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## Mechanistic Aspects of the De-novo-Synthesis of PCDD/PCDF on Model Fly Ash

K. Hell, L. Stieglitz, G. Zwick, R. Will

Institut für Technische Chemie, Bereich Physikalisch-Chemische Verfahren  
Forschungszentrum Karlsruhe, P.O. Box 3640, D-76021 Karlsruhe, Germany

### 1. Introduction

Thermal treatment of fly ash between 250 - 400°C results in the formation of a variety of chlorinated aromatic compounds, among others the highly toxic PCDD/PCDF<sup>1,2)</sup>. It could be shown that these compounds are formed de-novo from the residual carbon stemming from incomplete combustion<sup>3,4)</sup>. Heating residual carbon free fly ash that had been enriched with a mixture of <sup>12</sup>C- and <sup>13</sup>C-carbon resulted in the formation of <sup>12</sup>C<sub>12</sub>-, <sup>13</sup>C<sub>12</sub>- and <sup>12</sup>C<sub>6</sub>/<sup>13</sup>C<sub>6</sub>-PCDD (one aromatic ring consists of <sup>12</sup>C- and the other of <sup>13</sup>C-carbon), whereas only negligible amounts of <sup>12</sup>C<sub>6</sub>/<sup>13</sup>C<sub>6</sub>-PCDF were found<sup>5)</sup>. It has thus been concluded that PCDD and PCDF are built up according to the following pathways:

- PCDD are partly (20 - 30%) synthesized through condensation of intermediate monoaromatic compounds e.g. phenols<sup>6,7,8)</sup>
- PCDF are probably directly released from preformed structures in the carbon matrix, e.g. biphenyls<sup>9)</sup>.

Two questions now arise: i) Are these mechanisms also found on other matrices, and ii) what is the influence of a variation of temperature and reaction time on these two pathways. Therefore experiments were performed with a model fly ash that had been enriched with <sup>12</sup>C- and <sup>13</sup>C-carbon (ratio: 1:1). In order to compare the oxidation of <sup>12</sup>C- and <sup>13</sup>C-carbon to <sup>12</sup>CO<sub>2</sub> and <sup>13</sup>CO<sub>2</sub>, the main de-novo reaction, the combustion gases were measured on-line with a mass spectrometer. Besides PCDD/PCDF, PCPh and PCBz were also determined. In this paper the results of experiments in the temperature range 250 - 400°C and reaction times between 15 min. and 4 hrs. are discussed.

### 2. Experimental Methods

**Materials:** <sup>12</sup>C-carbon (amorphous, 99,95%, Cambridge Isotope Laboratories),  
<sup>13</sup>C-carbon (amorphous, 99,0%, Cambridge Isotope Laboratories).

**Composition of the model fly ash:**

4% carbon (18,98 mg <sup>12</sup>C-carbon, 21,01 mg <sup>13</sup>C-carbon, corresponding to a molar carbon ratio <sup>12</sup>C:<sup>13</sup>C = 1:1), 7% Cl as KCl, 0,4% Cu as CuCl<sub>2</sub>·2H<sub>2</sub>O, 80,2% Florisil (85% SiO<sub>2</sub>, 15% MgO).

The experiments were performed with an apparatus described earlier<sup>10)</sup>. The volatile compounds were collected in a XAD-16 resin trap. The model fly ash samples were extracted with toluene for 24 hrs. and the XAD-16 resin samples eluted with toluene and dichloromethane. After clean-up,

PCPh and PCBz were analyzed by HRGC-LRMS. PCDD/PCDF were measured by HRGC-HRMS (HP5890 - Fisons Autospec) with a 50 m SP2331 column in the Multi Detection Mode at a resolution of 10,000.

For quantification, the following internal standards were used: 1,3,5-trichloro-2,4,6-trifluorobenzene for the PCBz; 2,6-dichloro-4-fluorophenol for the PCPh and 1-bromo-2,3,7,8-tetrachlorodibenzofuran for the PCDD/PCDF. To determine the amounts of  $^{12}\text{C}$ O and  $^{12}\text{C}$ O<sub>2</sub>, the mass spectrometer was calibrated with a test gas (He 78,64%, O<sub>2</sub> 19,4%, CO<sub>2</sub> 1,87% and CO 885 ppmv).

Considering that labeled test gas is expensive and since ion streams are sufficient to compare the oxidation of the two carbon species to carbon dioxide, in some experiments only the ion streams of  $^{12}\text{C}$ O<sub>2</sub> and  $^{13}\text{C}$ O<sub>2</sub> were measured.

### 3. Results and Discussion

#### 3.1 Formation of PCDD/F as a Function of Temperature

The results of experiments with model fly ash ( $^{12}\text{C}:^{13}\text{C} = 1:1$ ) in dependence of reaction temperature are depicted in Table 1. For the formation of  $^{12}\text{C}_{12}$ -,  $^{13}\text{C}_{12}$ - and  $^{12}\text{C}_6/^{13}\text{C}_6$ -PCDD/F a maximum is reached at 350°C. The fraction of  $^{12}\text{C}_6/^{13}\text{C}_6$ -PCDD of the total amount of PCDD concentration decreases from 22% at 250°C to 11% at 300°C. It does not change significantly between 300 and 400°C. In all experiments the fraction of the  $^{12}\text{C}_6/^{13}\text{C}_6$ -PCDF species represents only 1% of the total PCDF.

Table 1. Formation of PCDD and PCDF on model fly ash ( $^{12}\text{C}:^{13}\text{C} = 1:1$ )  
reaction time 2 hrs.

temp.	compound	concentration ng/g model fly ash			
		$^{12}\text{C}$	$^{13}\text{C}$	$^{12}\text{C}_6/^{13}\text{C}_6$	sum
250°C	PCDD	158	262	123	543
	PCDF	279	512	4	795
300°C	PCDD	685	908	205	1798
	PCDF	1696	2436	39	4171
350°C	PCDD	1498	1806	372	3676
	PCDF	4855	6226	136	11217
400°C	PCDD	154	127	28	309
	PCDF	1338	1437	35	2810

We also performed experiments with model fly ashes with different  $^{12}\text{C}$ -: $^{13}\text{C}$ -carbon ratios. In all experiments, the ratio of the  $^{12}\text{C}$ -: $^{13}\text{C}$ -PCPh and  $^{12}\text{C}$ -: $^{13}\text{C}$ -PCBz produced corresponds to the  $^{12}\text{C}$ -: $^{13}\text{C}$ -carbon ratio present on the model fly ash. With a full scan measurement we have shown that there is no evident scrambling of the  $^{12}\text{C}$ - and  $^{13}\text{C}$ -carbon within the chlorobenzene or chlorophenyl rings. Knowing the data of the mixed dibenzodioxins as a fraction of the total PCDD, the fraction of the condensation reaction from the sum of formation pathways can be calculated. Therefore, it is assumed that the  $^{12}\text{C}$ - and  $^{13}\text{C}$ -precursors have similar reactivity. Thus we obtain the following results for the fraction of the condensation reaction in the range 250 - 400°C: condensation reaction of  $^{12}\text{C}$ -precursors to  $^{12}\text{C}_{12}$ -PCDD: decrease from 38 to 9%, condensation reaction of  $^{13}\text{C}$ -precursors to  $^{13}\text{C}_{12}$ -PCDD: decrease from 23 to 11%.

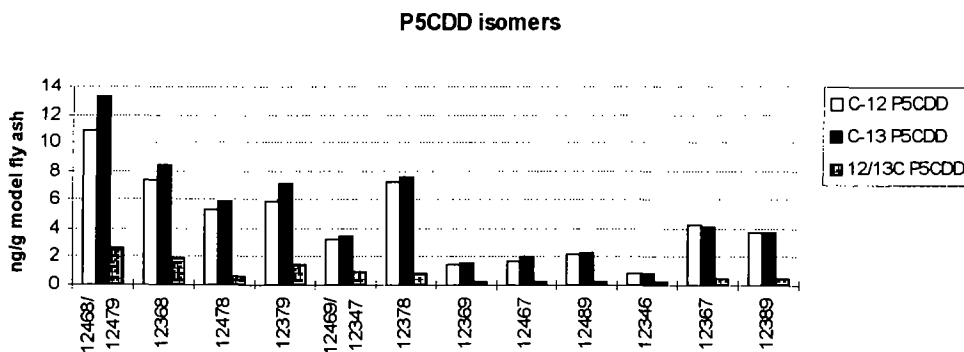
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This is due to increased evaporation of chlorophenols at elevated temperatures. The fraction of chlorophenols found in the gas trap increases from 2% at 250 to 91% at 350°C.

At 250 and 300°C the amounts of  $^{12}\text{C}_{12}$ - and  $^{13}\text{C}_{12}$ -PCDD/F congeners increase from T4CDD/F to O8CDD/F. At higher temperatures H6- and H7CDD and H6CDF are formed predominantly. This shift in the chlorination degree is due to the continued destruction of higher chlorinated PCDD/F at elevated temperatures. For the studied temperature and time range, the maximum in the chlorination degree for the  $^{12}\text{C}_6/^{13}\text{C}_6$ -PCDD was found for the octachlorinated isomer whereas for the mixed dibenzofurans the maximal concentration is reached for H6CDF. Comparing the chlorination degree of the different PCDD/F species, it seems that mixed dibenzodioxins are less dechlorinated than  $^{12}\text{C}_{12}$ - or  $^{13}\text{C}_{12}$ -PCDD/F.

It is remarkable that the isomer distribution of the mixed dibenzodioxins resembles that of the  $^{12}\text{C}_{12}$ - and  $^{13}\text{C}_{12}$ -dioxins. For example a typical isomer pattern for the P5CDD is represented in Fig. 1. From the condensation of 2,6-D2CPh with P5CPh and 2,4,6-T3CPh with 2,3,4,6-T4CPh only 1,2,3,4,6-, 1,2,4,6,8-, 1,2,4,7,9-, 1,2,3,6,8-, and 1,2,3,7,9-P5CDD are expected. These five isomers constitute only 60% of the total P5CDD isomers. The other isomers must be dechlorination products from higher chlorinated isomers.

Fig. 1. H5CDD isomer pattern  
reaction temperature: 300°C, reaction time 2 hrs.



## 3.2 Formation of PCDD/F as a Function of Time

The amounts of the PCDD/F species produced as a function of time are reported in Table 2. Even a prolongation of the reaction time to 4 hrs. did not lead to an increase in the fraction of the mixed dibenzofurans of the total amount of PCDF. The fraction of the mixed dibenzodioxins is almost independent of reaction time. According to the prior assumption, the condensation pathway for the  $^{12}\text{C}_{12}$ -dioxins is about 16% of the sum of reaction paths and for the  $^{13}\text{C}_{12}$ -dioxins 12%. A reaction time of 4 hrs. resulted in a decrease of this pathway to about 12% for the  $^{12}\text{C}_{12}$ -dioxins and 8% for the  $^{13}\text{C}_{12}$ -dioxins.

Table 2. Formation of PCDD and PCDF from model fly ash ( $^{12}\text{C}:^{13}\text{C} = 1:1$ )  
reaction temperature: 350°C

time [min]	compound	concentration ng/g model fly ash			
		$^{12}\text{C}$	$^{13}\text{C}$	$^{12}\text{C}_6/^{13}\text{C}_6$	sum
15	PCDD	137	133	42	312
	PCDF	404	429	8	841
30	PCDD	424	549	148	1121
	PCDF	1723	2274	52	4049
60	PCDD	753	1111	288	2152
	PCDF	3075	4355	98	7528
240	PCDD	719	982	167	1868
	PCDF	3514	4641	80	8235

### 3.3 Formation of PCPh and PCBz

With some exceptions the ratios of  $^{12}\text{C}:^{13}\text{C}$ -PCPh and  $^{12}\text{C}:^{13}\text{C}$ -PCBz are about 1. The data of the chlorophenol and chlorobenzene concentrations are shown in Table 3. The ratio of the chlorobenzenes in the experiments at 350°C as a function of time are not in agreement with the present carbon ratio on the fly ash.

The amount of PCBz increases continually with temperature and time, whereas for the P5CPh there is no obvious tendency. At lower temperatures, the P5CPh is the favored phenol product. The chlorination of the phenols is very selective. For each chlorination degree only one isomer is formed: 2,4/2,5-D2CPh, 2,4,6-T3CPh, 2,3,4,6-T4CPh and P5CPh. With the used GC conditions it was not possible to separate the 2,4- and 2,5-D2CPh. In all experiments the preferred congener for the benzenes is P5CBz.

Table 3. Formation of PCBz and PCPh from model fly ash ( $^{12}\text{C}:^{13}\text{C} = 1:1$ )

compound	concentration ng/g model fly ash							
	reaction time 120 min				reaction temperature 350°C			
	250°C	300°C	350°C	400°C	15 min	30 min	60 min	240 min
$^{12}\text{C}$ -PCBz	4908	17169	56678	80251	11262	28719	39544	106078
$^{13}\text{C}$ -PCBz	4894	15406	50375	71097	4966	15066	21535	59300
$^{12}\text{C}$ -PCPh	1317	465	351	748	373	196	165	329
$^{13}\text{C}$ -PCPh	2208	696	283	182	380	205	88	259

### 3.4 Comparison of the $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$ ion streams

The comparison of the  $^{12}\text{CO}_2$  and  $^{13}\text{CO}_2$  ion streams shows that the  $^{13}\text{C}$ -carbon is oxidized in a similar amount to carbon dioxide as  $^{12}\text{C}$ -carbon. It was only observed that the maximum of the  $^{13}\text{CO}_2$  concentration is reached 5 min. before that of the  $^{12}\text{CO}_2$  concentration. The  $^{12}\text{CO}_2$  and  $^{13}\text{CO}_2$  ion streams from an experiment with model fly ash enriched with  $^{12}\text{C}$ - and  $^{13}\text{C}$ -carbon (1:1) are depicted in Fig. 2.

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- Thermal treatment of model fly ash ( $^{12}\text{C}$ -: $^{13}\text{C}$  = 1:1) as a function of time did not lead to an increase of the fraction of the mixed dibenzofurans. The fraction of the mixed dibenzodioxins is nearly independent of time. Up to a reaction time of 60 min. the amount of all congeners increases; at longer reaction times the degradation becomes more important.
- The ratio of  $^{12}\text{C}$ -: $^{13}\text{C}$ -PCBz and  $^{12}\text{C}$ -: $^{13}\text{C}$ -PCPh is about 1 corresponding to the used  $^{12}\text{C}$ -: $^{13}\text{C}$ -carbon ratio.
- $^{13}\text{C}$ -carbon is oxidized to carbon dioxide in a resembling fraction as  $^{12}\text{C}$ -carbon and shows a similar reactivity in formation of PCDD/F, PCPh and PCBz as  $^{12}\text{C}$ -carbon. Therefore, it represents a good model compound for the studies.

## 5. References

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