UvA-DARE (Digital Academic Repository)

Dechlorination of octachlorodibenzo-p-dioxin and octachlorodibenzofuran on an alumina support.

Schoonenboom, M.H.; Zoetemeijer, H.E.; Olie, K.

DOI

[10.1016/0926-3373\(94\)00055-7](https://doi.org/10.1016/0926-3373(94)00055-7)

Publication date

1995

Published in

Applied Catalysis B-Environmental

[Link to publication](#)

Citation for published version (APA):

Schoonenboom, M. H., Zoetemeijer, H. E., & Olie, K. (1995). Dechlorination of octachlorodibenzo-p-dioxin and octachlorodibenzofuran on an alumina support. *Applied Catalysis B-Environmental*, 6, 11-20. [https://doi.org/10.1016/0926-3373\(94\)00055-7](https://doi.org/10.1016/0926-3373(94)00055-7)

General rights

It is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), other than for strictly personal, individual use, unless the work is under an open content license (like Creative Commons).

Disclaimer/Complaints regulations

If you believe that digital publication of certain material infringes any of your rights or (privacy) interests, please let the Library know, stating your reasons. In case of a legitimate complaint, the Library will make the material inaccessible and/or remove it from the website. Please Ask the Library: <https://uba.uva.nl/en/contact>, or a letter to: Library of the University of Amsterdam, Secretariat, Singel 425, 1012 WP Amsterdam, The Netherlands. You will be contacted as soon as possible.

Dechlorination of octachlorodibenzo-*p*-dioxin and octachlorodibenzofuran on an alumina support

Mirjam H. Schoonenboom *, Hans E. Zoetemeijer, Kees Olie

*Department of Environmental and Toxicological Chemistry, University of Amsterdam,
Nieuwe Achtergracht 166, 1018 WV Amsterdam, Netherlands*

Received 24 August 1994; revised 26 October 1994; accepted 26 October 1994

Abstract

We have studied the dechlorination/destruction of octachlorodibenzo-*p*-dioxin and octachlorodibenzofuran on alumina. The acidity of the alumina is an important parameter for the dechlorination of these compounds. Alkaline alumina is a better dechlorination agent than acidic alumina. Metal chlorides are less effective dechlorination catalysts than alumina. The dechlorination of octachlorodibenzo-*p*-dioxin and octachlorodibenzofuran on alumina proceeds probably via an electrophilic substitution mechanism.

Keywords: Acidity; Alumina; Dechlorination; Destruction; OCDD; OCDF; Metal chlorides

1. Introduction

The group of polychlorinated dibenzo-*p*-dioxins (PCDD's) and polychlorinated dibenzofurans (PCDF's) consists of tricyclic compounds substituted with one to eight chlorine atoms (see Fig. 1). This results in 210 different congeners: 75 PCDD congeners and 135 PCDF congeners, differing in number and position of the chlorine atoms¹. The positions of the chlorine atoms are numbered according to Fig. 1. When all 2,3,7,8-places are substituted with chlorine atoms, the compounds are extremely toxic.

De-novo synthesis from carbon is an important reaction pathway in the formation of PCDD's and PCDF's during municipal waste incineration [1,2]. Laboratory

* Corresponding author. Tel. (+31-20) 5256504, fax. (+31-20) 5255698.

¹ The number of chlorine atoms in the abbreviation of PCDD's and PCDF's is shown by the first character. M-mono, D-di, T-tri or tetra, P-penta, H-hexa or hepta and O-octa. This might be followed by a number, e.g. D₂CDD is a dibenzo-*p*-dioxin substituted with 2 chlorine atoms, T₄CDF is a dibenzofuran substituted with 4 chlorine atoms.

Fig. 1. Chemical structures of PCDD's and PCDF's.

experiments with fly ash have shown that PCDD and PCDF formation depends on parameters like reaction time, temperature, copper catalyst and oxygen concentration [2–7]. Also the influence of model supports, like alumina and Mg–Al-silicate, on the formation of these compounds from particulate organic carbon is studied [1,8,9]. The acidity of the alumina support is an important parameter in this formation pathway [8].

Oxygen is essential for de-novo synthesis from carbon. Without oxygen no PCDD and PCDF formation takes place. Under these conditions dechlorination reactions of PCDD's and PCDF's are observed [4,6,7]. In earlier experiments, it was established that alumina catalyzed dechlorination of PCDD's and PCDF's [8].

In order to get a better understanding of the formation process of PCDD's and PCDF's, it is necessary to know more about the behavior of these compounds on fly ash and alumina. Recently, we have looked into the influence of the acidity of the alumina support and the presence of metal chlorides on the dechlorination of octachlorodibenzo-*p*-dioxin (OCDD) and octachlorodibenzofuran (OCDF). OCDD and OCDF were chosen because all PCDD and PCDF congeners can be formed through dechlorination. Some results are presented in this paper.

2. Experimental

2.1. Dechlorination experiments

Alumina was impregnated with a solution of OCDD and OCDF (both 2 $\mu\text{g/g}$ alumina) in hexane and the hexane was evaporated. The impregnated alumina was heated at 275°C in a glass tube at a flow of 16 ml/min nitrogen or technical air for 30 min, as described previously [8]. All volatile organic substances were collected in a washing bottle filled with hexane, placed after the flow tube and cooled with ice. The various reaction conditions are described in Table 1; each experiment was performed in triplicate with the exception of experiment 3 which was performed 10 times and experiment 7 which was performed twice.

The pH of the alumina support was measured by suspending 1 g in 30 ml water, heating for 10 min, filtration and determining the pH of the filtrate with a pH meter [10]. This gave us an indication of the acidity of the alumina support.

2.2. Extraction, clean up and GC/MS analysis

After adding a solution of ^{13}C labeled PCDD's and PCDF's as internal standard, the sample was soxhlet-extracted with toluene. The extract was purified by using

Table 1
Experiments^a

No	Support	Gas composition
1	5 g alkaline alumina (pH = 8.9)	nitrogen
2	5 g neutral alumina (pH = 5.7)	nitrogen
3	5 g acidic alumina (pH = 4.6)	nitrogen
4	5 g alkaline alumina (pH = 8.9)	nitrogen with water
5	5 g alkaline alumina (pH = 8.9)	technical air
6	5 g alkaline alumina (pH = 8.9)	nitrogen
7	5 g alkaline alumina (pH = 8.9) + 0.8 % CuCl ₂	nitrogen
8	5 g alkaline alumina (pH = 8.9) + 0.8 % CuCl	nitrogen
9	0.5 g CuCl	nitrogen
10	0.5 g FeCl ₃	nitrogen
11	0.5 g AlCl ₃	nitrogen

^a The support is impregnated with 2 $\mu\text{g/g}$ OCDD and OCDF, temperature 275°C, reaction time 30 min, gas flow-rate 16 ml/min.

acidic, basic and silver nitrate modified silica gel, and aluminum oxide. After preparative reversed phase HPLC the PCDD's and PCDF's (tetra- to octa-chlorinated congeners) were identified and quantified with GC-MSD. This has been described in earlier experiments [8].

Experiment number 1 was performed again, but now the sample was extracted with toluene on an ultrasound bath. The toluene was evaporated by vacuum distillation. In the remaining extract we have looked for other chlorinated products, besides PCDD's and PCDF's, by GC-MSD in the full scan mode (100–800 AMU).

In some cases we have looked for lower chlorinated PCDD and PCDF congeners (mono- to tri-chlorinated) in the washing bottle after the flow tube (quantification by ¹³C labeled D₂CDD). The clean up of these compounds consists of a small acidic/basic silica column (4 cm) eluted with 15 ml hexane, and an alumina column, eluted with 40 ml hexane, 20 ml 10% CCl₄ in hexane and 30 ml dichloromethane.

3. Results and discussion

In two blank experiments (extraction and clean up of ¹³C labeled PCDD's and PCDF's) only trace amounts of OCDD and OCDF were found (<0.8 ng/g and <0.4 ng/g resp). No PCDD's and PCDF's were found in the washing bottle after the flow tube.

In Table 2 we present the results of the dechlorination of OCDD and OCDF on different kinds of alumina and in different atmospheres.

On alkaline alumina, the OCDD and OCDF are dechlorinated very rapidly in a nitrogen atmosphere. After 30 min less than 1% of the starting material is left. Besides OCDD and OCDF only trace amounts of hexa- and hepta-chlorinated

Table 2

The amount of PCDD's and PCDF's (ng/g) found after heating the starting material with 2 $\mu\text{g/g}$ OCDD and 2 $\mu\text{g/g}$ OCDF, for experiments 1–5 (Table 1) [The standard deviation is given in parentheses (%)]

Exp. No.	1	2	3	4	5
Support	Alkaline alumina	Neutral alumina	Acidic alumina	Alkaline alumina with water ^a	Alkaline alumina with air ^b
<i>H₆CDD</i>					
1,2,4,6,7,9- 1,2,4,6,8,9- 1,2,3,4,6,8-	n.d.	0.37 (28)	n.d.	n.d.	0.062 (17)
1,2,3,6,7,9- 1,2,3,6,8,9-	n.d.	0.23 (0.4)	n.d.	n.d.	n.d.
<i>H₇CDD</i>					
1,2,3,4,6,7,9-	0.38 (31)	8.5 (43)	2.9 (21)	0.14 (16)	1.68 (6.2)
1,2,3,4,6,7,8-	0.38 (31)	3.4 (39)	n.d.	0.13 (24)	1.03 (2.9)
OCDD	8.4 (15)	416 (17)	145 ^c	4.9 (12)	302 (8.9)
<i>H₆CDF</i>					
1,2,4,6,7,8-	n.d.	0.11 (12)	n.d.	n.d.	0.013 (50)
<i>H₇CDF</i>					
1,2,3,4,6,7,8-	0.13 (33)	0.97 (42)	0.84 (32)	0.052 (23)	0.22 (19)
OCDF	1.3 (8.9)	1.1 (15)	3.5 (10)	1.2 (14)	6.03 (4.9)

^a Water added to the nitrogen flow.

^b Air flow instead of a nitrogen flow.

^c Single experiment.

n.d. = not detected (detection limit = 0.06 ng/g).

congeners were found. This means that beside dechlorination another decomposition process can be present. Chlorinated degradation products other than PCDD's and PCDF's, however, were not detected. Also PCDD's or PCDF's with less than 4 chlorine atoms were not detected.

The fact that only hepta- and hexa-chlorinated congeners were detected and no lower chlorinated congeners indicates that the dechlorination products of hexa- and hepta-chlorinated congeners are less stable than the hexa- and hepta-chlorinated congeners itself. Further research is necessary to prove this.

OCDF is dechlorinated faster on alumina than OCDD (see Table 2). Assuming an electrophilic aromatic substitution mechanism, this could be explained by the electron pushing character of the oxygen atom. In this way oxygen is activating the aromatic ring towards electrophilic substitution of a hydrogen atom by a chlorine atom. The reverse reaction will therefore be inhibited by an oxygen atom at the aromatic ring. OCDF (with one oxygen atom) will therefore be dechlorinated faster than OCDD (with two oxygen atoms).

In an oxygen atmosphere the dechlorination rate is much less. The amount of OCDD left is increased from 8.4 ng/g in a nitrogen atmosphere to 302 ng/g in an air atmosphere. For OCDF the amounts are 1.3 ng/g and 6.03 ng/g, respectively. Oxygen probably blocks the reductive sites of alumina, thus retarding dechlorination.

The dechlorination of OCDD on alkaline alumina is faster than on neutral and acidic alumina. The dechlorination of OCDF on alkaline alumina is as fast as on neutral alumina. The dechlorination of OCDF on acidic alumina is slower. This can be explained by an electrophilic aromatic substitution reaction. The Cl^+ coming off can combine with the alkaline part of the alumina and hence more easily leave the aromatic ring under alkaline conditions.

Earlier we reported [8] the formation of PCDD's and PCDF's from particulate organic carbon via de-novo synthesis on different kinds of alumina. Acidic alumina gave a larger amount of PCDD's and PCDF's than neutral and alkaline alumina. No significant difference was observed between the amount of PCDD's and PCDF's formed on neutral and alkaline alumina. With respect to the results of the dechlorination study described above, the larger amount of PCDF's in the de-novo synthesis on an acidic alumina support can be explained by a low dechlorination rate of OCDF.

The influence of the acidity of the alumina support on the formation of PCDD's by de-novo synthesis and the dechlorination of OCDD is not as clear as for the PCDF's. Because of the relative slow dechlorination of OCDD on neutral alumina with regard to alkaline and acidic alumina, other processes have to play an important role in PCDD formation.

In the presence of water, no significant change in the dechlorination rate of OCDD and OCDF was observed. Water could enhance the acidity of the alumina

Table 3

The amount of PCDD's and PCDF's (ng/g) found after heating the starting material with 2 $\mu\text{g/g}$ OCDD and 2 $\mu\text{g/g}$ OCDF, for the experiments 6–11 (Table 1) [The standard deviation is given in parentheses (%)]

Exp. No.	6	7	8	9	10	11
Support	Al_2O_3	$\text{Al}_2\text{O}_3 + \text{CuCl}_2$	$\text{Al}_2\text{O}_3 + \text{CuCl}$	CuCl	FeCl_3	AlCl_3
T_4CDD	n.d.	2.1 (71 ^a)	0.23 (87)	n.d.	0.29 (114)	n.d.
P_5CDD	n.d.	2.4 (68 ^a)	0.35 (87)	n.d.	n.d.	n.d.
H_6CDD	n.d.	4.2 (24 ^a)	0.53 (87)	0.48 (23)	n.d.	4.1 (28)
H_7CDD	0.27 (34)	3.8 (10 ^a)	1.7 (8.7)	6.2 (12)	n.d.	21 (23)
O_8CDD	25 (29)	34 (22 ^a)	34 (7.2)	525 (25)	296 (27)	191 (39)
T_4CDF	n.d.	1.9 (22 ^a)	0.23 (88)	n.d.	10 (129)	n.d.
P_5CDF	n.d.	1.5 (32 ^a)	0.34 (87)	1.5 (52)	n.d.	n.d.
H_6CDF	n.d.	0.97 (86 ^a)	0.51 (87)	11 (35)	n.d.	7.6 (36)
H_7CDF	0.56 (37)	1.8 (42 ^a)	2.1 (16)	35 (14)	n.d.	47 (12)
O_8CDF	17 (40)	20 (51 ^a)	24 (26)	1820 (12)	457 (62)	135 (25)

^a Range of two experiments, the range is calculated by subtracting the values of the two experiments and dividing this by two.

Table 4

Percentage of a PCDD or PCDF isomer relative to the total isomer concentration (mean of two experiments) for the four most abundant isomers in experiments 7, 8 and 9 (Table 1); the range is given in brackets^a

Exp. No	7	8	9
Support	Al ₂ O ₃ + CuCl ₂	Al ₂ O ₃ + CuCl	CuCl
<i>T₄CDD</i>			
1,3,7,9-		11 (0.68)	
1,3,7,8-	15	27 (0.51)	
1,3,6,9-		11 (7.4)	
1,2,4,7-			
1,2,4,8-			
2,3,7,8-	29	27 (9.5)	
1,2,3,4-			
1,2,3,7-			
1,2,3,8-			
1,2,4,6-			
1,2,4,9-			
1,2,3,6-	8.3		
1,2,7,9-			
1,2,7,8-	17		
1,4,6,9-			
<i>T₄CDF</i>			
1,3,7,8-		20 (0.59)	
1,3,7,9-			
2,3,4,9-	19		
1,2,3,4-			
1,2,7,8-	24 (3.3)	34 (5.1)	
1,2,6,7-	14		
1,2,7,9-			
1,2,4,9-		14 (2.8)	
2,3,7,8-	15 (0.34)	15 (1.0)	
<i>P₅CDD</i>			
1,2,4,7,9-		21 (2.5)	
1,2,4,6,8-			
1,2,4,7,8-	13 (2.5)	13 (0.73)	
1,2,3,7,9-	16 (3.2)	15 (0.072)	
1,2,3,7,8-	30 (2.6)	22 (3.7)	
1,2,3,8,9-	16 (2.2)		

Exp. No	7	8	9
Support	Al ₂ O ₃ + CuCl ₂	Al ₂ O ₃ + CuCl	CuCl
<i>P₅CDF</i>			
1,2,4,6,8-	12 (3.0)		
1,3,4,7,8-	16 (2.6)	15 (0.60)	
1,2,3,6,8-			
1,2,4,7,8-	13 (0.070)	13 (0.59)	
1,2,3,4,7-			24 (2.8)
2,3,4,6,9-			
1,2,3,4,8-	30 (8.0)	25 (0.46)	23 (1.1)
1,2,3,7,8-			
1,2,4,6,9-			17 (0.91)
2,3,4,8,9-			
2,3,4,6,7-		11 (0.49)	48 (0.53)
<i>H₆CDD</i>			
1,2,4,6,7,9-	19 (0.28)	27 (1.9)	100 (0 ^b)
1,2,4,6,8,9-			
1,2,3,4,6,8-			
1,2,3,6,7,9-	37 (3.1)	34 (0.21)	
1,2,3,6,8,9-			
1,2,3,6,7,8-	8.9 (0.50)	9.8 (0.27)	
1,2,3,7,8,9-	27 (0.57)	19 (1.6)	
<i>H₆CDF</i>			
1,3,4,6,7,8-	18 (2.4)	13 (1.2)	
1,3,4,6,7,9-			
1,2,4,6,7,8	27 (1.5)	17 (0.82)	
1,2,3,4,7,8-	15 (2.1)	16 (0.12)	35 (3.1 ^a)
1,2,3,4,7,9-			
1,2,3,6,7,8-	27 (1.3)	23 (0.058)	14 (0.98 ^b)
1,2,3,4,6,7-			13 (1.5 ^b)
2,3,4,6,7,8-			12 (0.74 ^b)
<i>H₇CDD</i>			
1,2,3,4,6,7,9-	45 (6.0)	43 (0.32 ^b)	38 (1.7 ^b)
1,2,3,4,6,7,8-	55 (6.0)	57 (0.32 ^b)	62 (1.7 ^b)
<i>H₇CDF</i>			
1,2,3,4,6,7,8-	70	68 (13 ^b)	68 (0.58 ^b)
1,2,3,4,6,7,9-	12	13 (0.20)	11 (0.56 ^b)
1,2,3,4,6,8,9-	11	15 (1.7 ^b)	10 (0.70 ^b)
1,2,3,4,7,8,9-	7	12 (0.028)	11 (0.23 ^b)

^a When no range is given, the isomer is found in one experiment.

^b Standard deviation of three experiments.

Fig. 2. Dechlorination of OCDF on alumina impregnated with CuCl_2 , main dechlorination route.

and hence inhibit the dechlorination. In this case the amount of water added to the nitrogen flow was probably too low to have a significant effect on the acidity of the alumina and hence on the dechlorination. The earlier reported shift [8] in the formation of PCDD's and PCDF's via de-novo synthesis towards higher chlorinated congeners in the presence of water can therefore not be explained by a lower dechlorination rate.

In Table 3 the amount of PCDD's and PCDF's found after heating OCDD and OCDF in the presence of metal chlorides and alumina is given. The amount of OCDD and OCDF on alumina without metal chlorides is lower than on alumina with metal chlorides (25 ng/g and 34 ng/g, respectively, for OCDD and 17 ng/g and 20–24 ng/g, respectively, for OCDF). With regard to the starting amount of 2000 ng/g, this is not a significant difference. In the presence of metal chlorides more lower chlorinated congeners were found. This indicates that the dechlorination of the lower chlorinated congeners is inhibited while the dechlorination of the higher chlorinated congeners is more or less the same. An explanation could be that the metal chlorides occupy the active places of the alumina and hence inhibit the dechlorination. We can, however, not explain why this would only be true for the lower chlorinated congeners. Another possible explanation could be that lower chlorinated congeners are chlorinated by the metal chlorides. Again we cannot explain why this would only give higher amounts of the lower chlorinated congeners. Further research is necessary. The pure metal chlorides are less effective dechlorination catalysts than alumina or alumina impregnated with metal chlorides. Metal chlorides can dechlorinate aromatic compounds by a Friedel–Crafts reaction [11]. The equilibrium, however, lies in the other direction. AlCl_3 and FeCl_3 are known Friedel–Crafts catalysts, AlCl_3 is a stronger catalyst than FeCl_3 [12]. This

Fig. 3. Dechlorination of OCDF on alumina impregnated with CuCl, main dechlorination route.

is in agreement with our results, where the dechlorination rate of OCDD and OCDF on metal chlorides increases from CuCl, via FeCl₃, to AlCl₃.

In Table 4 the concentration of a PCDD or PCDF isomer relative to the total isomer concentration for the four most abundant isomers is given. On an alumina matrix impregnated with CuCl₂ OCDF is dechlorinated first at the 9 position. OCDD is dechlorinated in a less specific way; both the 8 and the 9 positions are dechlorinated first. Further dechlorination shows that the 2,3,7,8-positions of PCDD's are more resistant to dechlorination. One of the main routes of dechlorination for dibenzofurans is given in Fig. 2. Most of the other congeners are also found so there is not one specific dechlorination pathway. On an alumina matrix impregnated with CuCl, there is no specific route of dechlorination for OCDD, for OCDF one of the main routes of dechlorination is given in Fig. 3. We cannot give an explanation for these main dechlorination routes, the question remains whether this isomer pattern is thermodynamically controlled or kinetically: further research is necessary.

Comparing the isomer patterns on alumina with CuCl and alumina with CuCl₂ gives remarkable differences between PCDD's and PCDF's. For the PCDD's it seems that the chlorine atoms on the 2,3,7,8 places are earlier substituted on alumina with CuCl₂ than on alumina with CuCl. On the other hand for the PCDF's it seems to be the other way round, so chlorine atoms on the 2,3,7,8 places seem to be easier replaced on alumina with CuCl.

4. Conclusions

The dechlorination of OCDD on alkaline alumina is fast in comparison with that on neutral and acidic alumina.

The dechlorination rate of OCDF on acidic alumina is low in comparison with neutral and alkaline alumina.

From the effect of the acidity of the alumina support and the fact that OCDF is dechlorinated faster than OCDD we propose that the dechlorination of OCDD and OCDF on alumina proceeds via an electrophilic substitution mechanism.

On metal chlorides the dechlorination of OCDD and OCDF is less than on alumina or alumina impregnated with metal chlorides.

There is not one specific dechlorination route, a wide range of lower chlorinated congeners are formed from OCDD and OCDF. For OCDF the main dechlorination route is given on alumina impregnated with CuCl_2 as well as on alumina impregnated with CuCl .

Acknowledgements

We would like to thank Pieter Slot and Martin van Velzen for performing the GC–MS analysis, and Ruud Addink for critically reading the manuscript.

References

- [1] L. Stieglitz, G. Zwick, J. Beck, H. Bautz and W. Roth, *Chemosphere*, 19 (1989) 283.
- [2] L. Stieglitz, G. Zwick, J. Beck, W. Roth and H. Vogg, *Chemosphere*, 18 (1989) 1219.
- [3] R. Addink, D.J. Drijver and K. Olie, *Chemosphere*, 23 (1991) 1205.
- [4] H. Vogg, M. Metzger and L. Stieglitz, *Waste Manag. Res.*, 5 (1987) 285.
- [5] L. Stieglitz, G. Zwick, J. Beck, H. Bautz and W. Roth, *Chemosphere*, 20 (1990) 1953.
- [6] O.M. van Berkel, K. Olie and M. van den Berg, *Intern. J. Environ. Anal. Chem.*, 34 (1988) 51.
- [7] H. Hagenmaier, M. Kraft, H. Brunner and R. Haag, *Environ. Sci. Technol.*, 21 (1987) 1080.
- [8] M.H. Schoonenboom, P.N. Smit and K. Olie, *Chemosphere*, 25 (1992) 1897.
- [9] R. Addink, B. van Bavel, R. Visser, H. Wever, P. Slot and K. Olie, *Chemosphere*, 20 (1990) 1929.
- [10] O. Motl and L. Norotný, in O. Mikeš (Editor), *Laboratory Handbook of Chromatographic Methods*, Van Nostrand, London, 1966, p. 189.
- [11] J. March, *Advanced Organic Chemistry: Reactions, Mechanisms, and Structure*, McGraw-Hill, New York, 1968, p. 439.
- [12] L.F. Fieser and M. Fieser, *Advanced Organic Chemistry*, Reinhold, New York, 1961, p. 651.