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DESORPTION BEHAVIOUR OF POLYCHLORINATED DIBENZO-P-DIOXINS/
DIBENZOFURANS ON A PACKED FLY ASH BED

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Abstract - When incinerator fly ash is heated at 398 °C under a stream of N₂/O₂, polychlorinated dibenzo-p-
dioxin (PCDD) and polychlorinated dibenzofuran (PCDF) concentrations are lowered. Dechlorination/decomposition and desorption are competing processes. In this paper the desorption was
studied: within PCDD/F homologues, all isomers desorb at an equal rate. Obviously, values of the activation
energy of desorption from the fly ash surface (ΔG°₉₀,des) do not differ significantly between these isomers.

Key words - Desorption, fly ash, isomers, polychlorinated dibenzo-p-dioxins, polychlorinated dibenzofurans.

1. Introduction

Formation of polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) during the
process of waste incineration has been documented since the late seventies [1,2]. The formation of PCDD/F
takes place in the post combustion zone at temperatures < 600 °C [3]. Residue particles (fly ash) are carried
into this low-temperature area of the incinerator, in which the off-gas is cooled down and passed through an
air pollution control device. The fly ash particles act as a catalytic surface during the formation process [4].
Fly ash contains all material that is required for reactions yielding PCDD/F: carbon [5], small organic
compounds [6], metal ions [7] and inorganic chloride [8]. The macromolecular carbon structure on the fly
ash surface is catalytically oxidized to a great range of compounds, including PCDD/F. Especially Cu and Fe
ions catalyze these formation reactions [9]. Apart from inorganic Cl already present in the fly ash, Cl from
HCl can be incorporated in the PCDD/F structure as well [10]. PCDD/F can be formed on fly ash from
small organic molecules like chlorobenzenes, phenol and hexane too [11].

Once formed both PCDD and PCDF have a tendency to reside on the fly ash surface: with reaction times
of 1-2 h, below 300 °C desorption is negligible [12]. Between 300 and 350 °C PCDD/F start to evaporate
from the fly ash, at 350 °C 94% of all PCDD/F are in the gas phase [13]. With longer reactions times (16-
48 h), significant desorption is also possible at temperatures between 100-200 °C, suggesting a mass transfer limitation. PCDD/F which do not desorb are assumed to be chemisorbed [14].

In this article, we look into the desorption behaviour of PCDD/F isomers within homologues. Within a homologue the various isomers could have different values of $\Delta G^\circ_{\text{des}}$ and consequently exhibit different degrees of evaporation from the fly ash surface. We have studied the desorption behaviour of PCDD/F within homologues using original fly ash, i.e. untreated, still containing all organic material formed on its surface during the incineration process, at 398 °C.

2. Experimental

Chemicals

The chemicals used in our clean up have been described before [15]. Only the chemicals used in our experiments are reported: fly ash from the Municipal Waste Incinerator Zaanstad, The Netherlands; nitrogen (5.0 grade, Hoekloos, Schiedam, The Netherlands); oxygen (4.5 grade, Hoekloos, Schiedam, The Netherlands).

Experimental Apparatus

2.0 g of original fly ash was placed in a cylindrical sample basket and coupled with a glass inlet tube for introduction of a gas flow through the fly ash bed. Sample basket and inlet tube were fit into a horizontal pyrex glass reactor and put in a furnace (Lenton CSC 1100 Split Tube Furnace with PID 808 temperature controller, Leicestershire, UK). Experiments lasted for 50 min, preceded by 10 min of heating in order for sample basket, inlet tube and reactor to reach the setpoint temperature (398 °C, accuracy ± 7 °C). A gas stream of $101\pm3$ ml/min $N_2$ and $9.7\pm0.5$ ml/min $O_2$ passed the fly ash bed during the whole experiment (including the 10 min needed for warming up). The flow was controlled by Series 840 Side=Trak mass flow controllers (Sierra Instruments, Monterey, CA, USA). The flow was checked before and after experiments with a flow meter. The gases were mixed in a mixing chamber ($V=800$ ml) containing ceramic pellets. Products evaporating from the fly ash surface were collected using a cold trap (80 ml toluene cooled with ice). After the experiment the fly ash bed was taken out of the furnace immediately and cooled to room temperature. Cold traps were analyzed separately.

Clean Up and Analysis

These have been described before [15]. Only the $T_4$CDD-OCDD and $T_4$CDF-OCDF were analyzed. Blanks taken from the clean up procedure contained no significant amounts of PCDD/F.

3. Results and Discussion

Results of our experiments are shown in Table 1. We used original fly ash in our study, because this contains almost all possible tetra-octa CDD/F congeners. Initial experiments were carried out at 150 °C, but even after long reaction times (16 h) no significant desorption of PCDD/F took place. Therefore, we decided to conduct further experiments at higher temperatures (ca. 400 °C), where a significant amount of PCDD/F can be
expected in the gas phase.

When compared with the PCDD/F content of original fly ash, it is clear that under the experimental conditions used a decrease of both PCDD and PCDF is observed. Especially PCDD is prone to dechlorination and decomposition reactions, as the [PCDD]:[PCDF] ratio changes from 0.85 before the experiment to 0.12-0.15 after the experiment.

With our reaction conditions, dechlorination, decomposition and desorption take place. The isomer pattern within homologues found on the fly ash surface will be the result of these three processes; the isomer distribution in the cold trap will be the result of desorption only. This makes comparison of both isomer distributions difficult. Preliminary results suggested that the isomer distributions found on original fly ash (before the experiment), on fly ash after the experiment and in the cold trap are similar. This would mean that the thermal treatment, and consequently dechlorination, decomposition and desorption, do not alter the isomer distribution within homologues. Under such conditions, the isomer distribution found in the cold trap is entirely determined by the availability of PCDD/F on the fly ash surface and within homologues all isomers desorb at the same rate.

To test this hypothesis, we have looked at the degree of correlation between the isomer distributions of i) the fly ash after the experiment and the cold trap; ii) the fly ash after and before the experiment; iii) the cold trap and fly ash before the experiment. The degree of correlation was calculated using linear regression, either for all PCDD/F congeners together or for each homologue separately. When calculating the correlation coefficient \( r \) for all PCDD/F congeners together, within the tetra-hepta CDD/F homologues the isomer distribution is calculated by setting the sum of each homologue to 100%. This results in 102 percentages (each peak being a percentage) divided over 8 homologues. These 102 percentages represent 134 tetra-hepta CDD/F congeners, due to the fact that some isomers coelute on the GC column. Taking the isomer percentages of e.g. the fly ash after the experiment as \( x \) values, and those in the cold trap as \( y \) values, \( r \) can be calculated.

| Table 1. Yields of PCDD/F in nanomole/g fly ash and [PCDD]:[PCDF] ratios. (a) |
|------------------|------------------|------------------|
|                  | Fly ash          | Cold trap        | Original fly ash (b) |
| \( \Sigma \) PCDD | 0.06             | 0.03±0.01        | 4.36±0.32            |
| \( \Sigma \) PCDF | 0.55±0.05        | 0.21±0.04        | 5.13±0.37            |
| [PCDD]:[PCDF]    | 0.12             | 0.15             | 0.85                 |

a: Experiment performed twice, mean value ± range is given in nanomole/g fly ash. Conditions: 2.0 g of original fly ash, \( T=398±7 \, ^{\circ}\mathrm{C} \), 50 min, \( N_2 \) 101 ± 3 ml/min, \( O_2 \) 9.7 ± 0.5 ml/min.

b: Original fly ash was analyzed in duplicate to find the PCDD/F content and the [PCDD]:[PCDF] ratio before the experiment.
Table 2. Correlation coefficients (r) of the isomer distributions. (a)

<table>
<thead>
<tr>
<th></th>
<th>Fly ash - cold trap</th>
<th>Fly ash - original</th>
<th>Cold trap - original</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(b)</td>
<td>(c)</td>
<td>(d)</td>
</tr>
<tr>
<td>T₄CDD</td>
<td>0.94</td>
<td>0.87</td>
<td>0.89 ± 0.01</td>
</tr>
<tr>
<td>P₃CDD</td>
<td>0.85 ± 0.07</td>
<td>0.78 ± 0.02</td>
<td>0.93 ± 0.01</td>
</tr>
<tr>
<td>H₂CDD</td>
<td>0.96 ± 0.02</td>
<td>0.96</td>
<td>0.97</td>
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<tr>
<td>H₂CDD</td>
<td>e</td>
<td>e</td>
<td>e</td>
</tr>
<tr>
<td>T₄CDF</td>
<td>0.78 ± 0.02</td>
<td>0.62 ± 0.05</td>
<td>0.68 ± 0.02</td>
</tr>
<tr>
<td>P₃CDF</td>
<td>0.91 ± 0.03</td>
<td>0.91 ± 0.02</td>
<td>0.92 ± 0.01</td>
</tr>
<tr>
<td>H₂CDF</td>
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<td>0.84 ± 0.01</td>
<td>0.82 ± 0.07</td>
</tr>
<tr>
<td>H₂CDF</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
</tr>
</tbody>
</table>

a: The correlation coefficient r was calculated by linear regression. r was calculated for each experiment separately, resulting in two values of r for each entry in the table. The mean value ± range is given, unless the difference between the two values was negligible. Number of data points used for each homologue: T₄CDD = 14; P₃CDD = 11; H₂CDD = 7; T₄CDF = 28; P₃CDF = 23; H₂CDF = 13; H₂CDF = 4.
b: This column gives the degree of similarity of the isomer distribution found within a homologue on fly ash after the experiment and in the cold trap.
c: See b, but now for the fly ash before and after the experiment.
d: See b, but now for the cold trap and the fly ash before the experiment.
e: Homologue consists of two isomers only, hence r cannot be calculated.

Obviously, r can be calculated for each homologue separately in a similar way.

The correlation coefficients thus found are high when calculated for all PCDD/F together: r equals 0.95-0.98 when comparing the isomer distribution on fly ash after the experiment and in the cold trap. Both these isomer distributions are also very similar to the distribution found on fly ash before the experiment: r is 0.96 when comparing the distribution on fly ash after and before the experiment, and r is 0.95-0.97 when comparing the distribution of the cold trap with the fly ash before the experiment. Thus, when considering all homologues together, the isomer distribution on fly ash remains nearly constant during thermal treatment and within homologues all isomers desorb at an equal rate.
In Table 2 results are shown which are obtained by calculating \( r \) for each homologue separately. Correlation coefficients found are lower than those reported above now, but still > 0.8 for the T\(_4\)CDD-H\(_2\)CDD homologues. Values of 0.6-0.7 are found for T\(_5\)CDF, \( r \) is higher for the other homologues and nearly 1 for H\(_2\)CDF. When considering the various PCDD/F homologues, we can still conclude that the isomer distributions are not influenced significantly by the dechlorination/decomposition and desorption process.

4. Conclusions

Our experiments show that within PCDD/F homologues, all isomers evaporate from the fly ash surface at 398 °C with an equal rate. The position of the chlorine atoms in the PCDD/F does not influence this desorption process. This is also true for the dipole moment \( \mu \), which is different for the various isomers within a homologue [16]. The observation that \( \Delta G^* \) is more or less constant for the isomers within a homologue, implies that this also holds for \( \Delta H^* \) and \( \Delta S^* \).

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