Decomposition Behavior of PCDD/F Isomers in Incinerator Gases under Electron-Beam Irradiation

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The decomposition behavior under electron-beam irradiation was examined for polychlorinated dibenzo-*p*-dioxin (PCDD, polychlorinated dibenzo[*b*,*e*][1,4]dioxin) and polychlorinated dibenzofuran (PCDF) isomers in incinerator gases at a temperature of 473 K. Significant decomposition was obtained for all PCDD isomers over the investigated absorbed doses, which resulted from oxidation reactions with OH radicals yielded by electron-beam irradiation. In the case of PCDFs, specific isomers having symmetrical structures, such as 1,2,8,9-, 2,3,7,8-, and 3,4,6,7-TeCDFs, were yielded through the dechlorination of PeCDF isomers. Thermal electrons probably played a role in the dechlorination of PeCDF isomers. Simultaneous formation and subsequent destruction were observed in the electron-beam treatment of TeCDFs in incinerator gases.

Approximately 80% of all solid wastes have been incinerated in Japan because of the small amount of available landfill space, which has caused significant amounts of inorganic and organic pollutants. The emission of inorganic pollutants, such as NO_x, SO_2, and HCl, has been remarkably reduced by state-of-the-art technologies during the past 50 years. However, the deterioration of the environment with organic pollutants, such as dioxins and endocrine disruptors, was not taken very seriously because it was believed that trace amounts of the organic pollutants have no chemical or biological effects on the human body. Municipal solid waste incinerators (MSWI) are the largest emission source of dioxins in Japan. Treating dioxin emissions from MSWIs is the most effective way to reduce their total amounts emitted to the environment. Many efforts have been made to meet a new law on the emission of polychlorinated dibenzo-*p*-dioxin (PCDD, polychlorinated dibenzo[*b*,*e*][1,4]dioxin) and polychlorinated dibenzofuran (PCDF) established in 1999 by the Government of Japan.[1] A successful reduction from approximately 2040 g-TEQ/m^3_N in 1999 to 145 g-TEQ/m^3_N in 2003 was achieved by improving the incineration conditions, such as turbulence, temperature, and time.[2] The replacement of electric precipitators by bag filters also contributed to reduce PCDD/F emissions. Activated carbons are added prior to a bag house to adsorb PCDD/Fs in incinerator gases, after which the adsorbents are trapped by filters at 443–453 K. A bag-filter system for trapping PCDD/F in incinerator gases requires a secondary treatment for destroying PCDD/Fs.

Electron-beam technology for destroying air pollutants has been studied to treat NO_x, SO_2, HCl, and volatile organic compounds (VOCs).[3–7] Some electron-beam facilities at both the industrial and pilot scales have been successfully operating in China (300000 m^3_N/h), Poland (270000), and Bulgaria (100000) under collaboration of the Japan Atomic Energy Research Institute (JAERI), the International Atomic Energy Agency (IAEA), the Institute of Nuclear Chemistry and Technology (INCT) in Poland, and Ebara Co.[8] Electron-beam technology has a strong advantage when treating low concentrations of air pollutants, based on reactions with radicals yielded by the irradiation of wet air. When air containing hazardous substances is irradiated with electron beams, almost all electrons provide their energies to the basic components of air, such as nitrogen, oxygen, and H_2O. This process yields primary products, such as N_2^+, O_2^+, N, and O, by excitation and ionization. These primary products consequently cause ion–molecule, charge-transfer, and neutralization reactions with the basic components of air and yield secondary products, such as OH, O_3, and thermal electrons.[9] Target substances that should be treated are oxidized through reactions with the secondary products.

Experiments on PCDD/F treatment at a pilot-scale facility demonstrated that irradiation with electron beams to incinerator gases resulted in a significant reduction of PCDD/Fs in units of ng-TEQ/m^3_N, where 90% decomposition efficiencies were achieved at absorbed doses beyond 12 kGy for PCDD and 16 kGy for PCDF.[10] Polychlorinated dibenzofuran required a higher energy than that for PCDD over the investigated doses. In the treatment of PCDD, higher decomposition efficiencies were obtained from the irradiation of lower chlorinated homologues, such as Te- and Pe-CDDs. This decomposition behavior indicates that PCDD homologues were oxidized through reactions, mainly with OH radicals yielded as the second products, because lower chlorinated PCDD/F homologues have higher OH rate constants.[11,12] The decomposition efficiencies for PCDD homologues were found to be proportional to the corresponding OH rate constants. In contrast, the decomposition behavior of PCDF homologues did not show any relations to the OH rate constants. The amounts of OH radicals yielded by electron-beam irradiation at a rate of approximately 10 ppm/kGy[13] were sufficient to oxidize all

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PCDD/F molecules on the order of parts per trillion, even though a number of competitors (namely, other organic substances) in the incinerator gases consumed the OH radicals. Thus, the higher energy requirement for the PCDF decomposition suggests a discrepancy of the decomposition behavior between PCDD and PCDF molecules. As in our previous study, a few TeCDF isomers were yielded after irradiation.[10] The formation of isomers suggested that the dechlorination process took place during irradiation. However, a detailed study on the decomposition behavior of PCDD/F isomers was not carried out in the previous work.

The present work focuses on the decomposition behavior of PCDD/F isomers in incinerator gases under electron-beam irradiation.

Experimental

The test facility for the electron-beam treatment of PCDD/Fs in incinerator gases was constructed at the Takahama Clean Center, treating 450 t/day solid wastes using 3 furnaces. Each furnace generated a 40000 $\mathrm{m^3{}_N}$/h incinerator gas when incinerating a waste solid of 150 t/day. An incinerator gas of 1000 $\mathrm{m^3{}_N}$/h was diverted downstream of a dry electric precipitator, and was irradiated with electron beams using an electron accelerator (Iwasaki Electric Co., EC300/45/40) that supplied 300 kV with a maximum energy of 12 kW. The facility had an irradiation reactor (120 (length) × 45 (width) × 30 (height) $\mathrm{cm^3}$), PCDD/F sampling system, and monitors for NO_x, $\mathrm{SO_2}$, CO, and $\mathrm{O_2}$. The cooler and heater were equipped to keep the temperature of the incinerator gases constant. A computer system communicating with these devices was also installed to control the electron-beam energy and the flow rate and temperature of the incinerator gases diverted, and to save data from the monitors. The incinerator gases were directly irradiated with electron beams at 473 K through a thickness of 13 µm Ti foil attached to the window of the reactor. The accelerator, reactor, and tubes were covered with lead, namely a self-shielded accelerator unit, so that no additional shielding for any ionization radiation was required during irradiation.

The irradiation with electron beams started at least 30 min before sampling of the incinerator gases to obtain the steady state of PCDD/F concentrations during irradiation. Sampling at a flow rate of 1 $\mathrm{m^3{}_N}$/h was simultaneously and isokinetically carried out upstream and downstream of the reactor, which was continued for 4 h to trap significant amounts of PCDD/Fs into a filter for their quantitative analysis. The concentrations of PCDD/Fs in the incinerator gases which depended on the incineration condition and the content of garbage, ranged from 0.5 to 2.3 ng-TEQ/$\mathrm{m^3{}_N}$. The filter trapping PCDD/Fs was pre-treated after sampling to eliminate many organic substances disturbing the PCDD/F analysis. A quantitative analysis was conducted with HRGC/HRMS using splitless injection at 523 K, equipped with a 60 m × 0.25 mm i.d. × 0.1 µm column (Chrompack, CP-SIL88) for Te-, Pe-, and He-CDD/F isomers or with a 30 m × 0.25 mm i.d. × 0.25 µm column (Agilent, HP-50+) for Hp- and O-CDD/F isomers. The temperatures of the GC were programmed on 373 K (1 min), 20 K/min, 473 K, 2 K/min, and 573 K (10 min) for the lower chlorinated PCDD/Fs, and on 393 K (1 min), 20 K/min, and 543 K (26.5 min) for the higher chlorinated ones. Detailed information on the sampling devices, the procedure for pre-treatmenting HRGC/HRMS analysis, and the interpretation of HRGC/HRMS is available elsewhere.[10] The decomposition behavior of PCDF isomers is first discussed just for a simple explanation and understanding of the PCDD/F treatment under electron-beam irradiation.

Results and Discussion

Decomposition Behavior of PCDF Isomers. The decomposition pattern of PCDF homologues demonstrated that TeCDF decomposition required a higher energy input. Figure 1 shows the ratios of the concentrations (ng-TEQ/$\mathrm{m^3{}_N}$) after and before irradiation for PCDF homologues at five doses, ranging from 1.8 to 14.0 kGys. A ratio less than 1.0 indicates that target substances were decomposed with electron beams. Although the ratio for PeCDFs slightly increased from 0.63 to 0.71 at lower doses, Pe-, Hx-, Hp-, and OCDF homologues were decomposed with increasing doses. The ratio for TeCDFs was 1.30 at a dose of 3.5 kGy, indicating that 2,3,7,8-TeCDF was yielded after irradiation. This was not the trend only for 2,3,7,8-TeCDF, but for other TeCDF isomers. Figure 2 shows the ratios of the concentrations (ng/$\mathrm{m^3{}_N}$) after and before irradiation for all TeCDF isomers at three doses of 1.8, 3.5, and 7.0 kGys. Interestingly, the positions of the substituent chlorines on the aromatic rings affected the decomposition of TeCDF isomers. Ratios of more than 1.0, (i.e., the formation of isomers) were obviously obtained at 3.5 kGy for 2,3,7,8-, 3,4,6,7-, and 1,2,8,9-TeCDFs having symmetrical structures with two substituent chlorines next to each other. A symmetrical isomer of 2,4,6,8-TeCDF whose substitutions were not positioned next to each other had a ratio of 1.20 at 1.8 kGy. In the case of other symmetrical isomers,

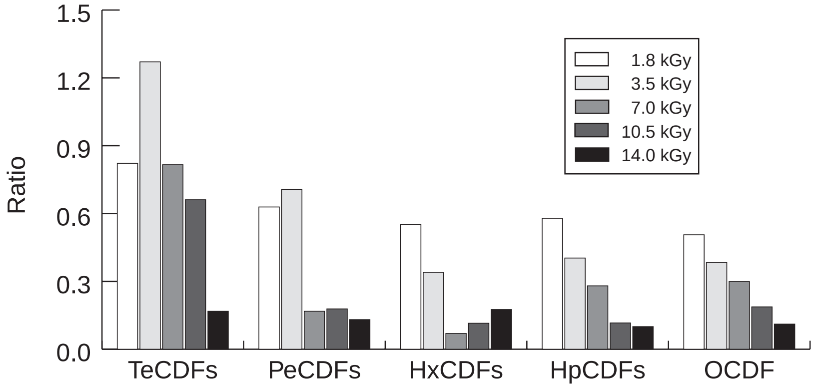

Fig. 1. Ratios of concentrations after and before irradiation for Te-, Pe-, Hx-, Hp-, and OCDF homologues.

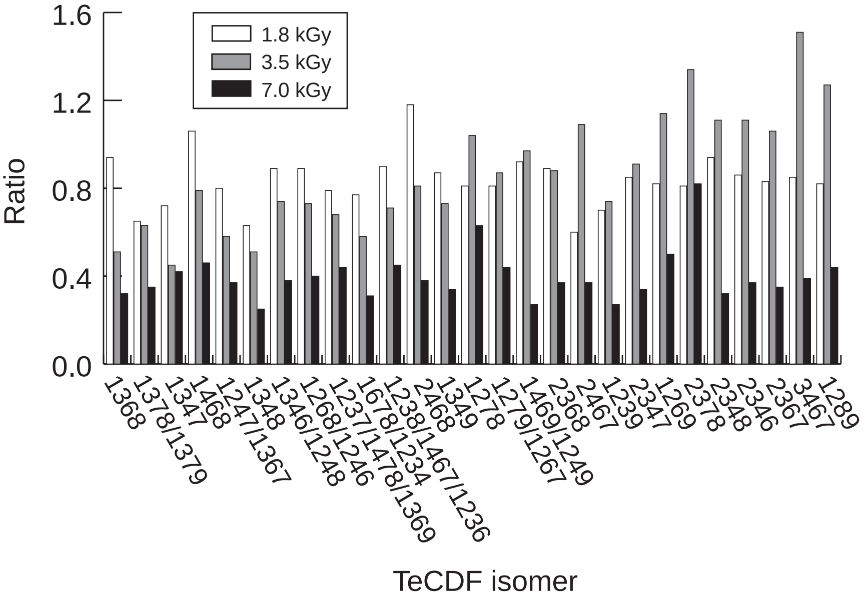

Fig. 2. Ratios of concentrations after and before irradiation for all TeCDF isomers.

Table 1. Ratios of Concentrations after and before Irradiation at a Dose of 3.5 kGy for TeCDF Isomers with Two Substituent Chlorines Next to Each Other

Isomer	Ratio
1367[a)]	<0.60
1378[a)], 1478[a)]	<0.70
1268[a)], 1467[a)]	<0.80
1267[a)], 1279[a)], 2368	<0.90
1278, 2367, 2467	>1.00
1269	>1.10
1289[b)]	>1.20
2378[b)]	>1.30
3467[b)]	>1.50

a) Not separated from other TeCDF isomers. b) Having symmetrical structures.

1,3,7,9- and 1,4,6,9-TeCDFs, their decomposition pattern could not be seen because no separation from other isomers was obtained by the temperature-programmed GC equipped with the special column for PCDD/F analysis. *Tetra*-chlorinated dibenzofuran isomers having symmetrical structures were yielded under electron-beam irradiation, of which the isomers with two substituent chlorines next to each other quantitatively increased by more than 1.2 times.

Asymmetrical TeCDF isomers with two substituent chlorines next to each other were also yielded with electron beams. Table 1 lists a summary of the ratios at 3.5 kGy for TeCDF isomers with two substituent chlorines next to each other, except for those with three or four substitutions on the aromatic ring. Although the separation of some isomers could not be obtained on HRGC/HRMS spectra, almost all separated isomers, such as 1,2,6,9-, 2,3,7,8-, and 2,4,6,7-TeCDFs, had ratios of more than 1.0, indicating that TeCDF isomers with two substituent chlorines next to each other were probably yielded after irradiation. The concentrations of isomers with the substitutions at 2, 3, and 4 positions such as 2,3,4,6- and 2,3,4,8-TeCDFs also increased after irradiation, as shown in Fig. 2. However, 2,3,4,7-TeCDF had a ratio less than 1.0, and 1,6,7,8-TeCDF could not be separated. The data are not sufficient to conceive that TeCDF isomers with substituent chlorines at the 2, 3, and 4 positions had chemical structural effects on their decomposition behavior.

Reactions of PCDF Isomers with Active Species. A few points have to be noted for specific isomers having ratios of more than 1.0, such as 1,2,6,9-, 2,3,7,8-, and 3,4,6,7-TeCDFs. In an electron process, hydrocarbons are oxidized by active species, such as OH, O_3, and thermal electrons. The oxidation process substantially occurred for the treatment of PCDD/Fs in incinerator gases, where the specific isomers were oxidized by the active species. Thus, the simultaneous formation and subsequent destruction of the specific TeCDF isomers occurred during irradiation. The destruction of the isomers by electron-beam irradiation can be estimated from oxidation by the OH radicals similarly to reactions observed in the atmosphere. Some data are available concerning the OH rate constants, in which Atkinson reported the rate constants for reactions with 2,4,6,8-TeCDF (1.4×10^{-12} cm^3 molecule^{-1} s^{-1}), 1,2,3,4-, 1,2,3,7-, 1,2,3,9-, 1,2,4,7-, 1,2,4,9-, 1,2,7,9-, 1,3,4,7-, 1,3,4,9-, 1,3,6,7-, 1,3,6,8-, 1,3,6,9-, 1,3,7,8-, 1,6,7,8-, and 2,3,4,7-TeCDF (4.9–6.0×10^{-12}), 1,3,7,9-TeCDF (8.3×10^{-12}), and remaining isomers (2.4–3.5×10^{-12}).[14] Less oxidation of specific isomers with the lower OH rate constants more or less contributed to their ratios of more than 1.0.

The specific TeCDF isomers could not be synthesized in an atmosphere of oxidation by the active species during irradiation, as described in our previous paper.[10] Polychlorinated dibenzofurans were dechlorinated to yield the lower chlorinated isomers. In general, chlorinated hydrocarbons are readily dechlorinated under electron-beam irradiation through reactions with thermal electrons to yield chloride ions.[15,16] The degree of the reactions, dissociative electron attachment, depends on the electron energy, the structures of the target substances, and their electron affinities, where the rate constants for the attachment increases with the number of substitutent chlorines.[17–20] There is no evidence that thermal electrons play a role in the dechlorination of PCDF isomers in incinerator gases during irradiation. However, thermal electrons with a high cross-section for dechlorination reactions with PCDF isomers are really yielded in the process of the interactions of higher energy electrons (namely, electron beams) with the basic components of air. It is conceivable that dissociative electron attachment to PCDF isomers occur during irradiation.

The incinerator gases at the facility contained many halogenated hydrocarbons, such as chlorophenol, chlorobenzene, and bromobenzene, on the order of parts per million, whose concentrations were quite higher than those of PCDF. Although a kinetic approach on dissociative electron attachment is difficult due to a lack of the rate constants for the reactions of thermal electrons with the halogenated hydrocarbons and PCDF isomers, significant amounts of thermal electrons yielded at a rate of approximately 10 ppm/kGy[9] allowed dissociative electron attachment to PCDF molecules. The attachment consequently induced the dissociation of C–Cl bonds of the molecules and yielded lower chlorinated PCDF. The specific TeCDF isomers having symmetrical structures, such as 1,2,8,9-, 2,3,7,8-, and 3,4,6,7-TeCDFs, were probably yielded by the dechlorination of PeCDF isomers after the attachment. The concentrations of the TeCDF increased after irradiation because higher chlorinated PCDF isomers had higher rate constants for reactions with the thermal electrons, as previously described.

There are two concerns about the formation of the specific TeCDF isomers during irradiation, recombination, and isomerization. If a specific isomer had been yielded in favor of the recombination of C–Cl bonds and/or the isomerization of other TeCDF isomers with an excess energy, their concentration would increase after irradiation. The recombination of C–Cl bonds was observed at a laboratory-scale study when crystal 1,2,7,8-TeCDF was evaporated and irradiated with electron beams. Approximately 60% decomposition obtained at a dose of 10 kGy was quite lower than that obtained at the Takahama Clean Center. The dissociated chloride ions were readily neutralized with positive ions of TrCDF back to 1,2,7,8-TeCDF, which lowered the dechlorination (i.e. decomposition) of 1,2,7,8-TeCDF. This is not the case in the incinerator gases. A dissociated chloride ion had a high possibility to react with many other positive ions of organic pollutants contained in the incinerator gases during irradiation. The depression of the recombination in the incinerator gases resulted in the higher decomposition efficiencies. The other possibility concerning the formation of specific isomers, isomerization, is also negligible because no other TeCDF isomers were yielded after irradiation of the gaseous 1,2,7,8-TeCDF.

Hydroxyl radicals yielded by electron-beam irradiation did not play an important role in the formation of the specific TeCDF isomers through dechlorination because the OH rate constants for reactions with TeCDF isomers were higher than those for PeCDF isomers.[12] The concentrations of the specific isomers would be increased only when the dechlorination of some PeCDF isomers through reactions with the OH radicals yielded one of the specific TeCDF isomers. Table 2 lists possible parent PeCDF isomers for the TeCDF isomers having a ratio of more than 1.0. Each of 1,2,8,9-, 2,3,7,8-, and 3,4,6,7-TeCDFs that ranked as the 3 highest ratios has two parent PeCDF isomers. These PeCDF isomers don't have higher OH rate constants than those for other PeCDF isomers.[14] Thus, the reactions of these PeCDF isomers with the OH radicals did not dominantly occur to yield the three isomers. The possibility for an increase in the concentrations of the three TeCDF isomers might be lower than those of other isomers, such as 1,2,7,8-, 2,3,4,6-, and 2,4,6,7-TeCDFs, having many parent PeCDF isomers because the dechlorination process of PeCDF isomers yielded a variety of different TeCDF isomers in different proportions. In addition, some of the parent isomers listed in Table 2 were also parents for other TeCDF isomers. For instance, 2,3,4,6,7-PeCDF is a parent isomer for 2,3,4,6-, 2,3,6,7-, 2,4,6,7-, and 3,4,6,7-TeCDFs. There are four pathways to yield the four different TeCDF isomers from the dechlorination of 2,3,4,6,7-PeCDF. The possibility for the formation of the TeCDF isomer with a ratio of more than 1.0 decreases as the number of dechlorination pathways increases. The dechlorination of PeCDF isomers through reactions with the OH radicals did not enhance the formation of specific TeCDF isomers.

Table 2. Possible Parent PeCDF Isomers that can be Dechlorinated to Yield TeCDF Isomers with Ratios of Concentrations after and before Irradiation More Than 1.0 at Doses of 1.8 and 3.5 kGys

TeCDFs	Ratio	Parent PeCDFs
1269	1.14	12369, 12469, 12489, 12679
1278	1.04	12378, 12389, 12478, 12678
1289	1.27	12389, 12489
1468	1.06	12468, 12469, 13468, 14678
2346	1.11	12346, 14678, 23467, 23468
2348	1.11	12348, 12678, 23468, 23478
2367	1.06	12367, 13478, 23467, 23478
2378	1.34	12378, 23478
2467	1.09	12467, 13468, 23467, 23468
2468	1.18	12468, 23468
3467	1.51	13467, 23467

Decomposition Behavior of PCDD Isomers. The ratios of the concentrations (ng/m$^3{}_N$) after and before irradiation for all PCDD isomers were less than 1.0 over the investigated doses. Oxidation dominantly proceeded for the electron-beam treatment of PCDD isomers. There was not significant difference in the ratios among the isomers at higher doses. To compare with the results for PCDF isomers, as shown in Fig. 2, the decomposition pattern was examined for TeCDD isomers. Figure 3 shows the ratios of the concentrations after and before irradiation for all TeCDD isomers at three doses of 1.8, 3.5, and 7.0 kGys. Although all isomers were decomposed with electron beams, the ratios increased for 1,2,6,7-, 1,2,6,9-, 1,2,7,8-, 1,2,8,9-, 1,4,6,9-, and 1,4,7,8-TeCDDs at 3.5 kGy. Isomers having symmetrical structures are 1,2,8,9-, 1,3,7,9-, 1,4,6,9-, and 2,3,7,8-TeCDDs, of which 1,2,8,9- and 1,4,6,9-TeCDDs had the increasing ratios at 3.5 kGy. In contrast to the decomposition TeCDFs, there was no relation between the chemical structures of TeCDD isomers and their decomposition behavior.

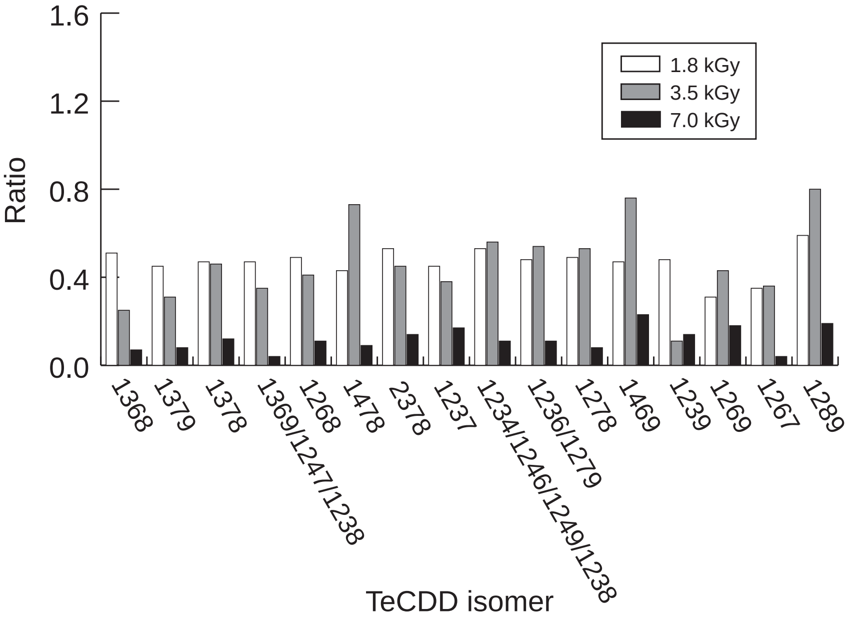

Fig. 3. Ratios of concentrations after and before irradiation for all TeCDD isomers.

Table 3. Possible Parent PeCDD Isomers that can be Dechlorinated to Yield TeCDD Isomers Having Ratios of Concentrations after and before Irradiation Increased with a Dose from 1.8 to 3.5 kGy

TeCDDs	Parent PeCDDs
1267	12367, 12467
1269	12369, 12469, 12467, 12489
1278	12367, 12378, 12389, 12467
1289	12389, 12489
1469	12469
1478	12369, 12478

Reactions of PCDD Isomers with Active Species. Polychlorinated dibenzo-*p*-dioxin was decomposed by reactions with OH radicals yielded by the irradiation of wet air, as previously described. *Tetra*-chlorinated dibenzo-*p*-dioxin isomers having the lowest OH rate constants (7.6×10^{-12} cm^3 $molecule^{-1}$ s^{-1}) were 1,2,6,7-, 1,2,6,9-, 1,2,7,8-, 1,2,8,9-, 1,4,6,9-, 1,4,7,8-, and 2,3,7,8-TeCDD.[14] All TeCDD isomers having increasing ratios have the lowest OH rate constants, so that the increment of the ratios at 3.5 kGy for the isomers was probably caused by less oxidation of the isomers during irradiation. Another possibility concerning the increment of the ratio is expected to the dechlorination of PeCDD isomers. Table 3 lists possible parent PeCDD isomers for TeCDD isomers having increasing ratios. All parent isomers had lower OH rate constants than other PeCDD isomers.[14] Although dechlorination through the OH radicals and/or thermal electrons was one of the possible processes for the electron-beam treatment of PCDD in the incinerator gases, the fate of PCDD isomers was determined by their oxidation through reactions with the OH radicals.

Electron-Beam Treatment of PCDD/Fs in Incinerator Gases. The dechlorination of PCDF isomers by dissociative electron attachment increases the dioxin toxicity when the dechlorination products are PCDF isomers with substituent chlorines at the 2, 3, 7, and 8 positions. The formation of lower chlorinated isomers having a toxic equivalency factor (TEQ) was observed at lower doses, as previously described. However, the total toxicity in the incinerator gases decreases at higher doses, where more than 90% decomposition is obtained. The dechlorination process of PCDF increases the operation cost of the accelerator because PCDF requires higher energy than PCDD to obtain 90% decomposition. Using an electron beam is a promising method for destroying PCDD/Fs in incinerator gases.

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