

The Role of Aliphatic Organic Chlorine in the Formation of PCDD/PCDF on Fly Ash in Comparison to Inorganic Chlorine

P. Weber, E. Altwicker*, E. Dinjus, L. Stieglitz

Institut für Technische Chemie, Forschungszentrum Karlsruhe
Postfach 3640, 76021 Karlsruhe, Germany

* Department of Chemical Engineering,
Rensselaer Polytechnic Institute, Troy, NY 12180, USA

Introduction

In the formation of polychlorinated aromatic hydrocarbons (PCDD/PCDF and related compounds) from particulate carbonaceous material of fly ash (de-novo-synthesis) two reactions have been recognized to be important: i) the transfer of chloride to the residual carbon with formation of carbon-chlorine bonds, and ii) the oxidative degradation of the macromolecular structure to carbon dioxide with volatile aromatic chlorinated compounds as side products. These reactions are catalyzed or promoted by metal ions, especially Cu(II) ions.^[1,2]

In many publications the role of inorganic chlorine (CuCl₂ or Cu²⁺/KCl) is determined^[3] and the dechlorination of higher chlorinated aromatic compounds investigated.^[4] Here is the question, whether the organic chlorine might be available for chlorination and formation of PCDD and PCDF. The topic of this presentation is the formation of PCDD and PCDF on fly ash with an aliphatic organic chlorine source (tetrachloromethane).

Therefore the difference of inorganic chlorine (KCl / CuCl₂) and organic chlorine (CCl₄) as source for the chlorination under de-novo conditions is determined in several experiments as well as the formation of PCDD and PCDF.

Material and Methods

As model fly ash a system containing CuSO₄*H₂O (0.1 – 0.75%) and charcoal (1.8% / 8%) in quartz sand was used. The samples were treated thermally in nitrogen or air at 300°C for 1,2,5,10,30 and 60 minutes. To add the organic chlorine source (CCl₄) a part of the total flow (50 ml/min) was saturated with CCl₄ at -10°C (impinger). In the short time runs (1 min to 5 min) the amount of CCl₄ was added manually with continuous injection over the reaction time.

The mixtures were analyzed for total organic chlorine (AOX) and PCDD/F by HRGC/MS. The total amount of CCl₄ in the gas phase was sampled in a gas trap (dichloromethane, -10°C) and analyzed by HRGC/MS.

In addition, experiments with pre-extracted fly ash^[3] (EPA) diluted 1:1 with quartz sand and different chlorine sources (KCl and CCl₄) were made. These experiments were performed in air (50 ml/min) for 30 minutes at 300°C. The EPA fly ash was pre-extracted by the following procedure: heating under nitrogen at 300°C for 1 h, extraction with toluene for 24 h, washing with hexane and drying in vacuum.

The mixtures were analyzed for total organic chlorine by AOX-measurements and residual CCl₄ in the gas trap (experiments with CCl₄ as organic chlorine source only) and PCDD/F by HRGC/MS.

All experiments were performed in an aluminum reactor with short heating (7-8 s) and cooling times (3-5 s). The total sample size was 1 gram.

Results and Discussion

Formation of non volatile organic chlorine with chlorinated aliphatic compounds (CCl₄) as chlorine source

In the experiment, the formation of non-volatile organic chlorine (AOX) is in the range of the blank samples. There is no formation of AOX from CCl₄ under nitrogen at 300°C.

In the experiments with air (Table 1) the formation of non volatile organic chlorine increase within the first minutes to about 1200-1300 µg Cl/g. With longer reaction times, the organic chlorine reaches a level of 1880 µg Cl/g. This is a transformation rate of 10% of chlorine from CCl₄ (total 18.5 mg Cl in the experiments) to nonvolatile organic chlorine. The ratio between organic chlorine formed and copper increases to 0.75 at 60 minutes.

Table 1: Formation of nonvolatile organic chlorine in air at 300°C from CCl₄ (0.45% Cu (CuSO₄*H₂O) / 1.8% C / 0.13 mmol CCl₄ / air 50 ml/min)

time [min]	AOX [µg Cl/g]	organic chlorine [µmol]	organic Cl/Cu [ratio]
0	0	0.00	0.00
1	619	17.42	0.25
2	1123	31.60	0.45
5	1317	37.06	0.52
10	1360	38.27	0.54
30	1754	49.35	0.70
60	1876	52.79	0.75

In comparison to earlier experiments^[5] with inorganic chlorine (CuCl₂/KCl) we found formation of organic chlorine under helium with a Cl/Cu ratio of 0.5 (in agreement with the reaction: 2 CuCl₂ + AR-H → 2 CuCl + Ar-Cl + HCl). With CCl₄ as chlorine source there is no formation of nonvolatile organic chlorine in the absence of oxygen. This leads to the conclusion, that for the dechlorination of CCl₄ or the chlorination of carbon (or nonvolatile compounds) at 300°C the presence of oxygen is necessary.

In air we found in the mixture a Cl/Cu ratio of 0.75 after 60 minutes. This is 10 times lower than the total Cl/Cu ratio in these experiments.

Formation of PCDD/F in model system with CCl₄ as chlorine source in air at 300°C in comparison to CuCl₂/KCl

These experiments show a very high formation of PCDD and PCDF although a low copper concentration down to 0.1% was used (Tables 2,3). The formation of PCDD and PCDF is very fast. After 1 minute there is a PCDD/F formation between 120 ng/g (0.1% Cu) and 850000 ng/g (0.75% Cu). In comparison to the formation of PCDD/F in the system with CCl₄ instead of KCl the formation is over 180 times higher after 60 min. (Table 2).

Table 2: Yield of PCDD/F [ng/g] in the experiments at 300°C in air (50 ml/min) with different chlorine sources (quartz sand containing 8% activated carbon and 0.18 mmol Cl (CCl₄ or CuCl₂/KCl).

Yield PCDD/F [ng/g]	1 min	2 min	5 min	10 min	30 min	60 min
0,75 % Cu (CuCl ₂ /KCl)	< 10	< 10	100	179	4284	4623
0.75 % Cu (CuSO ₄ /CCl ₄)	--	--	--	--	--	850245

Table 3: Yield of PCDD/F [ng/g] in the experiments at 300°C in air (50 ml/min) with CCl₄ and copper concentrations between 0.1% and 0.4% Cu (quartz sand containing 1.8 % activated carbon and 0.13 mmol CCl₄).

Yield PCDD/F [ng/g]	1 min	2 min	5 min	10 min	30 min	60 min
0.45 % Cu (CuSO ₄ /CCl ₄)	957	1382	1902	3556	8857	35452
0.30 % Cu (CuSO ₄ /CCl ₄)	494	791	1297	2605	6443	26892
0.20 % Cu (CuSO ₄ /CCl ₄)	329	491	869	2220	4891	18429
0.10 % Cu (CuSO ₄ /CCl ₄)	119	234	313	1578	2816	8963

In the formation of PCDD/F in the copper(II) containing model system with CCl₄ there is a strong shift to the higher chlorinated PCDD and PCDF isomers (Table 4). Mostly hepta and octa PCDD/PCDF are formed. This shows the very high chlorination potential of CCl₄ in combination with copper(II). In all these experiments the amount of CCl₄ in the gas trap was under 1% of the total amount of CCl₄ which indicates a conversion of CCl₄ over 99% in these experiments. In additional experiments the condition for the CCl₄ conversion was determined. With the empty reactor, or quartz sand or quartz sand and carbon (all at 300°C) no conversion was found. Only in the system with CuSO₄, carbon and quartz sand at 300°C conversion was observed.

Table 4: Congener pattern of the PCDD/F at 300°C in air (50 ml/min) with 60 min reaction time (0.75% Cu / 8% activated carbon / 2.2 mmol Cl (CuCl₂/KCl or CCl₄) / quartz sand)

Chlor-homologe	CuCl ₂ /KCl PCDD [ng/g]	CuCl ₂ /KCl PCDF [ng/g]	CCl ₄ PCDD [ng/g]	CCl ₄ PCDF [ng/g]
Tetra-	1	7	6	8
Penta-	2	24	8	9
Hexa-	9	109	8	11
Hepta-	128	262	5982	2913
Octa-	1255	2826	229681	611619

Formation of PCDD/F with inorganic and organic chlorine sources on EPA fly ash

In the case of EPA fly ash, the effect of the high formation of PCDD and PCDF is not observed (Table 5). The formation of PCDD/F is 3.4 times higher with CCl₄ (0.13 mmol CCl₄ total) in the gas phase. With the same amount of chlorine as KCl on the fly ash, there is no effect in the PCDD/F formation.

Formation and Sources I

Tab. 5: PCDD/F formation [ng/g fly ash] on EPA fly ash (diluted 1:1 with quartz sand) at 300°C and reaction time of 30 minutes in air with organic and inorganic chlorine.

Fly ash only		KCl (520 µmol Cl)		CCl ₄ (260 µmol Cl)		CCl ₄ (520 µmol Cl)	
PCDD	PCDF	PCDD	PCDF	PCDD	PCDF	PCDD	PCDF
228	243	284	369	214	317	681	828

Summary

These experiments lead to the following conclusions:

- I. Organic chlorine in aliphatic compounds can play an important role as a chlorine source for the de-novo synthesis. The chlorination potential in combination with copper (II) is very high at 300°C. The presence of copper(II) and oxygen is necessary for the transport of the chlorine from the CCl₄ to the carbon and polychlorinated compounds. The important role of copper(II) is also shown by the high CCl₄ conversion (destruction) of 99% which was only found in the presence of copper(II) at 300°C. The oxidative pyrolysis of CCl₄ needs temperatures over 880°C^[6]. The parent stability (99% destruction) is 880°C (1153 K).^[6]
- II. The formation of PCDD/F in the presence of CCl₄ is very high. There is a strong shift towards higher chlorinated homologues.
- III. On EPA fly ash, the effect of CCl₄ is not as high as in the model system. To determine this effect further experiments are underway.
- IV. Published experiments of J. Peddersen^[7] show an exchange between the carbon of the CCl₄ and PCDD/F at 400°C. To determine if this reaction also takes place at 300°C further experiments with ¹³C labeled activated carbon and CCl₄ are made.

Acknowledgements

Thanks to the Forschungszentrum Karlsruhe GmbH for the financial support of this work. Special thanks to Prof. E. Altwicker for the stay in his group at Rensselaer Polytechnic Institute (Troy, NY) where these experiments were performed, also to the members of his group assistance.

References

1. Stieglitz, L., Zwick, G., Beck, J., Roth, W., Vogg, H., Chemosphere **1989**, 18, 1219
2. Stieglitz, L., Vogg, H., Zwick, G., Beck, J., Bautz, H., Chemosphere **1991**, 23, 1255
3. Addink, R., Altwicker, E., Organohalogen Compounds **1996**, 27, 1-9
4. Collina, E. et al., Environ. Sci. Technol. **1995**, 29, 577-585
5. Weber P, Dinjus, E. Stieglitz, L.; 6th Int. Congress on Toxic Combustion Byproducts, Karlsruhe **1999**, Presentation
6. Taylor, P. H., Dellinger, B., Tirey, D. A., Int. J. Chem. Kinet. **1991**, 23, 1051-1047
7. Pedersen, J. R., Chemosphere **1989**, 18, 2311-2316