Behavior of Coplanar PCBs in Oxidative Condition of Municipal Waste Incineration

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

a)Environment Preservation Center, Kyoto Univ., Kyoto 606-01, Japan
b)Dept. of Environmental & Sanitary Engineering, Kyoto Univ., Kyoto 606-01, Japan
c)Kaneka Techno Research Co., Ltd., Yoshida-cho, Hyogo-ku, Kobe 605, Japan

1. Introduction

Recently Non-ortho PCBs (IUPAC #77, 126 and 169) have been detected in the exhaust gas and fly ash from the incineration of municipal solid waste (MSW) along with PCDDs/PCDFs[1-3]. Mono-ortho PCBs (IUPAC #105, 114, 118, 123, 156, 157, 167 and 189) are also present at the same order as Non-ortho PCBs[4]. However there is little information about the behavior and formation mechanism of these coplanar PCBs in thermal processes. This study has the objectives to obtain the information about the behavior of coplanar PCBs in oxidative conditions by the use of pilot-scale municipal waste incinerator and to discuss the formation mechanism.

2. Experimental Methods

Experiments were run on a pilot-scale two-stage incinerators which has a operating capacity of 1.5 ton/8 hours (1.6×10^6 KJ/hr). This furnace is used to test the optimal conditions of batch-type incineration of MSW and to simulate the behaviors of coplanar PCBs during the oxidative solid phase combustion. The total system consists of primary & secondary furnaces, heat exchanger of combustion air, gas cooling unit and bag filter. In this experiment, three runs were operated under total combustion air ratio of about 2.1, of which one was under the excess air (No.1) in the primary chamber and the others were under the starved-air combustion (No.2,3). No.1 had the primary air of 900 m^3N/hr (ϕ=1.9) and the secondary air of 150 m^3N/hr (ϕ=0.3). No. 2 & 3 were operated under ϕ=1.25 and 0.95 of the primary and ϕ=0.95 and 1.25 of the secondary air ratio respectively. The secondary combustion chamber was operated under tangential and eccentric gas input with gas exhaust from the centre axial point for the purpose of perfect gas mixing. The MSW sample used for the experiment had the calorific value of 7,300 KJ/kg which was actual one from the urban area. Furnace emissions were sampled in the downstream of each chambers. PCBs and PCDDs/PCDFs were sampled using isokinetic sampling protocols by the Japan Waste Research Foundation (JWRF). The probe rinse, filters, XAD resin and impinger were analyzed by HRGC/HRMS (HP5890 Series II and VG Autospec). The methods of extraction and cleanup was based on the JWRF method for PCDDs/PCDFs and the analytical procedures of Non-ortho and Mono-ortho PCBs have been reported[1,4]. A heating experiment of the fly ash was carried out using a quartz tube

(1 m × 31.5 mm i.d.) and combustion boat placed in a temperature controlled electric furnace. 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. A pair of toluene impingers were used to collect PCBs and PCDDs/PCDFs in the gas. After *heating, the combustion tube and other tubes were washed with acetone and toluene.* The following experiments heating 8 g of fly ash from municipal waste incineration were carried out: 0.5, 2, and 4 hours heat treatment at 300°C, with 667 mL/min air flow and 2 hours heat treatment at 300°C, with 667 mL/min nitrogen flow.

Tabale 1 PCBs and PCDDs/PCDFs in the Primary and Secondary chamber (O_2=9.6%)

		TEF WHO/IPCS (1994)	Primary Chamber [ng/m^{3}N at O_2=12%]		Secondary Chamber [ng/m^{3}N at O_2=12%]	
			Conc.	TEQ	Conc.	TEQ
Non-ortho PCBs 3,3',4,4'-TCB	# 77	0.0005	1.6	0.0008	1.0	0.00050
3,3',4,4',5-PeCB	#126	0.1	0.55	0.055	0.30	0.03
3,3',4,4',5,5'-HxCB	#169	0.01	0.31	0.0031	ND(<0.07)	0
Sub-Total			2.5	0.059	1.3	0.031
Mono-ortho PCBs 2,3,3',4,4'-PeCB	#105	0.0001	3.9	0.00039	1.8	0.00018
2,3,4,4',5-PeCB	#114	0.0005	0.66	0.00033	0.42	0.00021
2,3'4,4',5-PeCB	#118	0.0001	7.6	0.00076	4.1	0.00041
2',3,4,4'5-PeCB	#123	0.0001	1.2	0.00012	0.63	0.000063
2,3,3',4,4',5-HxCB	#156	0.0005	1.2	0.0006	0.69	0.00035
2,3,3',4,4',5'-HxCB	#157	0.0005	0.28	0.00014	0.14	0.00007
2,3'4,4',5,5'-HxCB	#167	0.00001	0.52	0.0000052	0.30	0.000003
2,3,3',4,4',5,5'-HpCB	#189	0.0001	0.28	0.000028	0.19	0.000019
Sub-Total			16	0.0024	8.3	0.0013
Coplanar PCBs Total			19	0.061	9.6	0.032
Percentage			2.8%		2.3%	
$M_1PCBs - D_{10}PCBs$ Total			690		420	
PCDDs/PCDFs 2,3,7,8-TCDD		1	0.16	0.16	ND(<0.09)	0
1,2,3,7,8-PeCDD		0.5	0.94	0.47	0.13	0.065
1,2,3,4,7,8-HxCDD		0.1	1.3	0.13	0.11	0.011
1,2,3,6,7,8-HxCDD		0.1	1.6	0.16	0.12	0.012
1,2,3,7,8,9-HxCDD		0.1	1.8	0.18	0.18	0.018
1,2,3,4,6,7,8-HpCDD		0.01	13	0.13	1.3	0.013
OCDD		0.001	16	0.02	1.9	0.0019
2,3,7,8-TCDF		0.1	1.2	0.12	0.22	0.02
1,2,3,7,8-PeCDF		0.05	4.6	0.23	0.56	0.028
2,3,4,7,8-PeCDF		0.5	4.3	2.2	0.48	0.24
1,2,3,4,7,8-HxCDF		0.1	7.8	0.78	0.80	0.08
1,2,3,6,7,8-HxCDF		0.1	7.8	0.78	0.57	0.057
1,2,3,7,8,9-HxCDF		0.1	1.6	0.16	0.19	0.019
2,3,4,6,7,8-HxCDF		0.1	8.6	0.86	0.65	0.065
1,2,3,4,6,7,8-HpCDF		0.01	30	0.30	2.8	0.028
1,2,3,4,7,8,9-HpCDF		0.01	7.8	0.078	0.71	0.0071
OCDF		0.001	20	0.02	2.6	0.0026
2,3,7,8-Substi.-Total				6.7		0.67
PCDDs/PCDFs Total			310		43	
TEQ PCDDs/PCDFs				6.7		0.67
PCBs				0.061		0.032
Σ				6.8		0.70
PCBs Percentage %				0.9 %		4.6 %

3. Results and Discussion

The concentrations of Non-ortho and Mono-ortho PCBs in the exhaust gas of primary and secondary chamber are given in Table 1. 2,3,7,8-TCDD equivalent are calculated according to the toxic equivalency factors proposed recently by WHO-ECEH and IPCS[5]. In this case O_2 concentration in the primary chamber was 9.6% and combustion temperature were 800±30°C in both chambers. 6.7 ng TEQ/m^3N of PCDDs/PCDFs in the primary chamber decreased to 0.66 ng TEQ/m^3N during the secondary combustion. CO also decreased from 90 ppm to 2 ppm. Non-ortho and Mono-ortho PCBs were detected on the order of 0.1 ng TEQ/m^3N in the primary chamber. After the secondary combustion coplanar PCBs have decreased, which is the same tendency as the PCDDs/PCDFs. In Figure 1, the concentrations of PCBs in the primary & secondary chamber are compared with the oxygen content of primary combustion. Coplanar PCBs in the starved-air combustion of O_2 content of about 3% are much higher than those in O_2 of 9.6%. CO in the primary starved combustion were 860 ppm (O_2 3.2%) and 2300 ppm (O_2 2.7%), which decreased to 11 and 24 ppm respectively after secondary combustion. Coplanar PCBs and PCDDs/PCDFs have the same behaviors in both primary and secondary combustion. These results have shown that Non-ortho & Mono-ortho PCBs have been formed in the oxidative solid combustion phase and have the same behaviors as PCDDs/PCDFs. Ballschmiter and others clarified that the PCB isomer patterns in fly ash are different from that commercial product PCB and also reported that the dimerization of chlorobenzene is the most acceptable possibility[6,7]. One of the reasons of the coplanar PCBs formation in this solid waste combustion phase is the dimerization of the chlorobenzenes to the PCB being proceeded in flames via radical reactions.

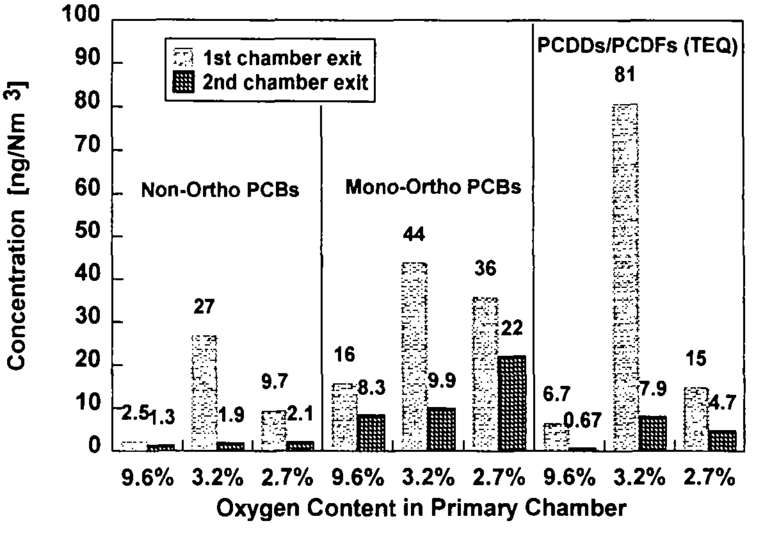

Figure 1 Coplanar PCBs behaviros by the oxygen content of primary chamber

Another formation mechanism of coplanar PCBs can be thought to be de novo synthesis. The results of a heating experiment using fly ash from the same plant above mentioned are shown in Figure 2. Heat treatment of fly ash in air has the remarkable increase of coplanar PCBs. The longer the heating time at 300°C was, the higher the concentrations of Non-ortho & Mono-ortho PCBs were found. 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°C air flow, PCBs are produced[8)]. Schoonenboom and others also confirmed that Non-ortho PCBs are formed from particulate organic carbon in a fly ash model system and the formation reaches maximum around 350°C[9)]. From both these results using fly ash model and the results of our heat experiment using actual MSW fly ash, de novo synthesis must be one of the formation routes.

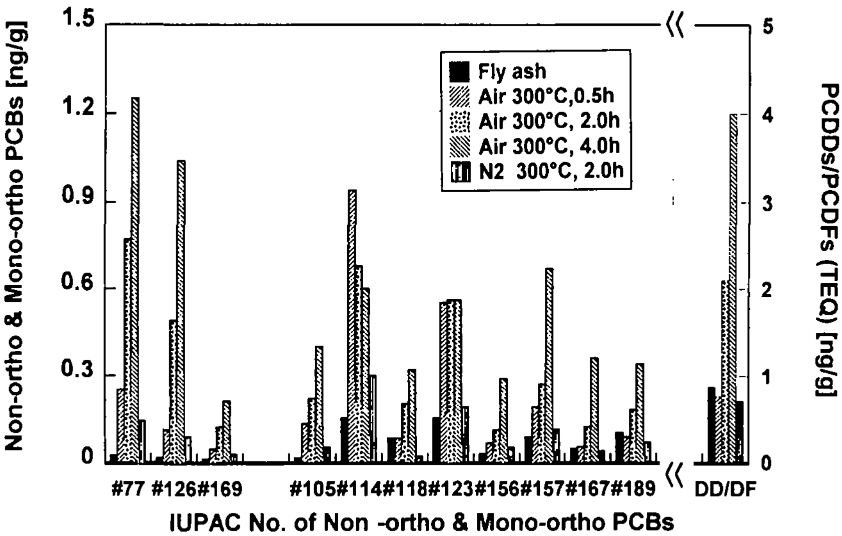

Figure 2 Non-ortho and Mono-ortho PCBs in heat treatment of fly ash

4. Conclusions

Non-ortho PCBs and Mono-ortho PCBs are formed during primary combustion of MSW in the oxidative conditions. In the secondary combustion, much of coplanar PCBs are destructed. There is the same behaviors between coplanar PCBs and PCDDs/PCDFs during the primary and secondary combustion. The de novo synthesis of coplanar PCBs are also observed.

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