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Decomposition Mechanism for Electron Beam Irradiation of Vaporized Trichloroethylene−Air Mixtures

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Decomposition of trichloroethylene (TCE) in electron beam irradiation was examined in order to get information on treatment of industrial off-gas. Air containing vaporized TCE was sealed into a glass vessel and irradiated with an electron beam. The concentration of TCE exponentially decreased with dose (air-absorbed energy). The doses necessary to decompose 90% of input TCE molecules had a value of 3.6 kGy independent of an initial concentrations ranging from 50 to 1800 ppmv. Between *G* values of decomposition and initial concentrations, the following equation was obtained: $G(-\text{TCE})\ [\mu\text{mol J}^{-1}] = 1.5\ [\mu\text{mol J}^{-1}] + 0.020\ [\mu\text{mol J}^{-1}\ \text{ppmv}^{-1}] \times \text{conc [ppmv]}$. The equation shows that concentrations of Cl radicals remained constant at 6.3×10^{-4} ppmv (at 298 K and 1 bar) independent of concentrations of TCE and products under a dose rate of 2.1 kGy/s. Termination reactions in the decomposition mechanism for EB irradiation of TCE and tetrachloroethylene (PCE) were also clarified on the basis of the relation of *G* value of decomposition and the initial concentrations. Dichloroacetyl chloride, which was identified as a primary product, was decomposed and oxidized to give CO and CO_2. Phosgene was also identified as a primary product. From the proportion of DCAC to $COCl_2$ concentrations, a branching ratio was calculated to be 5.3 in the Cl radical chain reaction of TCE. Formation of HCl and/or Cl_2 was analyzed and the collection of the products from the gas phase was examined with alkaline solution. The effect of water (400−25 000 ppmv) on decomposition efficiency was examined. The decomposition efficiencies had the same value as that in dry air.

Introduction

Volatile organic compounds (VOCs) have caused widespread environmental contamination such as groundwater and soil contamination. Off-gases from factories for semiconductor and paints also have been contaminated with VOCs. It is well-known that several kinds of VOCs are very harmful to human health because of carcinogenic and mutagenic effects. The Environmental Agency of Japan has started to evaluate the toxicity of various environmental pollutants, including VOCs in order to build the emission regulations from pollution sources.[1]

Among these VOCs, trichloroethylene (TCE) has been widely used as washing and de-oil solvents in various industrial fields. The pollution from TCE has caused severe problems, especially in the ground and drinking water or the soil at widely and highly industrialized areas. The VOCs including TCE have been treated with adsorption on activated carbon or catalytic combustion. These conventional methods can effectively and economically remove some kinds of VOCs from contaminated water and gas when their concentrations are large.[2] However, the removal efficiencies are relatively decreased in low concentrations of VOCs. The VOCs adsorbed on the activated carbon are not converted into nontoxic compounds and have the possibility of causing new pollution at places different from the original pollution sources (secondary pollution).

The ionizing radiation decomposition seems to be alternative technologies for removal of chlorinated hydrocarbon within low concentrations of VOCs and has the advantage of being performed at ambient temperature. The free radicals and ions, which are produced from base components (water, soil, and gas) by ionizing radiation, can directly oxidize and decompose VOC molecules. For TCE in groundwater, the study of radiation decomposition has been undertaken as a potential technology. These applications with ionizing radiation demonstrated the direct decomposition of TCE in water by γ ray irradiation,[3,4] as well as the decomposition of gas-phase TCE stripped from the contaminated water by electron beam (EB) irradiation.[5−7] These experiments were performed under fixed concentrations of TCE.

As compared with γ ray irradiation, an EB accelerator can produce large amounts of radicals and ions from base components within a very short time because of the high dose rate. A large amount of water, soil, and air contaminated with TCE is expected to be effectively treated with EB. Since the penetration range of EB in water and a solid is very small in comparison with that in a gas, EB treatment is suitable for purification of gas-phase TCE. Low-energy EB accelerators have recently been used in various industrial fields. It can be operated without a protection structure for bremsstrahlung X-ray and a skillful operator. It is cheaper to purchase a low one than a high one. The process will be more economical by using a low-energy EB accelerator.

For developing EB treatment of gas-phase TCE, basic information should be precisely obtained on decomposition efficiencies under input concentrations ranging from 50 to 1800 ppmv (parts per million by volume) as well as irradiation

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products. In the present work, gas-phase TCE was irradiated with EB. The decomposition efficiencies were examined under various initial TCE concentrations and water concentrations. The products were analyzed and the collection with an alkaline solution was investigated. The decomposition mechanism was discussed on the basis of product distribution.

Experimental Section

All sample gas was prepared by mixing dry air (<1 ppmv CO, <1 ppmv CO_2, and <1 ppmv CH_4) and vaporized TCE (>99.0% pure liquid TCE without further purification, Kanto Chemical Co. Ltd.). Pyrex glass vessels were used as an irradiation reactor.[8] The reactors (50 × 50 × 200 mm) have a volume of 500 mL and two stopcocks (without grease) at both ends. The sample gases were introduced into the reactors and were sealed with the stopcocks. The concentrations of TCE in the sample gases were measured by a gas chromatograph (GC-8A, Shimadzu Seisakusho Co. Ltd.) with FID and a packed column (BX-20 100/120, 2 mm i.d. × 3 m, GL Science Inc.), and the values were adjusted to 50−1800 ppmv. The water concentrations in the dry air were measured to be 200 ppmv by a moisture analyzer (Hygro-3M with D-2 detector, General Eastern Co. Ltd.). Vaporized water from a liquid water bubbling bottle was added to the sample gas, and the concentrations were adjusted to 400−25 000 ppmv.

The sample gases in the reactors were irradiated with 2 MeV electrons generated by an electron beam accelerator (3 MV 25 mA max., Cockcroft-Walton type, Radiation Dynamic, Inc.) with a constant beam current of 1.0 mA. The reactors were put on the conveyer for irradiation and passed under the scan horn. The sample gases in the reactors were exposed at doses ranging from 2.2 to 40 kGy. An average dose in the reactor was measured by a CTA film dosimeter and was 2.2 kGy/pass under these conditions. A calculated value of average dose rate was 2.1 kGy/s.

After irradiation, a rubber cap was attached to one side of the connection tubes of the reactor and the air between the rubber cap and the stopcock was evacuated by a syringe. Then, the stopcock was opened and a syringe sampled 2.0 mL of the inner gas.

Analyses of residual TCE and products were carried out as follows.

Trichloroethylene, dichloroacetyl chloride (DCAC), and chloroform ($CHCl_3$) were analyzed by the gas chromatograph. Other organic gaseous products were barely observed. Total carbon (TC) and carbon dioxide (CO_2) were analyzed by a total organic carbon (TOC) analyzer (TOC-5000A, Shimadzu Seisakusho Co. Ltd.). The TOC analyzer can convert all carbon compounds into CO_2 in a heating tube (923 K) with a catalyst. The resulting CO_2 formed in a TOC analyzer corresponds to TC. Carbon monoxide (CO) was analyzed by a CO analyzer (TH-D4 detector with TA-470 Monitor, Komyo Co. Ltd.). Phosgene ($COCl_2$) was indirectly analyzed by a TOC analyzer. When $COCl_2$ is dissolved in phosphoric acid solution (25% w H_3PO_4), CO_2 is produced from $COCl_2$ in the solution and released into the gas phase. The concentration of $COCl_2$ was calculated from the difference in CO_2 concentrations with and without H_3PO_4 solution. Hydrochloric acid and/or Cl_2 were analyzed by an ion chromatograph (LC-10A, Shimadzu Seisakusho Co. Ltd.) with a conductivity detector (CDD-6A, Shimadzu Seisakusho Co. Ltd.) and a column (Shim-Pack IC-A3, Shimadzu Seisakusho Co. Ltd.). The reactors were washed with NaOH solution (0.1 M) of 10.0 mL to mainly scavenge Cl_2 and HCl. A part of the solution was analyzed for Cl^- ions. Ozone (O_3) was analyzed by an ozone analyzer (model 4560 Sensor STIK with Type 4501 Monitor, EIT).

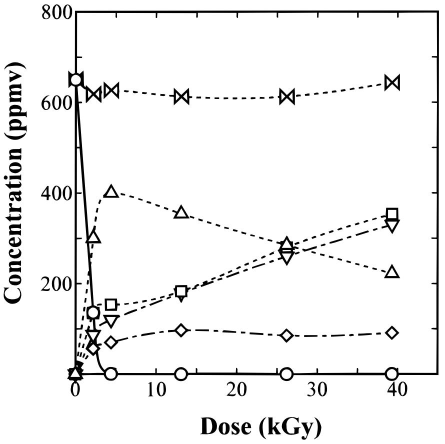

Figure 1. Concentrations of residual TCE and the products versus dose for EB irradiation of 650 ppmv TCE: (○) TCE; (△) dichloroacetyl chloride (DCAC); (▽) CO; (□) CO_2; (◇) phosgene ($COCl_2$); (⋈) TC (total carbon concentration) × $^{1}/_{2}$.

Result

Figure 1 shows concentrations of residual TCE and products versus dose at an initial concentration of 650 ppmv. Products were identified as dichloroacetyl chloride ($CHCl_2COCl$, DCAC), carbon monoxide (CO), carbon dioxide (CO_2), phosgene ($COCl_2$), and small amount of chloroform ($CHCl_3$). The concentration of total carbon (TC) remained constant up to 40 kGy so that any products containing carbon did not attach on the inner surface of the reactor. The concentration of DCAC increases and reaches a value of 390 ppmv (62%v of initial TCE concentration) at doses ranging from 0 to 4.4 kGy where TCE is decomposed. Then, the concentration gradually decreases at more than 4.4 kGy. For CO and CO_2, the concentrations rapidly increase up to 2.2 kGy and linearly increase at doses ranging from 2.2 to 40 kGy. For $COCl_2$, the concentration increases at doses ranging from 0 to 4.4 kGy and remains constant (ca. 90 ppmv). The concentration of $CHCl_3$ was measured to be 5 ppmv (0.8% v of initial TCE concentration) at 20 kGy.

Figure 2 shows the carbon concentrations for TCE and products in the gas phase with and without NaOH solution. Figure 2A (without $NaOH_{aq}$) corresponds to Figure 1. In this figure, the values in parentheses denote mass yield. The mass yield stands for the proportion of summation of the carbons contained in residual TCE and product molecules to input TC. These values are close to 100% so that all carbon compounds could be identified. As shown in Figure 2B (with $NaOH_{aq}$), DCAC, CO_2, and $COCl_2$ could be dissolved in NaOH solution. These compounds can be mineralized by hydrolysis and converted into sodium dichloroacetate (from DCAC) and NaCl and Na_2CO_3 (from CO_2 and $COCl_2$), respectively. The smallest mass yield after treatment with $NaOH_{aq}$ occurred at 4.4 kGy, which is where the largest removal efficiency of total VOCs including products was obtained. Trichloroethylene was almost completely decomposed at this dose. At more than 4.4 kGy, the efficiency gradually decreased with an increase in the concentration of CO. The solutions were also analyzed by the ion chromatograph to measure chloride ions (Cl^-). The result is shown in Table 1. The expected concentration denotes the concentration of Cl^- ions produced from DCAC, $COCl_2$, and HCl and/or Cl_2 when these products were dissolved in 10 mL of NaOH solution.

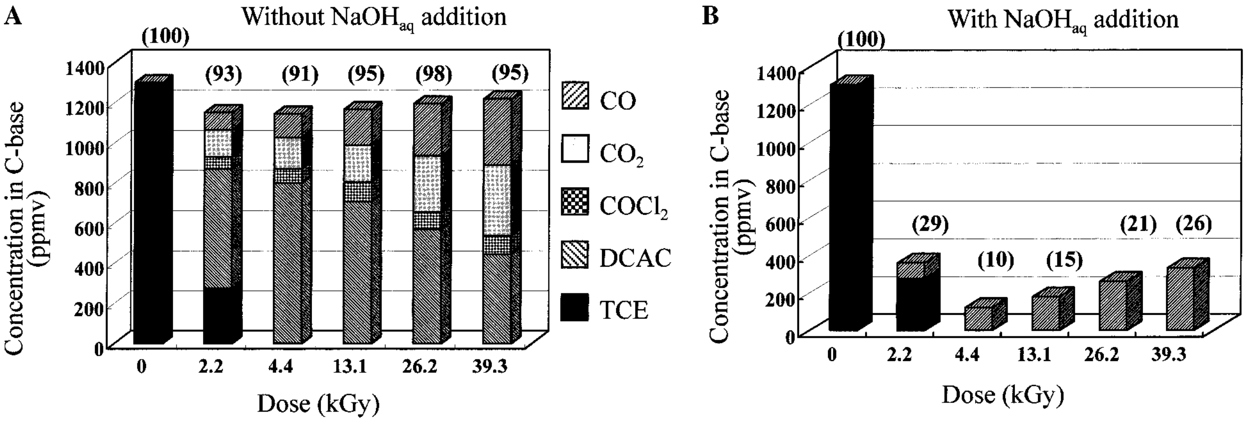

Figure 2. Distribution of TCE and the products with and without NaOH solution (0.1 M, 10 mL). The values in parentheses stand for the relative carbon concentration in the gas phase.

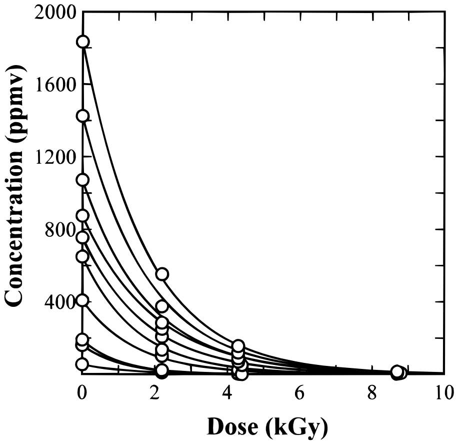

Figure 3. Concentrations of TCE versus dose in EB irradiation.

TABLE 1: Concentration of Cl^- Ion in Solution for EB Irradiation of 650 ppmv TCE

dose (kGy)	DCAC (ppmv)	expected Cl^- (10^{-3} mol/l)	measured Cl^- (10^{-3} mol/l)	mass yield (%)
2.2	298.0	2.76	2.68	97.1
4.4	412.0	2.35	2.15	91.5
13.1	345.2	2.54	2.36	92.9
26.2	284.9	2.82	2.76	97.9
35.3	222.5	3.08	3.10	100

Figure 3 shows concentrations versus dose for initial concentrations ranging from 50 to 1800 ppmv. A large initial concentration gives a large slope of the decomposition curve within a low dose. The doses necessary to decompose 90% of input TCE molecules ($Dose_{90\%}$) were calculated from decomposition curves. Most of the values of $Dose_{90\%}$ were calculated to be 3.6 ± 0.1 kGy. For 408 and 1834 ppmv, the relative concentrations of TCE and products showed the same distributions as those at 650 ppmv. The reason will be discussed in the next section.

Discussion

Formation of Activated Species. When air containing vaporized water is irradiated with ionizing radiation, OH, HO_2, O, N, and H radicals and O_3 molecules are produced as activated species. Electron beam irradiation of the sample gas can cause dissociation and ionization of the base gas (N_2 and O_2).[9–12]

$$e^- + N_2 \rightarrow e^- + (N_2^+ + e_{thr}^-),\ 2N^\bullet,\ N_2^* \tag{1}$$

$$e^- + O_2 \rightarrow e^- + (O_2^+ + e_{thr}^-),\ 2O^\bullet,\ O_2^* \tag{2}$$

The symbol star (*) stands for an excited state.

The charge transfer reaction mainly occurs between N_2^+ and O_2 molecules.

$$N_2^+ + O_2 \rightarrow N_2 + O_2^+ \tag{3}$$

The O_2^+ ions formed in reactions 2 and 3 produce H_2O cluster ions.

$$O_2^+ + H_2O \rightarrow O_2-H_2O^+ \tag{4}$$

The resulting $O_2-H_2O^+$ ions cause the dissociation reaction of water cluster ions to produce OH radicals

$$O_2-H_2O^+ + H_2O \rightarrow H_3O^+ + O_2 + OH^\bullet \tag{5}$$

$$O_2-H_2O^+ + 2H_2O \rightarrow\rightarrow H_3O^+ + H_2O + O_2 + OH^\bullet \tag{6}$$

Among O radicals produced in reaction 2, $O(^1D)$ radicals can react with H_2O molecules and produce OH radicals.

$$O(^1D)^\bullet + H_2O \rightarrow 2OH^\bullet \tag{7}$$

Secondary (thermal) electrons (e_{thr}^-) formed in reactions 1 and 2 are scavenged with O_2, H_2O, and TCE molecules

$$e_{thr}^- + O_2 + M \rightarrow O_2^- + M \tag{8}$$

$$O_2^- + H_2O + M \rightarrow O_2^-H_2O + M \tag{9}$$

$$e_{thr}^- + TCE \rightarrow Cl^- + \text{products} \tag{10}$$

Here the symbol M stands for a third body (such as N_2).

These ions are neutralized to produce H, HO_2, and O radicals and O_3 molecules.

$$H_3O^+ + O_2^-H_2O \rightarrow H^\bullet + O_2 + 2H_2O \tag{11}$$

$$\rightarrow HO_2^\bullet + 2H_2O \tag{12}$$

$$O_2^+ + O_2^- \rightarrow O^\bullet + O_3 \tag{13}$$

$$\rightarrow O_2^* + O_2 \tag{14}$$

$$\rightarrow 2O^\bullet + O_2 \tag{15}$$

$$O^\bullet + O_2 + M \rightarrow O_3 + M \tag{16}$$

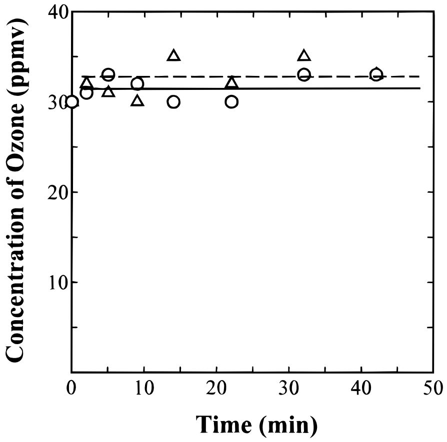

Figure 4. Concentrations of O_3 versus time after EB irradiation. (△, Original) and (dash line, mean value): for 250 ppmv TCE. (○, Original) and (solid line, mean value): for 1750 ppmv TCE.

A part of the ozone is decomposed to O_2 molecules through the reaction with O radicals.

First Step of Decomposition. In the decomposition process of TCE, OH radicals and O_3 molecules are dominant chemical oxidizing species attacking them. For decomposition of TCE in EB irradiation, the reactions with these activated species as well as reaction 10 are regarded as the first step of the decomposition reactions.[13−15]

For the reaction with the OH radicals [reaction-OH],[13]

$$OH^\bullet + C_2HCl_3 \rightarrow C_2HCl_3OH^\bullet \tag{17}$$

$$C_2HCl_3OH^\bullet + O_2 \rightarrow OOC_2HCl_3OH^\bullet \tag{18}$$

$$2(OOC_2HCl_3OH^\bullet) \rightarrow 2(OC_2HCl_3OH^\bullet) + O_2 \tag{19}$$

$$OC_2HCl_3OH^\bullet \rightarrow C_2HCl_2OH(O) + Cl^\bullet \tag{20}$$

For the reaction with O_3 molecules [reaction-O_3],[15]

$$O_3 + C_2HCl_3 \rightarrow CHClOO^\bullet + COCl_2 \tag{21}$$

$$CHClOO^\bullet \rightarrow Cl^\bullet + \text{products} \tag{22}$$

The main decomposition of TCE proceeds by Cl radical chain reaction. Therefore, reaction 10 producing Cl^- would be a minor reaction in the decomposition mechanism. The reaction rate constants of TCE molecules with OH radicals and O_3 molecules are $(2.0 \pm 0.4) \times 10^{-12}$ and $<3.0 \times 10^{-20}$ cm^3 $molecule^{-1}$ s^{-1}, respectively.[16,17] There is no large difference in formation of OH radicals [10,11] and O_3[18] in EB irradiation. Therefore, the reaction with OH radicals can be assumed to be the first step of the decomposition reaction. Figure 4 shows the changes in the concentrations of O_3 formed at 2.2 kGy for 40 min after the irradiation. The concentrations of O_3 remained constant for 40 min and had the same value as the concentration of O_3 in EB irradiation of air without TCE. The concentrations of TCE and products also did not change for 40 min after irradiation. These results show that OH radicals mainly cause the first step of decomposition reaction.

According to the decomposition mechanism proposed by Huybrechts et al.,[19,20] Cl radicals can attach to the double bond of TCE molecules to cause the oxidation of TCE (Cl radical chain reaction).

$$Cl^\bullet + C_2HCl_3 \rightarrow C_2HCl_4^\bullet \tag{23}$$

$$2C_2HCl_4^\bullet \rightarrow \text{chain termination} \tag{24}$$

$$C_2HCl_4^\bullet + O_2 \rightarrow C_2HCl_4OO^\bullet \tag{25}$$

$$C_2HCl_4OO^\bullet \rightarrow C_2HCl_4^\bullet + O_2 \tag{−25}$$

$$C_2HCl_4OO^\bullet + C_2HCl_4^\bullet \rightarrow C_2HCl_4O_2C_2HCl_4 \tag{26}$$

$$2C_2HCl_4OO^\bullet \rightarrow C_2HCl_4O_2C_2HCl_4 + O_2 \tag{27}$$

$$2C_2HCl_4OO^\bullet \rightarrow 2(C_2HCl_4O^\bullet) + O_2 \tag{28}$$

$$C_2HCl_4O^\bullet \rightarrow CHCl_2COCl + Cl^\bullet \tag{29}$$

$$\rightarrow CHCl_2^\bullet + COCl_2 \tag{30}$$

The $CHCl_2$ radicals given in reaction 30 can react with O_2 molecules to produce CHOCl molecules and ClO radicals. The ClO radicals would react with TCE molecules to produce Cl radicals.[21]

$$CHCl_2^\bullet + O_2 \rightarrow ClO^\bullet + CHClO \tag{31}$$

$$ClO^\bullet + C_2HCl_3 \rightarrow CHCl_2COCl + Cl^\bullet \tag{32}$$

The concentration of chloroform ($CHCl_3$), which would be produced from the reaction of $CHCl_2$ radicals and Cl radicals, was measured as 5 ppmv at 20 kGy in a 650 ppmv TCE−air mixture. Therefore, most of $CHCl_2$ radicals formed via reaction 30 would react with O_2 molecules to consequentially produce Cl radicals and DCAC molecules via reactions 31 and 32. The resulting Cl radicals from reactions 29 and 32 can reenter the same oxidation of TCE molecules.

As a result, the oxidation of TCE molecules mainly proceeds by the Cl radical chain process. From the present results (Figure 1), it can be concluded that DCAC is directly produced from TCE as primary products and decomposed with further oxidation to produce CO and CO_2. The Cl radical chain reaction seems to involve reactions 24, 26, and 27 as chain termination.

Effect of Water. Figure 5 shows concentrations of TCE, DCAC (dichloroacetyl chloride), and TC (total carbon) at water concentrations varying from 400 to 25 000 ppmv for a 650 ppmv TCE−air mixture. Under 400 and 1000 ppmv H_2O, the decomposition efficiencies and the concentration of DCAC have the same value as those in dry air. On the other hands, under 25 000 ppmv, the decomposition efficiency is slightly larger than that in dry air.

The vaporized H_2O in air would give a decrease in decomposition efficiency of TCE. The clusters and fragments from H_2O molecules can scavenge Cl radicals and result in a decrease in the concentration of Cl radicals (minus effect). These clusters and fragments can also give an increase in the decomposition efficiency of TCE by formation of more OH radicals (plus effect). Because the decomposition efficiencies under 400 and 1000 ppmv H_2O have the same values as in dry air, a plus effect can counteract a minus effect in the decomposition mechanism. Under 25 000 ppmv H_2O, the value was slightly larger than that in dry air. The concentrations of TC and DCAC were decreased with the dose. The decrease in concentrations of these products suggests that DCAC was adsorbed on the inner surface of glass reactors and removed from the gas phase under wet

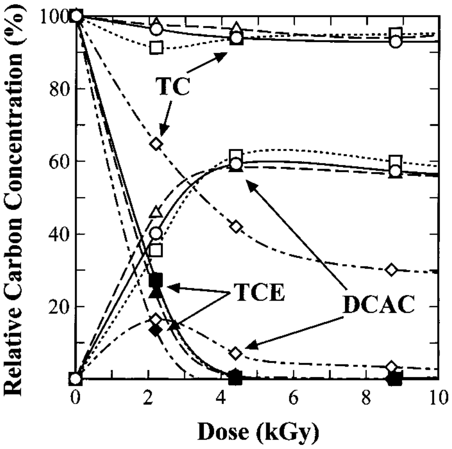

Figure 5. Concentrations of TCE and products versus dose in EB irradiation under different water concentrations: (○) dry air; (□) [H_2O] = 400 ppmv; (△) 1000 ppmv; (◇) 25 000 ppmv; (solid marks) TCE concentrations.

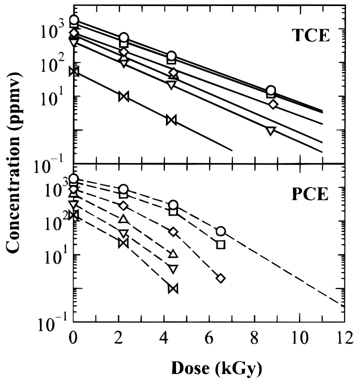

Figure 6. Concentrations versus dose for EB irradiation of TCE and PCE. The results for TCE and PCE are shown in the upper and lower figures, respectively. TCE: (⋈) 55, (▽) 408, (△) 650, (◇) 755, (□) 1425, (○) 1800 ppmv. PCE: (⋈) 150, (▽) 322, (△) 618, (◇) 880, (□) 1440, (○) 1800 ppmv.

conditions. Under this condition, OH radicals can effectively react with residual TCE molecules without reacting products.

Estimation of *G* Values. To quantitatively evaluate the decomposition efficiencies of TCE under various initial concentrations, the *G* value of decomposition was introduced. The value [number/100 eV] is defined as the number of decomposed TCE molecules when the sample gas absorbed 100 eV. In the present work, the *G* values are represented as the unit of μmol J^{-1} (=(1/0.1036) × [number/100 eV], at 298 K and 1 bar) instead of [number/100 eV]. Because the concentration of products is much smaller than that of residual TCE, the reaction of the activated species with products can be neglected at this small absorbed energy. Therefore, *G* values of decomposition can indicate the decomposition efficiency of TCE itself. The decomposition curves shown in Figure 3 can be well fitted with an exponential function (see Figure 6). The *G* values of decomposition ($G(-\mathrm{TCE})$) can be calculated from this fitting equation and are proportional to the slope of the exponential function at 0 kGy. Using the previous results for tetrachloroethylene (PCE),[22] an exponential equation cannot fit the decomposition curve at doses ranging from 0 to 12 kGy (see Figure 6). For the comparison with the values for TCE, $G(-\mathrm{PCE})$ values were also calculated from the slope of decomposition curve at doses ranging from 0 to 2.2 kGy. As shown in Figure 7, decomposition curve under each initial concentration agrees well with that under an initial concentration of 1800 ppmv for

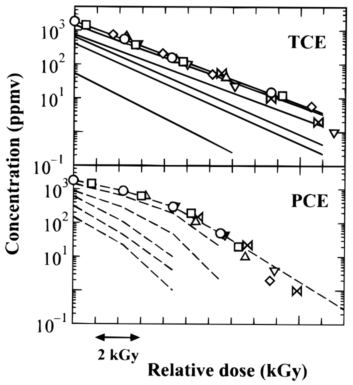

Figure 7. Concentrations of TCE and PCE versus relative dose in EB irradiation: (line) original data; (mark) data for a run with an initial concentration "C_0" plotted where the dose is offset from zero by the dose necessary to reduce the 1800 ppmv sample to concentration "C_0". The value of C_0 denotes the following concentrations of TCE and PCE. TCE: (⋈) 55, (▽) 408, (△) 650, (◇) 755, (□) 1425, (○) 1800 ppmv. PCE: (⋈) 150, (▽) 322, (△) 618, (◇) 880, (□) 1440, (○) 1800 ppmv.

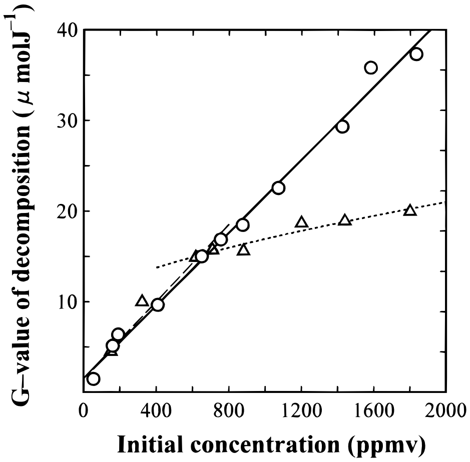

Figure 8. *G* values of decomposition versus initial concentrations for TCE and PCE in EB irradiation: (○) TCE; (□) PCE; (solid line) 1.5 + 0.020 × conc; (dash line) 1.5 + 0.021 × conc; (dotted line) 10.0 + 0.069 × conc$^{2/3}$.

TCE and PCE. Therefore, the decomposition efficiencies under each initial concentration will be affected by only the concentration of residual TCE or PCE and little affected by formation of the products. The value of $G(-\mathrm{PCE})$ calculated from the data at doses ranging from 0 to 2.2 kGy can also indicate the decomposition efficiency of PCE itself at all dose ranges. The values for TCE and PCE under each initial concentration are also shown in Figure 8. As shown in this figure, $G(-\mathrm{TCE})$ seems to linearly increase with the initial concentration at concentrations ranging from 50 to 1800 ppmv. The values of $G(-\mathrm{TCE})$ can be fitted with a following equation.

$$G(-\mathrm{TCE})[\mu\mathrm{mol\ J}^{-1}] = C + l_1 \times \mathrm{conc}\ [\mathrm{ppmv}^{-1}] \quad \text{(E1)}$$

where conc is the initial concentration of TCE. $C = 1.5$ [μmol J^{-1}] and $l_1 = 0.020$ [μmol J^{-1} ppmv^{-1}] at concentrations ranging from 50 to 1800 ppmv.

The chain length in the Cl radical chain reaction can be represented as a ratio of $G(-\mathrm{TCE})$ to the *G* value of formation of the OH radicals ($G(\mathrm{OH})$). As $G(\mathrm{OH})$ is reported as 0.44 [μmol J^{-1}],[10,11] the chain length can be estimated as the value of 85 (=37.3/0.44) at a concentration of 1800 ppmv. High initial concentration enhances the reaction possibility of Cl radicals with TCE molecules and results in an increase in chain length.

Slope and Intersect of Relationship of $G(-\mathrm{TCE})$ and Initial Concentration. During EB irradiation, the decrease in TCE concentration can be described as the following equation from reactions 17 and 23.

$$-\frac{\mathrm{d[TCE]}}{\mathrm{d}t} = k_{17}[\mathrm{OH}][\mathrm{TCE}] + k_{23}[\mathrm{Cl}][\mathrm{TCE}] \qquad \text{(E2)}$$

The dose rate (I) is represented as follows.

$$I = \frac{\mathrm{d}D}{\mathrm{d}t} \qquad (D\text{: dose [kGy = kJ kg}^{-1}]) \qquad \text{(E3)}$$

With eq E3, eq E2 can be represented as

$$-\frac{\mathrm{d[TCE]}}{\mathrm{d}D} = \frac{(k_{17}[\mathrm{OH}] + k_{23}[\mathrm{Cl}])[\mathrm{TCE}]}{I} \qquad \text{(E4)}$$

For OH radicals the reaction rate can be described as follows.

$$\frac{\mathrm{d[OH]}}{\mathrm{d}t} = \frac{1}{0.0346}G(\mathrm{OH}) \times I - k_{17}[\mathrm{OH}][\mathrm{TCE}] \qquad \text{(E5)}$$

If the steady-state treatment can apply to OH radicals, eq E4 can be described as

$$-\frac{\mathrm{d[TCE]}}{\mathrm{d}D} = \frac{G(\mathrm{OH})}{0.0346} + \frac{k_{23}[\mathrm{Cl}][\mathrm{TCE}]}{I} \qquad \text{(E6)}$$

The G value of decomposition for TCE has the following relationship with eq E5.

$$G(-\mathrm{TCE}) = \frac{\Delta N}{\Delta E} \approx -0.0346 \left.\frac{\mathrm{d[TCE]}}{\mathrm{d}D}\right|_{t=0} = G(\mathrm{OH}) + 0.0346\frac{k_{23}[\mathrm{Cl}]}{I}[\mathrm{TCE}]_0 \qquad \text{(E7)}$$

where ΔN is the number of decomposed TCE molecules, ΔE is 100 eV = 1.6×10^{-17} J, and $[\mathrm{TCE}]_0$ is the initial concentration of TCE.

The slope of eq E1 corresponds to the value of $0.0346 \times k_{23}[\mathrm{Cl}]/I$.

$$l_1 = 0.0346\frac{k_{23}[\mathrm{Cl}]}{I} \qquad \text{(E8)}$$

The values of l_1 (= 0.020 μmol J^{-1} ppmv^{-1}), I (=2.1 kGy s^{-1} = 2.7×10^{-3} J cm^{-3} s^{-1}), and k_{17} (=7.8×10^{-11} cm^3 molecule^{-1} s^{-1})[13] are inserted into eq E8: the concentration of Cl radicals can be calculated as 6.3×10^{-4} ppmv (at 298 K and 1 bar). The slope of eq E1 suggests that the concentrations of Cl radicals remained constant at 6.3×10^{-4} ppmv within a small dose range (100 eV) under different initial concentrations and a constant dose rate of 2.1 kGy/s. At all dose ranges, the Cl radicals also have the constant concentration of 6.3×10^{-4} ppmv, because the decomposition curve under each initial concentration agrees well with that under an initial concentration of 1800 ppmv (see Figure 7). For concentrations ranging from 50 to 1800 ppmv, the Cl radicals have the constant concentration under decomposition process at doses ranging from 0 to 12 kGy.

The Cl radical chain oxidation of TCE molecules from reactions 23−32 can predict the initial formation rate of DCAC, and phosgene molecules can be described by the following equation, if chain termination exclusively occurred through reaction 27.

$$\frac{\mathrm{d}}{\mathrm{d}t}([\mathrm{DCAC}] + [\mathrm{COCl_2}]) = \frac{k_{28}k_{\mathrm{OH}}[\mathrm{OH}][\mathrm{TCE}]_0}{k_{27}} \qquad \text{(E9)}$$

The symbol of k_{OH} denotes the overall reaction rate constant in which OH radicals react with TCE molecules and consequently produce Cl radicals via reactions 17−20.

On the other hands, if chain termination exclusively occurred through reaction 26, the initial formation of DCAC and phosgene molecules can be described by the following equation.

$$\frac{\mathrm{d}}{\mathrm{d}t}([\mathrm{DCAC}] + [\mathrm{COCl_2}]) = \left(\frac{{k_{25}}^2 k_{28}}{2{k_{26}}^2}\right)^{1/3} (k_{\mathrm{OH}}[\mathrm{OH}][\mathrm{TCE}]_0[\mathrm{O_2}])^{2/3} \qquad \text{(E10)}$$

The initial oxidation (or decomposition) of TCE molecules has the same value as the initial formation of DCAC and phosgene molecules. Therefore, the G value of decomposition of TCE can be described as next equation so long as the energy (100 eV) is going into air and none is going into the TCE molecules.

If chain termination is exclusively reaction 27, eq E11 can be obtained.

$$G(-\mathrm{TCE}) \propto \frac{2k_{28}k_{\mathrm{OH}}[\mathrm{OH}]}{Ik_{27}}[\mathrm{TCE}]_0 \qquad \text{(E11)}$$

If chain termination is exclusively reaction 26, eq E12 can be obtained.

$$G(-\mathrm{TCE}) \propto \frac{\left(\frac{{k_{25}}^2 k_{28}}{2{k_{26}}^2}\right)^{1/3} (k_{\mathrm{OH}}[\mathrm{OH}][\mathrm{O_2}])^{2/3}}{I}{[\mathrm{TCE}]_0}^{2/3} \qquad \text{(E12)}$$

As shown in Figure 8, $G(-\mathrm{TCE})$ is proportional to the initial concentration of TCE. Therefore, reaction 27 seems to mainly occur as chain termination reaction in the decomposition mechanism of TCE.

The G value of formation for OH radicals should correspond to the intercept of eq E1. The intercept of eq E1 (=1.5 μmol J^{-1}) had a large value in comparison with $G(\mathrm{OH})$ (=0.44 μmol J^{-1}). The difference in two values suggests that decomposition of TCE molecules should be also caused by the activated species except for OH radicals, such as O radicals, ClO radicals given in reaction 31, and thermal electrons formed via reaction 10.

Comparison with $G(-\mathrm{PCE})$. As shown in Figure 8, the values of $G(-\mathrm{PCE})$ nonlinearly increase with initial concentration. At initial concentrations ranging from 150 to 700 ppmv, the values of $G(-\mathrm{PCE})$ have the same values of slope (=0.021 μmol J^{-1} ppmv^{-1}) and intercept (=1.5 μmol J^{-1}) as those of $G(-\mathrm{TCE})$. However, the values of $G(-\mathrm{PCE})$ at more than 700 ppmv deviated from those of $G(-\mathrm{TCE})$. The deviation can be explained by the difference in the kinds of chain termination. For gas-phase chlorine-photosensitized oxidation of PCE, Huybrechts et al.[23] also proposed the same Cl radical chain reaction as the oxidation of the gas-phase PCE and $\mathrm{Cl_2}$ mixture.

$$\mathrm{Cl^{\bullet} + C_2Cl_4 \rightarrow C_2Cl_5^{\bullet}} \qquad (23')$$

$$\mathrm{2C_2HCl_5^{\bullet} \rightarrow chain\ termination} \qquad (24')$$

$$\mathrm{C_2Cl_5^{\bullet} + O_2 \rightarrow C_2Cl_5OO^{\bullet}} \qquad (25')$$

$$\mathrm{C_2Cl_5OO^{\bullet} \rightarrow C_2Cl_5^{\bullet} + O_2} \qquad (-25')$$

$$C_2Cl_5OO^\bullet + C_2Cl_5{}^\bullet \rightarrow C_2Cl_5O_2C_2Cl_5 \qquad (26')$$

$$2C_2Cl_5OO^\bullet \rightarrow C_2Cl_5O_2C_2Cl_5 + O_2 \qquad (27')$$

$$2C_2Cl_5OO^\bullet \rightarrow 2(C_2Cl_5O^\bullet) + O_2 \qquad (28')$$

Application of the oxidation mechanism to EB irradiation of PCE can lead to the following equations.

If chain termination is exclusively reaction 27′, eq E13 can be obtained.

$$G(-\mathrm{PCE}) \propto \frac{k_{28}'k_{\mathrm{OH}}'[\mathrm{OH}]}{Ik_{27}'}[\mathrm{PCE}]_0 \qquad (\mathrm{E13})$$

If chain termination is exclusively reaction 26′, eq E14 can be obtained.

$$G(-\mathrm{PCE}) \propto \frac{\left(\frac{k_{25}'^2k_{28}'}{2k_{26}'^2}\right)^{1/3}(k_{\mathrm{OH}}'[\mathrm{OH}][\mathrm{O_2}])^{2/3}}{I}[\mathrm{PCE}]_0 \qquad (\mathrm{E14})$$

Accurate reaction rate constants indicated at the oxidation mechanism for TCE and PCE are not available. If the reaction rate constant for PCE molecules has the same value as those for TCE ones, the relation between the value of $G(-\mathrm{PCE})$ and initial concentrations ranging from 150 to 700 ppmv would correspond to eq E13. At these initial concentrations, reaction 27′ will exclusively occur as chain termination. If $k_{26}'[C_2Cl_5{}^\bullet]$ is slightly larger than $k_{27}'[C_2Cl_5OO^\bullet]$, not only reaction 27′ but also reaction 26′ can start to occur as chain termination for a long chain length (or large initial concentration) range. Two kinds of chain termination (reactions 26′ and 27′) would give different slopes of change of $G(-\mathrm{PCE})$.

Formation of Products. Previous workers[2,24] reported that dichloroacetyl chloride (DCAC) molecules, produced directly from TCE molecules, react with Cl radicals and consequently produce phosgene molecules. To clarify the mechanism of DCAC decomposition and phosgene formation, the following experiment was carried out. Air containing 50 ppmv TCE, 390 ppmv dichloroacetyl chloride (DCAC), and 200 ppmv Cl_2 were irradiated with EB to examine the formation mechanism of carbon monoxide (CO), carbon dioxide (CO_2), and phosgene ($COCl_2$). The components of the sample gas, except phosgene, are reproductions of those of the irradiated gas obtained at 2.2 kGy in EB irradiation of the 650 ppmv TCE−air mixture. The result is shown in Figure 9. The concentrations of CO and CO_2 increase with a decrease in concentration of DCAC. The decrease in DCAC concentration and the increase in CO and CO_2 were calculated as 5.2, 6.0, and 6.0 ppmv/kGy, which had the same values as those in the TCE−air mixture. These values suggest that DCAC molecules produced as primary products from TCE molecules should be decomposed to produce CO and CO_2 molecules with further oxidation.

$$CHCl_2COCl \xrightarrow{O_2} CO + CO_2 + HCl + Cl_2 \qquad (3)$$

Phosgene molecules are supposed to be directly produced from TCE molecules, because formation of phosgene was barely observed in the TCE−DCAC−Cl_2−air mixture. From these results, phosgene molecules seem to be directly produced from TCE molecules via reaction 30. The Cl radical initiated chain reaction of TCE has two main paths in the decomposition mechanism. The Cl radicals can react with TCE molecules to produce DCAC and phosgene molecules. The increases in concentrations of DCAC and phosgene at doses up to 2.2 kGy were calculated as 136.4 and 25.7 ppmv/kGy, respectively. It was elucidated that a branching ratio was estimated to be 5.3 in the Cl radical chain reaction for TCE (=reaction 29/reaction 30).

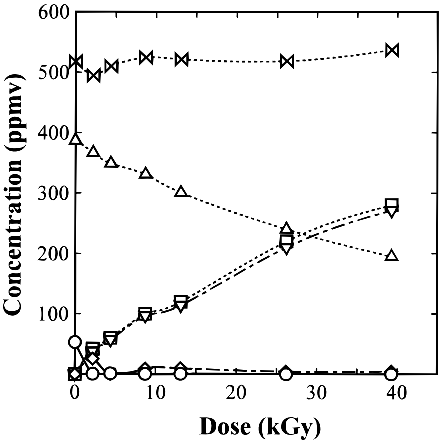

Figure 9. Concentrations of the products versus dose for 390 ppmv DCAC, 50 ppmv TCE, and 200 ppmv Cl_2 in EB irradiation: (○) TCE; (△) dichloroacetyl chloride (DCAC); (▽) CO; (□) CO_2; (◇) phosgene; (⋈) TC (total carbon concentration) × 1/2.

Conclusion

The main results of the present work can be summarized as follows:

(1) Dichloroacetyl chloride (DCAC), CO, CO_2, phosgene, and a small amount of chloroform were identified as products.

(2) With an alkaline solution (0.1 M NaOH), the products except for CO were completely removed from the gas phase. The largest removal efficiency was obtained at 4.4 kGy for EB irradiation of 650 ppmv TCE.

(3) The Cl radical chain reaction occurred as the main decomposition mechanism. Dichloroacetyl chloride, a primary product, was decomposed and converted into CO and CO_2 with further oxidation. Phosgene was also identified as a primary product. The branching ratio for formation of DCAC and phosgene was estimated as 5.3.

(4) Between G values of decomposition and initial concentrations for TCE, the following relationship was obtained: $G(-\mathrm{TCE})$ [μmol J^{-1}] = 1.5 [μmol J^{-1}] + 0.020 [μmol J^{-1} ppmv^{-1}] × conc [ppmv] for concentrations ranging from 50 to 1800 ppmv. The slope of the equation showed that concentrations of Cl radicals remained constant at 6.3×10^{-4} ppmv (at 298 K and 1 bar), independent of concentrations of TCE and products under a dose rate of 2.1 kGy/s.

(5) The values of $G(-\mathrm{TCE})$ linearly increased with initial concentrations up to 1800 ppmv. Those of $G(-\mathrm{PCE})$ linearly increased with the same slope of $G(-\mathrm{TCE})$ up to 700 ppmv. At more than 700 ppmv, the values deviated from those of $G(-\mathrm{TCE})$. The difference in a change of G values of decomposition for TCE and PCE can be contributed to the kind of chain termination.

(6) The decomposition efficiencies under 400 and 1000 ppmv H_2O have the same values as those in dry air. Under 25 000 ppmv H_2O, that value was slightly larger than that under dry air, because the products were adsorbed on the inner surface of the reactors and removed from the gas phase.

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