

Polyfluorinated Dibenzodioxins/furans - Synthesis, Analysis and Formation

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1. Introduction

In the last years the question has been raised repeatedly, whether polyfluorinated dibenzodioxins and polyfluorinated dibenzofurans are formed during chemical and /or thermal processes, as it has been shown for chlorinated, brominated and mixed chlorinated-brominated dibenzodioxins and dibenzofurans.

In order to analyse products, emissions, and environmental samples for the occurrence of polyfluorinated dibenzodioxins and dibenzofurans, it is necessary to know their analytical properties. For this purpose we synthesized all 75 PFDD and about half of the 135 PFDF, developed a clean-up procedure, and determined their chromatographic properties.

The possibility of a *de novo* synthesis of polyfluorinated dibenzodioxins was studied and some processes were tested for the occurrence of polyfluorinated dibenzodioxins and dibenzofurans.

A preliminary toxicological evaluation of 2,3,7,8-tetrafluorodibenzodioxin was carried out and is reported in the Toxicology Section.

2. Materials and Methods

Synthesis of PFDD:

The different congeners of PFDD were synthesised by pyrolysis of fluorophenols or fluorophenates, analogous to PCDD [1, 2].

1 to 100 mg of the fluorophenol and a corresponding stoichiometric amount of KOH or CaH₂ were heated in a closed quartz ampule (10 cm x 2 cm i.d.) for 1 to 3 h at 280 °C. After cooling to room temperature the ampule was opened carefully. The reaction product was dissolved in 10 ml toluene by treatment in an ultrasonic bath for 15 minutes. The toluene solution was extracted 3 times with a 1 M KOH-solution. The organic layer was dried with Na₂SO₄ and the solvent was reduced to approximately 1 ml. This solution was placed on a column filled with 2.5 g of Alumina B Super I for Dioxin Analysis (ICN Biomedicals, Wesel, FRG). The column was eluted first with 20 ml of heptane/dichloromethane (98:2) followed by 20 ml of heptane/dichloromethane (1:1). The latter fraction contained the PFDD. The solvent was removed with a rotary evaporator under controlled pressure. Due to the relatively high vapour pressure of the PFDD complete removal of solvent has to be avoided. The PFDD were transferred to a 3 ml vial with dichloromethane as solvent. The solvent was removed under a gentle stream of nitrogen avoiding complete dryness.

Synthesis of PFDF:

PFDF were synthesized by pyrolysis of fluorophenols and fluorobenzenes. In addition pyrolysis of fluorophenols without fluorine substitution in ortho position to the hydroxyl group was carried out.

1-20 mg of fluorophenol and approximately a three fold amount of fluorobenzene or only fluorophenols without substitution in 2 position were heated in a closed quartz ampule (10 cm x 2 cm i.d.) for 1-5 h at 280-380 °C. As catalysts for the condensation CuO/Zn/Ca were used.

The isolation was carried out analogous to the PFDD.

GC/MS analysis:

The analysis for PFDD/PFDF was carried out with a HP 5890 gaschromatograph coupled directly to a HP 5970 mass selective detector. A CPSil-88 fused silica column (50 m, 0.25 mm i.d., 0.2 µm film thickness, CHROMPACK, Frankfurt) was used. Sample aliquots of 1-3 µl were injected splitless (injector temperature 250 °C) and the column temperature was programmed as follows: 90 °C; 2.7 °C/min to 150 °C, 4 min isothermal; 8 °C/min to 170 °C, 3 min isothermal; 20 °C/min to 245 °C. Carrier gas was helium at a head pressure of 150 kPa. For characterization of the PFDD/PFDF full scan mass spectra were obtained. For quantitative analyses the mass spectrometer was run in the SIM mode. For PFDD mass fragmentograms at M^+ , $(M-47)^+$ and $(M-56)^+$, for PFDF M^+ , $(M-29)^+$ and $(M-47)^+$ were registered. Quantitation was carried out either by external or internal standardisation with octafluorodibenzodioxin and 2,3,7,8-TCDD, respectively.

Study of *de novo* synthesis of PFDD/PFDF on fly ash:

5 g of fly ash from a municipal waste incinerator, with a high PCDD/PCDF formation potential were treated with aqueous CuF_2 -solution (containing about 100 mg CuF_2) and dried. The mixture was heated in an open glass tube (100 cm, 2.5 cm i.d.) in a stream of oxygen (2 - 20 ml O_2 /minute). The cool end of the glass tube was filled with alumina to adsorb any volatilized PFDD/PFDF. Several experiments were carried out, varying the temperature between 250 and 500 °C and the time of treatment between 0.5 and 3 h. The treated fly ash and the alumina adsorbent were extracted under refluxing with a mixture of toluene, ethoxyethanol and HCl. The clean up of the toluene extract was carried out on 25 g Alumina B Super I ("macro-alumina column") using 150 ml of heptane/dichloromethane (98:2) and 150 ml of heptane/dichloromethane (1:1) as eluents.

Pyrolysis of hexafluorobenzene:

30 mg hexafluorobenzene was pyrolyzed in a quartz ampule for 2h at 250-350 °C. As matrices for the catalysis SiO_2 , Al_2O_3 , Ni, CuO/Zn were used.

Pyrolysis of fluorotrichloromethan (Freon 11):

2 ml of Freon 11 were heated in a closed quartz ampule (7 cm, 4 cm i.d.) for 1-5 h at 300-600 °C. To catalyze the condensation, different matrices (Al_2O_3 , SiO_2 , MgO , ZnO) with various concentrations of metal (Pt, Ni, Cu, Zn, Fe) were used.

Burning of polyfluorinated carbon (PFK) and PFK containing material:

PFK and PFK containing material were placed in a porcelain dish, vaporised and burnt, respectively, within 0.5 h. The soot formed was collected on a glass funnel, the tubing of which was filled with alumina as adsorbent. The soot, the adsorbent, and the residue in the dish were extracted with toluene. After clean up of the extract on a "macro-alumina column" analysis for PFDD/PFDF was carried out.

Extraction of samples from aluminium production:

Samples from the oven base, dust from the production hall, anode material and a soil sample from the production area were extracted under refluxing with a mixture of toluene, ethoxyethanol and HCl. Clean up was carried out on a "macro-alumina column".

3. Results and Discussion

Synthesis of PFDD and PFDF:

The various polyfluorinated dibenzodioxins were synthesized by pyrolysis of fluorophenols and fluorophenates according to the synthesis of PCDD [1,2].

By this route were synthesized:

- individual congeners of "symmetrical" substitution, e.g. 2,3,7,8- T_4 FDD from 2,4,5-trifluorophenol.
- pairs of products of "asymmetrical" substitution, e.g. 1,2,6,7- and 1,2,8,9- T_4 FDD from 2,3,4-trifluorophenol.

- simple mixtures of products of different ring substitution, e.g. from a mixture of 2,3-difluorophenol and 2,3,5,6-tetrafluorophenol a mixture of 1,6- and 1,9- D₂FDD, 1,2,4,6- and 1,2,4,9-T₄FDD, and 1,2,4,6,7,9- and 1,2,4,6,8,9-H₆FDD is formed.
 - side products. This is the case for PFDD which are 1,2,3-substituted, since the corresponding phenols, the 2,3,4,5- and the 2,3,4,6-tetrafluorophenol are not commercially available. These fluorophenols are however present as by-products in pentafluorophenol. Therefore these 1,2,3-substituted PFDD could be identified in the pyrolysis product of pentafluorophenol with other phenols.
- Various polyfluorinated dibenzofurans were synthesized by pyrolysis of fluorophenols and fluorobenzene or only fluorophenols without fluorine in 2 position.
- Analogous to the condensation of PFDD individual congeners and simple mixtures of PFDF were synthesized. The mechanism of the condensations and the product distribution will be discussed elsewhere.

Extraction, enrichment and clean-up from samples containing PFDD/PFDF:

So far no significant differences were found in the extraction, enrichment, and clean-up of PFDD/PFDF in comparison to the chlorinated analogues in different matrices. Optionally, the PFDD/PFDF could be analysed by GC/MS simultaneously with PCDD/PCDF. The main difference is the high volatility of the fluorinated compounds. Therefore it is essential to avoid complete dryness if the solvent is removed during the clean-up. For future emission sampling for PFDD/PFDF the high volatility of these compounds has to be taken in account.

Separation and identification:

The separation and identification of PFDD/PFDF in the pyrolysis products was achieved by HRGC/LRMS. Three capillary columns were tested for highest resolution, DB-5 and DB-5MS, both from J&W, and CPSil-88 from CHROMPACK. The CPSil-88 capillary column was found to be most effective for this purpose, despite the fact, that 2,3,7,8-TFDD overlaps with 1,3,7,9-TFDD. The separation of this pair can however be achieved on a DB-5MS.

All 75 PFDD and approximately half of the 135 PFDF could be identified and the retention times relative to dibenzodioxin were determined.

Mass spectrometric detection of PFDD/PFDF:

Fluorine occurs in nature as a pure element. Therefore, one cannot identify fluorinated compounds in mass spectrometry by isotope clusters in the molecular ion or in fragment ions, as is the case with chlorinated and brominated compounds. The (M+1)⁺ peak resulting from the ¹³C-abundance with 13.4% is not very useful for identification purposes. Therefore the mass spectra of the fluorinated dibenzodioxins were examined for characteristic fragment ions. Analogous to the characteristic elimination COCl from PCDD leading to a (M-63)⁺ fragment ion, an elimination of COF was found for all PFDD, leading to a characteristic (M-47)⁺. Contrary to the PCDD in PFDD an elimination of two CO is always observed, resulting in a (M-56)⁺ fragment ion. This fragmentation is also seen with dibenzodioxin and results in the formation of naphthalene. For the identification of PFDD three ions were always monitored, M⁺, (M-47)⁺ and (M-56)⁺. M⁺, (M-29)⁺ and (M-47)⁺ were detected for the identification of the PFDF.

Gas chromatographic retention behavior:

With chlorinated, brominated, and mixed chlorinated-brominated dibenzodioxins/furans, retention times on gas chromatographic columns increase with the degree of substitution, independent from the stationary phase. With fluorinated dibenzodioxins/furans, a completely different retention behaviour is observed. The 22 tetrafluorinated dibenzodioxins elute in a rather wide time window. All of the other fluorinated dibenzodioxins elute within the time window of the tetrafluorinated dibenzodioxins. Octa-, hepta-, and most of the hexa-substituted compounds elute early, and most of the mono-, di-, and tri-substituted compounds elute late in this time window, with pentafluorinated compounds also spread out more or less over the total time window of the T₄FDDs. The PFDF generally elute earlier

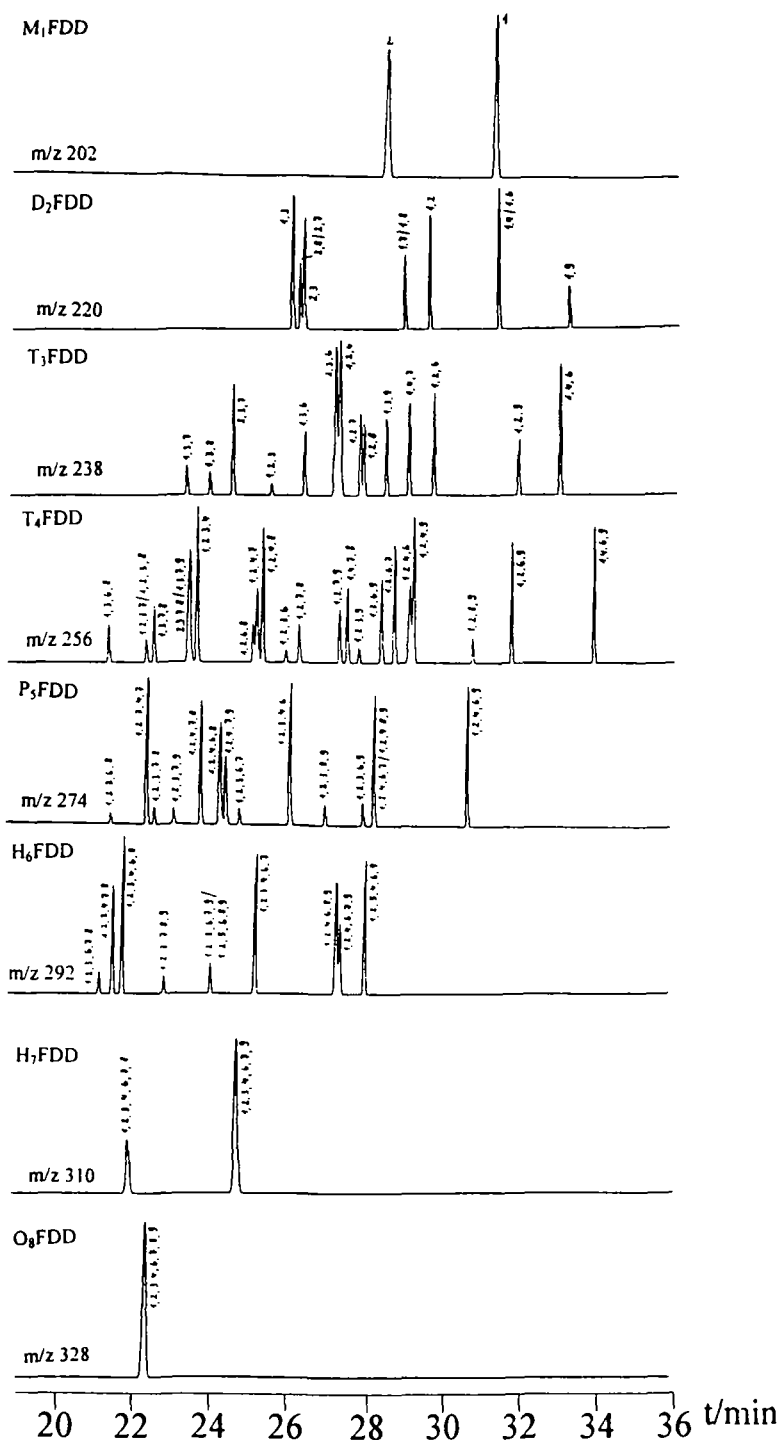


Figure 1: Reconstructed mass fragmentograms of the mono- to octafluorodibenzodioxins

than the PFDD. The reason for the retention behavior is the low polarizability of the fluorine atoms. The substitution using fluorine atoms also lowers the polarizability of the whole dioxin/furan molecule compared to the unsubstituted molecule, which explains the shorter retention times of most PFDD/PFDF compared to the unsubstituted dibenzodioxin/furan. A more detailed discussion of the theoretical aspects of the retention behavior of PFDD/PFDF will be reported elsewhere.

Are PFDD formed in industrial processes?

Possibility of a *de novo* synthesis in thermal processes:

When fly ash from municipal waste incinerators is heated at 300 °C for 30 min in a stream of air, the concentration of PCDD and PCDF increases. This phenomenon has been shown to be caused by a *de novo* synthesis of PCDD/PCDF [3]. By the addition of chloride or bromide to the fly ash the heat treatment in an air stream leads to an additional formation of chlorinated or brominated dibenzodioxins and dibenzofurans. When a mixture of CuF₂ and NaF was added to fly ash the subsequent heat treatment in a stream of air at temperatures between 300 °C and 500 °C did not result in the formation of fluorinated dibenzodioxins or dibenzofurans. A number of fly ash samples from municipal waste incinerators were analyzed for PFDD and PFDF. With detection limits in the range of 0.01 ng/g for individual congeners no PFDD/PFDF could be detected.

The reason for this result is the lack of formation of the C-F bond. It is assumed that for the *de novo* synthesis of PCDD/PCDF the formation of Cl₂ is the essential starting reaction, leading to the C-Cl bond formation [4, 5]. This mechanism is impossible for fluorine due to its redox potential.

Formation of the C-F bond from carbon and metal fluoride occurs only at temperatures above 900 °C [6]. At these temperatures, dioxins are destroyed rather than formed. This might be the reason why the analysis of samples from aluminium production, despite the formation of C-F bonds did not reveal any PFDD/PFDF and only very low concentrations of PCDD/PCDF..

Possibility for the formation of PFDD/PFDF from fluororganic compounds:

Formation of PFDD/PFDF from praedioxins:

Heating of hexafluorobenzene with various matrices yielded different concentrations of octafluorodibenzodioxin/decafluorobiphenylether and octafluordibenzofuran/decafluorbiphenyl.

PFDD were also found in the fluorophenols, used for synthesizing the PFDD. The concentrations of the PFDD were comparable to the concentration of PCDD in chlorophenols found by Buser.

Possibility for the formation of fluorinated praedioxins:

Heating a stream of fluorotribromomethan in a nickel tube leads to the formation of hexafluorobenzene in 40% yield [7]. In a preliminary analysis of pyrolysis products of fluorotrichloromethan (Freon 11), a widely used fluorochlorohydrocarbon, no PFDD/PFDF could be detected. Also in burning of polyfluorinated carbon and polyfluorinated carbon containing materials, no formation of PFDD or PFDF could be detected.

The possibility of PFDD/PFDF formation in other processes is under further investigation.

4. References

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