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Radiolytic degradation of octachlorodibenzo-*p*-dioxin and octachlorodibenzofuran in organic solvents and treatment of dioxin-containing liquid wastes

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Abstract

Degradations of octachlorodibenzo-*p*-dioxin (OCDD) and octachlorodibenzofuran (OCDF) were studied by ^{60}Co γ-ray in organic solvents: ethanol, *n*-nonane, and toluene. Both OCDD and OCDF were degraded more efficiently in ethanol than in *n*-nonane or toluene. The degradation is mainly attributed to electrons and in part to solvent radicals. The addition of ethanol to dioxin-containing liquid wastes enhanced effectively the degradation of dioxins; the liquid wastes did not exhibit the dioxin toxicity at a dose of 100 kGy.

Keywords: Dioxin; Octachlorodibenzo-*p*-dioxin; Octachlorodibenzofuran; γ-ray irradiation; Organic solvent; Dioxin-containing waste

1. Introduction

Polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs), namely dioxins as shown in Scheme 1, are some of the most toxic persistent organic pollutants (Ballschmiter and Bacher 1996). Among the 75 PCDDs and 135 PCDFs, all toxic congeners are relative to 2,3,7,8-position substituted PCDDs and PCDFs. These chemicals have widely contaminated the air, water, and soil. Because of their chemical stabilities and resistances to degradation under the natural conditions, they would bioaccumulate in the living body through the food chains, leading to a serious public health hazard.

Dioxin-containing liquid wastes are commonly generated in *n*-nonane or toluene in the dioxin laboratories. They have to be stored in laboratories due to lack of suitable methods for their disposal. So far practical methods such as incineration, UV-Vis photolysis and radiolysis have been investigated to degrade dioxins in organic solution. Incineration is the most common and effective method for degradation of dioxins in liquid wastes. Dioxins would, however, be re-generated in exhaust gas, and this limits to obtain fully public approval. UV-Vis photolyses have been widely studied for dioxins in organic solvents (Dung and O'Keefe, 1994; Isosaari et al., 2001; Kim and O'Keefe, 2000; Konstantinov et al., 2000; Rayne et al., 2002; Wagenaar et al., 1995), but its practical application is limited due to low penetration of light. While ionizing radiations, especially commercially available ^{60}Co γ-rays have high penetration and their radiolysis is a promising technique

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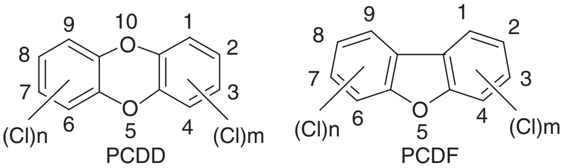

Scheme 1. The structure of PCDD and PCDF.

for the waste treatment (Getoff, 1999; Solpan et al., 2003; Hirota and Kojima, 2005). Moreover, γ-ray irradiation demonstrates effectiveness to the degradation of dioxin-like compounds, polychlorinated biphenyls (PCB) in organic solvents (Curry and Mincher, 1999).

There have been a few γ-ray radiolytic studies on the degradation of dioxins in organic solvents (Fanelli et al., 1978; Buser, 1976), except for on soil (Gray and Hilarides, 1995; Hilarides et al., 1994, 1996). After γ-ray irradiation of octachlorodibenzo-*p*-dioxin (OCDD) and octachlorodibenzo furan (OCDF) in hexane, *penta*-, *hexa*-, and *hepta*-chlorinated dioxins were qualitatively observed as irradiation products (Buser, 1976). Fanelli et al. (1978) have studied the radiolysis of 2,3,7,8-*tetra*-chlorodibenzo-*p*-dioxin (2,3,7,8-*tetra*-CDD) in dioxane, acetone or ethanol, and reported that the type of solvents is important for the degradation efficiency. However, the degradation products and the reaction mechanism have not been mentioned in the literature.

In the present paper, radiolytic degradations of OCDD and OCDF in ethanol, *n*-nonane or toluene were studied with the aim of identification of degradation products and clarification of the degradation mechanism. Both OCDD and OCDF were chosen to understand the degradation pathway of dioxins and analyze quantitatively low chlorinated dioxins through mass balance. The practical radiolytic method for treatment of dioxin-containing liquid wastes was developed based on the results of radiolyses of OCDD and OCDF in organic solvents.

2. Experimental

2.1. Reagents and sample preparation

OCDD and OCDF were supplied from Cambridge Isotope Laboratories, Inc. (CIL). All solvents (ethanol, *n*-nonane and toluene) were supplied from Wako Pure Chemical Industries, Ltd. as analytical grade and used without further purification. Internal standards ($^{13}C_{12}$-labeled 2,3,7,8-position substituted PCDDs and PCDFs (16 isomers)) and recovery standards ($^{13}C_{12}$-labeled 2,4-*di*-chlorodibenzofuran (2,4-*di*-CDF), 2,3,4,7,8-*penta*-CDF, and 1,2,3,4,7,8,9-*hepta*-CDF) were purchased from CIL.

Some amounts of OCDD or OCDF were dissolved in ethanol, *n*-nonane or toluene, respectively. The concentration was adjusted about 22 ± 1 nmol/L for OCDD and about 25 ± 1 nmol/L for OCDF in the three solvents. Dioxin-containing liquid wastes were prepared by extraction from the real fly ashes using *n*-nonane or toluene. The concentration of dioxins was about 1.6×10^{6} ng/L (corresponding concentration of toxic equivalency quantity (TEQ): 45 000 ng-TEQ/L).

2.2. ^{60}Co γ irradiation

All samples (2 mL) in glass vial sealed with a glass cap were irradiated by ^{60}Co γ-ray source at Japan Atomic Energy Agency at room temperature. The samples of OCDD or OCDF in the three solvents were irradiated to the absorbed doses ranging from 5 to 160 kGy (Gy = J/kg) at a dose rate of 10 kGy/h; the liquid wastes were irradiated to 100 kGy at a dose rate of 20 kGy/h.

2.3. Pre-treatment and analysis by GC/MS

After γ-ray irradiation, the internal standards and *n*-nonane were added to each sample. The samples were subsequently concentrated to ~50 μL at 80 °C under nitrogen gas at a flow rate of 100 mL/min. Recovery standards were added prior to capping the microvial for monitoring recovery of internal standards.

Identification and quantification of degradation products of OCDD and OCDF in organic solvents were carried out using a JEOL JMS-700 GC/MS equipped with an EI-SIM mode (Takigami et al., 2004; Hirota and Kojima, 2005). The samples were injected automatically into a split/splitless injector port with the volumes of injection not exceeding 1.0 μL. The analytical column employed by turn was HP-50+ (Agilent, 30 m × 0.25 mm × 0.25 μm column) dedicated for 7–8 chlorinated PCDDs and PCDFs, CP-SIL88 (Chrompack, 60 m × 0.25 mm × 0.10 μm column) for 4–6 chlorinated PCDDs and PCDFs, and SP-2331 (Supelco, 60 m × 0.50 mm × 0.25 μm column) for 0–3 chlorinated PCDDs and PCDFs. Each column was used with helium carrier gas at a flow rate of 1 mL/min. The temperature of GC was programmed on 120 °C (1 min), 20 °C/min, 270 °C (26.5 min) for 7–8 chlorinated PCDDs and PCDFs, on 100 °C (1 min), 20 °C/min, 200 °C, 2 °C/min, 250 °C (29 min) for 4–6 chlorinated PCDDs and PCDFs, and on 120 °C (1 min), 30 °C/min, 200 °C, 2 °C/min, 260 °C (30 min) for 0–3 chlorinated PCDDs and PCDFs, respectively.