

Formation of PCDD/F from anthraquinone derivatives on fly ash.

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Introduction

Formation of polychlorinated dibenzo-p-dioxins/dibenzofurans (PCDD/PCDF) has been studied using various organic starting materials. Macromolecular carbon is capable of PCDD/F formation on fly ash.¹ Phenol and various chlorophenols have also been studied and give coupling reactions leading mainly to PCDD.² Monocyclic aromatic compounds like toluene, benzaldehyde and benzoic acid, containing no chlorine, also give rise to PCDD/F formation.³ Residual carbon on fly ash (i.e. carbon left after extraction of original fly ash with an organic solvent) probably contains various functional groups like carboxylic and ether groups and also quinoid structures.⁴ To investigate the role of functional groups in PCDD/F formation we have looked at anthraquinone, 2,6-dihydroxy-anthraquinone (here after: 2,6-diOH) and 2-anthraquinone-carboxylic acid (2-aca) as possible precursors.

Experimental

Only essential data are given here, experimental details and clean up have been described elsewhere.⁵ Fly ash from the MWI Zaanstad (92.6%), reactant (5.3%) and CuCl₂ (2.1%) were mixed by shaking. From the incinerator fly ash all organic material had been removed previously. 2.0 g of this mixture 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 placed in a horizontal pyrex glass reactor, which had been pre-heated in a tube furnace for 30 min. All experiments were performed in duplo for 50 min at 348 °C (accuracy ± 7 °C). Blank controls were made of fly ash, reactants and CuCl₂. Fly ash and CuCl₂ together contained 5ng/g PCDD/F. Reactants were more contaminated and contained between 53-130 ng/g Σ PCDD/F. A gas stream (101 ± 2 ml/min N₂, 12.9 ± 0.2 ml/min O₂ and 5.1 ± 0.3 ml/min HCl) was passed through the fly ash bed. Products evaporating from the fly

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ash surface were collected using a cold trap.

Results and discussion

The chemical structure of the three compounds studied is presented in figure 1. Results are shown in table 1. Heating of anthraquinone on fly ash does not result in PCDD/F formation. The total amount of PCDD/F formed is 113 ± 1 ng/g fly ash, which is slightly less than the PCDD/F concentration found in anthraquinone itself (130 ng/g).

With a carboxyl group present at the 2-position in the molecule (i.e. 2-aca), formation proceeds smoothly: Σ PCDD + PCDF is 8140 ± 170 ng/g. Before the experiment 2-aca contained only 1.3% of that amount (102 ng/g). Quantification of PCDD/F formed with the 2,6-diOH compound was not possible. This is due to: a. extensive clean up of the fly ash samples necessary to remove the 2,6-diOH compound, resulting in low recoveries of ^{13}C -labeled internal standards; b. injection of the sample from a diluted solution in order to avoid too high concentrations of PCDD/F in the GC/MSD, making determination of the ^{13}C -PCDD/F standards impossible. However, some internal standards could be determined and during one experiment with 2,6-diOH 59 $\mu\text{g/g}$ of P5CDD was formed, indicating that the 2,6-diOH compound is more reactive in PCDD/F formation than 2-aca.

The parent anthraquinone structure with its two carbonyl groups is not reactive as far as PCDD/F formation is concerned. Of course, other compounds may have been formed, e.g. through fly ash mediated oxychlorination. This was not investigated. The other two compounds 2-aca and 2,6-diOH do form PCDD/F and have the presence of one (in carboxyl) and two hydroxy groups in common. Apparently this enhances their reactivity, possibly through better adsorption on the fly ash surface. As all three compounds contain two C=O groups the presence of carbonyl itself does not prevent PCDD/F formation. When we consider the reactants as carbon model compounds, the OH- and COOH groups in carbon will have a stimulating effect on PCDD/F formation, whereas C=O plays not an important role.

The [PCDD] : [PCDF] ratio found for 2-aca is ca. 1.2, which is higher than usually found with carbon as reactant (rarely above 0.5). The formation of more PCDD than PCDF from 2-aca is accompanied with an isomer distribution which shows a typical 'chlorophenol' pattern for T4CDD. Formation via chlorophenol intermediates leads to a higher [PCDD] : [PCDF] ratio. However, the 'chlorophenol' pattern is seen less with the other isomer groups.

Formation from 2-aca has a tendency for the higher chlorinated congeners: Σ H7CDD + OCDD is 90 ± 6 % and Σ H7CDF + OCDF is 62 ± 3 % (Σ PCDD, Σ PCDF=100%).

The T4CDD isomer distribution formed from 2-aca has 1,3,6,8 and 1,3,7,9 as the predominant isomers. They are present at $53.8 \pm 0.1\%$ and $34.8 \pm 0.8\%$ respectively,

Table 1, yields of PCDD/F in ng/g fly ash.^a

	anthraquinone	2-aca	2,6-diOH
Σ PCDD	27 \pm 1	4430 \pm 170	not quantified
Σ PCDF	86 \pm 3	3710 \pm 0	idem
Σ PCDD + PCDF	113 \pm 1	8140 \pm 170	idem
[PCDD] : [PCDF]	0.31 \pm 0.02	1.19 \pm 0.05	idem

a: All experiments 92.6% fly ash, 5.3% reactant, 2.1% CuCl₂, 50 min at 348 \pm 7 °C, N₂ 101 \pm 2 ml/min, O₂ 12.9 \pm 0.2 ml/min, HCl 5.1 \pm 0.3 ml/min, in duplo, mean value \pm range.

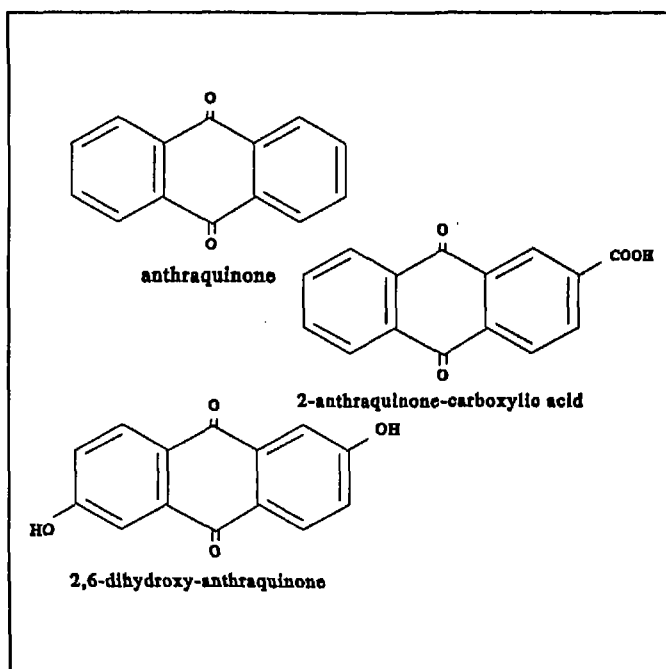


Figure 1 Chemical structure of compounds tested.

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compared to $16.2 \pm 5.4\%$ and $20.1 \pm 2.0\%$ in the original fly ash from which our carbon-free fly ash is derived ($\Sigma T4CDD=100\%$). Formation of these two T4CDD-isomers can be explained by condensation of two 2,3,5- or 2,4,6-trichlorophenol molecules, either directly or via the Smiles-rearrangement.⁶ Apparently the 2-aca is converted to one of these intermediates during the experiment. 1,2,3,6,8-P5CDD is formed for $32.1 \pm 0.5\%$, compared to $13.2 \pm 3.2\%$ in original fly ash ($\Sigma P5CDD=100\%$). This isomer could be formed through coupling of 2,4,6-trichlorophenol and 2,3,4,6-tetrachlorophenol. However the Smiles rearranged product of this coupling, 1,2,3,7,9-P5CDD is formed in the same amounts as on original fly ash (ca. 20%). This suggests that the specific formation of 1,2,3,6,8-P5CDD stems from direct chlorination of 1,3,6,8-T4CDD rather than from condensation of chlorophenols. The co-eluting isomers 1,2,4,6,7,9-, 1,2,4,6,8,9,- and 1,2,3,4,6,8-H6CDD are also formed more than on original fly ash ($44.9 \pm 0.1\%$ versus $29.9 \pm 3.8\%$, $\Sigma H6CDD=100\%$). It is likely that this is due to additional formation of the 1,2,3,4,6,8 isomer from 1,2,3,6,8.

No specific 'chlorophenol' pattern is seen with 2,6-diOH. On the contrary, the 1,3,6,8- and 1,3,7,9-T4CDD are formed in smaller concentrations than on original fly ash. A 'chlorophenol' pattern could be expected if cleavage of the molecule occurs with formation of two phenol and two CO molecules. Apparently this does not take place.

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