volume was 0.2 mL.

GC-MS Determination: A GC (Hewlett-Packard, CA)-MS (JEOL, Tokyo) was used for identifying intermediates of the radiolytic dehalgenation. The GC column was supelcowax 10 (60 m × 0.53 mm i.d.). The GC oven was temperature-programmed from 30 °C to 60 °C at a rate of 1 °C/min. The carrier gas was He, and the flow rate was 310 mL/min. Ionization potential of the MS was 70 eV and the ionization current was 200 μA. The scanning range of MS was from 10 to 200 *m*/*z*.

Results and Discussion

1. Effect of Radiation Dose on the Radiolytic Degradation. Figure 1 shows the decomposition ratios of chlorinated hydrocarbons in water with different radiation doses. The decomposition ratios were calculated from the concentrations of chlorinated hydrocarbons determined by gas chromatography. It can be seen that the chlorinated compounds decomposed fast at the beginning, and then the decomposition process slowed as the irradiation continued. For a certain radiation dose, the lower the concentration of the chlorinated compounds, the higher the decomposition ratio. When the radiation dose increased to 100 kGy, the decomposition ratio was above 90% except for the saturated hydrocarbon solutions.

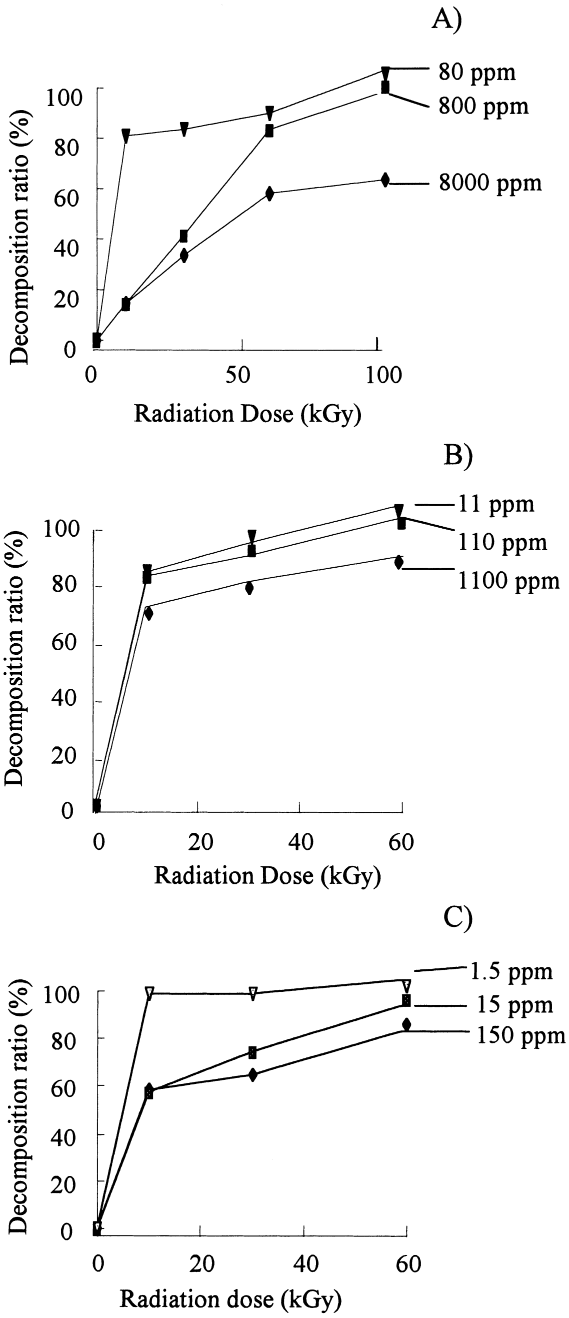

Fig. 1. Dependences of decomposition ratios calculated from the gas chromatographic determinations of chlorinated hydrocarbons on radiation doses. A) chloroform solution; B) trichloroethylene solution; C) tetrachloroethylene solution.

2. Production of Chloride Ions and Decrease of pH Values in the Irradiated Solution. In view of water treatment, it is desirable and ideal that all Cl atoms in the chlorinated solvents are converted into Cl^-. Figure 2 shows the decomposition ratio to Cl^- calculated from the ion chromatographic determination of Cl^- concentration. It can be seen that the decomposition ratios to Cl^- are larger than 90%, except for the saturated chlorinated hydrocarbon solutions when the radiation dose was 60 kGy. It can be seen by comparison of Figs. 1 and 2 that the decomposition ratio calculated from Cl^- concentration is a little smaller than that from concentration of the chlorinated hydrocarbon. As discussed below, this is because that small amounts of chlorinated intermediates were also formed.

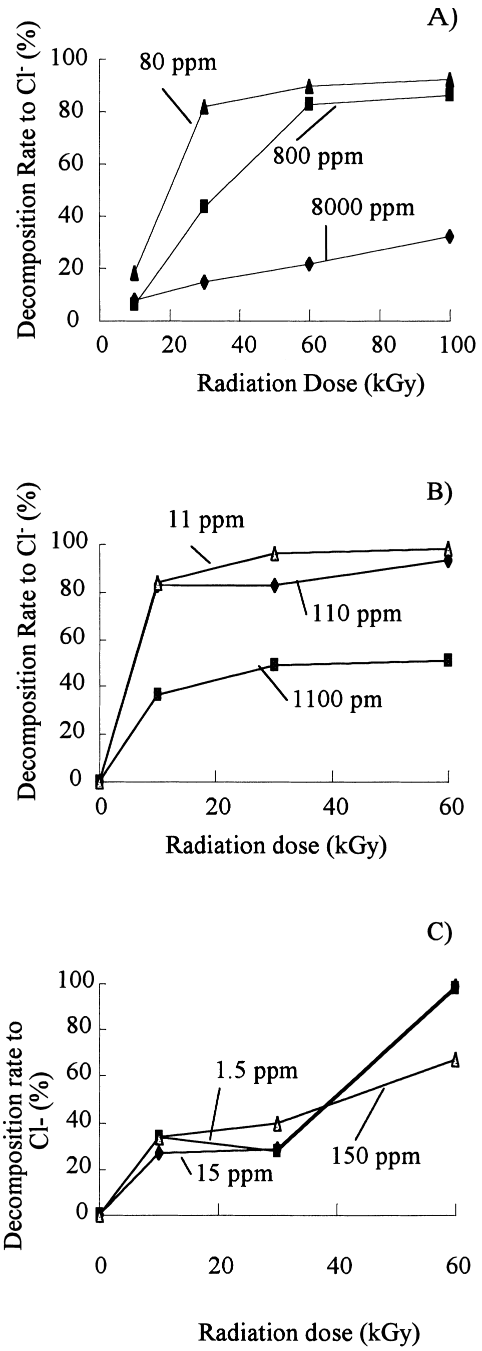

Fig. 2. Dependences of decomposition ratios calculated from the ion chromatographic determinations of chloride ions on radiation doses. A) chloroform solution; B) trichloroethylene solution; C) tetrachloroethylene solution.

Figure 3 shows pH change of the chloroform solution after irradiation. It is clear that pH decreased with the radiation dose and concentration of chloroform. Similar pH changes were observed for other chlorinated solvents too. Figure 3 indicates that the irradiated solution was greatly acidic, i.e., a large amount of H^+ was produced. Since most of the Cl atoms in the chloroform were transformed to Cl^-, the negative charge of the Cl^- was balanced by H^+ in the irradiated solution.

3. Production of CO, CO_2, CH_4, and C_2H_6. To what were C atoms in the chlorinated solvents transformed is also investigated. Methane, ethane, CO, and CO_2 were detected. Figure 4 shows production of methane in chloroform solution with different radiation doses and different concentrations. It is clear that the produced methane increased with the irradiation dose and the chloroform concentration. The dependences of C_2H_6 concentration on the irradiation dose and chloroform concentration are similar to those of CH_4. However, the concentration of C_2H_6 was only about 1/100 of CH_4. Other chlorinated solvents gave results similar to those of chloroform. Since methane and ethane are clean fuels and important chemical materials, it is meaningful to convert organic pollutants into methane and ethane by ionizing irradiation.

Figure 5 shows the dependences of concentrations of CO and CO_2 on radiation dose. Concentration of CO firstly increased with the radiation dose. It reached a maximum at about 30 kGy, then it decreased with the radiation dose. On the other hand, the concentration of CO_2 increased with radiation dose when chloroform concentrations were 8000 or 800 ppm. Comparing Fig. 4 with Fig. 5, we concluded that CO_2 and CO concentrations were larger than that of methane. This means that conversion ratios of C in the chloroform to CO_2 and CO were larger than those to methane and ethane.

4. Production of H_2 and Decrease of O_2. Figure 6 shows concentration changes of H_2 and O_2 with the radiation dose. It is well known that H_2 can be produced by the radiolysis of water. However, as shown in Fig. 6-A, H_2 concentration in chloroform solution increased in comparison with that in water. Moreover, H_2 concentration increased with chloroform concentration. This suggests that either H_2 production efficiency from the radiolysis of water has been improved or that H in chloroform has been transformed into H_2. Since H_2 is an ideal energy source, the improvement of H_2 production efficiency is meaningful.

Figure 6-B shows that O_2 concentration decreased with radiation dose. Moreover, the larger the chloroform concentration, the faster the O_2 concentration decreased. This suggests that O_2 was consumed during the degradation of chloroform. The consumed O_2 should have been converted into CO and CO_2. Since O_2 concentration in the saturated chloroform solution was greatly decreased as shown in Fig. 6-B, its amount might be not enough for transforming most of the C atoms in chloroform into CO_2 or CO. As a result, a larger concentration of methane was produced in the saturated chloroform solution.

5. Effect of H_2O_2 Addition on the Radiolytic Degradation. As stated above, O_2 amount might be not enough for the chloroform-saturated solution. This might be one reason why only about half of the chloroform could be degraded even

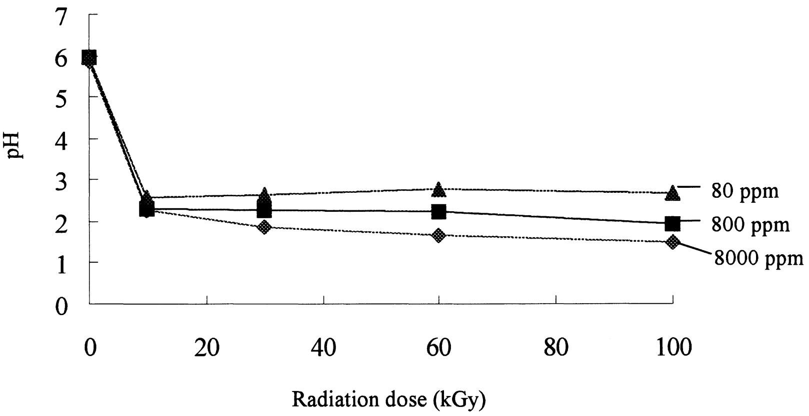

Fig. 3. pH change of the irradiated chloroform solution.

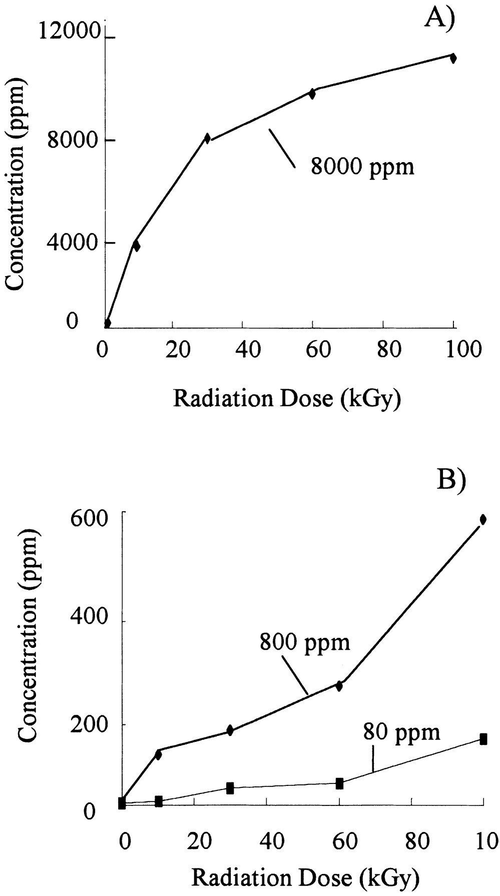

Fig. 4. Relationship between methane concentration and radiation dose. In A), concentration of chloroform was 8000 ppm; in B), chloroform concentration was 800 and 80 ppm, respectively.

with irradiation dose of 100 kGy (Fig. 1). As a source of oxygen, H_2O_2 was added into the chloroform-saturated solution. Figure 7 shows the effect of H_2O_2 addition on the radiolytic decomposition of chloroform. Nearly 90% of degradation ratio was obtained even at radiation dose of 10 kGy with the addi-

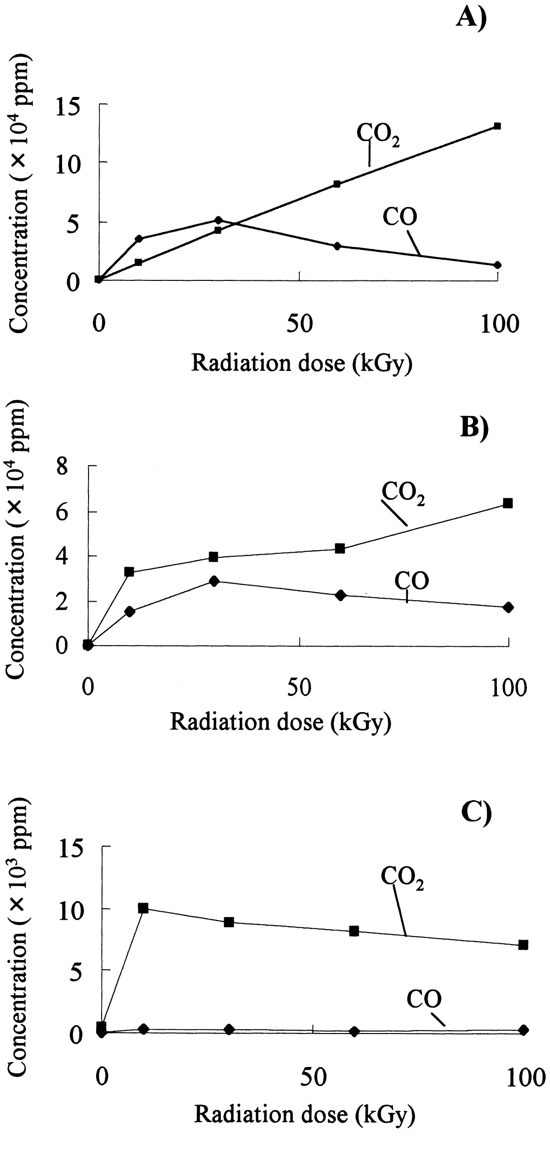

Fig. 5. Dependences of concentrations of CO and CO_2 on radiation doses. Concentrations of chloroform were 8000 (A), 800 (B), and 80 (C) ppm, respectively.

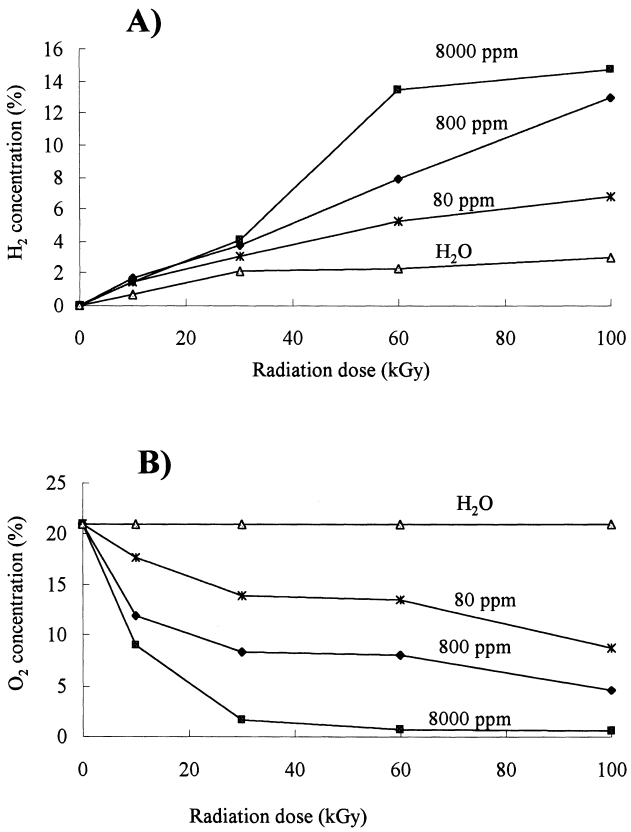

Fig. 6. Dependences of concentrations of H_2 (A) and O_2 (B) on radiation doses for chloroform solutions with different concentrations.

tion of H_2O_2, while the degradation ratio was only about 10% without addition of H_2O_2. Therefore, fast radiolyic degradation could be realized with the addition of H_2O_2. Figure 7 also shows that oxygen concentration was nearly constant during the irradiation process. This means that the added H_2O_2 compensated the consumption of the oxygen in the irradiation process.

6. GC-MS Determinations. In addition to above products, small amounts of chlorinated intermediates such as $CCl_2{=}CCl_2$, $CH_2{=}CCl_2$, $CHCl{=}CHCl$, $CHCl_2{-}CHCl_2$, and $CHCl_2{-}O{-}CHCl_2$ are also detected by GC-MS from the irradiated chloroform solution. Existence of such intermediates is the reason why the decomposition ratio calculated from Cl^- concentration was a little smaller than that obtained from chlorinated solvent concentration.

7. Radiolytic Decomposition Mechanism. The dehalogenation in the irradiation process is generally carried out by the attack of active species such as hydrated electron (e_{aq}), hydrogen atom (H), and hydroxyl radical ($^\bullet OH$) produced by the radiolysis of water in oxygen-free condition. On the other hand, dehalogenation is carried out by the $^\bullet OH$ and superoxide ion radical ($O_2^{\bullet -}$), which is produced by electron scavenging of oxygen in the presence of dissolved oxygen.[18–20] In either case, a series of radical reactions are followed. It has been reported that as many as 55 reactions may occur in the irradiated aqueous chloroform solutions.[11] As a result, stable radiolytic products of Cl^-, CO, CO_2 are formed. Some relative stable intermediates or products such as HCHO and oxalate are also detected or are expected in the dehalogenation process of chloroorganic compounds.[18] However, methane and ethane have neither been reported nor expected in these studies. Hence, there must be other reaction mechanisms in addition to the proposed ones. Here the production mechanism of methane and ethane is proposed as follows, based on the above experimental results.

$$H_2O + \gamma \text{ rays} \sim e_{aq}^-, H, OH, H_2O_2, H_2, H^+, OH^- \quad (1)$$

In the presence of dissolved oxygen, e_{aq}^-, and H atoms are scavenged by oxygen as follows:

$$e_{aq}^- + O_2 \rightarrow O_2^- \quad (2)$$

$$H + O_2 \rightarrow HO_2^- \quad (3)$$

Since the concentration of chlorinated solvents was relatively high in this experiment (for example, the concentration of chloroform is about 0.067 mol/L in the chloroform saturated

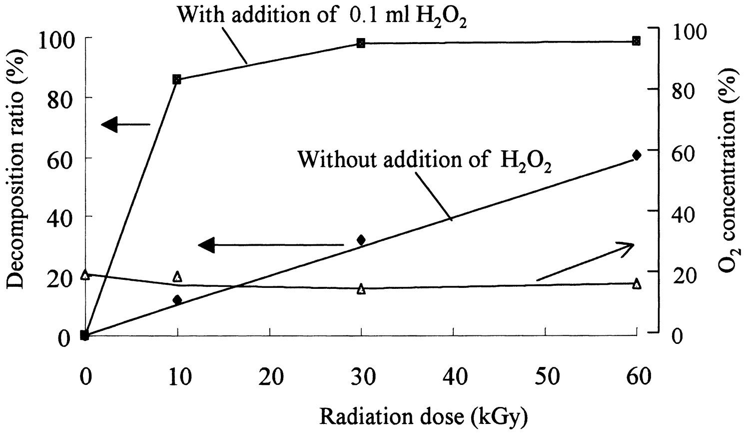

Fig. 7. Effect of H_2O_2 addition on radiolytic decomposition of chloroform and O_2 concentration. Concentration of chloroform was 8000 ppm.

solution, which was much higher than concentration of dissolved oxygen (2.5×10^{-4} mol/L)), a part of hydrated electrons, H atoms, and OH radicals were expected to attack the chlorinated solvents directly. Thus a series of radical reactions are followed:

$$e_{aq}^{-} + CHCl_3 \rightarrow {}^{\bullet}CHCl_2 + Cl^{-} \quad (4)$$

$$H + CHCl_3 \rightarrow CH_2Cl_2 + Cl^{-} \quad (5)$$

$$^{\bullet}OH + CHCl_3 \rightarrow {}^{\bullet}CCl_3 + H_2O \quad (6)$$

$$^{\bullet}CHCl_2 + H \rightarrow CH_2Cl_2 \quad (7)$$

$$^{\bullet}CHCl_2 + {}^{\bullet}CHCl_2 \rightarrow CHCl_2\text{–}CHCl_2 \quad (8)$$

$$CH_2Cl_2 + e_{aq}^{-} \rightarrow {}^{\bullet}CH_2Cl + Cl^{-} \quad (9)$$

$$^{\bullet}CH_2Cl + H \rightarrow CH_3Cl \quad (10)$$

$$CH_3Cl + e_{aq}^{-} \rightarrow {}^{\bullet}CH_3 + Cl^{-} \quad (11)$$

$$^{\bullet}CH_3 + H \rightarrow CH_4 \quad (12)$$

$$^{\bullet}CH_3 + {}^{\bullet}CH_3 \rightarrow C_2H_6 \quad (13)$$

In addition to above reactions that induced production of methane and ethane, the radicals such as $^{\bullet}CCl_3$, $^{\bullet}CHCl_2$, and $^{\bullet}CH_2Cl$ might react with oxygen to produce peroxyradicals that are finally transferred into CO_2 and CO by hydrolysis reaction. For example, the following reactions for $^{\bullet}CCl_3$ are expected.

$$^{\bullet}CCl_3 + O_2 \rightarrow O_2CCl_3 \quad (14)$$

$$O_2CCl_3 + H_2O \rightarrow CO + 2OH + 3\,Cl^{-} \quad (15)$$

$$O_2CCl_3 + 2H_2O \rightarrow CO_2 + HO_2 + 3\,HCl \quad (16)$$

The radical reactions and the following hydrolysis reactions as expressed in Eqs. 14–16 accounted for the consumption of O_2 (Fig. 6-B) and the production of CO and CO_2 (Fig. 5) in the irradiation process.

On the other hand, little consumption of O_2 was observed when H_2O_2 was added into the system (Fig. 7). One reason for this might be due to reactions between the active OH radical and H_2O_2:[11]

$$^{\bullet}OH + H_2O_2 \rightarrow H_2O + HO_2 \quad (17)$$

$$2HO_2 \rightarrow H_2O_2 + O_2 \quad (18)$$

net reaction of Eqs. 17 and 18 is as follows:

$$2^{\bullet}OH + H_2O_2 \rightarrow 2H_2O + O_2 \quad (19)$$

Therefore, O_2 consumed by Eqs. 14–15 was compensated by the existence of H_2O_2 as expressed by Eq. 19.

Conclusions

As a conclusion, γ ray irradiation is a simple and effective method for degradation of chlorinated hydrocarbons in water. Addition of a small amount of H_2O_2 can greatly accelerate the degradation process. Most of the chlorine in chlorinated hydrocarbon is transformed into chloride ions. Methane and ethane, which are clean energy, are produced during the radiolytic decomposition process. Production of H_2 is increased compared with that obtained in water radiolysis. In addition to chlorinated hydrocarbons, this method is expected to be useful for other chlorinated organic compounds and other organic pollutants.

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