

## Investigation of Precursor Reactions in the De-Novo-Synthesis of PCDD/PCDF on Fly Ash

**L. Stieglitz, H. Bautz, W. Roth, G. Zwick**

Institut für Technische Chemie, Bereich Chemisch-Physikalische Verfahren  
Forschungszentrum Karlsruhe, P.O.Box 3640, 76021 Karlsruhe, Germany

### 1. Introduction

In thermal experiments with fly ash it could be shown that in the temperature range between 275°C and 450°C a great variety of aromatic halogenated compounds are formed de-novo and released.<sup>1-4)</sup> In these heterogeneous reactions the residual carbon from incomplete combustion acts as a direct source for the aromatic compounds. So far two reaction steps have been identified: a.) the metal ion -catalyzed transfer of chloride to the carbon lattice with the formation of carbon-chlorine bonds, and b.) the subsequent oxidation, also metal catalyzed, with the formation and release of volatile, thermodynamically stable aromatic halogen compounds.<sup>5,6)</sup> Detailed investigations of the influence of different parameters were carried out by a series of research groups to elucidate the mechanism of these reactions and its significance for incineration processes.<sup>7,8,9)</sup> A great variety of compounds has been identified to be formed such as chlorobenzenes, -phenoles, -biphenyls, -naphthalenes, - benzothiophenes, -xanthenes, etc. Special interest was focused from the beginning on the formation of polychlorodibenzodioxins (PCDD) and -furans (PCDF) from the carbon. Generally the formation of these three-ring-systems might proceed in two different ways: a) by condensation of one-ring compounds. E.g. PCDD may be synthesized by condensation of chlorophenoles, produced from the carbon structures. Similarly PCDF might result from chlorobenzenes. b.) On the other hand also the direct formation from structures preformed in the carbon could be discussed without intermediate reactions of the precursor compounds. A contribution to this up to now open question can be made by experiments with fly ash containing <sup>12</sup>C and <sup>13</sup>C labeled carbon and mixtures thereof.<sup>10)</sup> The concept is that if intermediates, such as phenoles and benzenes react, besides <sup>13</sup>C<sub>12</sub>- and <sup>12</sup>C<sub>12</sub> labeled PCDD/PCDF also mixed compounds with <sup>13</sup>C<sub>6</sub> - <sup>12</sup>C<sub>6</sub> labeled ring systems should be formed. Consequently for these studies special fly ash was spiked with the appropriate carbon specimens and after thermal treatment the reaction products investigated by HRCG/HRMS. The first results from an extensive investigation are presented here, with the main emphasis on the formation of PCDD/PCDF.

### 2. Experimental

**Materials:** From carbon-free fly ash (<0,2% C), isotopically purified <sup>12</sup>C - carbon (amorphous, 99,95%, Cambridge Isotope Laboratories) and <sup>13</sup>C-enriched carbon (amorphous, 99%, Cambridge Isotope Laboratories) four different mixtures were prepared: Mixture A with 35,3 mg <sup>12</sup>C/g fly ash; mixture B with 38,75 <sup>13</sup>C/g fly ash, mixture C with 17,5 mg <sup>12</sup>C and 19,4 mg <sup>13</sup>C, corresponding to a carbon ratio <sup>12</sup>C/<sup>13</sup>C = 1:1; mixture D with 23,33 mg <sup>12</sup>C and 12,92 mg <sup>13</sup>C (carbon ratio 2:1).

**Thermal treatment and Analysis.** The mixtures were heated at 300°C for 2hrs. in an apparatus described earlier [ 2 ] with an air flow of 50 ml/min containing 150 mg water vapor/l. Volatile compounds were sampled by passing the gas stream through an XAD-16 resin trap. After the thermal treatment the annealed sample and the resin was extracted by toluene. Clean-up and fractionation was

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performed with an alumina column using hexane, hexane:dichloromethane (98:2) and hexane:dichloromethane (1:1) as eluents. With mixture A  $^{13}\text{C}$  labeled tetra - octaCDD/CDF were added including decachlorobiphenyl. To mixture B the corresponding  $^{12}\text{C}$  labeled tetra to octa CDD/CDF and decachlorobiphenyl was added. With mixtures C and D only decachlorobiphenyl served as internal standard. The PCDD/PCDF fraction was measured by HRGC-HRMS (HP5890-Fisons Autospec) with a 50 m SP2331 column in the multi detection mode at a resolution of 10 000. With each sample two masses (M, M+2) characteristic for the  $^{12}\text{C}_{12}$ -  $^{13}\text{C}_{12}$ - and  $^{12}\text{C}_6/^{13}\text{C}_6$  labeled PCDD/PCDF species were recorded. Quantification was achieved with mixtures A and B via the corresponding labeled PCDD/PCDF, with mixtures C and D by substance specific response factors for PCDD/PCDF related to decachlorobiphenyl.

### 3. Results and Discussion

The total concentrations of PCDD/PCDF( residual and volatile) formed after a 120min. thermal treatment of the fly ash are presented in table 1 for the mixtures A, B containing pure  $^{12}\text{C}$ - and  $^{13}\text{C}$ - carbon respectively. The symbol  $^{12}\text{C}_{12}$  and  $^{13}\text{C}_{12}$  stands for PCDD or PCDF compounds in which all twelve carbon atoms in the molecule are isotopically pure either  $^{12}\text{C}$  or  $^{13}\text{C}$  labeled. The expression  $^{12}\text{C}_6/^{13}\text{C}_6$  means that one aromatic ring consists of six  $^{12}\text{C}$ -atoms and the other one of six  $^{13}\text{C}$  atoms.

Table 1: Formation of PCDD/PCDF from  $^{12}\text{C}$  and  $^{13}\text{C}$  -Carbon in Fly Ash

| compound | MIXTURE A<br>12C: 35.5 mg/g FA |                      | MIXTURE B<br>13C: 38.8 mg/g FA |                      |
|----------|--------------------------------|----------------------|--------------------------------|----------------------|
|          | concentration ng/g FA          |                      | concentration ng/g FA          |                      |
|          | $^{12}\text{C}_{12}$           | $^{13}\text{C}_{12}$ | $^{12}\text{C}_{12}$           | $^{13}\text{C}_{12}$ |
| TetraCDD | 46.0                           | <0.1                 | <0.1                           | 59.0                 |
| PentaCDD | 45.8                           | <0.1                 | <0.1                           | 70.1                 |
| HexaCDD  | 14.6                           | <0.1                 | <0.1                           | 18.5                 |
| HeptaCDD | 2.4                            | <0.1                 | <0.1                           | 2.8                  |
| OctaCDD  | 0.6                            | <0.1                 | <0.1                           | 0.4                  |
| PCDD     | 109.5                          | <0.1                 | <0.1                           | 150.8                |
| TetraCDF | 666.7                          | <0.1                 | <0.1                           | 957.0                |
| PentaCDF | 514.9                          | <0.1                 | <0.1                           | 711.5                |
| HexaCDF  | 144.4                          | <0.1                 | <0.1                           | 175.6                |
| HeptaCDF | 1.6                            | <0.1                 | <0.1                           | 17.0                 |
| OctaCDF  | 1.0                            | <0.1                 | <0.1                           | 0.4                  |
| PCDF     | 1328.6                         | <0.1                 | <0.1                           | 1861.4               |

Formation of PCDD/PCDF in the Pure  $^{12}\text{C}$ - $^{13}\text{C}$  Systems In the isotopically pure systems of mixture A and B only either  $^{12}\text{C}_{12}$  or  $^{13}\text{C}_{12}$  PCDD are found. The sum of tetra- to octaCDD is 109,5 and 150,8 ng/g fly ash. The yield of the congener groups in  $\mu\text{g/g}$  related to carbon in the  $^{12}\text{C}$  system is 1.3 for T4CDD and P5CDD, 0.42 for H6CDD, 0,07 for H7CDD and 0,018 for OCDD. The  $^{13}\text{C}$  carbon shows a slightly higher conversion. Here the yields (  $\mu\text{g/g}$  carbon) are 1.52 and 1.81 for T4CDD and P5CDD

respectively, 0.48 for H6CDD, 0.07 for H7CDD and 0.01 for OCDD. The lower chlorinated species are the main compounds.

The PCDF are formed as major compounds. The concentration of T4CDF-OCDF are 1329 ng/g in mixture A and 1860 ng/g in mixture B. The pattern is a strong preference of the lower chlorinated species. The yields of the tetra to hexachloro-congeners are higher by a factor of 10 to 15 compared with the PCDD, while the hepta and octachlorospecies are in the same concentration range as the corresponding PCDD. The yields in  $\mu\text{g/g}$  carbon in the  $^{12}\text{C}$  system are 19 and 14.7 for T4CDF and P5CDF, 4.1 H6CDF and 0.05 and 0.03 for H7CDF and OCDF. The formation in the  $^{13}\text{C}$  mixture is also slightly higher for the furans

Table 2: Formation of PCDD/PCDF in  $^{12}\text{C}$ - $^{13}\text{C}$  Mixtures

| compound | MIXTURE C                              |       |               |        | MIXTURE D                              |       |               |        |
|----------|--|-------|---------------|--------|--|-------|---------------|--------|
|          | 12C: 17.5 mg/g FA<br>13C: 19.4 mg/g FA |       |               |        | 12C: 23.3 mg/g FA<br>13C: 12.9 mg/g FA |       |               |        |
|          | concentration ng/g FA                  |       |               |        | concentration ng/g FA                  |       |               |        |
|          | 12C12                                  | 13C12 | 12C6-<br>13C6 | sum    | 12C12                                  | 13C12 | 12C6-<br>13C6 | sum    |
| TetraCDD | 17.0                                   | 28.3  | 12.6          | 57.8   | 20.1                                   | 11.4  | 5.9           | 37.4   |
| PentaCDD | 16.9                                   | 31.1  | 17.7          | 65.7   | 22.2                                   | 14.7  | 9.8           | 46.7   |
| HecaCDD  | 4.8                                    | 16.2  | 7.4           | 28.4   | 8.2                                    | 4.9   | 7.1           | 20.3   |
| HeptaCDD | 0.7                                    | 1.6   | 1.2           | 3.6    | 1.7                                    | 0.7   | 0.7           | 3.0    |
| OctaCDD  | 0.3                                    | <0.1  | 0.2           | 0.5    | 0.5                                    | 0.2   | 0.1           | 0.8    |
| PCDD     | 39.7                                   | 77.2  | 39.0          | 155.9  | 52.7                                   | 31.8  | 23.6          | 108.1  |
| TetraCDF | 255.4                                  | 464.8 | 14.9          | 735.1  | 369.4                                  | 592.3 | 6.5           | 968.2  |
| PentaCDF | 207.2                                  | 400.5 | 12.2          | 619.8  | 290.8                                  | 198.8 | 5.8           | 495.4  |
| HexaCDF  | 57.2                                   | 118.4 | 4.0           | 179.6  | 97.4                                   | 70.3  | 1.7           | 169.3  |
| HeptaCDF | 5.8                                    | 13.2  | 0.5           | 19.5   | 12.7                                   | 10.3  | 0.3           | 23.3   |
| OctaCDF  | 0.6                                    | 2.8   | <0.1          | 3.5    | 1.0                                    | 0.4   | <0.1          | 1.4    |
| PCDF     | 526.2                                  | 999.8 | 31.5          | 1557.5 | 771.3                                  | 872.1 | 14.1          | 1657.5 |

**Behaviour of  $^{12}\text{C}$ - $^{13}\text{C}$ -Mixtures:** The results from the thermal treatment of fly ash with mixtures of  $^{12}\text{C}$ - $^{13}\text{C}$  are presented in table 2. The formation of PCDD and PCDF is discussed separately due to the different behaviour:

a.) **Formation of PCDD:** All three species  $^{12}\text{C}_{12}$ ,  $^{13}\text{C}_{12}$  and the mixed  $^{12}\text{C}_6/^{13}\text{C}_6$  PCDD are formed. The sum is between 108 and 155 ng/g and corresponds within the experimental error to the amounts formed in the pure systems A and B. In the data also the small differences found in the reactivity of 12C and 13C carbon are reflected. The total yield ( $\mu\text{g/g}$  carbon) is 1.03 for T4CDD, 1.29 for P5CDD, 0.56 for H6CDD, 0.08 for H7CDD and 0.02 for OCDD, similar to the pure systems. The fraction of the mixed species  $^{12}\text{C}_6$ - $^{13}\text{C}_6$  is relatively constant at 20 to 30% of the total production in the system with 12C:13C ratio = 1:1 (mixture C) With the mixture D (12C:13C = 2:1) the fraction varies depending on the chlorination degree from 16 to 47%. The presence of the mixed  $^{12}\text{C}_6$ - $^{13}\text{C}_6$ -PCDD species strongly indicates that in the formation of the PCDD molecule intermediates with separate benzene rings such as chlorophenols formed from the carbon lattice play a role. So from  $^{12}\text{C}$  and  $^{13}\text{C}$  carbon the corresponding  $^{12}\text{C}_6$ - and  $^{13}\text{C}_6$  chlorophenols are released as products of the oxidative degradation of

the carbon and react in situ with each other to form chlorodioxins. The fraction of the  $^{12}\text{C}_{12}$ -,  $^{13}\text{C}_{12}$ - and  $^{12}\text{C}_6$ - $^{13}\text{C}_6$ - species depends on the reactivity of the carbon and the probability for the subsequent interaction of the intermediates. The ratio between condensation reaction and direct formation is currently evaluated.

**b.) Formation of PCDF:** The data for the formation of PCDF, presented in table 2, show that the total yield (mg/g) in the mixture is in the same order as with the systems with  $^{12}\text{C}$  and  $^{13}\text{C}$  separate. In strong contrast to the behaviour of the PCDD are the data for the synthesis of PCDF: In both mixtures C and D only PCDF compounds are formed in which both aromatic rings consist either of pure  $^{12}\text{C}_{12}$  or  $^{13}\text{C}_{12}$  structures. The fraction of the  $^{12}\text{C}_6$ - $^{13}\text{C}_6$  species is only 1 - 2% of the total PCDF concentration produced and must be considered as negligible. Mixed dibenzo-dioxin species are formed with a probability higher by a factor of 10 to 20 than PCDF. This finding is the experimental proof that with the de-novo-synthesis of PCDF intermediate reactions of chlorphenoles or chlorbenzenes cannot be involved. It must be assumed that in the synthesis process dibenzofuran structures are preformed and present in the carbon lattice or that at least preformed biphenyl structures are involved and kept intact throughout the formation of the dibenzofuran molecule.

#### 4. Conclusions

Using  $^{12}\text{C}$  and  $^{13}\text{C}$  carbon in fly ash intermediate reactions in the de-novo-synthesis of PCDD/PCDF may be investigated. From the annealing of isotopically pure carbon systems as well as of defined  $^{12}\text{C}/^{13}\text{C}$  mixtures the following conclusions may be arrived at with regard to reactions of intermediate precursors:

- With the PCDD formed a substantial fraction (20-30%) consists of compounds in which one phenyl ring is  $^{12}\text{C}$ , the other one  $^{13}\text{C}$  labeled. The appearance of these  $^{12}\text{C}_6$ - $^{13}\text{C}_6$  structures indicates that the synthesis of PCDD from carbon proceeds at least in part via the condensation of intermediately formed phenyl rings. e.g. phenoles.
- In strong contrast to this fact,  $^{12}\text{C}_6$ - $^{13}\text{C}_6$  structures are not found with the formation PCDF. Consequently the reaction of single phenyl compounds play no role in the synthesis of dibenzofurans from carbon. Instead it must be concluded that preformed biphenyl structures are the precursor compounds in the de-novo-synthesis.

The experimental data prove that in the formation of the two compound classes on fly ash two completely different precursor compounds and reaction paths are involved, with carbon still being the primary source of the intermediates.

#### 5. References

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