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DOI

[10.1016/0045-6535\(95\)00038-A](https://doi.org/10.1016/0045-6535(95)00038-A)

Publication date

1995

Published in

Chemosphere

[Link to publication](#)

Citation for published version (APA):

Schoonenboom, M. H., Tromp, P. C., & Olie, K. (1995). The formation of coplanar PCBs, PCDDs and PCDFs in a fly ash model system. *Chemosphere*, 30, 1341-1349.
[https://doi.org/10.1016/0045-6535\(95\)00038-A](https://doi.org/10.1016/0045-6535(95)00038-A)

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THE FORMATION OF COPLANAR PCBs, PCDDs AND PCDFs IN A FLY ASH MODEL SYSTEM

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(Received in Germany 11 November 1994; accepted 22 December 1994)

ABSTRACT

Coplanar PCBs as well as PCDDs and PCDFs are formed from particulate organic carbon on an alumina support. The formation of all three of these compounds reaches its maximum around 350°C. The 3,4,6,7-substituted PCDD and PCDF congeners are the predominant congeners formed, indicating a side by side chlorination of the carbon, after which oxidative breakdown of the chlorinated carbon skeleton to PCDDs and PCDFs can take place.

INTRODUCTION

PCDDs and PCDFs are trace compounds formed during the incineration of municipal waste¹. Two main formation routes have been postulated, de novo synthesis from particulate organic carbon and formation from chlorinated precursors². Recently coplanar PCBs were also detected in the fly ash and flue gas of municipal waste incinerators^{3,4}. It is important to study coplanar PCBs at the same time with PCDDs and PCDFs because of their similar toxicological behavior.

It is not known yet whether these compounds are formed in the incineration process, as the PCDDs and PCDFs, or already are present in the waste and survive the incineration process. Stieglitz et al.⁵ have shown that PCBs (as a group) are formed from particulate organic carbon in a fly ash model system. For coplanar PCBs we can also expect this behavior. In this paper we present a method for simultaneous determination of PCDDs, PCDFs as well as coplanar PCBs and its application to the study of the de novo synthesis of these compounds at different temperatures. We are also looking at the isomer distribution of the PCDDs and PCDFs in order to get a better understanding of the formation mechanism of these compounds.

EXPERIMENTAL

Extraction, clean up and GC/MS analysis

Coplanar PCBs and PCDD/Fs cannot be quantified in the same sample by GC-MSD due to an overlap in masses and retention times, as can be seen in Table 1. We have modified the standard procedure for extraction and clean up of PCDDs and PCDFs⁶ to separate the coplanar PCBs from the PCDDs and PCDFs.

Table 1 Mass and retention overlap for coplanar PCBs with PCDDs and PCDFs.^c

Mass	PCBs			PCDD/Fs		
	*		RT ^b			RT ^b
323.9 325.9 327.9	M M+2 M+4	¹² C P ₅ CB	24.8	M+4 M+6 M+8	¹² C T ₄ CDD	17.4-25.6
357.8/357.9 359.8/359.9 361.8/361.9	M M+2 M+4	¹² C H ₆ CB	30.4	M+4 M+6 M+8	¹² C P ₅ CDD	22.8-30.2
303.9 305.9 307.9	M+2 M+4 M+6	¹³ C T ₄ CB	20.7	M M+2 M+4	¹² C T ₄ CDF	16.7-27.8
337.9 339.9 341.9	M+2 M+4 M+6	¹³ C P ₅ CB	24.8	M M+2 M+4	¹² C P ₅ CDF	21-33
371.8 373.8 375.8	M+2 M+4 M+6	¹³ C H ₆ CB	30.4	M M+2 M+4	¹² C H ₆ CDF	27.6-42

* M is the molecular mass when all chlorine atoms are present as ³⁵Cl-isotope, M+2 is the molecular mass with one ³⁷Cl-isotope, etc.

* RT = retention time (min)

^cThere is also an overlap in mass and retention time for P_xCB with the -Cl fragment of P_xCDD with one ¹³C atom. The response of this mass will be very low for PCDD, because it is a minor peak in the mass spectrum of a PCDD molecule.

Besides a solution of ¹³C labeled PCDDs and PCDFs, 200 µl 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 an 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 were 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 (Carbosphere, 80-100 mesh, Chrompack, Middelburg, The Netherlands), which then was eluted by hot dichloromethane for 1 hour. The dichloromethane then contained the non-planar PCBs. The column was turned upside down and eluted for 24 hours with hot toluene. The toluene fraction was concentrated to a few milliliters and brought onto a column (i.d. = 6 mm) filled with 4.5 g Al_2O_3 , to separate the P_3CB and the H_6CB from the PCDDs and PCDFs. Subsequently the column was eluted with 150 ml 10% CCl_4 in hexane. This fraction contained the P_3CB , H_6CB and some T_4CB . Afterwards the column was eluted with 30 ml dichloromethane, which contained the T_4CB , PCDDs and PCDFs. The dichloromethane fraction was evaporated to dryness.

A reversed phase HPLC was used for the separation of T_4CB from the PCDDs and PCDFs. The PCBs, PCDDs and PCDFs from the dichloromethane fraction of the aluminum oxide column were dissolved in 50 μl CHCl_3 and injected into a HPLC. The first fraction contained the T_4CB (6-12 min = 13.8 ml), the second fraction contained the PCDDs and PCDFs (15-58 min = 101.9 ml) except the O_8CDF which was in the third fraction (69-74 min = 11.5 ml). This was described elsewhere⁶.

The PCBs, PCDDs and PCDFs were identified and quantified with GC-MSD. The PCBs and O_8CDF on a J & W DB-5 column, the other PCDDs and PCDFs on a Supelco SP 2331. This was applied in earlier experiments⁶.

Detection limits (pg) for the PCB-, PCDD- and PCDF-congeners are $\text{T}_4\text{CDD} = 26$, $\text{P}_3\text{CDD} = 55$, $\text{H}_6\text{CDD} = 97$, $\text{H}_7\text{CDD} = 105$, $\text{O}_8\text{CDD} = 260$, $\text{T}_4\text{CDF} = 31$, $\text{P}_3\text{CDF} = 55$, $\text{H}_6\text{CDF} = 65$, $\text{H}_7\text{CDF} = 85$, $\text{O}_8\text{CDF} = 190$, $\text{T}_4\text{CB} = 130$, $\text{P}_3\text{CB} = 300$, $\text{H}_6\text{CB} = 75$.

De novo synthesis

Alumina was impregnated with 5.4% KCl, 0.83% CuCl_2 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 previously⁶. Each experiment was performed in triplicate.

RESULTS AND DISCUSSION

In four blank experiments (extraction and clean up of ^{13}C labeled PCDDs, PCDFs and coplanar PCBs) only trace amounts of O_8CDD , O_8CDF and T_4CB 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- P_3CB and the 3,3',4,4',5,5'- H_6CB were not detected in all experiments. The formation of PCDDs and PCDFs reaches its maximum around 350°C. This is in agreement with the results of Addink⁷ and Stieglitz⁸. Ross⁹ and Vogt¹⁰ both found an optimum reaction temperature of 300°C. Differences in reaction conditions could explain the various optimum temperatures found. 3,3',4,4'- T_4CB has a maximum formation at the same temperature region as the PCDDs and PCDFs. Therefore we expect that coplanar PCBs are formed by similar reactions as PCDDs and PCDFs.

Table 2 Amount of PCDDs, PCDFs and coplanar PCBs formed at different reaction temperatures (ng/g).

	300°C		350°C		400°C	
		STD		STD		STD
T ₄ CDD	0.10	0.04*	0.11	0.06	nd	
P ₃ CDD	nd		0.8	0.3	nd	
H ₆ CDD	nd		2.3	1.1	0.068	0.017
H ₇ CDD	0.095	0.011	2.8	1.5	0.52	0.16
O ₈ CDD	nd		5	3	1.6	0.6
total PCDD	0.16	0.06	11	6	2.2	0.8
T ₄ CDF	0.9	0.3	11	3	1.0	0.3
P ₃ CDF	0.6	0.2	17	8	2.0	0.7
H ₆ CDF	0.356	0.013	27	11*	3.8	1.3
H ₇ CDF	0.26	0.02	15	9	5.6	1.1
O ₈ CDF	0.536	0.019	14	8	4.5	1.4
total PCDF	2.6	0.5	83	39*	17	4
PCDD+PCDF	2.7	0.5	85	39*	19	5
3,3',4,4'-T ₄ CB	0.094	0.017	0.15	0.08	0.072	@
T ₄ CB/T ₄ CDD	1.1	0.2*	1.6	0.8		
T ₄ CB/T ₄ CDF	0.11	0.04	0.015	0.005	0.06	
PCDD/PCDF	0.061	0.011	0.121	0.018	0.125	0.016

STD = standard deviation of three experiments, * range of two experiments, @ single experiment

nd = not detected (for detection limits see experimental section).

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. For the T₄CB/T₄CDD ratio results are not conclusive.

The ratio between PCDDs and PCDFs increases slightly with increasing temperature. This is not in agreement with temperature studies in the literature. Addink⁷ found a sharp decrease in PCDD/PCDF ratio going from 250°C to 300°C and a slight decrease going from 300°C to 350°C, but with the results of Vogg¹⁰ we found no correlation between the temperature and the PCDD/PCDF ratio. The difference in [PCDD]:[PCDF] ratio between 300°C and 350°C in this study can be due to the fact that we found only a few PCDD congeners at 300°C. When a lot of not detected PCDD congeners have concentrations just below the detection limit, the total PCDD concentration can be underestimated giving rise to low [PCDD]:[PCDF] ratio's.

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 octa chlorinated dioxin is formed predominantly. For dibenzofurans

the hexa and hepta congeners are formed most and for the PCBs only the tetrachlorinated congener is formed. So when we assume that coplanar PCBs act in the same way as all the other PCBs, there is a shift towards lower chlorinated congeners with decreasing internal oxygen. The internal oxygen is increasing going from PCB via PCDF to PCDD. The degree of chlorination is also increasing going from PCB via PCDF to PCDD. This suggests an electrophilic aromatic substitution because oxygen is activating the aromatic ring towards electrophilic substitution.

Table 3 Percentage of a PCDD/PCDF isomer relative to one (or more) isomer(s)¹ at different temperatures. For each homologue group the concentrations of all isomers are calculated with respect to one isomer (or group of isomers) of the group.

¹ T₄CDD: 1,2,3,4-, 1,2,3,7-, 1,2,3,8-, 1,2,4,6- and 1,2,4,9- T₄CDF: 3,4,6,7- P₅CDD: 1,2,3,8,9- P₅CDF: 2,3,4,6,7- H₆CDD: 1,2,3,4,6,7- H₆CDF: 1,2,3,4,6,7- H₇CDD: 1,2,3,4,6,7,8- H₇CDF: 1,2,3,4,6,7,8-

When more than one isomer is given, the concentration of these isomers is given as the sum.

	300°C		350°C		400°C			300°C		350°C		400°C	
T ₄ CDD		STD		STD		STD	T ₄ CDF		STD		STD		STD
1,3,7,9-	33	5*	nd		nd		1,2,3,8- 1,4,6,7- 2,4,6,8- 1,2,3,6-	6.8	0.5*	0.8	0.6	9	5
1,3,7,8-	35	6*	nd		nd		1,2,7,8-	6.8	0.5	2.5	1.3	6.0	0.3
1,3,6,9- 1,2,4,7- 1,2,4,8-	35	7*	nd		nd		1,2,6,7- 1,2,7,9-	9.9	1.1*	1.6	0.7	4	3
1,2,6,8-	23	4*	nd		nd		1,2,4,9-	6.0	1.0*	nd		2.2	0.4*
2,3,7,8-	nd		72	14	nd		2,4,6,7-	15.3	1.4	6	3	8.1	0.6
1,2,3,4- 1,2,3,7- 1,2,3,8- 1,2,4,6- 1,2,4,9-	100	0*	100	0	nd		1,2,3,9- 2,3,4,7-	12.1	1.6	5.7	1.9	8.3	0.6
1,2,3,6- 1,2,7,9-	26.6	1.9*	58	15*	nd		2,3,7,8- 2,3,4,8-	8.8	0.5	3.3	0.6	4.52	0.007*
1,2,8,9-	nd		111	14	nd		2,3,4,6-	18.2	0.2	10	3	13.0	1.3
T ₄ CDF							2,3,6,7-	20.5	1.5	20	4	19.0	0.5
1,3,7,8- 1,3,7,9-	4.3	0.2*	0.41	0.14*	5.3	1.4	3,4,6,7-	100	0	100	0	100	0
1,3,4,6- 1,2,4,8-	nd		nd		2.5	1.6	1,2,8,9-	nd		2.79	0.13	nd	
1,2,6,8- 1,2,3,7- 1,4,7,8- 1,3,6,9-	4.14	0.16*	1.4	0.2*	5	3							

	300°C		350°C		400°C			300°C		350°C		400°C	
P ₂ CDD							H ₆ CDD						
1,2,3,7,8-	nd		80	30	nd		1,2,4,6,7,9- 1,2,4,6,8,9- 1,2,3,4,6,8-	nd		13	3*	nd	
1,2,4,8,9- 1,2,4,6,7-	nd		50	20	nd		1,2,3,6,7,9- 1,2,3,6,8,9-	nd		37	15	nd	
1,2,3,4,6- 1,2,3,6,7-	nd		50	20	nd		1,2,3,4,7,8- 1,2,3,6,7,8-	nd		46	10	nd	
1,2,3,8,9-	nd		100	0	nd		1,2,3,7,8,9-	nd		50	15	nd	
P ₃ CDF							1,2,3,4,6,7-	nd		100	0	100	0
2,3,4,7,9-	nd		nd		5	2*	H ₆ CDF						
1,3,4,7,8- 1,2,3,6,8-	4.3	0.9*	nd		8	6	1,2,3,4,6,8-	12.2	0.9*	nd		nd	
1,2,4,7,8-	3.77	0.19*	nd		5	2	1,3,4,6,7,8- 1,3,4,6,7,9-	50	20	nd		71	16
1,3,4,6,7- 1,2,4,7,9-	12.6	1.8*	nd		19	10	1,2,4,6,7,8-	26	9	nd		26	10
1,2,4,6,7-	4.4	0.6*	nd		7	3	1,2,4,6,7,9-	nd		nd		7.6	0.9*
1,2,3,4,7- 2,3,4,6,9-	8.2	1.3*	nd		13	5	1,2,3,4,7,8- 1,2,3,4,7,9- 1,2,3,6,7,8- 1,2,4,6,8,9-	89	8	50	11	64	4
1,2,3,4,8- 1,2,3,7,8-	9	2	6.8	0.5	15.0	1.3	1,2,3,4,6,7-	100	0	100	0	100	0
1,2,3,4,6-	5.2	0.9*			8.9	0.7*	1,2,3,6,7,9-	nd		nd		6.2	1.1
1,2,3,7,9-	nd		1.38	0.17*	3.8	0.9	1,2,3,4,6,9- 1,2,3,6,8,9-	54	15	38	18	16.2	1.2
1,2,3,6,7-	11	3	3.4	1.3*	19.3	1.5	1,2,3,7,8,9-	nd		50	60	8.4	0.5
1,2,4,6,9- 2,3,4,8,9-	10	2	1.6	0.8*	18.0	1.2	1,2,3,4,8,9-	41	14	120	110	16.0	1.8
1,3,4,8,9-	3.22	0.15*	nd		5.4	0.8	2,3,4,6,7,8-	100	50	340	380	28.8	1.4
1,2,3,6,9- 2,3,4,6,8-	11	3*	2.2	1.5	8	2	H ₇ CDD						
1,2,3,4,9-	4.0	0.4*	0.6	0.2*	3.5	1.7	1,2,3,4,6,7,9-	90	16	41	2	80	8
1,2,4,8,9-	4.4	0.7*	1.4	1.2	3.9	1.1	1,2,3,4,6,7,8-	100	0	100	0	100	0
2,3,4,7,8-	12.7	0.7	8	2	13.3	0.6	H ₇ CDF						
1,2,3,8,9-	nd		4.0	0.3	3.83	0.16	1,2,3,4,6,7,8-	100	0	100	0	100	0
2,3,4,6,7-	100	0	100	0	100	0	1,2,3,4,6,7,9-	30	5	12	7	15.0	1.2
							1,2,3,4,6,8,9-	23	3	16	2	6.3	0.8
							1,2,3,4,7,8,9-	17	3*	24	16	13	17

STD = standard deviation of three experiments * Range (n=2)

nd = not detected (for detection limits see experimental section)

In table 3 the isomer distribution at different temperatures is given. Mainly 3,4,6,7-substituted PCDF congeners are formed, especially at 350°C, as is shown in figure 1. The 3,4,6,7-substituted dioxins are also formed most, but only at 350°C, as can be seen in figure 2.

This indicates a two stage mechanism as is described before by Heinbuch and Stieglitz¹¹ for brominated compounds. The first step is the chlorination of the surface of carbon. After that the second step is the oxidative decomposition of the chlorinated carbon yielding side by side chlorinated PCDDs and PCDFs. Earlier in this paper we suggested chlorination by an electrophilic aromatic substitution mechanism. The 3,4,6,7-substitution we found is not in agreement with the 2,3,7,8-substitution of electrophilic aromatic substitution. This 2,3,7,8-substitution however is based on chlorination of free PCDD and PCDF molecules. In the case of a two stage mechanism chlorination takes place before the release of PCDD/F molecules and therefore do not necessarily give 2,3,7,8-substitution.

Figure 1 Most abundant PCDF congeners formed at 350°C. The arrows indicate a possible chlorination/dechlorination route.

Figure 2 Most abundant PCDD congeners formed at 350°C. The arrows indicate a possible chlorination/ dechlorination route.

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 its maximum around 350°C.

There is a shift towards lower chlorinated congeners with decreasing internal oxygen (PCDD-PCDF-PCB). This suggests an electrophilic aromatic substitution.

The 3,4,6,7-substituted PCDF (and PCDD) congeners are the predominant congeners formed, especially at 350°C. This indicates a two stage mechanism of chlorination and oxidation of the carbon yielding side by side chlorinated PCDDs and PCDFs.

In summary the mechanism of formation of PCDDs, PCDFs and coplanar PCBs possibly proceeds via a two stage mechanism. The first step is chlorination of the surface of carbon by electrophilic aromatic substitution. After that the second step is oxidative decomposition of the chlorinated carbon yielding side by side chlorinated PCDDs and PCDFs.

ACKNOWLEDGEMENT

We would like to thank Pieter C. Slot and Martin J.M. van Velzen for performing the GC/MS analysis, and Ruud Addink and Harrie A.J. Govers for critically reading the manuscript.

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