

Electron-Beam Decomposition of Carbon Tetrachloride in Air/Nitrogen

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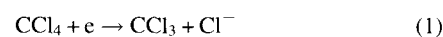
Carbon tetrachloride (CCl₄, approximately 10, 50, and 100 ppm) in air and nitrogen was irradiated with electron beams in both the presence and absence of water. The absorbed doses ranged from 1.2 to 18.0 kGys. An absorbed dose of 18 kGy led to approximately 90% decomposition of CCl₄ at a concentration of 10 ppm in dry air. The presence of water lowered the decomposition rate in air by 20%, but not in nitrogen. Negative oxygen ions (O₂⁻) formed upon the irradiation of wet air played a role in the oxidation of CCl₄. Water molecules became negative cluster ions (O₂⁻(H₂O)_n) with negative oxygen ions, which depressed the oxidation.

New technologies invented in the 20th century have been remarkably changing our life styles. We have benefited from these technologies, which are expected to create a sophisticated society and comfortable lives from many years to come. However, every technology leading to the comfortable lives is not necessarily welcome by the environment. Sometimes it causes the destruction of nature on Earth, which puts us in a dangerous situation. Many sources emitting volatile organic compounds (VOCs) exist everywhere around us. For instance, exhaust gases from cars, car-body painting, petroleum refines, and so on are common emission sources. Volatile organic compounds are essential substances in many industrial processes. However, they cause a heavy damage to the environment. Photochemical oxidant formation, stratospheric ozone depletion and tropospheric ozone formation are representative indirect effects of VOCs. Stratospheric ozone depletion leads to excess radiation of UV-rays on the human body. This induces skin cancer. Photochemical oxidant formation is caused by tropospheric ozone formation, that is accelerated as hydrocarbon concentrations increase. Other problems of VOCs involve direct effects on the human body. Long exposure in a VOC atmosphere, even at a low concentration, may cause cancer. Headache, nausea, and the stimulation of the eyes and nose are acute toxic symptoms of VOCs. Carcinogenicity and mutagenicity are the most dangerous effects of VOCs.

To eliminate these harmful effects on human health, we have started research on the electron-beam treatment of VOCs using aromatics and aliphatics, like benzene, xylene, chlorobenzene, butylacetate, and trichloroethylene.^{1–4} They were decomposed through oxidation reactions with active species formed by the irradiation of wet air. Their decomposition rates were found to be in proportion to the rate constants for reactions with hydroxyl radical (OH), which was one of the active species. The radicals decomposed the VOCs by oxidation. The oxidation was initiated through the addition of the OH radical to the aromatic ring at ambient

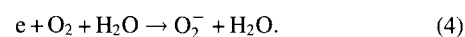
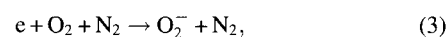
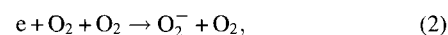
temperature. In the case of butylacetate, a H abstraction reaction occurred in the first place. Trichloroethylene was oxidized through a chain reaction with the chlorine radical that was generated by OH addition to the double bond (C=C). The oxidation process by the electron beam is terminated to produce CO₂.

In the case of chloromethane, such as CCl₄, CH₂Cl₂, reactions with OH radicals are not the main oxidation processes. Penetrante et al.⁵ have reported that the oxidation of chloromethane occurred through reactions with thermal electrons when chloromethane-air mixtures were irradiated with electron beams. A thermal electron is generated from electron-beam irradiation of air.⁶ When a thermal electron collides with a chloromethane molecule in the gas phase, a short-live parent negative ion is formed. The ion immediately dissociates to a fragment negative ion (Cl⁻) together with a radical. For instance, the CCl₄ molecule is oxidized by a thermal electron as follows:



The rate constant of reaction (1) is $3.3 \times 10^{-7} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.⁷ This value is five orders of magnitude higher than that of the reaction of CCl₄ with the OH radical.⁸ Dissociative electron attachment is a main decomposition route for the electron-beam irradiation of chloromethane.

In processing electron beams, the oxygen molecule can also react with a thermal electron:



Penetrante et al.^{8,9} have reported, using related rate constants, that reactions (2), (3), and (4) were significant electron-loss processes when the concentration of CCl₄ was less than approximately 10 ppm. However, they have not experimentally

shown whether oxygen really has an influence on the decomposition of CCl_4 in an electron-beam treatment. It is very important to clarify the role of oxygen concerning the feasibility of electron-beam technology to chloromethane that is oxidized through the reactions with thermal electrons. We thus started a study on the electron-beam treatment of chloromethane.

Carbon tetrachloride was chosen for our research, since it had the highest rate constant for the reaction with a thermal electron of all chloromethane.¹⁰ In the present work, we showed the effect of oxygen on the decomposition of CCl_4 . The reason for the depression in the CCl_4 decomposition rate by the addition of water was also considered.

Experimental

Apparatus. Laboratory-scaled experiments on electron-beam treatments were carried out for CCl_4 in air (CO , CO_2 , and $\text{CH}_4 < 0.1$ ppm) and nitrogen (99.999%) in both the presence and absence of water. Vaporized CCl_4 was mixed with a carrier gas of air or N_2 to obtain the desired concentrations of 10, 50 and 100 ppm. Water was supplied to the system with the carrier gas into water. Sample gases were exposed to electron beams when introduced into a reactor ($200 \times 70 \times 25 \text{ mm}^3$) placed at the irradiation zone of an electron accelerator (Iwasaki: Electrocurtain CB175/15/180LS). The reactor, made of stainless steel, was designed to have sample gases exposed as uniformly as possible. A cooling panel attached to the reactor was able to keep the gas temperature at 25°C during irradiation. Sample gases were analyzed with a gas chromatograph (Shimadzu: GC-14B) that was calibrated with a CCl_4 standard gas at a concentration of 10.6 ppm. The accelerator supplied 170 kV with a current of up to 10 mA. The flow rate of the sample gases was 5 L min^{-1} and the exposure time was approximately 0.21 s. The irradiation of sample gases formed particles and gaseous products. A Fourier-transform infrared spectrometer (Perkin Elmer: Spectrum 2000) was placed downstream from the reactor to analyze the decomposition products, such as CO and CO_2 . Particles were measured with a particle counter (TSI: SMPS 3025A) 3 min after irradiation. Detailed information on the apparatus is available elsewhere.³

G-Value. Finding the G -value is one of the approaches to measure the radiation-chemical yield. The G -value is defined as the number of molecules charged for each 100 eV of energy absorbed,

$$G = M/(E/100) = 100 \times (M/E) \quad (5)$$

where E is the energy that the irradiated target absorbed and M is the number of molecules formed from the irradiated target. Thus, $G(X)$ refers to the number of molecules X that are formed upon irradiation per 100 eV, and $G(-Y)$ refers to the number of molecules Y that are decomposed in the same way. One molecule per 100 eV (G -value = 1.0) is equivalent to $0.1036 \mu\text{mol J}^{-1}$.¹¹

Results and Discussion

Oxidation in Dry Air. Carbon tetrachloride in dry air was irradiated with electron beams at initial concentrations of approximately 10, 50 and 100 ppm. The irradiation doses ranged from 1.2 to 18.0 kGys. The oxidation of CCl_4 in the absence of water by electron-beam irradiation is shown in Fig. 1. The remaining concentration at 18 kGy absorbed dose was 1.2 ppm, giving more than an 85% decomposition rate of CCl_4 at an initial concentration of 10 ppm. The

decomposition rate was lower as its higher concentrations over the investigated doses. The decomposition G -values ($G(-\text{CCl}_4)$) of 1.3, 2.7, and 3.3 were calculated from the initial slope (0–1.2 kGy) for 10, 50 and 100 ppm, respectively. A higher G -value was obtained from a higher concentration of CCl_4 . Considering the reaction probability between CCl_4 molecules and the active species produced by the electron-beam irradiation of air, the more CCl_4 molecules that exist, the greater is the chance to collide with the active species. The active species effectively reacted with CCl_4 molecules when the concentration of CCl_4 was high.

The solid lines in Fig. 1 were obtained from our data points using the equation $[X] = [X]_0 \exp(-E/\beta)$, where $[X]_0$ is the initial concentration of CCl_4 , E is the input energy density and β is the experimental holding factor. Penetrante et al.⁵ used this equation to compare the energy efficiency for the oxidation of vaporized CCl_4 . They showed that the experimental holding factor was 9 J L^{-1} for the electron-beam decomposition of 100 ppm CCl_4 in dry air. This value is lower than our experimental holding factor of 19 J L^{-1} . Our electron-beam processing required more energy to decompose CCl_4 compared with their results.

In dry-air experiments, reactions (2) and (3) are significant electron-loss processes when the concentration of CCl_4 is less than approximately 10 ppm, as Penetrante et al.^{8,9} have reported. This is not consistent with our results, as shown in Fig. 1. If electron-loss processes occur in our experiments, the decomposition of CCl_4 should be depressed. However, the decomposition rate at an initial concentration of 10 ppm is higher than in two other experiments over the investigated doses. No influence of the consumption of thermal electrons by oxygen molecules was observed. We thus predicted that other reactants existed to oxidize CCl_4 . The reactants probably reacted with CCl_4 , which compensated for the electron-loss processes.

Oxidation in Wet Air. The addition of water drastically

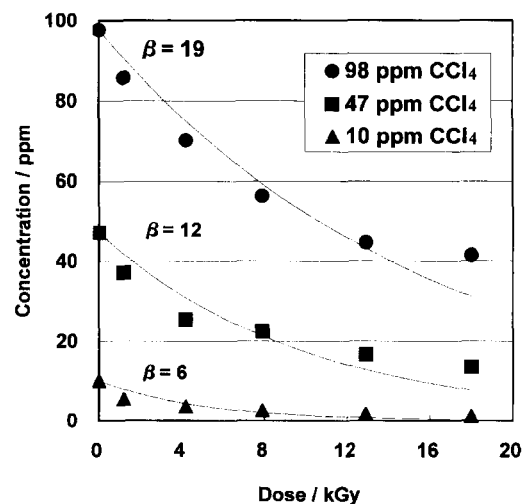


Fig. 1. Oxidation of carbon tetrachloride in dry air. The solid lines are fits to the experimental data points using the expression of $[X] = [X]_0 \exp(-E/\beta)$. $[\text{H}_2\text{O}] < 1$ ppm, Temp = 25°C .

dropped the decomposition rate of CCl_4 . The results are shown in Fig. 2. The initial concentrations of CCl_4 in wet air are similar to those in dry air. An absorbed dose of 18 kGy decomposed 70% of CCl_4 at the lowest concentration, 10 ppm. This decomposition rate was 15% lower than that in dry air. Two other experiments also exhibited that the presence of water depressed the CCl_4 decomposition over the investigated doses. In addition, the $G(-\text{CCl}_4)$ values (0–1.2 kGy) of 0.7, 1.4, and 2.1 in wet-air experiments were smaller than those in dry air for experiments of 10, 50 and 100 ppm, respectively. At doses below 1.2 kGys, few reaction products from the oxidation of CCl_4 exist in the irradiated wet air, where the reactions of thermal electrons with the products are minor. Also, electron attachment to water molecules is negligible. When accelerated electrons penetrate into polluted air, almost all electrons lose energy to collide with nitrogen, oxygen, and water molecules, which are the main components of air. The collisions produce many primary products such as N_2^+ , O_2^+ , N , O , and e . Mätzing reported the following stoichiometric equations for the electron-beam irradiation of air.¹²

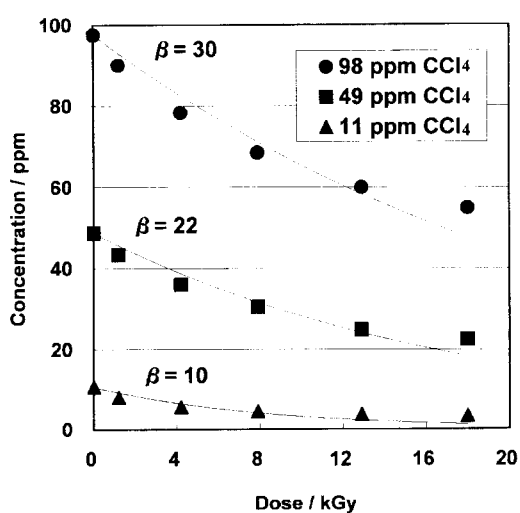
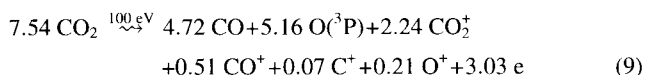
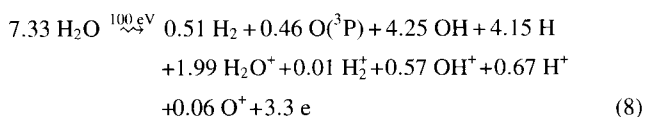
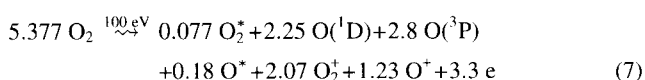
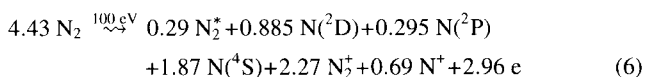
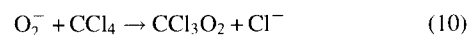


Fig. 2. Oxidation of carbon tetrachloride in wet air. The solid lines are fits to the experimental data points using the expression of $[X] = [X]_0 \exp(-E/\beta)$. $[\text{H}_2\text{O}] = 1.5\%$, $\text{Temp} = 25^\circ\text{C}$.

Ion-molecular reactions, charge-transfer reactions, neutralization and so on then take place among the primary products and the components of air. In the process of these reactions, carbon tetrachloride molecules collide with electrons to dissociate before redistribution of the excess energy takes place.¹³ The electron-attachment rate of carbon tetrachloride suddenly increases because the mean electron energy is less than 0.1 eV.¹⁴ Consequently, the dominant reactions occur between CCl_4 molecules and thermal electrons in not only dry air, but also in wet air. Thus, the $G(-\text{CCl}_4)$ values in wet air are attributable to reactions with thermal electrons. The drop in $G(-\text{CCl}_4)$ in wet air points out that other reactants, except for a thermal electron, existed and could oxidize CCl_4 molecules in the case of a dry-air condition. The oxidation by other reactants was affected in the presence of water.

Oxidation Mechanism. The addition of water had no influence on the oxidation of CCl_4 in nitrogen, as shown in Fig. 3 and Fig. 4. The results gave us an important issue. Namely, the addition of water had no influence on the decomposition of CCl_4 under the nitrogen condition. This implies that the oxidation of CCl_4 is affected by the addition of water in the presence of oxygen. From our experiments, we propose the following oxidation process of CCl_4 by an electron beam. A product in reactions (2) and (3), the negative oxygen ion, is responsible for the oxidation of CCl_4 molecules in dry air. This oxidation occurs with a rate constant of $1.4 \times 10^{-9} \text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$.¹⁵



In fact, our computer simulation demonstrated that approximately 55% of the decomposed CCl_4 was attributed to reactions with negative oxygen ion when 10 ppm CCl_4 in dry air was irradiated at a dose of 8 kGy. The simulation was made via the Runge–Kutta–Gill method using $G(e)$ of 3.06^{16} and the 10 reactions listed in Table 1. The contribution

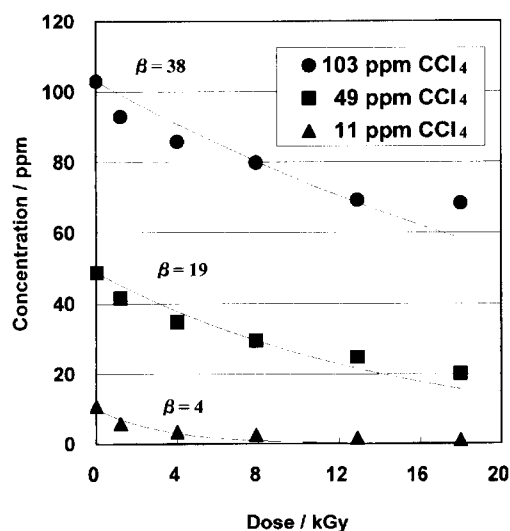


Fig. 3. Oxidation of carbon tetrachloride in dry nitrogen. The solid lines are fits to the experimental data points using the expression of $[X] = [X]_0 \exp(-E/\beta)$. $[\text{H}_2\text{O}] < 1 \text{ ppm}$, $\text{Temp} = 25^\circ\text{C}$.

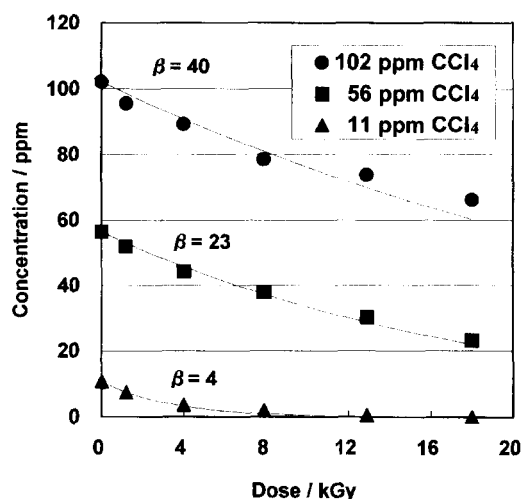


Fig. 4. Oxidation of carbon tetrachloride in wet nitrogen. The solid lines are fits to the experimental data points using the expression of $[X] = [X]_0 \exp(-E/\beta)$. $[H_2O] = 1.5\%$, Temp = 25 °C.

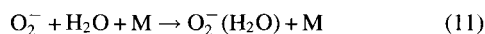
Table 1. Rate Constants k for the Computer Simulation of CCl_4 Oxidation

Reaction	$k/cm^3 \text{ mol}^{-1} \text{ s}^{-1}$	Reference
$CCl_4 + e \rightarrow CCl_3 + Cl^-$	3.3×10^{-7}	7
$CCl_3 + e \rightarrow CCl_2 + Cl^-$	2.4×10^{-7}	7
$e + O_2 + O_2 \rightarrow O_2^- + O_2$	1.2×10^{-11}	8
$e + O_2 + N_2 \rightarrow O_2^- + N_2$	3.1×10^{-12}	8
$O_2^- + CCl_4 \rightarrow CCl_3O_2 + Cl^-$	1.4×10^{-9}	15
$O_2^- + N_2^+ \rightarrow N_2 + O_2$	7.7×10^{-6} a)	17
$N_2^+ + O_2 \rightarrow O_2^+ + N_2$	4.9×10^{-11} a)	17
$O_2^- + O_2^+ \rightarrow O_2 + O_2$	7.9×10^{-6} a)	17
$O_2^+ + e \rightarrow O_2$	1.5×10^{-7} a)	17
$O_2^+ + e \rightarrow O + O$	2.1×10^{-7} a)	17

a) Calculated at 25 °C

of secondary electrons (e) and negative oxygen molecules (O_2^-) to the decomposition of CCl_4 was compared with the products of their concentrations and the rate constants. It is found from our experimental results and simulation that not only thermal electrons, but also negative oxygen ions are important substances to oxidize CCl_4 in dry air.

In the presence of water, negative oxygen ions collide with water molecules to be a negative cluster ions of $O_2^-(H_2O)$:



The rate constant of this reaction is $7.4 \times 10^{-9} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.¹⁷ To confirm the formation of the cluster ion, we measured the particles in air in both the presence and absence of water. The particles were detected when wet air was irradiated with electron beams, as shown in Fig. 5. No particles were observed when using electron beams in dry air. A mean diameter of 15.1 nm was obtained with a number concentration of 2.4×10^3 particles/cm³ at a dose of 1.2 kGy. The size and number concentration of particles increased with the dose. The size of the particle formed even at 1.2 kGy dose was beyond the size range of the cluster. However,

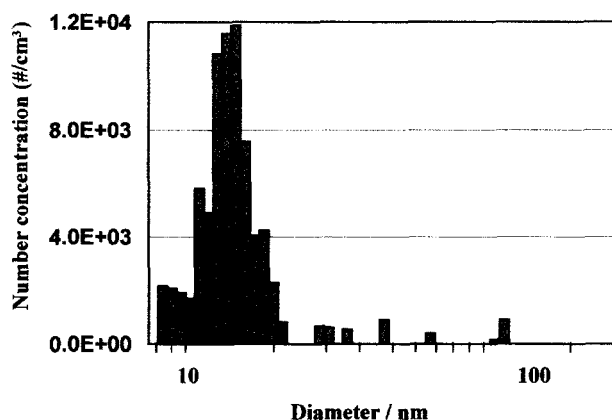


Fig. 5. Distribution of particles formed in wet air at a dose of 1.2 kGy. $[H_2O] < 1 \text{ ppm}$, Temp = 25 °C.

it is possible for the cluster ion to be larger in collisions with water molecules after irradiation. Indeed, Handa et al.¹⁸ showed that $O_2^-(H_2O)_n$ was formed in wet air irradiated by a corona discharge plasma. The plasma processing is based on radical reactions as well as the electron beam. Consequently, the particles which we detected under a wet-air condition probably contained $O_2^-(H_2O)_n$ cluster ions that were formed through collisions with nH_2O . The formation of the cluster ions demonstrated that there was competition for the reactions with negative oxygen ions between CCl_4 and water molecules, giving a lower decomposition rate of CCl_4 in wet air, as shown in Fig. 2.

However, negative oxygen ions formed exclusively through reactions (2), (3), and (4) when the concentration of CCl_4 was less than approximately 10 ppm, as mentioned above. Little effect of water on the oxidation of CCl_4 can be expected at concentrations of 50 and 100 ppm, since thermal electrons react substantially with CCl_4 molecules. Why was the decomposition rate of CCl_4 lowered by the addition of water at concentrations of 50 and 100 ppm, as shown in Fig. 2? The answer to this question is given as follows. The irradiation of CCl_4 at higher concentrations in wet air leads to the formation of many products that have a rela-

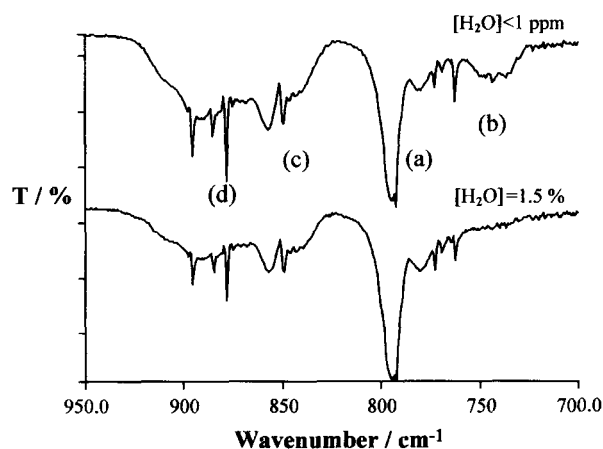
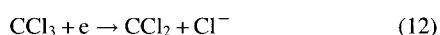


Fig. 6. FTIR spectrum of carbon tetrachloride in dry and wet air at a dose of 9.8 kGy. $[CCl_4] \approx 10 \text{ ppm}$, $[H_2O] < 1 \text{ ppm}$, Temp = 25 °C.

tively higher electron affinity, such as CCl_3 and Cl .¹⁰ These products are strong competitors for reacting with the thermal electrons against CCl_4 . In addition, the irradiation of wet air produces HNO_3 . This product is a strong scavenger of thermal electrons. As a result, the products and HNO_3 probably depressed the oxidation of CCl_4 at concentrations of 50 and 100 ppm.

The effect of water on CCl_4 oxidation was also observed by spectrophotometry. Figure 6 shows the FTIR spectrum of CCl_4 in dry and wet air at a dose of 9.8 kGy. Strong and weak absorption peaks (a) in the region $770\text{--}800\text{ cm}^{-1}$ on the spectrum are assigned to CCl_4 . The absorption band of $-\text{CCl}_2$ and/or $-\text{CCl}_3$ generally lies at around 740 cm^{-1} . In the FTIR spectrum, many peaks (b) are seen in a similar region of $730\text{--}760\text{ cm}^{-1}$. The irradiation of CCl_4 in dry air leads to the dissociation of chlorine from carbon through reactions (1), as mentioned above. A primary product of CCl_3 in reaction (1) also consumes thermal electrons with a rate constant of $2.4 \times 10^{-7}\text{ cm}^3\text{ mol}^{-1}\text{ s}^{-1}$.

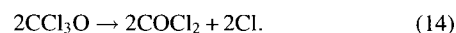
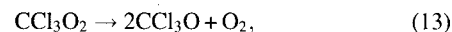


The analysis time with FTIR spectrometry is far beyond the lifetime of the primary and secondary products in reactions (1) and (12). Therefore, the products from the reactions of CCl_4 with negative oxygen ions in reaction (10) and the following reaction products probably contribute to the many absorption peaks in the region $730\text{--}760\text{ cm}^{-1}$ in the FTIR spectrum. Actually, as shown in Fig. 6, these peaks completely disappeared from the spectrum when CCl_4 in wet air was irradiated. It is found from our FTIR spectrum that water depresses the reactions of negative oxygen ions with CCl_4 . In addition, the spectrum revealed that the oxidation of CCl_4 in dry air with electron beams produced phosgene (COCl_2) (c), seen in the region $840\text{--}860\text{ cm}^{-1}$. Other peaks (d) in the region $860\text{--}900\text{ cm}^{-1}$ are attributable to nitric acid (HNO_3).

Although $\text{O}_2^-(\text{H}_2\text{O})$, the product in reaction (11), can oxidize CCl_4 , its rate constant is much lower than that of reaction (10). Also, $\text{O}_2^-(\text{H}_2\text{O})$ reacts with water molecules one after another to form $\text{O}_2^-(\text{H}_2\text{O})_n$. The more the cluster ion reacts with water molecules, the lower is the rate constant for the

reactions with CCl_4 . The oxidation of CCl_4 in wet air is not due to the reactions with negative oxygen ions, but to the reactions with thermal electrons.

Reaction Products. In the case of the oxidation of CCl_4 by negative oxygen ion in reaction (10), CCl_3O_2 decomposes to produce phosgene (COCl_2):¹⁹



On the other hand, CCl_2 , the product from the dissociative electron attachment in reaction (12) reacts with an oxygen molecule:²⁰



Representative oxidation processes to produce CO and CO_2 are available in Table 2. Other chemical mechanisms have been reported elsewhere for the fragmentation products from the decomposition of CCl_4 .^{21,22} Figures 7(a) and 7(b) show the concentrations of CO_2 and CO produced by the irradiation of 10 ppm CCl_4 in dry and wet air. The formation of CO_2 and CO indicates that CCl_4 is completely dechlorinated. The concentration ratio of $[\text{CO}_2] + [\text{CO}]$ to $[\text{CCl}_4]_{\text{oxidized}}$ increased with the dose. More than 80% of the oxidized CCl_4 in dry air was completely dechlorinated beyond the 4 kGy dose. Wet-air irradiation required an absorbed dose of 8 kGy to get 80% of complete dechlorination.

Table 2. Rate Constants k for the reactions to produce CO and CO_2

Reaction	$k/\text{cm}^3\text{ mol}^{-1}\text{ s}^{-1}$	Reference
$\text{ClO} + \text{COCl} \rightarrow \text{CO} + \text{Cl}_2\text{O}$	1.7×10^{-10}	21
$\text{ClO} + \text{COCl} \rightarrow \text{CO}_2 + \text{Cl}_2$	1.7×10^{-10}	21
$\text{ClO} + \text{CO} \rightarrow \text{CO}_2 + \text{Cl}$	3.6×10^{-18} a)	21
$\text{COCl} + \text{O}_2 \rightarrow \text{CO}_2 + \text{ClO}$	1.0×10^{-13}	21
$\text{COCl} + \text{M} \rightarrow \text{CO} + \text{Cl} + \text{M}$	5.4×10^{-15} a)	21
$\text{COCl} + \text{OH} \rightarrow \text{CO} + \text{HOCl}$	1.6×10^{-11}	21
$\text{COCl}_2 + e \rightarrow \text{CO} + \text{Cl}_2^-$	5.0×10^{-8}	10

a) Calculated at 25 °C

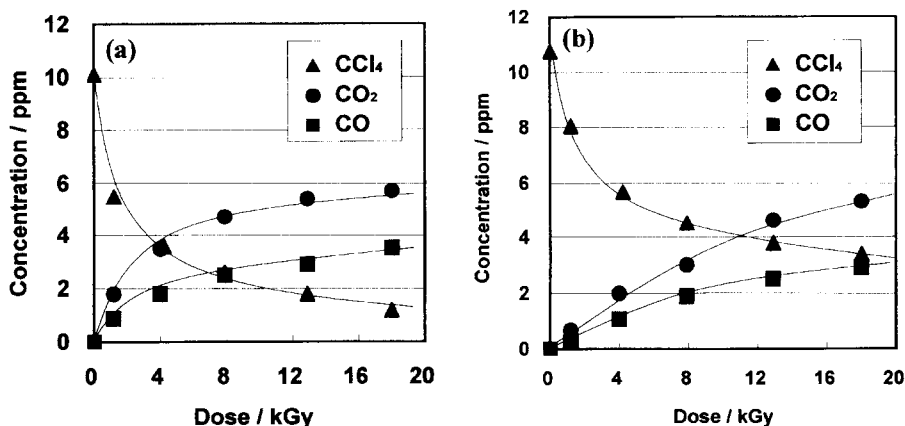


Fig. 7. Formation of carbon monoxide and carbon dioxide in dry and wet air. $[\text{H}_2\text{O}] < 1\text{ ppm}$ (a), $[\text{H}_2\text{O}] = 1.5\%$ (b), Temp = 25 °C.

Conclusion

Gaseous CCl₄ in air and nitrogen was irradiated with electron beams in both the presence and absence of water. Approximately 90% of the decomposition was obtained when 10 ppm CCl₄ in dry air was irradiated at a dose of 18 kGy. Negative oxygen ions played a role in the oxidation of CCl₄ in dry air. The addition of water depressed the decomposition by 20%, since the reactions of water molecules with negative oxygen ions controlled the decomposition. More than 80% of the oxidized CCl₄ in dry air was completely dechlorinated beyond the 4 kGy dose when 10 ppm CCl₄ was irradiated with electron beams. Wet-air irradiation required an absorbed dose of 8 kGy to obtain the same dechlorination rate.

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