

Hydrothermal decomposition of PCDD/F

Hans-Peter Gräbel and Hanspaul Hagenmaier

Institute of Organic Chemistry, University of Tübingen, Auf der Morgenstelle 18, D-72076 Tübingen, Germany

Abstract

The decomposition of polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) in fly ash samples and in heavily contaminated soil was studied under hydrothermal conditions, especially the effect of the pH-value and temperature on the rate of decomposition. PCDF as well as PCDD can be decomposed in an aqueous alkaline solution. The decomposition starts at 200°C and reaches 99% at 300°C. At constant reaction times the decomposition rate increases with increasing pH. The higher chlorinated PCDD/F are destroyed faster than the lower chlorinated. The behavior of high concentrations of polychlorinated aromatic compounds such as PCB and PCP under hydrothermal conditions was studied also. It was found that at neutral pH the presence of PCB leads to the formation of PCDF, while from PCP no PCDD formation was observed.

The decomposition products were analysed for 2,4,8-Trichlorodibenzofuran and Octachlorodibenzodioxin. It was shown that the first step in the decomposition reaction is a nucleophilic substitution of chlorine by the hydroxylion which works best under alkaline conditions. The dechlorination/hydrogenation (the main reaction at the copper-catalyzed low temperature destruction [1]) which would lead to lower chlorinated, and under certain circumstances higher toxic, congeners plays only a minor role.

Introduction

The physical and chemical properties of water are changing dramatically with increasing temperature [2,3]. The increasing solubility of organic substances in water with higher temperatures is accompanied by an increasing reactivity. Cycloalkyl-aryl-ether, e.g. are cleaved to the alcohols at 250-300°C [4]. It appeared of practical interest to study the hydrothermal reaction on PCDD/PCDF. This has already been done for PCBs [5]. The mechanism has been investigated for 4-Chlorobiphenyl which lead to biphenyl-4-ol. The decomposition of samples contaminated with PCDD/PCDF was so far not investigated in detail.

Materials and Methods

Hydrothermal treatment

2 g of either fly ash or soil sample are placed in an autoclave (100 ml) and 60 ml of the respective aqueous solution is added. After closing the autoclave is heated in an aluminum heating block, which is placed on a shaker, to the desired temperature. During treatment the autoclave is shaken. The pressure rises to about 40 bar at 250°C and about 100 bar at 300°C.

In case of treatment of PCP, PCB, 2,4,8-triCDF and OCDD 60 ml of the respective aqueous solution are added to the autoclave and the substances added in 0.1 ml of acetone or toluene.

Extraction and clean-up

After treatment a standard mixture of ^{13}C -labeled 2,3,7,8-substituted PCDD/PCDF was added to the reaction mixture. The aqueous solution was transferred to a separatory funnel, the autoclave washed several times with toluene. The toluene solution is subsequently used to extract the aqueous solution. The residue (soil sample, fly ash) is mixed with 30 g Na_2SO_4 and Soxhlet-extracted with the toluene fraction obtained from the liquid/liquid extraction. The organic solvent is concentrated to a few milliliters and a clean-up carried out as described elsewhere [6].

Results and Discussion

The temperature dependence of the hydrothermal reaction was studied at 200, 250, 280 and 300°C. The duration of treatment was 1h in a 1N NaOH solution. At 200°C considerable rates of decomposition were only observed for the higher chlorinated homologues hexa- to octaCDD/F. The concentration of tetraCDD even increased slightly at this temperature. When

Table 1: Temperature dependence of the hydrothermal decomposition of PCDD/PCDF in fly ash; conditions: 1 n NaOH, 1 h; concentrations in ng/g

	Untreated	200°C	250°C	280°C	300°C
T4CDD	25	48	20.9	0.52	0.27
P5CDD	70	53	1.2	<0.01	0.36
H6CDD	127	11	1.0	<0.01	0.00
H7CDD	88	2	0.8	0.14	0.04
OCDD	40	1	1.0	0.19	0.18
Σ PCDD	350	115	24.9	0.85	0.85
T4CDF	89	63	12.8	0.79	0.68
P5CDF	101	33	0.8	0.28	0.44
H6CDF	67	1	0.5	0.07	0.17
H7CDF	29	0.2	0.1	0.06	0.04
OCDF	9	0.7	0.2	0.21	0.06
Σ PCDF	295	97.8	14.4	1.41	1.39
D4	0.5	2.4	0.60	0.07	0.03
D5	3.5	3.4	0.13	<0.01	<0.01
D6/1	7.4	0.8	0.08	<0.01	<0.01
D6/2	11.1	1.0	0.09	<0.01	<0.01
D6/3	3.7	0.4	0.09	<0.01	<0.01
D7	46.1	0.8	0.41	0.10	0.03
F4	6.9	4.1	1.01	0.06	0.05
F5/1	3.1	1.3	0.06	0.03	0.02
F5/2	7.8	0.8	0.06	0.01	0.01
F6/1	8.4	0.1	0.07	<0.01	0.02
F6/2	8.4	0.2	0.07	<0.01	0.03
F6/3	0.6	<0.1	<0.01	<0.01	<0.01
F6/4	7.5	0.1	<0.01	<0.01	<0.01
F7/1	18.1	0.1	0.07	0.06	0.04
F7/2	2.7	<0.1	<0.01	<0.01	<0.01
I/TEQ	12.4	5.2	0.84	0.08	0.05

the temperature was increased to 250°C already 97% of all homologues with the exception of tetraCDD/F were decomposed. At 300°C more than 99% of all homologues had reacted.

pH-dependence

At pH 1 and a temperature of 250°C no decomposition of PCDD/PCDF was observed. At this pH the destruction of hepta- and octaCDD starts at 280°C. At pH 6 hepta- and octaCDD are partly destroyed at 250°C. At 280°C the destruction of all homologues with exception of TetraCDDs is evident. PCDFs are again destroyed more readily.

Table 2: pH dependence of hydrothermal treatment of PCDD/F conditions: 1 h treatment; concentrations in ng/g

	Untreated	pH 1/250°C	pH 1/280°C	pH 6/250°C	pH 6/280°C
T4CDD	25	32	30	42	32
P5CDD	70	85	99	82	61
H6CDD	127	123	106	95	56
H7CDD	88	105	64	74	29
OCDD	40	52	14	25	7
Σ PCDD	350	397	313	318	185
T4CDF	89	106	78	105	67
P5CDF	101	86	73	85	51
H6CDF	67	58	41	92	24
H7CDF	29	22	10	14	5
OCDF	9	4	1	3	1
Σ PCDF	295	276	203	299	148
I/TEQ	12	13	11	12	7

Time-dependence

For the determination of the concentration in dependence of the duration of treatment we used 1N NaOH at a temperature of 280°C. PCDF were again faster destroyed than PCDD. It is also evident that the decomposition is not only increasing with increasing number of Cl-atoms, but that the decomposition of dioxins with an odd number of Cl-atoms is faster than that of dioxins with an even number of Cl-atoms. PentaCDD are for example faster destroyed than tetraCDD and HexaCDD. For the PCDF no such dependence is seen. The destruction rate for tetraCDD leads from 86% after 10 minutes over 95% after 30 min to 98% after 60 min. For the other PCDD/F congeners the destruction rate is almost 99% after 30 minutes.

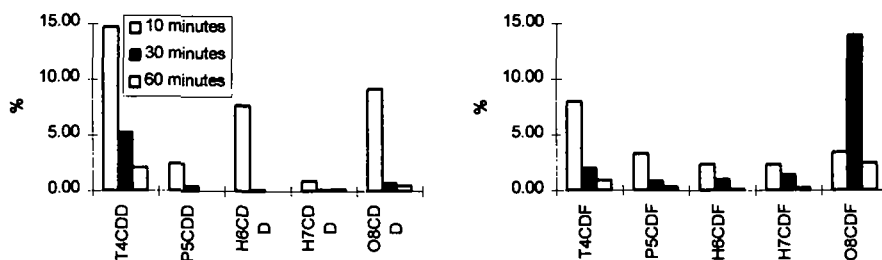


Figure 1: PCDD/F residual concentrations after 10, 30 and 60 minutes in 1N NaOH at 280°C. These results were tested on a second fly ash sample. The peculiarity of this fly-ash was the absence (<0.01 ng/g) of 2,3,7,8-TCDD and high concentrations of PCDF. After the decomposition we found low concentrations (max. 0.19 ng/g) of 2,3,7,8-TCDD.

Soil samples

The decomposition of PCDD/F was also tested on soil samples. The soil samples were collected at a contaminated area of a former production site for 2,4,5-trichlorophenol which explains the high concentration of 2,3,7,8-TCDD. The results obtained are shown in Table 2.

Table 3: Time dependence of PCDD/PCDF decomposition in a soil sample by hydrothermal treatment; conditions: 1 N NaOH, 280°C, concentrations in ng/g.

	Untreated	10 min	40 min	60 min
T4CDD	115	17.1	2.4	1.4
P5CDD	47	3.8	1.7	1.6
H6CDD	423	3.7	1.9	1.4
H7CDD	1017	1.5	1.1	0.7
OCDD	2327	3.0	0.7	0.1
Σ PCDD	3928	29.2	7.7	5.1
T4CDF	330	10.7	15.0	8.9
P5CDF	515	14.8	45.1	4.7
H6CDF	550	5.1	9.1	1.4
H7CDF	161	1.9	0.6	0.6
OCDF	650	1.6	1.1	1.3
Σ PCDF	2206	34.1	71.0	16.9
D4	99	4.0	1.2	0.50
D5	12	0.7	0.4	0.31
D6/1	16	0.2	0.1	0.04
D6/2	76	0.6	0.4	0.20
D6/3	38	0.4	0.2	0.14
D7	586	0.9	0.6	0.41
F4	<0.01	0.7	0.1	<0.01
F5/1	11.7	0.3	0.5	0.12
F5/2	2.9	0.7	0.5	0.15
F6/1	62.4	0.7	0.2	0.15
F6/2	17.0	0.5	0.1	0.12
F6/3	<0.01	<0.01	<0.01	<0.01
F6/4	22.7	0.3	0.1	0.09
F7/1	134.0	1.4	<0.01	<0.01
F7/2	<0.01	0.2	<0.01	0.08
I/TEQ	141	5.0	1.8	0.81

The behavior of PCDD/PCDF in the soil sample is comparable to that in fly ash samples. The decomposition rate is about the same. That shows that there is practically no catalytic effect of the heavy metal ions present in the fly ash. This was verified in experiments with the addition of various heavy metal ions.

Decomposition products

The copper catalyzed low temperature decomposition of octaCDD at 285°C is a dechlorination/hydrogenation reaction with the intermediate formation of lower chlorinated

PCDD congeners. When octaCDD is decomposed under hydrothermal conditions in alkaline solution no formation of tetra- to heptaCDD is observed.

To detect other decomposition products of octaCDD we analyzed the reaction mixture for all OH/Cl substituted dibenzodioxins, biphenylether, biphenyls and phenols. The result of this analysis with the most likely reaction pathways is shown in Figure 2.

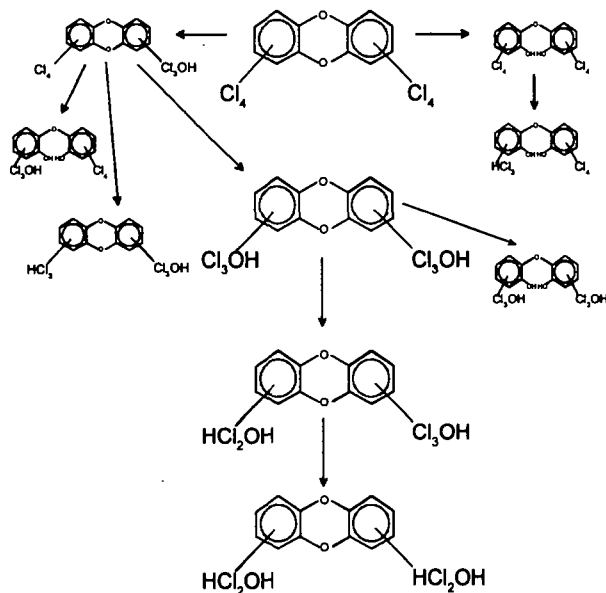


Figure 2: Main products of the hydrothermal treatment of OCDD.

In alkaline solution only the molecules shown in large in Figure 2 can be found. The other compounds were found only in neutral or acid solution, when dechlorination/hydrogenation becomes a competitive reaction.

In a second experiment the reaction products of the hydrothermal treatment of 2,4,8-trichlorodibenzofuran were identified. Table 4 shows the results.

Table 4: Reaction products of 2,4,8-triCDF (relative concentrations) in 1 N NaOH.

xxDF	280°C		300°C	
	1min	30min	1min	30min
DF	0	n.n.	2	2
Cl	1	2	5	0
Cl2	10	6	5	2
Cl3	18	100	58	15
OH	0	8	9	25
Cl(OH)	14	42	46	5
Cl2(OH)	100	49	56	2
(OH)2	2	18	23	100
Cl(OH)2	4	88	100	23

For 2,4,8-TriCDF we found dechlorination/hydrogenation as well as OH-substitution. In comparison to OCDD, the OH-substitution is slower, so that dechlorination/hydrogenation can be observed. Trisubstitution by OH could not be found.

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