On Emission and Formation of Non-Ortho CBs and Mono-Ortho CBs in Municipal Waste Incineration

Sakai,S.[a], Hiraoka,M.[b], Takeda,N.[b], Shiozaki,K.[c]

a)Environment Preservation Center, Kyoto Univ., Kyoto 606, Japan
b)Dept. of Environmental & Sanitary Engineering, Kyoto Univ., Kyoto 606, Japan
c)Kaneka Techno Research Co., Ltd., Yoshida-cho, Hyogo-ku, Kobe 602, Japan

INTRODUCTION

It has been found before that Non-ortho PCBs and PCDDs/PCDFs can be analyzed simultaneously by improving alumina column fractionation of PCDDs/PCDFs analysis; and that the contribution of the toxicity of Non-ortho CBs, in the exhaust gas of refuse incineration, to the 2,3,7,8-TCDD toxic equivalent concentration of PCDDs/PCDFs is a few percent. This is not as high as that in fish and human tissues[1,2]. The number of samples was small, however. The PCBs previously studied were three species of Non-ortho CBs (IUPAC #77, 126, 169), which have no chlorine substitution at the ortho positions. Like Non-ortho CBs, Mono-ortho coplanar type PCBs (hereafter referred to as Mono-ortho CBs), which have one chlorine substitution at their ortho positions, have a similar mechanism of toxic response to that of PCDDs/PCDFs. 2,3,7,8-TCDD toxicity equivalent factors for Mono-ortho CBs have been already proposed[3] as 0.001. In addition to PCDDs/PCDFs and Non-ortho CBs, Mono-ortho CBs are also present in exhaust gas and fly ash from municipal waste incineration. Also, the mechanism of Non-ortho CBs formation was discussed.

EXPERIMENTAL METHODS

After acid treatment and toluene extraction, the samples are cleaned up with a silica gel column, and then with an alumina column. At this point, the column is fractionated into: a PCBs fraction (including Mono-ortho CBs), a Non-ortho CBs fraction, and a PCDDs/PCDFs fraction. The alumina column has a 10 mm inside diameter and 300 mm length; and 14 g of neutral activated alumina was packed in the tube, and 1 cm of sodium sulfate anhydride was loaded onto the alumina. The column was eluted with 100 mL of n-hexane containing 2% dichloromethane, to yield a first fraction; this was followed by passage of 150 mL of n-hexane, containing 5% dichloromethane, to yield a second fraction; this was followed by passage of 150 mL of n-hexane containing 50% dichloromethane to yield a third fraction. Each fraction was concentrated to a volume of 100 μ L with dry nitrogen gas, to yield a GC/MS analytical sample. The Mono-ortho CBs studied are the following isomers: IUPAC #105, 114, 118, 123, 156, 157, 167, and 189. A heating experiment on fly ash was carried out according to the following procedure. Smaller ash than 2.8 mm (6.6 mesh) was ground to make it finer, and used as samples. A quartz tube (1 m × 31.5 mm i.d.) and combustion boat were placed in a temperature controlled electric furnace (± 2℃). Air was supplied through an activated carbon column, and nitrogen gas of purity A (more than 99.999%) was passed through an activated carbon column as well. The following experiments heating 8 g of fly ash from municipal waste incineration were carried out: ① 0.5, 2, and 4 hours heat treatment at 300℃, with 667 ml/min air flow, ② 0.5, 2, and 4 hours heat treatment at 300℃, with 667 ml/min nitrogen flow, and ③ 2 hour heat treatment at 120℃ and 500℃, with 667 ml/min air flow.

FORM

RESULTS AND DISCUSSION

Non-ortho CBs, Mono-ortho CBs and PCDDs/PCDFs in the gas and fly ash samples from municipal waste incineration were analyzed quantitatively, and the results are shown in Table 1. The PCBs recovery percentage of exhaust gas and fly ash were 89.3 and 107.8 %. The results of this quantitative analysis show that the total concentrations of Non-ortho CBs and Mono-ortho CBs are at the same level, but the toxicity equivalent concentration of Mono-ortho CBs is smaller than that of Non-ortho CBs. In recent years, Mono-ortho CBs in biological samples have been studied; it has been reported that the concentrations of Mono-ortho CBs are about two orders of magnitude higher than those of Non-ortho CBs. On the basis of these results, it can be said that the amount of Non-ortho CBs and Mono-ortho CBs produced by municipal waste incineration is small compared with the PCB toxicity load in biological samples. The number of samples, however, is too small to generalized about PCB behavior in municipal waste incineration, and very little of the PCB formation mechanism is known.

Vogg and Stieglitz[4,5] observed de novo synthesis of dioxins in a heating test of fly ash in a municipal waste incinerator, in an oxidizing atmosphere at about 300 ℃. A similar heating experiment was carried out here, and the results of the measurements of Non-ortho CBs and PCDDs/PCDFs are shown in Table 2. The remarkable increase of PCDDs/PCDFs after the heat treatment in 300℃ air, which Stieglitz and others had reported, was not observed. With nitrogen flow the decrease was greater than with air flow. The three kinds of Non-ortho CBs showed the same behavior as PCDDs/PCDFs. It is of interest that in this study, the concentration of Non-ortho CBs in the 300℃ air flow was higher than that in the nitrogen flow. In the competitive reaction system between the formation and decomposition, the high concentration in the air flow implies the possibility of de novo synthesis, producing Non-ortho CBs as well. Ballschmiter and others carried out the identification of PCB isomers in fly ash from municipal waste incineration, and they clarified that the PCB isomers are different from that of commercial product PCB[6]. They reported that, for its formation mechanism, dimerization of chlorobenzene is the most acceptable possibility. Stieglitz and others reported that PCDDs/PCDFs are produced in de novo synthesis, and later they confirmed experimentally that chlorobenzene, chloronaphthalenes and PCBs are produced in the same way. A model compound Mg-Al-Silicate was used, activated carbon, KCl and $CuCl_2$ are added, and through heat treatment in the 300 ℃ air flow, PCBs are produced[7]. Our results did not show sufficient evidence of formation, but they did imply the possibility of synthesis.

REFERENCES

1) Sakai,S., Hiraoka,M., Takeda,N., Shiozaki,K. : Coplanar PCBs and PCDDs/PCDFs in municipal waste incineration, Chemosphere, in press

2) van Bavel,B., Fängmark,I., Marklund,S., Söderström,G., Ljung,K., Rappe,C. : Quantitative analysis of organic trace compounds by isotope dilution: Formation of the Non-ortho PCBs 77, 126, 169 during incineration, Dioxin '92

3) Safe,S. : Polychlorinated Biphenyls (PCBs), Dibenzo-p-Dioxins (PCDDs), Dibenzofurans (PCDFs), and related compounds: Environmental and mechanistic considerations which support development of toxic equivalency factors (TEFs), CRC Critical Reviews in Toxicology, Vol.21, No.1, pp.51-88 (1990)

4) Vogg,H., Stieglitz,L. : Thermal behavior of PCDD/PCDF in fly ash from municipal incinerators, Chemosphere, Vol.15, Nos.9-12, pp.1373-1378 (1986)

Table 1 Non-ortho CBs, Mono-ortho CBs and 2,3,7,8-T$_4$CDD TEQ Concentration

		Concentration	
	I-TEF	Exhaust gas [ng/Nm^3]	Fly ash [ng/g]
2,3,7,8-T$_4$CDD	1	1.2	0.39
1,2,3,7,8-P$_5$CDD	0.5	7.7	3.0
2,3,7,8-substituted H$_6$CDD	0.1	13	9.6
1,2,3,4,6,7,8-H$_7$CDD	0.01	90	26
O$_8$CDD	0.001	130	25
2,3,7,8-T$_4$CDF	0.1	6.5	1.2
1,2,3,7,8-P$_5$CDF	0.05	17	3.1
2,3,4,7,8-P$_5$CDF	0.5	17	3.2
2,3,7,8-subsituted H$_6$CDF	0.1	55	10
2,3,7,8-subsituted H$_7$CDF	0.01	87	13
O$_8$CDF	0.001	38	5.2
PCDDs+PCDFs (TEQ)		28	5.2
PCDDs+PCDFs(Total)		1800	610
Non-ortho CBs IUPAC #			
3,3',4,4'-T$_4$CB 77	0.01	12	1.6
3,3',4,4',5-P$_5$CB 126	0.1	7.9	1.3
3,3',4,4',5,5'-H$_6$CB 169	0.05	1.8	0.34
Non-ortho CBs (Total)		22	3.2
Non-ortho CBs (TEQ)		1.0	0.16
Non-ortho CBs (TEQ %)		4%	3%
Mono-ortho CBs IUPAC #			
2,3,3',4,4'-P$_5$CB 105	0.001	0.52	0.042
2,3,4,4',5-P$_5$CB 114	0.001	5.2	0.35
2,3',4,4',5-P$_5$CB 118	0.001	0.79	0.099
2',3,4,4',5-P$_5$CB 123	0.001	0.41	0.057
2,3,3',4,4',5-H$_6$CB 156	0.001	1.6	0.24
2,3,3',4,4',5'-H$_6$CB 157	0.001	4.2	0.62
2,3',4,4',5,5'-H$_6$CB 167	0.001	2.1	0.39
2,3,3',4,4',5,5'-H$_7$CB 189	0.001	3.5	0.81
Mono-ortho CBs (Total)		18	2.6
Mono-ortho CBs (TEQ)		0.018	0.0026
Mono-ortho CBs (TEQ %)		0.08%	0.05%
Other PCBs			
D$_2$CBs		53	3.8
T$_3$CBs		102	4.4
T$_4$CBs		142	4.7
P$_5$CBs		59	3.4
H$_6$CBs		30	2.4
H$_7$CBs		29	2.4
O$_8$CBs		16	2.2
N$_9$CBs		13	2.0
Total PCBs		466	28
Non-ortho CBs (percentage)		5%	11%
Mono-ortho CBs(percentage)		4%	9%

FORM

REFERENCES (continued)

5) Stieglitz,L., Vogg,H. : On formation conditions of PCDD/PCDF in fly ash from municipal waste incinerators, Chemosphere, Vol.16, Nos.8/9, pp.1917-1922 (1987)

6) Ballschmiter,K., Niemczyk,R., Schäfer,W., Zoller,W. : Isomer-specific identification of polychlorinated benzenes (PCBz) and -biphenyls (PCBs) in effluents of municipal waste incineration, Fresenius Z Anal. Chem., Vol.328, pp.583-587 (1987)

7) Stieglitz,L., Zwick,G., Beck,J., Bautz,H., Roth,W. : Carbonaceous particles in fly ash - A source for the de-novo-synthesis of organochlorocompounds, Chemosphere, Vol.19, Nos.1/6, pp.283-290 (1989)

Table 2 Heat treatment of fly ash from municipal waste incineration (ng/g)

	Fly Ash	Air 300℃ 0.5 hr	Air 300℃ 2.0 hr	Air 300℃ 4.0 hr	Air 120℃ 2.0 hr
3,3',4,4'-T$_4$CB	1.2	1.1	1.0	1.0	1.1
3,3',4,4',5-P$_5$CB	1.3	1.1	0.73	0.5	1.3
3,3',4,4',5,5'-H$_6$CB	0.35	0.44	0.21	0.11	0.53
Total	3.0	2.6	1.9	1.6	2.9
T$_4$CDD	140	190	120	83	120
P$_5$CDD	240	240	140	72	220
H$_6$CDD	310	230	87	35	340
H$_7$CDD	110	82	21	8.7	100
O$_8$CDD	51	26	4.1	2.2	47
Total	850	770	370	200	830
T$_4$CDF	54	66	57	70	43
P$_5$CDF	92	81	51	38	85
H$_6$CDF	120	65	26	13	120
H$_7$CDF	49	24	5.9	2.5	45
O$_8$CDF	12	3.9	0.52	0.27	11
Total	330	240	140	120	300

	N_2 300℃ 0.5 hr	N_2 300℃ 2.0 hr	N_2 300℃ 4.0 hr	Air 500℃ 2.0 hr	Air 500℃ gas phase
3,3',4,4'-T$_4$CB	0.52	0.30	0.17	< 0.005	< 0.005
3,3',4,4',5-P$_5$CB	0.30	0.15	0.071	< 0.005	< 0.005
3,3',4,4',5,5'-H$_6$CB	0.085	0.050	0.023	< 0.005	< 0.005
Total	0.91	0.50	0.26	< 0.005	< 0.005
T$_4$CDD	150	94	49	1.5	0.53
P$_5$CDD	96	45	21	1.4	0.37
H$_6$CDD	46	19	8.7	1.1	0.39
H$_7$CDD	11	6.3	2.5	0.33	0.068
O$_8$CDD	4.0	3.2	0.72	0.70	0.061
Total	310	170	82	5.0	1.4
T$_4$CDF	39	26	14	0.41	0.31
P$_5$CDF	30	13	6.5	0.39	0.18
H$_6$CDF	13	5.4	2.5	0.43	0.15
H$_7$CDF	3.6	2.1	0.81	0.18	0.045
O$_8$CDF	0.67	0.51	0.19	0.11	0.024
Total	86	47	24	1.5	0.71