Subject Area 6.4: Monitoring and fate of persistent chemicals (POPs) including new compounds

Research Article

Formation of Polychlorinated Diphenyl Ethers from Condensation of Chlorophenols with Chlorobenzenes

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Abstract

Background and Aims. Polychlorinated diphenyl ethers (PCDEs), which are among the members of persistent organic pollutants, and PCDEs have been determined in a number of environmental samples. The main possible sources are the technical production of chlorinated phenols and all processes of incomplete combustion. PCDEs were observed in the fly ash from a municipal waste incinerator (MWI). It was speculated that the condensation of chlorophenols with chlorobenzenes occurred via PCDEs to form polychlorinated dibenzofurans (PCDFs). Nevertheless, PCDEs formation from condensation of chlorophenols with chlorobenzenes has not been confirmed by experimental observation. The objective of this paper is to investigate the formation mechanism of PCDEs from the condensation of chlorophenols with chlorobenzenes. The results are expected to be helpful in understanding the formation of PCDEs and in controlling and abating PCDEs emissions from MWI.

Methods. The pyrolysis of pentachlorophenol (PCP) and/or polychlorobenzenes (PCBz) was carried out in a sealed glass tube. The reaction products were extracted and purified with K₂CO₃ solution. The samples were concentrated and then cleaned up on an alumina column. GC/MS was used for identification and quantification of reaction products.

Results and Discussion. The results showed that the pyrolysis of hexachlorobenzene (HCB) at 340°C for 6 h led to the formation of decachlorodiphenyl ether (DCDE) (2.41 µg/mg) and octachlorodibenzo-*p*-dioxins (OCDD) (0.24 µg/mg), while the pyrolysis of PCP yielded DCDE (13.08 µg/mg) and OCDD (180.13 µg/mg). In addition, the amount of DCDE formation from the pyrolysis of the mixture of PCP and HCB was 4.65 times higher than the total amount of DCDE formation from the pyrolysis of HCB and PCP, respectively. This indicated that PCP and HCB were prone to condensation and formation of DCDE. DCDE was the main congener of PCDEs from condensation of PCP with HCB at 340, 400 and 450°C. A small amount of nonachlorodiphenyl ether (NCDE) was formed by dechlorination reaction at 450°C. The condensation of PCP with 1,2,4,5-tetrachlorobenzene (Cl₄Bz) formed 2,2',3,4,4',5,5',6-octa-

chlorodiphenyl ether (OCDE). Small amounts of heptachlorodiphenyl ether (HpCDE) and hexachlorodiphenyl ether (HxCDE) were detected at 450°C. Meanwhile, polychlorinated dibenzo-*p*-dioxins (PCDDs) and PCDFs were detected from the condensation of PCP and PCBz.

Conclusions. Experimental studies clarified the behavior of the formation of PCDEs from condensation of polychlorophenols and PCBz. The condensation of polychlorophenols with PCBz formed PCDEs through elimination of HCl between polychlorophenols and PCBz molecules. Another pathway of PCDEs formation was elimination of H₂O between two polychlorophenol molecules. In addition, dechlorination processes had caused the specific homologous pattern of PCDEs under higher temperatures.

Glossary. Cl₄Bz – Tetrachlorobenzene; DCDE – Decachlorodiphenyl ether; HCB – Hexachlorobenzene; HpCDD – Heptachlorodibenzo-*p*-dioxin; HpCDE – Heptachlorodiphenyl ether; HpCDF – Heptachlorodibenzofuran; HxCDD – Hexachlorodibenzo-*p*-dioxin; HxCDE – Hexachlorodiphenyl ether; HxCDF – Hexachlorodibenzofurans; MWI – Municipal waste incinerator; NCDE – Nonachlorodiphenyl ether; OCDD – Octachlorodibenzo-*p*-dioxins; OCDE – Octachlorodiphenyl ether; OCDF – Octachlorodibenzofuran; PCBz – Polychlorobenzenes; PCDDs – Polychlorinated dibenzo-*p*-dioxins; PCDEs – Polychlorinated diphenyl ethers; PCDFs – Polychlorinated dibenzofurans; PCP – Pentachlorophenol; PeCDD – Pentachlorodibenzo-*p*-dioxins; PeCDF – Pentachlorodibenzofuran; TCDD – Tetrachlorodibenzo-*p*-dioxins; TCDF – Tetrachlorodibenzofurans

Keywords: Condensation; pentachlorophenol; polychlorinated dibenzofurans; polychlorinated dibenzo-*p*-dioxins; polychlorinated diphenyl ethers; polychlorobenzenes

Introduction

Polychlorinated diphenyl ethers (PCDEs) are among the members of persistent organic pollutants, which are lipophilic substances with long half-lives in the environment. PCDEs are becoming of great concern because of their structural and toxicological similarity to polychlorinated biphenyls (Becker et al. 1991). Studies indicate that PCDE congeners show a broad spectrum of toxic and biochemical responses in laboratory animals, including the induction of

cytochrome P-450-dependent mono-oxygenase enzymes. Attempts have been made to define toxic equivalency factors for the PCDEs similar to those defined for polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) (Safe 1992, Hornung et al. 1996). The main possible sources are the technical production of chlorinated phenols and all processes of incomplete combustion. PCDEs were observed in the fly ash from municipal waste incinerator (MWI) (Passivirta et al. 1986, Kurz et al. 1995). Moreover, PCDEs are a group of ubiquitous pollutants and can bioaccumulate in the food chain. In fact, PCDEs have been determined in a number of environmental samples including sediments, fish, cod liver oils, bird eggs, white-tailed eagle muscles, salmon and human adipose tissue (Sinkkonen and Paasivirta 2000, Stanley et al. 1990, Koistinen et al. 1995, 1997, Nevalainen et al. 1994). In addition, the levels of PCDEs are often higher than those of PCDFs in the environment. For example, the levels of PCDEs in fish have been measured 10–50 times higher than that of PCDFs (Huestis et al. 1992). Furthermore, PCDEs are crucial precursors of PCDFs. These compounds are transformed by irradiation or pyrolysis with a dehydrogenation or dehydrochlorination step into PCDFs (Norström et al. 1977, Lindahl et al. 1980). Recently, there are some reports on the physicochemical properties of PCDEs such as vapor pressures (P_L), partition coefficients (K_{ow}), aqueous solubilities ($S_{w,L}$) and Henry's law constants (Öberg 2002, 2003, Kurz et al. 1999, Yang et al. 2003). The toxic effects and human exposure to PCDEs were studied (Bocio et al. 2004, Domingo 2006, Falcó et al. 2005). However, little attention has been paid to the formation of unintentional production of PCDEs.

PCDD/Fs are among the most toxic environmental pollutants known. Their presence in MWI effluents has sparked a variety of laboratory investigations over 20 years in the hope of learning more about the formation and destruction mechanisms of these compounds (Isosaari et al. 2004). Chlorophenols and chlorobenzenes have been discussed as both potential precursors and structurally related to PCDD/Fs in effluents of MWI (Ballschmiter et al. 1988, Altwicker et al. 1990). The formation of PCDD/Fs from respective chlorophenols and chlorobenzenes via condensation reaction was reported (Evans and Dellinger 2003, 2005, Buser 1979, Weber et al. 1999a). Weber (1999b) elucidated the pathways for PCDD/Fs formation in fluidized bed incineration and made assumptions that the condensation of chlorophenols with chlorobenzenes occurred via biphenyl ethers to form PCDFs. However, the condensation of chlorophenols with chlorobenzenes has not been confirmed by experimental observation.

The present paper reported on the experimental results of condensation of pentachlorophenol (PCP) and polychlorobenzenes (PCBz). The occurrence and distribution of PCDEs and PCDD/Fs were investigated systematically at different temperatures in this study. A mechanism of condensation of PCP with PCBz was proposed. The results are expected to be helpful in understanding the formation of PCDEs and in controlling and abating PCDEs emission from MWI.

1 Materials and Methods

The experiment was carried out in a sealed glass tube (8 cm × 3 mm, i.d.). The glass tube that contained 2 mg of PCP and/or 2 mg of PCBz was sealed under atmospheric pressure, and then heated in an oven. After cooling to room temperature, the tube was crushed carefully. The reaction products were extracted three times with 20 ml each of *n*-hexane/toluene (20/1 v/v) under ultrasonication and the extracts were combined, and then 10 ml 0.1 mol/L K_2CO_3 solution was added to the extracts. After mixing and layering, the water phase containing chlorophenols was removed. The organic phase was washed three times with 15 ml each of water, and then dried over anhydrous Na_2SO_4 . The sample was concentrated using a rotary evaporator and then cleaned up on an alumina column (25 cm × 8 mm i.d., with basic alumina, which was activated at a temperature of 660°C for 6 h). The column was first eluted with 50 ml *n*-hexane (discarded), then 60 ml *n*-hexane/dichloromethane (49/1 v/v) (LC1), and then 50 ml *n*-hexane/dichloromethane (1/1 v/v) (LC2). The PCDEs fraction (LC1) and the PCDD/Fs fraction (LC2) were concentrated using a rotary evaporator, and then used for GC/MS analysis. Replicates were performed.

An Agilent 6890 GC equipped with 5973 MSD and DB-5 fused-silica capillary column (30 m × 1.2 mm i.d., 0.25 µm film thickness, J&W) was used for identification and quantification of reaction products. Identification of the compounds was based on the scan mode. The quantitative analyses of PCDEs and PCDD/Fs were based on the selected-ion monitoring (SIM) mode using two most abundant ions of PCDEs and PCDD/Fs molecular ion clusters. The quantification was done by external standards.

2 Results and Discussion

2.1 Formation of PCDEs from the condensation of PCP with hexachlorobenzene

The main products of pyrolysis of the mixture of PCP and hexachlorobenzene (HCB) at 340°C for 4 h were decachlorodiphenyl ether (DCDE) and octachlorodibenzo-*p*-dioxins (OCDD) in this study. The EI mass spectra of DCDE are presented in Fig. 1. The characteristic features of the mass spectra of DCDE were the chlorine clusters of molecular ion (M^+) and fragment ion ($M-2Cl$)⁺. The latter was the base peak for the DCDE that had *ortho*-chlorines in its molecule (Nevalainen et al. 1994).

Fig. 2 illustrates the amounts of DCDE and OCDD formed from the pyrolysis of various samples at 340°C for 6 h. There was significant variation in the amount of DCDE in the three cases. The amount of DCDE formation from the pyrolysis of the mixture of PCP and HCB was 4.65 times higher than the total amount of DCDE formation from the pyrolysis of HCB and PCP, respectively. This phenomenon indicated that PCP and HCB were prone to condensation to form of DCDE. In conclusion, experimental observation confirmed that the condensation of chlorophenols with chlorobenzenes occurred via biphenyl ethers.

Fig. 1: Mass fragmentogram of DCDE and OCDD from the condensation of PCP with HCB at 340°C for 4 h (Peak assignment: 1= DCDE, 2=OCDD)

Fig. 2: The formation of DCDE and OCDD under different conditions (340°C, 6 h, 2 mg HCB, 2 mg PCP, 2 mg PCP + 2 mg HCB)

The pyrolysis of HCB at 340°C for 6 h led to the formation of DCDE (2.41 µg/mg) and OCDD (0.24 µg/mg). The amount of DCDE was noticeably higher than the amount of OCDD. This can be explained that chlorophenols formed by oxidation of HCB could possibly serve as reaction intermediates and condensate with the initial chlorobenzenes, and their condensation was preferred to form PCDEs.

The pyrolysis of PCP at 340°C for 6 h yielded DCDE (13.08 µg/mg) and OCDD (180.13 µg/mg). DCDE could be formed by the elimination of H₂O between two PCP molecules. It was obvious that the formation of OCDD by condensation of PCP was a precedence pathway.

Table 1 presents the analytical results of PCDEs and PCDD/Fs from pyrolysis of the mixture of PCP and HCB for 30 min. Table 1 contains the experimental results obtained as a function of three temperature profiles. PCDEs, PCDD/Fs congeners together with their sums (ΣPCDE, ΣPCDD, ΣPCDF) were given in the table. The main product among the PCDEs was DCDE. Nonachlorodiphenyl ether (NCDE), which represented only 6.95% of ΣPCDE, was observed at 450°C. Meanwhile, octachlorodibenzofuran (OCDF), heptachlorodibenzofuran (HpCDF), OCDD and heptachlorodibenzo-*p*-dioxin (HpCDD) were observed from pyrolysis of PCP and HCB.

Table 1: Formation of PCDEs and PCDD/Fs from pyrolysis of PCP and HCB for 30 min (PCP: HCB =1:1) (ng/mg)

Congeners	340°C	400°C	450°C
DCDE	5,773	17,558	3,330
2,2',3,3',4,4',5,5',6-NCDE	n.d.	n.d.	189
2,2',3,3',4,4',5,6,6'-NCDE	n.d.	n.d.	60
ΣNCDE	n.d.	n.d.	249
ΣPCDE	5,773	17,558	3,579
OCDF	n.m.	6,735	11,610
1,2,3,4,6,7,8-HpCDF	n.m.	495	828
ΣPCDF	n.m.	7,230	12,438
OCDD	13,105	72,465	58,890
1,2,3,4,6,7,8-HpCDD	150	1,925	1,078
1,2,3,4,6,7,9-HpCDD	77	1,608	1,005
ΣHpCDD	227	3,533	2,083
ΣPCDD	13,332	75,998	60,973

n.d. < 10 ng/mg; n.m. = not measured

On the basis of this study and the previous research works (Louw and Ahonkhai 2002, Bozzelli et al. 1991), the formation pathway of PCDEs from condensation of PCP and HCB was depicted as follows. The initiation pathway appeared to be the formation of pentachlorophenoxy radicals by loss of the hydroxyl-hydrogen, the pentachlorophenoxy radicals then displaced the Cl atom of HCB to form DCDE. Simultaneously, the pentachlorophenoxy radicals displaced OH of PCP to form DCDE. At a higher temperature, two isomers of NCDE were formed by dechlorination reaction.

2.2 Formation of PCDEs from the condensation of PCP with 1,2,4,5-tetrachlorobenzene

The concentrations of PCDEs together with PCDD/Fs formation from pyrolysis of PCP and 1,2,4,5-tetrachlorobenzene (Cl₄Bz) were measured as a function of temperature profiles (Table 2). A high concentration of 2,2',3,4,4',5,5',6-octachlorodiphenyl ether (OCDE) was detected, and OCDE

Table 2: Formation of PCDEs and PCDD/Fs from pyrolysis of PCP and 1,2,4,5-Cl₄Bz for 30 min (PCP: Cl₄Bz = 1:1) (ng/mg)

Congeners	340°C	400°C	450°C
DCDE	148	330	2,258
2,2',3,3',4,4',5,5',6-NCDE	n.d.	n.d.	n.d.
2,2',3,4,4',5,5',6-OCDE	29,540	31,698	51,573
2,2',3,4,4',5,5'-HpCDE	n.d.	n.d.	808
2,3,3',4,4',5,6-HpCDE	n.d.	n.d.	483
ΣHpCDE	n.d.	n.d.	1,291
2,3,3',4,4',5-HxCDE	n.d.	n.d.	2,290
ΣPCDE	29,688	32,028	57,412
OCDF	n.d.	n.d.	4,620
1,2,3,4,6,7,8-HpCDF	n.d.	n.d.	255
1,2,3,4,6,8,9-HpCDF	n.d.	n.d.	1,735
ΣHpCDF	n.d.	n.d.	1,990
1,2,3,4,7,8-HxCDF	n.d.	n.d.	320
1,2,3,6,8,9-HxCDF	n.d.	63	100
1,2,4,6,7,8-HxCDF	n.d.	n.d.	508
1,2,3,4,6,8-HxCDF	n.d.	n.d.	45
ΣHxCDF	n.d.	63	973
PeCDF ^a	n.d.	n.d.	25
TCDF ^a	n.d.	n.d.	280
ΣPCDF	n.d.	63	7,888
OCDD	9,370	30,150	36,130
1,2,3,4,6,7,8-HpCDD	175	174	4,845
1,2,3,4,6,7,9-HpCDD	83	135	2,355
ΣHpCDD	258	309	7,200
1,2,3,4,7,8-HxCDD	73	84	4,274
1,2,4,7,8-PeCDD	n.d.	n.d.	61
1,2,3,7,8-PeCDD	n.d.	n.d.	69
ΣPeCDD	n.d.	n.d.	130
2,3,7,8-TCDD	n.d.	n.d.	24
ΣPCDD	9,701	30,543	47,758

^a Substitution pattern of congener not identified; n.d. < 10 ng/mg

yield increased with the increasing reaction temperature. Small amounts of 2,2',3,4,4',5,5'-heptachlorodiphenyl ether (HpCDE), 2,3,3',4,4',5,6-HpCDE and 2,3,3',4,4',5-hexachlorodiphenyl ether (HxCDE) were also detected at 450°C. A low level of DCDE was found at different temperatures. The condensation of PCP with 1,2,4,5-Cl₄Bz to form OCDE was the main reaction, while the condensation of two PCP molecules to form DCDE was an inferior reaction.

Small amounts of PCDFs homologues were observed from the condensation of PCP and 1,2,4,5-Cl₄Bz at 450°C. The PCDFs products included HpCDF, hexachlorodibenzofuran (HxCDF), pentachlorodibenzofuran (PeCDF) and tetrachlorodibenzofuran (TCDF). The formation of OCDD, HpCDD and hexachlorodibenzo-*p*-dioxin (HxCDD) were also observed at three temperature profiles, and small amounts of pentachlorodibenzo-*p*-dioxin (PeCDD) and tetrachlorodibenzo-*p*-dioxin (TCDD) were detected at 450°C.

The formation pathway of PCDEs from the condensation of PCP with 1,2,4,5-Cl₄Bz can be explained as follows. The pentachlorophenoxy radicals displaced the Cl atom of 1,2,4,5-Cl₄Bz to form 2,2',3,4,4',5,5',6-OCDE. Slight amounts of 2,2',3,4,4',5,5'-HpCDE, 2,3,3',4,4',5,6-HpCDE and 2,3,3',4,4',5-HxCDE were formed by dechlorination reaction at 450°C. At the same time, DCDE was formed by the elimination of H₂O between two PCP molecules. On the basis of the present study, the speculated pathways of formation of PCDEs from condensation of polychlorophenols and PCBz were depicted in Fig. 3. The condensation of polychlorophenols with PCBz can be a radical/molecule reaction mechanism. Polychlorophenoxy radicals were formed owing to the oxidation of oxygen under heated conditions, then polychlorophenoxy radicals addition reactions to chlorobenzene or chlorophenol formed the ether linkages and, following the elimination of chlorination or hydroxyl, respectively, PCDEs were formed. These radicals were important intermediate products. Further studies should be conducted to elucidate their detailed processes.

Fig. 3: Formation mechanism of PCDEs from the condensation of polychlorophenols and PCBz

3 Conclusions

In the current study, formation pathways of PCDEs from condensation of polychlorophenols and PCBz are experimentally verified. The condensation of polychlorophenols with PCBz forms PCDEs through elimination of HCl between polychlorophenols and PCBz molecules. Another pathway of PCDEs formation is elimination of H₂O between two polychlorophenol molecules. Furthermore, dechlorination processes cause the specific homologue pattern of PCDEs under higher temperatures.

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