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Effect of Water and Oxygen Contents on the Decomposition of Gaseous Trichloroethylene in Air under Electron Beam Irradiation

Teruyuki Hakoda,* **Shoji Hashimoto, and Takuji Kojima**

Takasaki Radiation Chemistry Research Establishment, Japan Atomic Energy Research Institute,
1233 Watanuki, Takasaki, Gunma 370-1292

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An electron beam (EB) treatment of gaseous trichloroethylene (TCE) in air was studied as a purification method of off-gases containing gaseous chloroethylenes. The model air containing TCE at input concentrations of 5–75 ppmv, detected mostly in actual off-gases, was irradiated with 1-MeV EBs in a gas-flow vessel at 10 L/min under the conditions of atmospheric pressure, 298 K, and different H_2O contents. The decomposition of 75 ppmv TCE was also examined in humid air under different O_2 contents of 1×10^3–2.1×10^5 ppmv. In the existence of H_2O and O_2 contents with $\geq 3 \times 10^2$ ppmv and $\geq 5 \times 10^3$ ppmv, respectively, the decomposition ratios of TCE were enhanced and TCE was decomposed into $83.0 \pm 1.5\%$ of dichloroacetyl chloride (DCAC) and $17.5 \pm 0.6\%$ of carbonyl chloride ($COCl_2$) independently of the input TCE concentrations based on the carbon balance. Trichloroethylene of 5–75 ppmv was effectively decomposed by the OH radical through Cl-radical chain oxidation under the above-mentioned air conditions.

Volatile organic compounds (VOCs) have been widely used in various industrial fields, and consequently cause widespread environment contamination. Several kinds of VOCs are very harmful to human health because of their carcinogenicity and mutagenicity. Trichloroethylene (TCE), one of such VOCs, has been used as washing and de-oil solvents in various industrial fields, such as in the production of semiconductor and electronic devices. The VOCs including TCE have so far been treated with adsorption on activated carbon or combustion using a catalyst. These methods can effectively and economically remove several kinds of VOCs from contaminated gases or water when their concentrations are higher than a few thousands ppmv (parts per million by volume). The removal ratios, however, become lower at lower concentrations in the order of a few hundred ppmv. The VOCs adsorbed on activated carbon are not changed into nontoxic substances, and have the possibility of causing other pollution at different places from the original pollution sources.

An electron beam (EB) treatment has been proposed as a new technology for the decomposition of ppmv-order gaseous chloroethylenes in air.[1–4] The OH radical and the O radical are produced from humid air through the dissociation and/or excitation of N_2 and O_2 molecules by EB irradiation. Chloroethylene at their lower concentrations in humid air is probably completely oxidized into CO_2, Cl_2, and HCl by these free radicals in the gas phase through the oxidation of primary and intermediate irradiation products. In previous work, a termination reaction of the Cl-radical chain oxidation of TCE at input concentrations of 1.5×10^2–2.0×10^3 ppmv in humid air was exclusively studied using a batch-type irradiation glass vessel.[5] Gaseous H_2O molecules produce OH radicals, which can oxidize TCE, while they scavenge free radicals formed under EB irradiation. However, the effect of gaseous H_2O on the TCE decomposition could not be examined by the batch-type experiment because of contributions of small amounts of H_2O deposited on the inner wall of the irradiation vessel.

In the present work, TCE at lower input concentrations of 5–75 ppmv, detected mostly in actual contaminated air, was irradiated with EBs in a flow system to examine the effect of gaseous H_2O on TCE decomposition in air. The flow-type experiment enables one to minimize the contributions of TCE and H_2O deposited on the inner wall of the irradiation vessel to TCE decomposition in the gas phase, and to optimize the necessary conditions to balance the formation of OH radicals and the scavenging of free radicals. The decomposition ratio was examined under different H_2O contents to clarify the OH-radical contribution to the initiation reaction in Cl-radical chain oxidation. Oxygen radicals and secondary electrons would react with TCE and O_2 as a competitive reaction. The Cl-radical chain oxidation of TCE involves reactions of alkyl radicals and O_2. The effect of the O_2 contents was examined on the reaction of O radicals and the electrons with TCE as well as the Cl-radical chain oxidation.

Experimental

Gaseous samples of TCE and those of H_2O were prepared, respectively, from a liquid TCE (> 99.5% pure liquid TCE, Wako Pure Chemical Industries, Ltd.) and MILLIQ water (≥ 17 MΩ) by bubbling them with pure N_2 gas (> 99.999 %, Nippon Sanso Co. Ltd.). The mixture gases containing TCE of 5–75 ppmv, H_2O of 3×10^2–1×10^4 ppmv, and O_2 of 1×10^3–2.1×10^5 ppmv were prepared by mixing the above-mentioned TCE, H_2O, and N_2 gases and pure O_2 gas (> 99.99%, Nippon Sanso Co. Ltd.). The concentration of O_2 in the mixture gases was measured by a gas chromatograph (GC-8A, Shimadzu Seisakusho Co. Ltd.) equipped with a thermal-conductivity detector (TCD) and a packed column (molecular sieve 5A, 3 mm i.d. × 1.5 m, Shimadzu GLC, Inc.). The concentration of H_2O was measured by a moisture analyzer (Hygro-3M with D-2 detector, General Eastern Co. Ltd.) in terms of dew points of gases by 65 K lower than ambient temperature. The detector in a cold storage chamber (273 K) was used to measure dew points higher than 208 K, which corresponds to 10 ppmv H_2O under 1.013×10^5 Pa and 298 K. The concentration of H_2O in dry synthesis air was less than 10 ppmv. Trichloroethylene of 5–75 ppmv without H_2O content was prepared as dry air mixture samples to examine the effect of H_2O on the TCE decomposition.

The mixture gas was irradiated with 1 MeV horizontal EBs using a Cockcroft–Walton type electron accelerator (NISSIN-HIGH VOLTAGE Co. Ltd., Scan width: 60 cm) in a stainless-steal flow-type irradiation vessel.[6] The experimental set-up is shown in Fig. 1. The vessel (H50 × W177 × D100 mm) has two stainless-steel foil windows (thickness: 50 μm) along the beam pass to irradiate the mixture gas flow between them. Electron beams deposit a part of their energy to the mixture gas along the beam pass. The temperature of the mixture gas was kept constant at 298 K during irradiation by the circulation of cooling water outside of the vessel. The flow rate of the mixture gas was kept constant at 10 L/min and the resident time of the mixture gas in the vessel was 5.3 s.

The absorbed dose in the mixture gas was estimated using pure dinitrogen monoxide (N_2O) gas under the same irradiation conditions. The concentration of N_2 formed from the dissociation of N_2O was measured by the GC-TCD equipped with the packed column. The dose rate was calculated from the concentration of N_2 for different beam currents of 0.1 to 3.75 mA using the G values of N_2 generation, 1.0 [μmol J^{-1}][7]. Based on this dose estimation, the mixture gas was irradiated to doses in the range from 0.4 to 15 kGy.

The yield of free radicals to oxidize trace substances in gases significantly depends on the depth-dose distribution in the vessel. The dose rates before and after passing the mixture gas layer were estimated in terms of the energy deposition rate per 1 mA by a simulation code, EDMULT5.[8] Because the dose rates ranged from 3.002×10^3 to 3.056×10^3 J cm^2 g^{-1} s^{-1} along the incident beam direction, the dose-rate uniformity in the mixture gas was within ±1%.

The temperature of the plumbing between the outlet of the irradiation vessel and the gas-sampling ports was controlled at around 373 K so as to avoid irradiation product deposition on the inner walls of the plumbing. A part of the irradiated gas obtained from the gas-sampling ports was analyzed using the following analytical instruments. Organic gaseous products were analyzed by a gas chromatograph equipped with a flame ionizing detector (FID) and a packed column (BX − 20 100/120, 2 mm i.d. × 3 m, GL Science Inc.). The concentration of CO_2 was measured by a total organic carbon (TOC) analyzer (TOC-5000A, Shimadzu Seisakusho Co. Ltd.) customized for the gas-phase sample. Carbon monoxide was analyzed by a CO analyzer (TH-D4 detector with TA-470 Monitor, Komyo Co. Ltd.). Dichloroacetyl chloride, $COCl_2$, and Cl_2 were analyzed by a real-time gas mass filter system having a minimum detectable limit of 0.2 ppmv.[6] The mixture gases were immediately bubbled in $NaOH_{aq}$ (0.01 M) (1 M = 1 mol dm^{-3}) at the irradiation product sampler after passing the irradiation vessel. The concentration of total Cl^- in the solution was 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.).

Results

Decomposition Curves. The changes in the TCE concentrations for different input concentrations were studied as a function of dose under air containing 2.1×10^5 ppmv O_2 with different H_2O contents. The changes in the TCE concentrations as a function of the dose were also examined under different O_2 contents ranging over 1×10^3–2.1×10^5 ppmv in air

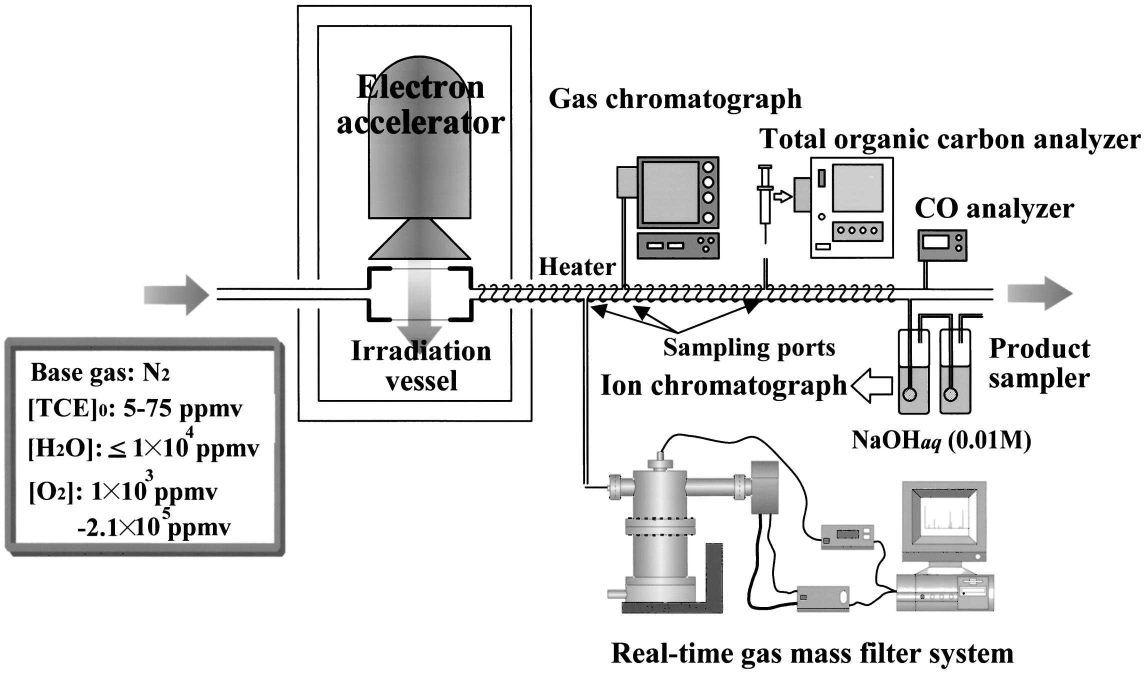

Fig. 1. Apparatus for electron beam irradiation of TCE/air mixture.

containing 75 ppmv TCE and 3×10^2 ppmv H_2O.

Under Different H_2O Contents. The changes in the TCE concentration for different input concentrations in humid air and dry air were studied as a function of the dose. The results for humid air containing 3×10^2 ppmv H_2O and dry air are shown in Fig. 2. The concentrations of TCE in humid air containing 1×10^3, 5×10^3, and 1×10^4 ppmv H_2O decrease with the dose on the same curves as those containing 3×10^2 ppmv H_2O for the corresponding input concentration. In the case of input TCE concentrations of 5 and 10 ppmv, the difference in the decrease of the TCE concentration with the dose is negligible between in humid air and dry air. The decrease of TCE at input concentrations of 30–75 ppmv in dry air is lower than that in humid air. The concentrations of TCE in humid air decrease with the dose exponentially, while those in dry air decrease linearly with the dose at input concentrations of 30–75 ppmv. About 95% of the input TCE in humid air is decomposed at 0.8 kGy independently of any input TCE concentrations. In dry air, the doses for 95% decomposition of the input TCE at concentrations of 30, 55, and 75 ppmv are 0.9, 1.2, and 1.6 kGy, respectively.

The decomposition ratios, relative concentration changes per 1 kGy, estimated from the decomposition curves in Fig. 2, generally depend on the concentrations of the irradiation products. For comparing the decomposition curves with and without the products, the decomposition curve for each input concentration was shifted to that of 75 ppmv so as to adjust the input concentration plots on the curves for 75 ppmv, as shown in Fig. 3 with the ordinate in logarithmic scale. Under both air conditions, the decomposition curve for each input concentration agrees with that for an input concentration of 75 ppmv. The decomposition ratios, therefore, depend only on the concentration of the residual TCE, and namely irradiation products do not influence the ratios. This result shows that most of TCE molecules are decomposed through different mechanisms from those of the primary products.

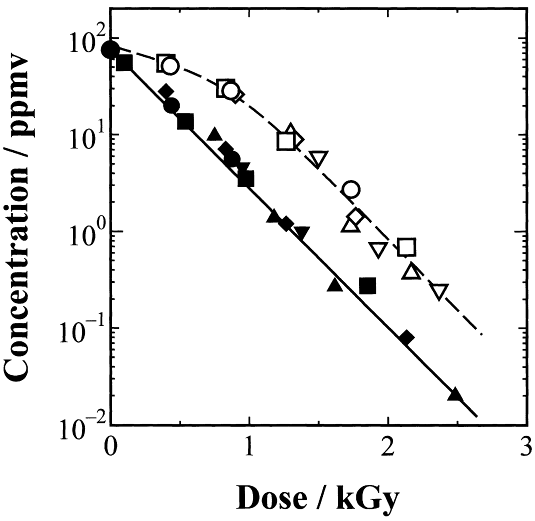

Fig. 3. The concentrations of TCE in humid and dry air as a function of dose in logarithmic expression. The decomposition curves for each input concentration shifted to that of 75 ppmv so as to adjust input concentration plots on the curves for 75 ppmv. TCE ▼: 5, ▲: 10, ◆: 30, ■: 50, ●: 75 ppmv in humid air. ▽: 5, △: 10, ◇: 30, □: 50, ○: 75 ppmv in dry air.

Under Different O_2 Contents. The changes in the TCE concentration for an input concentration of 75 ppmv in air containing 3×10^2 ppmv H_2O were studied as a function of the dose under different O_2 contents. The results for humid air containing 1×10^3, 3×10^3, and 5×10^3 ppmv O_2 are shown in Fig. 4. The concentrations of TCE in humid air containing O_2 contents higher than 5×10^3 ppmv decrease with the dose on the same curves as that containing 5×10^3 ppmv O_2. The higher is the O_2 contents in the mixture air, the larger is the decomposition ratios of TCE. For example, the decomposition

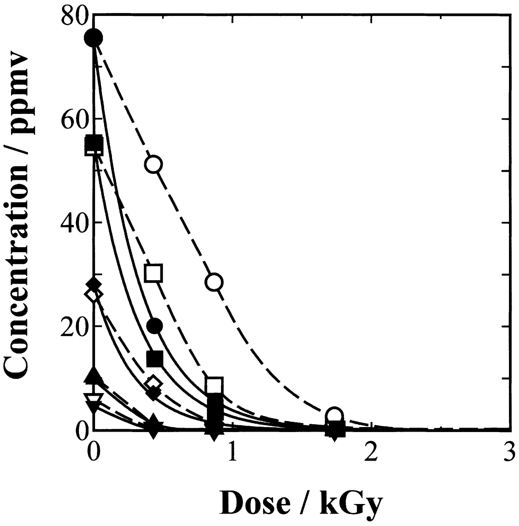

Fig. 2. The concentrations of TCE in humid and dry air as a function of dose. TCE ▼: 5, ▲: 10, ◆: 30, ■: 50, ●: 75 ppmv in humid air. ▽: 5, △: 10, ◇: 30, □: 50, ○: 75 ppmv in dry air.

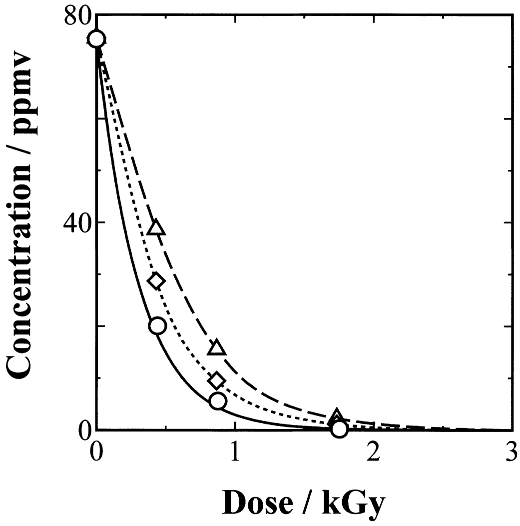

Fig. 4. The concentrations of TCE as a function of dose in N_2 containing 300 ppmv H_2O under O_2. Contents of 1×10^3, 3×10^3, and 5×10^3 ppmv or higher. ○: $\geq 5 \times 10^3$ ppmv, □: 3×10^3 ppmv, and △: 1×10^3 ppmv.

ratios at 0.8 kGy were obtained as 48.4, 61.7, and 73.3% for O_2 contents of 1×10^3, 3×10^3, and 5×10^3 ppmv or higher, respectively.

Irradiation Products. Under Different H_2O Contents. At input TCE concentrations of 5–30 ppmv, irradiation products in humid air and dry air were identified as dichloroacetyl chloride (DCAC), carbonyl chloride ($COCl_2$), CO_2, Cl_2, and HCl. Carbon monoxide was additionally identified as an irradiation product of 55 or 75 ppmv TCE in humid air and dry air. The products in humid air ($[H_2O] = 3 \times 10^2$–1×10^4 ppmv) and dry air have the same tendency of product concentration changes as a function of the dose at input TCE concentrations of 5–10 ppmv, while the changes in the product concentration as a function of the dose is different between humid air and dry air for each input TCE concentration of 30–75 ppmv. The product composition without and with CO is described in the following sections.

Without CO Production: The changes in the product concentrations were measured as a function of the dose to examine the formation mechanism of the products. The result for 5 ppmv TCE in humid air is shown in Fig. 5 as one of the results without CO production. The input TCE decreases completely at a dose of 1.6 kGy. The concentrations of DCAC and $COCl_2$ increased up to 0.8 kGy and, subsequently, decreased at higher doses. Trichloroethylene at input concentrations of 5–30 ppmv were decomposed into DCAC, $COCl_2$, and CO_2 as 83.3 ± 1.5, 18.1 ± 0.5, and 17.1 ± 1.0% of the decrease of the TCE concentration through Cl-radical chain oxidation based on the carbon balance, respectively.

Among these products, $COCl_2$ is more harmful than TCE, and has a lower decomposition rate than TCE or other primary products. The dissolution of $COCl_2$ in an alkaline solution is a common method of its natural hydrolysis into carbonate ions (CO_3^{2-}) and chloride ion (Cl^-) as nontoxic substances. The complete oxidation of TCE and the primary products were performed at lower doses by the combination of EB irradiation and hydrolysis. In the case of 5 and 10 ppmv TCE under both air conditions, the doses for the complete oxidation were lowered from 12 and 15 kGy to 5 and 7 kGy, respectively.

With CO production: Under humid air and dry air conditions, TCE at input concentrations of 50–75 ppmv were decomposed into 82.6 ± 0.3% of DCAC, 16.9 ± 0.2% of $COCl_2$, 3.2 ± 0.2% of CO_2, and 12.6 ± 0.1% of CO through the Cl-radical chain oxidation based on the carbon balance, respectively. Dichloroacetyl chloride and $COCl_2$ were decomposed into CO_2 and CO with increasing the dose.

Under different O_2 Contents. The same decomposition curves and product distributions as a function of the dose were obtained for the irradiation of TCE in humid air (3×10^2 ppmv H_2O/N_2 mixture gas) containing 5×10^3–2.1×10^5 ppmv O_2. Trichloromethane ($CHCl_3$) was observed as a product in mixture gases containing 1×10^3 and 3×10^3 ppmv O_2. The ratios of the $CHCl_3$ concentration to the decomposed TCE concentration were 5.8 and 2.2% under O_2 contents of 1×10^3 and 3×10^3 ppmv, respectively.

Discussion

The effect of the H_2O contents on the initiation reactions of the TCE decomposition and the effect of the O_2 contents on Cl-radical chain oxidation are discussed in the following section.

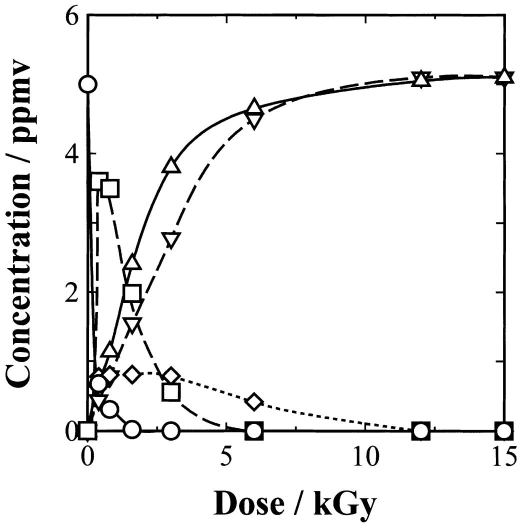

Fig. 5. The concentrations of the products in irradiated 5 ppmv TCE/humid air mixture. The concentration of CO_2, as shown in this figure, is a half of its actual concentration. ○: TCE, □: DCAC, ◇: $COCl_2$, △: CO_2, and ▽: Cl_2.

Study on Initiation Reactions. Oxidizing free radicals, O_3, ions, and secondary hot electrons are produced by EB irradiation through the dissociation and ionization of the air components. Hydroxyl radicals are formed from positive ions scavenged with H_2O molecules in humid air.[9] The *G* values of formation for N_2^+, O_2^+, and $O(^3P)$ radical are reported as 0.249, 0.068, and 0.128 µmol J^{-1} in normal air,[10] respectively. The yields of OH and $O(^3P)$ radicals per 1 kGy were, respectively, estimated to be 9.16 and 3.71 ppmv in humid air under 1.013×10^5 Pa and 298 K by considering the above G values. The secondary hot electrons are quickly changed into thermalized electrons with a reaction rate constant[9] of 1.0×10^9 cm^3 $molecule^{-1}$ s^{-1}. The yield of thermal electrons per 1 kGy was obtained as the same values of OH radicals. The reactions of these active species with TCE molecules were examined by comparing the concentrations of decomposed TCE per 1 kGy (ΔC_i) in humid air and dry air at the same input TCE concentration (*i* ppmv). The reaction of O_3 with TCE is regarded to be negligible in TCE decomposition because of a smaller reaction rate constant[11] of $\leq 3 \times 10^{-20}$ cm^3 $molecule^{-1}$ s^{-1}.

The values of ΔC_i were obtained as the differential of the decomposition curves, shown in Fig. 2, at zero dose. The concentrations of TCE in humid air as a function of the dose were well-fitted with an exponential function of $[TCE]_0 \cdot \exp(-k \cdot D)$; here $[TCE]_0$ is the input TCE concentration and *k* is a constant value for input TCE concentrations of 5–75 ppmv. At input TCE concentrations of 5 and 10 ppmv in dry air, the concentrations of TCE as a function of the dose were fitted with a similar exponential function for the humid-air condition. At an input TCE concentration of 30 ppmv, the concentration of TCE was fitted with a quadratic function. In the case of input concentrations of 50 and 75 ppmv, the concentrations were fitted with linear functions. In humid air and dry air, the decomposition ratios of TCE depend on the concentrations of residual TCE, as

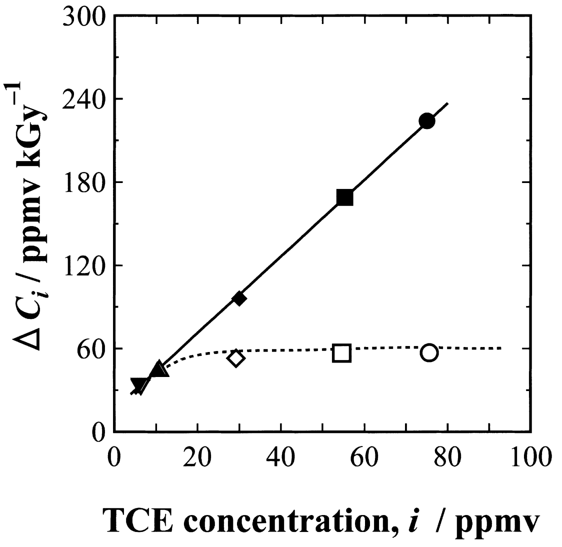

Fig. 6. Residual TCE concentrations and decrease in the concentration of TCE per 1 kGy in humid air and dry air. TCE ▼: 5, ▲: 10, ◆: 30, ■: 50, ●: 75 ppmv in humid air. ▽: 5, △: 10, ◇: 30, □: 50, ○: 75 ppmv in dry air.

shown in Fig. 3. The values of ΔC_i are used as the concentration of residual TCE per 1 kGy, even for the existence of irradiation products.

The relations between ΔC_i [ppmv kGy^{-1}] and the residual TCE concentration [ppmv] for both air conditions are shown in Fig. 6. The value of ΔC_i in humid air increases linearly with the residual TCE concentration, and reaches 224.0 ppmv kGy^{-1} at a residual concentration of 75 ppmv. The value of ΔC_i at 75 ppmv is ten-times as large as the summation of the yields of OH, O radicals and electrons per 1 kGy. In the case of residual concentrations of 5 and 10 ppmv, the values of ΔC_i in dry air are equal to those in humid air. The value of ΔC_i in dry air increases with residual TCE concentrations of lower than around 20 ppmv, and reaches a constant value at higher concentrations. The difference in ΔC_i under humid air and dry air clearly suggests a significant contribution of H_2O, namely OH radicals formed from H_2O by EB irradiation.

The formation of a Cl radical in a CH_3ON/NO/TCE/air mixture gas through the reaction of the OH radical with TCE was examined for UV irradiation by Kleindienst et al.[12] The mechanism of Cl-radical formation in the absence of gaseous H_2O was reported as follows:

$$\mathrm{OH\bullet + CHClCCl_2} \begin{array}{l} \nearrow \ \mathrm{CHCl(OH)CCl_2\bullet} \quad \text{(a)} \\ \searrow \ \mathrm{CCl_2(OH)CHCl\bullet} \quad \text{(b)} \end{array} \qquad (1)$$

$$\mathrm{CHCl(OH)CCl_2\bullet\ (or\ CCl_2(OH)CHCl\bullet) + O_2} \longrightarrow \mathrm{CHCl(OH)CCl_2O_2\bullet\ (or\ CCl_2(OH)CHClO_2\bullet)} \qquad (2)$$

$$\mathrm{CHCl(OH)CCl_2O_2\bullet\ (orCCl_2(OH)CHClO_2\bullet) + NO} \longrightarrow \mathrm{CHCl(OH)CCl_2O\bullet\ (or\ CCl_2(OH)CHClO\bullet) + NO_2} \qquad (3)$$

$$\mathrm{CHCl(OH)CCl_2O\bullet} \begin{array}{l} \nearrow \ \mathrm{CHCl(OH)COCl + Cl\bullet} \quad \text{(a)} \\ \searrow \ \mathrm{CHCl(OH)\bullet + COCl_2} \quad \text{(b)} \end{array} \qquad (4)$$

$$\mathrm{CCl_2(OH)CHClO\bullet} \begin{array}{l} \nearrow \ \mathrm{CCl_2(OH)COH + Cl\bullet} \quad \text{(a)} \\ \searrow \ \mathrm{CCl_2(OH)\bullet + HCOCl} \quad \text{(b)} \end{array} \qquad (5)$$

The yield of the Cl radical was 0.63 ± 0.34 in a reaction of OH radicals with TCE molecules. Nitrogen monoxide production from N_2 and O_2 is well-known under EB irradiation. In the present work, the Cl radical could be produced from the reaction of OH radicals and TCE molecules in the presence of sufficient O_2. The peroxy radicals, e.g., free radicals resulted in Eq. 2, are generally stable compared with other free radicals.[13] Alkoxy radicals, $\mathrm{CHCl(OH)CCl_2O^\bullet}$ or $\mathrm{CCl_2(OH)CHClO^\bullet}$, are expected to be produced from a bimolecular reaction of the corresponding peroxy radicals under OH radical formation by EB irradiation in high density. The OH radicals would also be diminished by OH–OH recombination, the OH–O_3 reaction and so on.[9] The probability of the reaction of OH radicals with TCE at higher TCE concentrations is higher than that at lower TCE concentrations, which resulted in a lower probability for the recombination of OH radicals.

The reactions of the $O(^3P)$ radical and the thermal electron with TCE and O_2 were examined as a competitive reaction as follows. Possible reactions of $O(^3P)$ radical with TCE are shown as follows:[14]

$$\mathrm{O(^3P)\bullet + CHClCCl_2} \longrightarrow \mathrm{HCOCl + CCl_2\bullet} \qquad (6)$$

$$\mathrm{CCl_2\bullet + O_2} \longrightarrow \mathrm{COCl\bullet + ClO\bullet} \qquad (7)$$

The $\mathrm{COCl\bullet}$ reacts further with an O_2 molecule as follows:[15]

$$\mathrm{COCl\bullet + O_2} \longrightarrow \mathrm{CO_2 + ClO\bullet} \qquad (8)$$

The resulting ClO radicals, formed through Eqs. 7 and 8, react with TCE molecules to produce Cl radicals via several reaction steps.[15] The decomposition ratios of TCE at a certain dose are independent of the O_2 contents, ranging over 5×10^3–2.1×10^5 ppmv, as shown in Fig. 4. This is probably due to scavenging of the $O(^3P)$ radical by O_2. The reaction rate constant of the $O(^3P)$ radical with the TCE molecule is reported[14] as 5.60×10^{-13} cm^3 molecule^{-1} s^{-1} at 298 K. On the other hand, $O(^3P)$ is scavenged with O_2 to produce O_3 with a reaction rate constant[9] of $\sim 6 \times 10^{-34}$ cm^6 molecule^{-2} s^{-1}. In the present work, the reaction rate of $O(^3P)$ radical with 75 ppmv TCE was estimated to be 9.912×10^2 [O] s^{-1} under 1.013×10^5 Pa at 298 K: here [O] is the concentration of the $O(^3P)$ radical. The reaction rates of the $O(^3P)$ radical with 5×10^3, 1×10^5, 1×10^5, and 2.1×10^5 ppmv O_2 were calculated to be 8.35[O], 3.34×10^1[O], 3.34×10^3[O], and 1.47×10^4[O] s^{-1}, respectively. For example, 30% of the $O(^3P)$ radicals react with TCE molecules in air containing 1×10^4 ppmv O_2. The $O(^3P)$ radicals probably react with TCE molecule to produce Cl radicals, which initiate Cl-radical chain oxidation. However, the decomposition of TCE is considered to be independent of the O_2 contents, ranging over 5×10^3–2.1×10^5 ppmv. As a result, the chain reaction is depressed by insufficient O_2, as mentioned in the section on Cl-radical chain oxidation.

The thermalized electron can also react with a TCE molecule and an O_2 molecule. The thermalized electrons are scavenged with O_2 molecules through the following reactions:

$$e^- + O_2 + M \longrightarrow O_2^- + M \quad (9)$$

The M is N_2, O_2, and H_2O as a third body. The reaction rate constants[16] for N_2, O_2, and H_2O are reported to be 1.6×10^{-31}, 2.5×10^{-30}, and 1.4×10^{-29} cm^6 $molecule^{-2}$ s^{-1}, respectively. For example, the reaction rates are estimated to be $1.02 \times 10^6[e^-]$, $7.72 \times 10^6[e^-]$, and $2.19 \times 10^7[e^-]$ s^{-1} in dry N_2 gas containing 1×10^4, 5×10^4, and 1×10^5 ppmv of O_2, respectively. The reaction rate with 75 ppmv TCE is estimated to be $3.54 \times 10^6[e^-]$ s^{-1} from a reaction rate constant[17] of 2.0×10^{-9} cm^3 $molecule^{-1}$ s^{-1}. The reaction between O_2^- and TCE molecules hardly occurs as an indirect reaction, because the electron affinity[18,19] of O_2 is slightly higher than that of TCE. The reaction of the thermalized electrons with TCE is negligible in air containing O_2 for values higher than 1×10^5 ppmv. In air with O_2 contents lower than 1×10^5 ppmv, the thermalized electron probably reacts with a TCE molecule to produce a Cl^- and corresponding radicals[20] analogously to the reaction in an aqueous solution containing TCE induced by ionizing radiation.[21]

$$e^- + CHClCCl_2 \longrightarrow \begin{cases} CHClCCl\bullet + Cl^- & \text{(a)} \\ CHCCl_2\bullet + Cl^- & \text{(b)} \end{cases} \quad (10)$$

The CHClCCl and $CHCCl_2$ radicals react with O_2 to produce the corresponding peroxy radicals. The following two processes are considered to be a possible degradation mechanism of the resulting peroxy radicals. The CHClCCl or $CHCCl_2$ radical would be degraded to HCOCl and $COCl^\bullet$ or $COCl_2$ and $HCO^\bullet$ via a C–C cleavage. As another one, Gehringer et al.[22] examined the decomposition of TCE in aqueous solution under γ-ray irradiation, and pointed out that a Cl radical should be formed from the above peroxy radicals based on the detection of glyoxylic acid as a product. The chain oxidation of TCE is probably initiated by such resulting Cl radicals. The decomposition ratios of TCE remained constant under humid air containing O_2 contents of 5×10^3–2.1×10^5 ppmv. The chain reaction is, therefore, probably depressed by insufficient O_2 contents, the same as the case for the $O(^3P)$ radical.

Even using high-purity dry air, a trace amount of H_2O-producing OH radicals would contaminate from the inner wall of the irradiation vessel and auxiliary plumbing. Such a trace amount of OH radical is consumed by TCE at residual concentrations of 55–75 ppmv without OH–OH recombination. A part of OH radicals is consumed by TCE at residual concentrations lower than 55 ppmv by competing with the recombination. The concentration of the contaminant OH radical is considered to be proportional to the dose. The concentration of TCE, therefore, decreases lineally with the dose for input TCE concentrations higher than 55 ppmv, and exponentially with the dose for input TCE concentrations lower than 30 ppmv, as shown in Figs. 2 and 3.

Cl-Radical Chain Oxidation of TCE. In the Cl-radical chain oxidation of TCE, the reactions of alkyl radicals with O_2 molecules are reported as follows:[5,23]

$$CHCl_2CCl_2\bullet + O_2 \longrightarrow CHCl_2CCl_2O_2\bullet \quad (11)$$

$$CHCl_2\bullet + O_2 \longrightarrow CHCl_2O_2\bullet \quad (12)$$

The peroxy radicals proceed the chain oxidation of TCE through their degradation. In air containing 1×10^3 and 3×10^3 ppmv O_2, the depression of the above reactions due to insufficient O_2 contents results in the formation of $CHCl_3$ as a product. These alkyl radicals react with other radicals, including a Cl radical as chain termination reactions under insufficient O_2. As a result, the decomposition ratios of TCE become lower in air under lower O_2 contents.

Formyl chloride (HCOCl) is produced at the same concentrations as $COCl_2$ through the Cl-radical chain oxidation initiated by OH radicals.[5] In the presence of Cl radicals, HCOCl is rapidly decomposed to CO and HCl.[24] Carbon monoxide is oxidized to CO_2 by an OH radical at a rate constant[9] of 2.4×10^{-13} cm^3 $molecule^{-1}$ s^{-1}. In air containing TCE at input concentrations lower than 30 ppmv, residual OH radicals after the reaction with TCE completely oxidize CO into CO_2. On the other hand, CO is not completely oxidized into CO_2 in air containing TCE at input concentrations higher than 55 ppmv.

Conclusions

Model gases containing TCE at input concentrations of 5-75 ppmv with different H_2O and O_2 contents were irradiated with 1 MeV EBs in a flow system at 10 L/min for developing a purification method of off-gases containing gaseous chloroethylenes. The decomposition of 75 ppmv TCE was also examined in humid air under different O_2 contents of 1×10^3–2.1×10^5 ppmv. For the existence of H_2O and O_2 contents with $\geq 3 \times 10^2$ ppmv and $\geq 5 \times 10^3$ ppmv, respectively, the decomposition ratios of TCE were enhanced and TCE was decomposed into $83.0 \pm 1.5\%$ of dichloroacetyl chloride (DCAC) and $17.5 \pm 0.6\%$ of carbonyl chloride ($COCl_2$) independently of the input TCE concentrations based on the carbon balance. Alky and peroxy radicals proceed Cl-radical chain oxidation without inactivation by H_2O, even in air containing a higher H_2O content. Trichloroethylene of 5–75 ppmv was effectively decomposed by the OH radical through Cl-radical chain oxidation under the above-mentioned air conditions. Among these products, $COCl_2$ is more harmful than TCE, and has a lower decomposition rate than TCE or other primary products. The complete oxidation of TCE and the primary products are performed at lower doses by the combination of EB irradiation and hydrolysis.

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