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On the Mechanism of the Formation of Polychlorinated Dibenzofurans from Chlorophenols

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#### Introduction

The pyrolysis of chlorinated phenates at a temperature of about 280 °C results in the formation of definite chlorinated dibenzodioxin congeners. [1-3].

In the pyrolysis of a mixture of two trichlorophenols Ballschmiter et al. found the expected congeners up to temperatures of 390 °C [4]. At temperatures above 400 °C (400-440°C) the PCDD congeners formed still reflected the starting chlorophenols to some extent, but now nearly all of the possible  $T_3CDD-H_7CDD$  were formed. In addition to these PCDD congeners pyrolysis at the higher temperatures yielded up to 20% of a complex mixture of  $T_4CDF$  and  $P_5CDF$ . The mechanism of formation of the dibenzofurans under these conditions was not examined by Ballschmiter.

Only few studies on the formation of PCDF from chlorophenols at higher temperatures have been published [5,6]. Louw and coworkers describe the formation of dibenzofurans in a homogeneous gas phase reaction from monochlorophenols at a temperature of 490 °C. In these investigations the mechanism remained unresolved and only assumptions are made on a mechanism of formation.

It is somewhat surprising that the condensation reaction of chlorophenols by pyrolysis has not drawn more attention, as it might constitute an elementary mechanism in the formation of PCDD/PCDF in combustion processes. In the controversial discussion on the mechanism of PCDD/PCDF formation in combustion processes two different pathways are postulated. One favors the formation of PCDD/PCDF via intermediates such as chlorophenols, chlorobenzenes or chlorinated biphenyls. The other claims that for PCDD/PCDF formation carbon in a particulate form is essential, from which, in the presence of oxygen, the PCDD/PCDF are released without prior gas phase intermediate formation [10,11]. For these hypotheses the misleading terminology of "precursor theory" and "de novo synthesis" has been used in recent years. Whatever the prevailing pathway may be, the synthesis via intermediates is certainly also a *de novo* synthesis.

Recently Altwicker emphasized the importance of chlorophenols in the formation of PCDD/PCDF. From his kinetic calculations he concluded that PCDD/PCDF are formed much faster from precursors than from from carbon in fly ash, and that therefore chlorophenols represent key molecules in PCDD/PCDF formation in combustion processes [7, 12].

One of the problems with chlorophenols as key intermediates in PCDD/PCDF formation is the discrepancy between the PCDD/PCDF ratios observed in laboratory experiments in the presence of fly ash (>>1) and the PCDD/PCDF ratios typically observed in incinerator fly ash which often are less than 1.

The ratio of PCDD to PCDF obviously depends on which location in an incineration plant the PCDD/PCDF formation is observed, the temperature being the most important parameter [12-14] with

## FORMATION

PCDF formed at higher temperatures than PCDD. Without knowledge of the mechanism of the condensation of chlorophenols to PCDD and PCDF it is not possible to explain this temperature dependence of the PCDD/PCDF ratio nor is it possible to correlate the congener (isomer) pattern of PCDD/PCDF with the relative concentration of chlorophenols in waste combustion.

#### Materials and methods

#### **Reagents and standards**

Chlorophenols were purchased from Supelco, INC., Bellefonte, Pennsylvania, USA <sup>13</sup>C<sub>12</sub>-PCDD/PCDF-standards were obtained from Promochem, Wesel, Germany)

#### Pyrolysis of chlorophenols

All pyrolysis experiments were carried out in sealed glass or quartz ampoules with about 1 mg of chlorophenol. After cooling to room temperature the ampoules were opened carefully. The reaction products were dissolved in toluene (two times 200  $\mu$ l) with treatment in an ultrasonic bath for 15 minutes. For the analysis of the hydroxylated products, 10 % of this toluene solution was methylated. For the analysis of PCDD/PCDF 90% of the toluene fraction was subjected to clean up on an alumina column [2] and analyzed for PCDD/PCDF.

#### Methylation of the hydroxylated compounds

40  $\mu$ l of the toluene solution were treated with 20  $\mu$ l of phenyltrimethylammonium hydroxide (0.1 molar in methanol, Fluka Chemika, Buchs, Switzerland). Phenolic hydroxy groups are methylated practically instantaneously. The samples were analyzed by GC/MS.

#### **HRGC/LRMS** Detection

The analysis was carried out with a HP 5890 gas chromatograph coupled directly to a HP 5970 mass selective detector.

A DB-5 fused silica column (30 m, 0.32 mm i.d., 0.25  $\mu$ m film thickness, J&W Scientific, Folsom/USA) was used for the separation of the methoxy compounds and the H7CDD/F and OCDD/F.

For isomer specific separation of the M1CDD/M1CDF - H6CDD/H6CDF a CP-SIL 88 column (50 m, 0.25 mm i.d., 0.2 µm film thickness, CHROMPACK, Frankfurt/Germany) was used.

Sample aliquots (1µl) were injected splitless (injector temperature 290 °C). With the DB-5 column the following temperature program was used: 100°C, 4 min. isothermal; 10°C/min. to 200°C, 5 min. isothermal; 5°C/min. to 300°C, 10 min. isothermal. Carrier gas was helium at a head pressure of 90 kPa. Temperature program for the CP-SIL 88 column: 130°C, 1 min. isothermal; 20°C/min. to 220°C, 1 min. isothermal; 2°C/min. to 245°C, 7 min. isothermal; 5°C/min. to 255°C, 20 min. isothermal. Carrier gas was helium at a head pressure of 150 kPa.

#### Results

When the alkali salts of chlorinated [1-3] or fluorinated [15,16] phenols are heated, PCDD are formed at temperatures above approximately 250 °C. In this process the condensation occurs by nucleophilic substitution in which phenoxyphenols (ortho-hydroxybiphenylethers) are formed as intermediates in a first step. In the second step they condense directly or after a Smiles rearrangement [17] to form PCDD [Figure 1].

When chlorophenols are pyrolyzed up to a temperature of about 350 °C only dibenzodioxins are formed. Above this temeprature dibenzofurans are formed also. In our experiments chlorinated phenols and air were sealed in ampoules and heated for 10 minutes at the respective temperatures. The PCDD/PCDF ratio

### Dioxin '97, Indianapolis, Indiana, USA

is dependent very strongly on the reaction temperature, the substitution pattern of the chlorophenols and the oxygen concentration.



Figure 1: Condensation of 2,3,5-trichlorophenate to 1,3,6,8-TCDD and 1,3,7,9-TCDD (via Smiles rearrangement)

#### Pyrolysis of non substituted phenol

Pyrolysis of phenol yields dibenzofuran. During this dimerization of two phenol molecules an oxygen bridge and a C-C bond has to be formed. Theoretically three intermediates are possible (Figure 2): biphenylether, phenoxyphenol, and dihydroxybiphenyl.





# FORMATION

By identification of intermediates and by analyzing the PCDF resulting from the different chlorophenols, the pathway of PCDF formation from chlorophenols can be elucidated..

No formation of dibenzodioxin is observed when non substituted phenol is pyrolyzed in the temperature range of 200-600°C. Of the above mentioned possible intermediates only phenoxyphenol (POP) and dihydroxybiphenyl (DOHB) are formed. The formation of these intermediates starts below 300 °C, while the onset of formation of dibenzofuran is approximately 350 °C. Above about 430 °C the main product is dibenzofuran which is formed very rapidly. The biphenylether is also formed at temperatures above 450 °C, but only in insignificant amounts.

Therefore phenoxyphenol (POP) and/or dihydroxybiphenyl (DOHB) are possible intermediates in PCDF formation. Conclusive evidence of whether POP or DOHB or both are the actual intermediates is available from the results of the analysis of the PCDF isomers formed from various chlorophenols (see below).

#### Intermediates in the condensation of chlorophenols to PCDF

The advantages of investigating and describing the basic mechanisms of the condensation of phenols by means of monochlorophenols are:

- The basic mechanism of condensation does not change with the degree of chlorination.
- The mechanism can be understood most easily and described most clearly by starting with monochlorophenols and then proceeding to higher degrees of chlorination.
- Non specific dechlorination and exchange of chlorine, occurring with the higher chlorinated phenols and preventing a detailed elucidation of the mechanisms (as it was e.g. the case in Ballschmitters work), are insignificant with monochlorophenols.
- The M1CDDs/M1CDFs and D2CDFs formed through condensation of monochlorophenols are toxicologically relatively harmless.

In the pyrolysis of ortho-chlorophenol the only DCDF formed is 4,6-D<sub>2</sub>CDF (additionally 4-M<sub>1</sub>CDF, 1-M1CDD, DD and the chlorinated POP and DOHB are formed) (Table 1). From para-chlorophenol 2,8-D2CDF is produced as the only D<sub>2</sub>CDF and from meta-chlorophenol three different D<sub>2</sub>CDF congeners are formed: 1,7-; 1,9-; 3,7-D<sub>2</sub>CDF. These are exactly the products one would expect via DOHB as intermediate (Figure 3).

If the condensation would occur via the POP, the ortho-chlorophenol would form the  $1,6-D_2CDF$ , the para-chlorophenol the  $2,7-D_2CDF$  (Figure 3) and the meta-chlorophenol the 1,8-, 2,7-, and  $3,6-D_2CDF$  (not shown) (additionally one would expect further products via the smiles rearrangement). However, these compounds are not formed.

Consequently the intermediates in the formation of PCDFs from chlorophenols are the polychlorinated dihydroxybiphenyls (PCDOHB). Formation of PCDF via the phenoxyphenols occurs only at temperatures >500°C and only to a minor extent: e.g. when pyrolyzing para-chlorophenol at 600°C the ratio of 2,7-DCDF (via POP) to 2,8-DCDF (via DOHB) is about 1:20.

The mechanism of the formation of PCDF is also relevant for phenols with a higher degree of chlorination. From 2,4-dichlorophenol the 2,4,6,8-T<sub>4</sub>CDF and from 2,3,4-trichlorophenol the 2,3,4,6,7,8-H<sub>6</sub>CDF are formed (in addition to the respective PCDDs) (Fig.3).

With increasing degree of chlorination the trend towards PCDD formation increases. This is probably due to the fact that the nucleophilic attack of the phenolic oxygen atom at the second phenol is facilitated during the formation of the phenoxyphenol (intermediate for PCDDs) by the withdrawel of electron density from the aromatic system by the chlorine substituents. On the other hand the sterically demanding formation of the DOHB is inhibited by the voluminous chlorine atoms (as in the case of formation of 2,2'-dihydroxy-6,6'-dichlorobiphenyls; see below). If both ortho-positions of the phenol are substituted with



Dioxin '97, Indianapolis, Indiana, USA

Figure 3: Condensation of 2- and 4-chlorophenol, 2,4- dichlorophenol and 2,3,4-trichlorophenol to the possible PCDF congeners via phenoxyphenols (POP) and dihydroxyphenols (DOHB).

484

ORGANOHALOGEN COMPOUNDS Vol. 31 (1997) chlorine (e.g.  $2,4,6-T_3CP$ ,  $2,3,4,6-T_4CP$ )the formation of PCDFs is almost completely inhibited and only PCDDs are formed.

The assumption that the DOHBs could be intermediates in the formation of PCDF was first made by Born and Louw [5, 6]. Their assumption was based on the observation that dibenzofuran is formed during heating of 2,2'-dihydroxybiphenyl. Yet, they were not able to show that the DOHBs actually are formed as intermediates during pyrolysis of phenols.

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Temperature (°C)	600	530	500	470	430	400	375	330
Congeners								
Dibenzodioxin	150	120	47,4	67	97,5	89	62,7	25,8
Dibenzofuran	80	5,9	0,4	n.d.	n.d.	n.d.	n.d.	<b>n.d</b> .
1-MCDD	43	40,4	15,2	18,3	73,2	74,1	216	3,8
4-MCDF	113	57	20	28,3	29	24,1	19,6	<u>n.d.</u>
OHCIDF	20,7	13,8						
	8,1	2,2						
4,6-DCDF	100	100	_100	100	100	100	100	n.d.
T3CDF	1,5	0,1	n.d.	n. <b>d</b> .	n.d.	n.d.	n.d.	n.d.
CIPOP	0,14	0,3	0,8	2,6	25,5	20,3	78,4	37
C2POP	n.d.	0,2	0,5	<0,1	4,9	5,6	114	77
	n.d.			<0,1	1,2	1,8	51	29
	n.d.			<0,1	24,2	37	156	32
	n.d			<0,1	5,3	5,6	19,6	13
CIDOHB	4x<1	5x<1		1,7	2,8	2,1	3,1	<3
				0,3	1,7	2,5	7,8	<3
C2DOHB	n.d.	n.d.	1,45	3,5	17	33,3	147	100
	n.d.	n.d.	7,5	0,7	<0,1		7,9	12,9
	n.d.	n.d.	n.n	0,4	1,6	2,2	<0,1	22,5
	n.d.	0,6	9,8	2,1	4,1	1,4	4,5	
	n.d.	1,3	9,8	3,1	12,6	7,1	27,5	
2,2'-dichlorobi-	0,4	0,3	0,1	n.d.	n.d.	n.d.	n.d.	n.d.
phenylether			L					

 

 Table 1: Temperature dependence of the condensation products of 2-chlorophenol (concentration of the congeners relativ to 4,6-DCDF)

#### References

- [1] O. Aniline, Adv. Chem. Ser., 120, 126 (1973).
- [2] G. R. Higginbotham, A. Huang, D. Firestone, J. Verret, J. Ress, A. D. Campell, Nature, 220, 702 (1986).
- [3] H.-R. Buser, Ph.D. thesis, University of Umea, Sweden, 1978.
- [4] W. Zoller, K. Ballschmiter, Fresenius Z. Anal. Chem., 323, 19 (1986).
- [5] J. G. P. Born, R. Louw and P. Mulder, Chemosphere, 19, 401 (1989).
- [6] R. Louw, H.-H. Grotheer, M. J. Kanters and I. Wiater, Organohalogen Compounds, 27, 26 (1996).
- [7] E. R. Altwicker, Municipal Waste Combustion, Proceedings, Air & Waste Manage. Assoc., VIP-32, 202 (1993).
- [10] L. Stieglitz, H. Vogg, Chemosphere 16, 1917 (1987).
- [11] H. Huang, A. Buekens, Chemosphere 31, 4099 (1995).
- [12] E.R. Altwicker, Chemosphere 33, 1897 (1996).
- [13] L. Takacs, A. McQueen, and G. L. Moilanen, J. Air & Waste Mgt. Assoc., 43, 889 (1993).
- [14] U. Düwel, A. Nottrodt, K. Ballschmiter, Chemosphere 20, 1839 (1990).
- [15] R. Weber, D. Schrenk, A. Hagenmaier, H. Hagenmaier, Chemosphere, 30, 629 (1995).
- [16] U. Haffer, W. Rotard, Organohalogen Compounds, 11, 87 (1993).
- [17] W. E. Truce, E. M. Kreider, W. W. Brand, Organic Reactions, 18, 99 (1970).

ORGANOHALOGEN COMPOUNDS Vol. 31 (1997)