

The formation of coplanar PCBs, PCDDs and PCDFs in a fly-ash model system.

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INTRODUCTION

PCDDs and PCDFs are trace compounds formed during the incineration of municipal waste¹. Recently coplanar PCBs were also detected in the fly ash and flue gas of a municipal waste incinerator^{2,3}. For PCDDs and PCDFs two main formation routes have been postulated, de novo synthesis from particulate organic carbon and formation from chlorinated precursors⁴. In this paper we present a method for simultaneous determination of PCDDs, PCDFs as well as coplanar PCBs. We also present the results of a study of the de novo synthesis of these compounds.

EXPERIMENTAL

Extraction, clean up and GC/MS analysis

Coplanar PCBs and PCDD/Fs can not be quantified in the same sample by GC-MSD due to an overlap in masses and retention times. We have modified the standard procedure for extraction and clean up of PCDDs and PCDFs⁵ to separate the coplanar PCBs from the PCDDs and PCDFs.

Besides a solution of ¹³C labeled PCDDs and PCDFs, 200 μ l of a solution of three ¹³C labeled coplanar PCBs (3,3',4,4'-, 3,3',4,4',5- and 3,3',4,4',5,5'-PCB) was added as internal standard. After soxhlet extraction, the extract was concentrated to a few milliliters and brought onto a column (i.d. = 10 mm), filled -from top to bottom- with 2 cm 22% H₂SO₄ on silica, 9 cm 44% H₂SO₄ on silica, 1 cm silica, 8 cm 33% 1N NaOH on silica and 2 cm AgNO₃ on silica. The column was eluted with 50 ml hexane and the hexane was evaporated.

The coplanar PCBs are separated from the non-planar PCBs with activated carbon: the PCBs, PCDDs and PCDFs were dissolved in 20 ml dichloromethane. This was brought onto a column (i.d.= 1 cm) filled with activated carbon, which was then eluted with refluxing dichloromethane for 1 hour. The dichloromethane now contains the non-planar PCBs. The column was turned upside down and eluted for 24 hours with toluene. The toluene fraction was concentrated to a few milliliters and brought onto a column (i.d. = 6 mm) filled with 4.5 g Al₂O₃, to separate the P₅CB and the H₆CB from the PCDDs and PCDFs. The column was eluted with 150 ml 10% CCl₄ in hexane. This fraction contains

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the P₅CB, H₆CB and some T₄CB. Afterwards the column was eluted with 30 ml dichloromethane, which contains the T₄CB, PCDDs and PCDFs. The dichloromethane fraction was evaporated to dryness.

A HPLC is used for the separation of T₄CB from the PCDDs and PCDFs: the PCBs, PCDDs and PCDFs from the dichloromethane fraction of the aluminum oxide column were dissolved in 50 µl CHCl₃ and injected into a HPLC. The first fraction contains the T₄CB, the second fraction contains the PCDDs and PCDFs except the O₆CDF which is in the third fraction. This has been described before⁵.

The PCBs, PCDDs and PCDFs were identified and quantified with GC-MSD. The PCBs and O₆CDF on a J & W DB-5 column, the other PCDDs and PCDFs on a Supelco SP 2331. This has also been described before⁵.

De novo synthesis

Alumina was impregnated with 5.4% KCl, 0.83% CuCl₂ and 5.4% activated carbon, and heated at different temperatures (200°C, 250°C, 300°C, 350°C, 400°C) in a glass tube under a flow of 50 ml/min technical air for 2 hours, as described before⁵. Each experiment was performed three times.

RESULTS AND DISCUSSION

In four blank experiments (extraction and clean up of ¹³C labeled PCDDs, PCDFs and coplanar PCBs) only trace amounts of O₆CDD, O₆CDF and T₄CB were found (439, 94 and < 28 pg/g respectively).

In table 2 the amounts of PCDDs, PCDFs and coplanar PCBs during de novo synthesis at 300°C, 350°C and 400°C are given. At 200°C and 250°C only trace amounts of a few PCB, PCDD and PCDF congeners could be detected. The 3,3',4,4',5-P₅CB and the 3,3',4,4',5,5'-H₆CB were not detected. The formation of PCDDs and PCDFs reaches maximum around 350°C. This is in agreement with the results of Addink⁶ and Stieglitz⁷. Ross⁸ and Vogg⁹ both found an optimum reaction temperature of 300°C. Differences in reaction conditions could explain the various optimum temperatures found. 3,3',4,4'-T₄CB has a maximum formation at the same temperature region as the PCDDs and PCDFs. Therefore we expect those compounds will be formed by similar reactions.

The T₄CB/T₄CDF ratio is lower at 350°C than at 300°C and 400°C. Values found at 300°C and 400°C do not differ significantly. As formation reaches maximum at 350°C, the lowest ratio is found at the highest absolute concentrations of PCBs, PCDDs and PCDFs. The same seems to be true for the T₄CB/T₄CDD ratio, but here the differences are not significant.

The ratio between PCDDs and PCDFs decreases slightly with increasing temperature. Addink⁶ found a decrease in PCDD/PCDF ratio going from 250°C to 300°C, but with the results of Vogg⁹ we found no correlation between the temperature and the PCDD/PCDF ratio.

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Table 2 Amount of PCDDs, PCDFs and coplanar PCBs formed at different reaction temperatures (ng/g). nd = not detected, detection limit T₁CDD = 5.2, P₅CDD = 11, H₆CDD = 19, H₇CDD = 21, O₈CDD = 52, T₁CDF = 6.2, P₅CDF = 11, H₆CDF = 13, H₇CDF = 17, O₈CDF = 38, T₁CB = 26, P₃CB = 60, H₆CB = 15 pg/g.

	300°C		350°C		400°C	
		STD		STD		STD
T ₁ CDD	0.061	*	0.11	0.06	nd	
P ₅ CDD	nd		0.8	0.3	nd	
H ₆ CDD	nd		2.3	1.1	0.08	0.02
H ₇ CDD	0.101	0.013	2.8	1.5	0.52	0.16
O ₈ CDD	nd		5	3	1.6	0.6
total PCDD	0.52	0.03	11	6	2.2	0.8
T ₁ CDF	0.9	0.3	11	3	1.0	0.2
P ₅ CDF	0.5	0.2	17	9	2.1	0.8
H ₆ CDF	0.32	0.03	27	*	3.9	1.2
H ₇ CDF	0.24	0.04	15	9	5.6	1.0
O ₈ CDF	0.536	0.019	14	8	4.5	1.4
total PCDF	2.5	0.5	74	33	17	4
PCDD+PCDF	3.1	0.5	85	39	19	5
3,3',4,4'-T ₁ CB	0.094	0.017	0.15	0.08	0.072	°
T ₁ CB/T ₁ CDD	1.7	0.6	1.56	0.93		
T ₁ CB/T ₁ CDF	0.11	0.03	0.015	0.005	0.06	
PCDD/PCDF	0.21	0.03	0.15	0.05	0.124	0.015

* n=2, range = 0.023 ng/g, * n=2, range = 11 ng/g, ° n=1.

With increasing temperature, more higher chlorinated PCDF congeners are formed. This tendency is also seen with the PCDDs, but less clear. At 350°C and 400°C most octa chlorinated dioxin is formed. For dibenzofurans the hexa and hepta congeners are formed most and for the PCBs only the tetrachlorinated congener is formed. So there is a shift towards lower chlorinated congeners with decreasing internal oxygen. This suggests an

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electrophilic aromatic substitution because oxygen is activating the aromatic ring towards electrophilic substitution.

CONCLUSIONS

Coplanar PCBs are formed from particulate organic carbon in a fly ash model system, via so-called de-novo synthesis.

The formation of PCDDs, PCDFs as well as coplanar PCBs reaches maximum around 350°C.

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