

Behaviour of PCDD under Pyrolysis Conditions

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Abstract

A regular sample of real municipal solid waste (MSW) spiked with a ¹³C₁₂-OCDD standard has been pyrolysed in a model reactor. Dechlorination has occurred and isomeric profiles are found for the homologue groups of tetra- to octachlorinated PCDD. A mass balance over the labelled carbon introduced by the ¹³C₁₂-OCDD standard and emitted by the formed tetra- to octachlorinated ¹³C₁₂-PCDD shows that 85% of the input ¹³C₁₂-PCDD get through the pyrolysis without thermal decomposition. Decomposition rates and homologue patterns of native and labelled dioxins differ a lot due to different transit times in the oven. But the congener profiles of the labelled PCDD correspond with those of the native PCDD. This seems to indicate that the congener pattern determining step does not take place during pyrolysis but in the gas phase.

Introduction

The incineration of wastes has been identified as a source of PCDDs and PCDFs. Investigations particularly related to the incineration of municipal solid waste resulted in the postulation of two main formation routes for PCDD/F, the de novo synthesis from particulate organic carbon and the formation from chlorinated precursors¹⁾. However, the contribution of the two processes to the total emission of PCDD/Fs is still being debated. Nottrodt et al.²⁾ found the de novo synthesis to be the main process for the formation of PCDD/Fs in MSWI. Experiments performed on fly ash showed the amount of PCDD to be governed by the formation from precursors³⁾. Aside from the two mechanisms mentioned above, a third theory explains that the appearance of PCDD/F in flue gas of MSWIs is caused by the chlorination and dechlorination of dioxins and furans already existing in the MSW. An approximate mass balance shows that the PCDD/F entering an incinerator with MSW and leaving the system with fly ash and stack gas are of the same order of magnitude⁴⁾. Nevertheless, the isomeric pattern of PCDD/F in the feed and in the emissions are different. This leads to the exclusion of a mechanism of formation according to which PCDD/Fs remain unaltered in the combustion process.

The homologue patterns of PCDD in MSW⁵⁾ and biocompost⁶⁾ are predominated by the octachlorinated dibenzodioxin. Therefore the OCDD presents the main fraction of PCDD entering an incinerator. Assuming that the emitted PCDDs originate mainly from a transformation of the feed PCDD, a mass balance could be reduced to the amount of OCDD in the MSW observed. In order to confirm this, MSW spiked with OCDD has been treated under pyrolysis conditions.

Experimental

For the laboratory-scale investigation a representative sample of Hessian MSW, spiked with 10µg of a $^{13}\text{C}_{12}$ -OCDD standard, was pressed into a high-grade steel tube which was then placed in an oven. Pyrolysis was performed by heating the oven up to 600°C, with a heating rate of 2°C/min. During operation the reactor temperature was continuously controlled with a CrAlCr-thermoelement. Further parameters like loss of weight, volume stream and amount of gas produced were measured and the composition of the gas concerning inorganic and volatile aliphatic compounds was analyzed. The pyrolysis gas was condensed, giving an oily condensate. In addition to the oily condensate the solid residue left in the reactor was analyzed. In order to obtain a mass balance for the native dioxins and furans the sample of MSW has been analyzed before performing the pyrolysis. Analytical preparation followed procedures referring to a German official standard (VDI 3499). The samples were extracted and the raw extracts cleaned up and fractionated by adsorption chromatography on silicagel- and aluminum oxid columns. The fraction containing PCDD/F was concentrated with dry nitrogen gas and an aliquot of the final volume was injected into a HRGC/HRMS. Screening analysis and detection of higher chlorinated congeners was performed with a non-polar DB-5 capillary column. For isomer specific detection a polar capillary column (CP Sil 88) was used. The MS was performed in MID-mode (multiple ion detection). For additional information, the attained PCDD/F-data is expressed as toxic equivalents according to the international scale (I-TEQ).

Results and Discussion

The results of the native and $^{13}\text{C}_{12}$ -labelled dioxins and furans analysis are given in Table 1. Under pyrolysis conditions dechlorination of the $^{13}\text{C}_{12}$ -OCDD has occurred and congener profiles are found for the homologue groups of tetra- to octachlorinated $^{13}\text{C}_{12}$ -PCDD. No labelled PCDFs have been detected, as was expected, since a conversion from dibenzodioxines into dibenzofurans and vice versa has never been observed. The amount of labelled PCDD present in the solid residue is not detectable.

A mass balance over the labelled carbon introduced by the $^{13}\text{C}_{12}$ -OCDD standard and emitted by the formed tetra- to octachlorinated $^{13}\text{C}_{12}$ -PCDD shows that 85% of the input PCDD get through the pyrolysis process undergoing dechlorination but without undergoing thermal decomposition. Nevertheless, parts of the PCDD could also undergo chlorination due to the fact that many chlorine sources exist in MSW. Contrary to this result the mass balance over the native PCDD/F introduced by the sample of MSW and emitted by the PCDD/F in the oily condensate shows that the decomposition rate for the native dioxins is about 57%. The difference in percentage of decomposition of 15% for the labelled and 57% for the native dioxins can be explained by the diversified transit times of the compounds in the oven. The application of the $^{13}\text{C}_{12}$ -OCDD standard to the MSW only leads to a bondage of the compounds to the surface of waste particles. Therefore, the appearance of evaporation with increasing temperature during which dechlorination occurs is very likely. The native dioxins and furans already existing in the MSW are partially inserted by chemical processes. The bondage to solid particles is not restricted to the surface but the compounds are also bound in the pores of particles. In that way the transit time and hence the chance of decomposition increases.

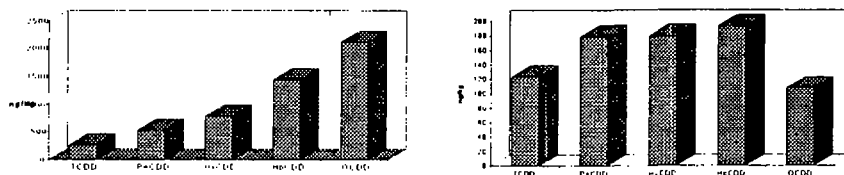


Figure 1 Homologue patterns of native and labelled PCDD

The homologue profile of the labelled dioxins in the oily condensate (see Figure 1) is characterized by an elevated percentage of the congeners with a higher chlorination degree (HpCDD and OCDD being over 50% of the total amount), while the TCDD is the congener present in the lowest percent. As can be seen from Figure 1 the homologue profile of the native dioxins in the condensate fraction is governed by the penta- to heptachlorinated PCDD, while the tetra- and octachlorinated dioxins are represented in minor percentages. The different homologue profile of native PCDD is due to the input homologue pattern (see Table 1), the increased transit times and the related chance of decomposition and the contribution of de novo synthesis and formation from precursors to the total amount of native PCDD. Most striking is the result that the congener profiles of the labelled PCDD correspond largely with those of the native PCDD (see Figure 2). Only the congener profiles of the native and labelled TCDD show a minor difference which could be explained by the formation of native PCDD from precursors or by de novo synthesis. The results obtained seem to indicate that the congener distribution determining step is not related to the transit time in the pyrolysis oven while the decomposition rate and the homologue distribution seem to show a dependency of the transit time. With the experiment carried out it could not be shown that the emitted PCDD/F originate mainly from transformation of the feed PCDD/F. The contribution of de novo synthesis, formation from precursors and input PCDD/F has to be verified by further experiments.

Table 1 Native and labelled PCDD/F concentrations in input and condensate

| polychlorinated dibenzo-dioxins und -furans (PCDD/F) | input native PCDD/F [ng/kg] | oily condensate native PCDD/F [ng/kg] | oily condensate labelled PCDD/F [ng/kg] |
|--|-----------------------------|---------------------------------------|---|
| ∑ TCDD | 5,93 | 123,9 | 264,7 |
| ∑ PeCDD | 10,8 | 178,9 | 536,7 |
| ∑ HxCDD | 28,1 | 179,6 | 790,6 |
| ∑ HpCDD | 308 | 193,0 | 1447,2 |
| OCDD | 1750 | 107,2 | 2123,9 |
| ∑ PCDD | 2102,83 | 782,6 | 5163 |
| ∑ TCDF | 35,7 | 83,8 | 0,13 |
| ∑ PeCDF | 29,9 | 53,7 | 0,27 |
| ∑ HxCDF | 17,5 | 26,7 | 0,27 |
| ∑ HpCDF | 32,3 | 23,9 | 0,27 |
| OCDF | 37,3 | 9,78 | 0,7 |
| ∑ PCDF | 152,7 | 197,9 | n.d. |
| ∑ PCDD + PCDF | 2255,53 | 980,5 | 5163 |
| 2,3,7,8-substituted PCDD | | | |
| 2378-TCDD | 0,2 | 2,12 | 4,85 |
| 12378-PeCDD | 0,44 | 13,4 | 38,28 |
| 123478-HxCDD | 1,27 | 3,49 | 17,62 |
| 123678-HxCDD | 2,84 | 14,54 | 51,86 |
| 123789-HxCDD | 1,90 | 14,27 | 56,21 |
| 1234678-HpCDD | 1,56 | 87,8 | 562 |
| 2,3,7,8-substituted PCDF | | | |
| 2378-TCDF | 2,62 | 5,09 | 0,13 |
| 12378 + 12348-PeCDF | 0,99 | 3,79 | 0,27 |
| 23478-PeCDF | 1,49 | 2,24 | 0,27 |
| 123478 + 123479-HxCDF | 1,41 | 3,03 | 0,27 |
| 123678-HxCDF | 0,90 | 2,65 | 0,27 |
| 123789-HxCDF | 0,4 | 0,15 | 0,27 |
| 234678-HxCDF | 0,94 | 1,23 | 0,27 |
| 1234678-HpCDF | 15,8 | 18,31 | 0,27 |
| 1234789-HpCDF | 0,68 | 0,66 | 0,27 |
| 1-TEQ | 5,7 | 15,7 | 44,6 |

n.d. = not determined

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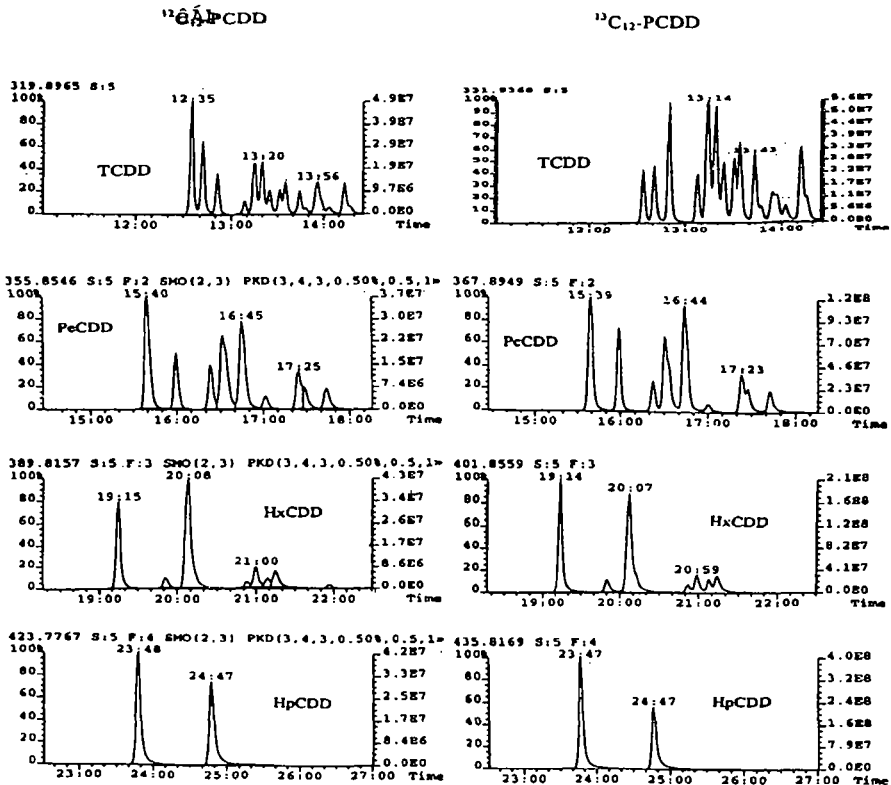


Figure 2 Congener profiles of native and labelled tetra- to heptachlorinated PCDD