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EXPERIMENTAL DECHLORINATION ISOMER PATTERNS OF PCDFs, PCDDs, PCNs, AND PCBs FROM THEIR FULLY CHLORINATED SPECIES

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Introduction

Copper-catalyzed dechlorination and hydrogenation of polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), and polychlorinated biphenyls (PCBs) were examined in detail by Hagenmaier et al.¹ They reported PCDD isomer patterns obtained from octachlorodibenzo-*p*-dioxin (O8CDD) and discussed the distinctions between the isomer patterns from the experiment and fly ash samples collected from municipal waste incinerators (MWIs). In their paper, neither the PCDF nor PCB isomer patterns were shown. Although we consider this paper to provide significant insights into PCDD/F formation mechanisms, no research reports have followed other than a thesis by Wiesmüller².

Based on the isomer patterns of the *N*-1 chlorinated species (*N* = the number of chlorine atoms of the fully chlorinated species), an isomer pattern prediction model was proposed by Iino et al.^{3,4} The prediction of PCDFs showed an excellent fit to the field fly ash data from the eight MWIs in Japan³. The PCDD prediction was not as successful as that of PCDFs⁴.

In this report, dechlorination experiments of PCDFs, PCDDs, polychlorinated naphthalenes (PCNs), and PCBs were performed in order to determine if a simple dechlorination experiment can provide isomer patterns similar to those found in MWIs. Hagenmaier et al. found that the catalytic effect of copper resembles that of fly ash from MWIs¹, and copper oxide was selected as a dechlorination catalyst in this research.

Experimental Methods

The fully chlorinated species [i.e., octachlorodibenzofuran (O8CDF; Cambridge Isotope Laboratories, Inc., USA), O8CDD (Cambridge Isotope Laboratories, Inc.), octachloronaphthalene (O8CN; Cambridge Isotope Laboratories, Inc.), and decachlorobiphenyl (DeCB; Accustandard Inc., USA)] were tested separately via injection into a 1 g mixture of silica gel (Alfa Aesar, USA) and 1 wt % copper oxide (CuO) (J. T. Baker Chemical Co., USA). The concentrations of the original solutions are 50±5 µg/mL of O8CDF, 10±1 µg/mL of O8CDD, 100±10 µg/mL of O8CN, and 35 µg/mL of DeCB. For most experiments, 50 or 100 µL of each original standard solution was injected. To prove that no chlorination occurs under this experimental condition, two

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heptachlorodibenzofuran (H7CDF) and one heptachlorodibenzo-*p*-dioxin (H7CDD) standards (Cambridge Isotope Laboratories, Inc.) were also separately used as a starting chemical.

The mixture was dried overnight and was moved into a 10 mL glass ampoule (Wheaton Scientific, USA). The ampoule was sealed off by an oxygen/gas torch in an atmospheric environment and heated to 300 °C in a preheated furnace for 2, 5, 10, 15, and 30 min. (CAUTION: The ampoule containing PCBs may explode under this experimental condition.) After the reaction, the silica gel mixture was transferred to a filter and about 50 mL of toluene was used for extraction. The toluene solution was evaporated to about 100 µL prior to injection into a Gas-Chromatograph/Mass-Spectrometer (GC/MS). Internal and recovery standards were spiked for quantitative analyses. A DB-Dioxin (J&W) column for quantitative analyses and an SP-2331 column (SUPELCO) for isomer pattern analyses were used in the GC/MS (Hewlett Packard, GC5890/MS5971A and GC5890/MS5970). Since the concentration range of the analyzed samples is higher than that of the usual samples from combustion sources, calibration curves for O8CDF and 1,2,3,4,7,8,9-H7CDF were made to cover the concentration range (5 – 25 mg / mL) of the samples in this experiment. The fact that the GC/MS response of 1,2,3,4,7,8,9-H7CDF is about 0.75 times smaller than that of 1,2,3,4,6,7,8-H7CDF for the same amount was used to determine the concentration of the total H7CDF homologue. The temperature profile of the ampoule with silica gel is shown in Fig. 1. At 5 min, the temperature inside the ampoule reached 300 °C. Each ampoule was heated up from the room

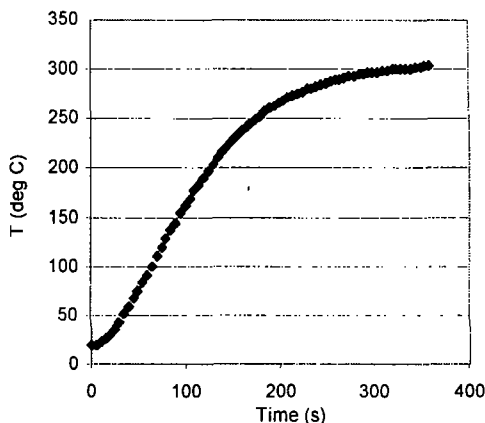


Fig.1 A temperature profile of the ampoule (10mL) in the furnace with silica gel (1g)

Results and Discussion

The experiment with O8CDF in an ampoule was repeated twice for quantitative analysis. The time profile of the homologue concentrations is shown in Table 1. Due to the closed ampoule with no added chlorine source, 75% of the original O8CDF was destroyed or dechlorinated before 5 min (300 °C). In Fig. 2, the H7CDF isomer patterns of these samples are compared with those of fly ash samples collected from MWIs in Japan. The isomer of

Table 1 Homologue concentrations of the O8CDF experiments.

	ng/train	0min	2min	5min	10min	15min	30min
Run1	O8CDF	2410	1785	631	28.3	0.8	0
	H7CDF	22.4 [†]	56.7	303.6	215.4	107.1	16.1
	H6CDF	0	1.8	20.8	86.6	94.4	52
	P5CDF	0	0.6	3	17.3	28.7	28.7
	T4CDF	0	2.9	19.9	84.5	87.5	16.1
	T3CDF	0	1.3	7	36.8	72.4	16.4
	D2CDF	0	0	0	16.1	21.6	0
	M1CDF	0	0	0	0	0	0
Run2	O8CDF	2410	2002	584.8	15.2	0	0
	H7CDF	22.4 [†]	56.4	312.1	204.9	57.4	2.1
	H6CDF	0	2.5	30.4	91.4	75	26
	P5CDF	0	0	6.7	23.4	25.7	29.8
	T4CDF	0	1.7	76.3	136.4	98.4	83.4
	T3CDF	0	0.7	31.8	73.8	76.2	111.2
	D2CDF	0	0	14	29.9	25.9	41.8
	M1CDF	0	0	0	0	0	0

[†]H7CDF originated from the standard O8CDF solution

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1,2,3,4,6,7,8-H7CDF shows a predominant peak, confirming that the 9-chlorine atom from O8CDF is easily released, probably because of the steric effect of the 1- and 9- chlorine atoms on an O8CDF molecule. The other three peaks in Fig. 2 correspond to dechlorination from the 8-, 7-, and 6-positions in order, respectively. Since dechlorination from H7CDFs to hexachlorodibenzofurans (H6CDFs) also occurs at the same time, the observed isomer patterns also reflect the dechlorination kinetics from O8CDF to the H7CDF isomers and from the H7CDF isomers to H6CDFs as well as to each successive, less chlorinated homologue. At 2 min, 1,2,3,4,7,8,9-H7CDF is higher than 1,2,3,4,6,8,9-H7CDF. The peak of 1,2,3,4,7,8,9-H7CDF becomes relatively smaller, as the reaction proceeds. The isomer patterns from 5 to 15 min obtained from the O8CDF experiment are very similar to those from MWIs. The dechlorination of each H7CDF isomer, instead of O8CDF, did not form any isomers which have to be formed via rearrangement and/or dechlorination from the H7CDF isomers.

The H6CDF isomer patterns obtained from O8CDF are shown in Fig. 3. The sampled data from MWIs in Japan are also shown for comparison. The isomers of 1,2,3,6,7,8- and 1,2,4,6,8,9-H6CDFs were not well separated in the experimental samples due to the close elution times of the two H6CDF isomers. It is known that the peak of 1,2,3,7,8,9-H6CDF analyzed by the SP-2331 column interferes with that of 1,2,3,4,6,7,8-H7CDF. This interference may be the reason of the larger peak of 1,2,3,7,8,9-H6CDF than that of the sampled data at 5 and 10 min. The peak of 2,3,4,6,7,8-H6CDF showed a distinctive difference from the sampled data.

Starting from only O8CDD, the ratio of the two H7CDDs was 1,2,3,4,6,7,9-H7CDD:1,2,3,4,6,7,8-H7CDD = 0.56:0.44 based on the GC/MS peak area after 30 min. This ratio is within the range of those normally observed from MWI samples. The H6CDD isomer pattern was fairly similar to those from the MWIs except for a coeluting peak of 1,2,4,6,7,9-, 1,2,4,6,8,9-, and 1,2,3,4,6,8-H6CDDs.

The ratio of the two heptachloronaphthalenes (HpCNs) produced from OccN at 5 min was 1,2,3,4,5,6,7-HpCN:1,2,3,4,5,6,8-HpCN = 0.029:0.97. The average ratio observed in the six fly ash samples from the MWIs is 0.81:0.19, which is completely opposite from the experimental findings. However, this result does not mean that the chlorine at the α position (1-, 4-, 5-, and 8-

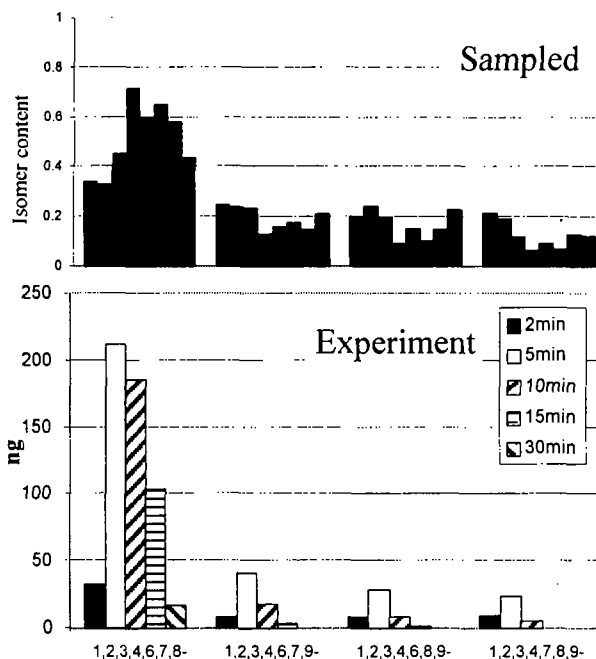


Fig. 2 H7CDF isomer pattern from sampled data and O8CDF experiments

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positions) of an OcCN molecule is rarely released, because we observed a predominant peak of 1,2,3,4,6,7- and 1,2,3,5,6,7-hexachloronaphthalenes (HxCNs) in the HxCN homologue at 5 min. The two isomers lost two chlorine atoms at the α position from OcCN, and cannot be formed from 1,2,3,4,5,6,8-HpCN. Because of the steric effect of the α position chlorine atoms, it is possible that 1,2,3,5,6,7-HxCN is more predominantly formed than 1,2,3,4,6,7-HxCN, which will have to be confirmed by using another column to separate the two isomers.

The experiments with DeCB were done in a quartz tube reactor with a flow of 10%O₂/N₂ 200 mL/min. The isomer patterns of nonachlorobiphenyls (NoCBs) were barely detected under this experimental condition.

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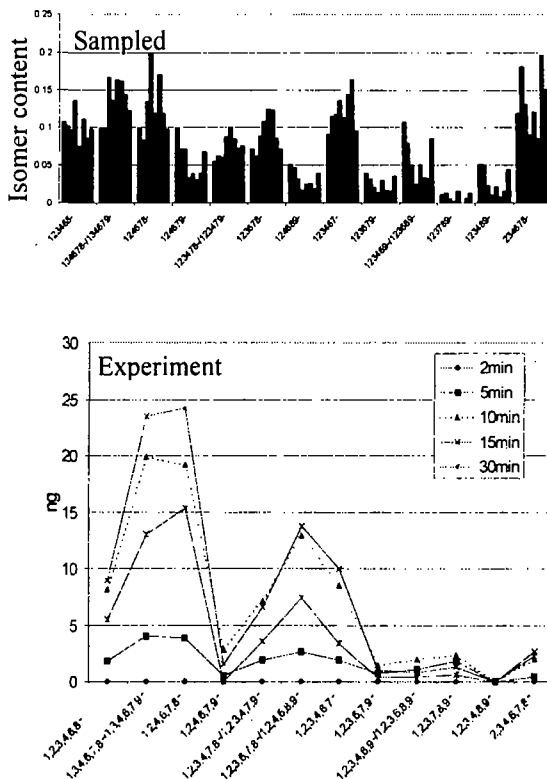


Fig. 3 H6CDF isomer pattern from sampled data and O8CDF experiments