Physical-Chemical Properties of Polyfluorinated Dibenzo-p-dioxins and Dibenzofurans

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Introduction

Polyfluorinated organic compounds are usually more stable than their unsubstituted and their chlorinated and brominated corresponding compounds. While especially polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/F) but polybrominated dibenzo-p-dioxins and dibenzofurans (PBDD/F) too, were intensively investigated, little information is available on corresponding polyfluorinated dibenzo-p-dioxins and dibenzofurans (PFDD/F). Some evidence of their existence beside mixed F/Cl dioxins and furans were found in ash samples of waste incineration, primary aluminium industry and pyrolysis of some fluorinated aromatics (1-3).

In general polyfluorinated aromatic compounds in contrast to their chlorinated corresponding compounds have higher vapour pressure, surface tension and dielectric constant because of their week polarity and week intermolecular interactions. Therefore the physical-chemical properties of PFDD/F should be completely different than PCDD/F. Physical-chemical properties like the aqueous solubility, the n-octanol water partition constant, the henry's law constant and the vapour pressure for example, determine the environmental behaviour of chemical compounds.

For that reason we determined the aqueous solubility (S), the octanol water constant (K_{OW}), the henry's law constant (H) and the vapour pressure (P) of some synthesised PFDD/F. To keep further information of the thermal behaviour we additionally carried out thermal analysis exemplary with 2,3,7,8-tetrafluoro-dibenzodioxin (TeFDD).

Materials and Methods

Chemicals: All PFDD/F were synthesised as described earlier (1, 4).

Aqueous solubility S : We used the generator column method (GCM) developed for hydrophobic substances (5). The substance was homogeneous dispersed at the surface of glass bead in a column The pure water flow of 1 mL/min through the column at T = 25°C was slow enough to avoid colloidal dispersions (6). The equilibrium was quickly achieved. The water solution was extracted with dichloromethane and the extract was analysed by GC-MS.

Octanol water partition constant K_{OW} : A similar experiment was used for the determination of K_{OW} as described above (5). Chromosorb W/AW in a column was coated with the substance in n-octanol and than treated with a water flow at 25°C.

Henry's law constant (H): A saturated solution of a PFDD/F congener in pure water (100-1000 µg each congener) was transferred in a stripping vessel. Each of the V = 50, 100, 150 and 200 mL solution were purged with a water saturated nitrogen stream (F_G = 25 L/h) at T = 25°C. Aliquots of the solutions were extracted with dichloromethane and analysed with GC/MS after t = 15, 30, 60, 90, 120 min. H was determined by using the results of the 200 mL experiment (equilibrium

achieved): **ln S/S_o = -(H · F_G / V · R · T) · t** ; S_o concentration at the beginning, R universal gas constant. Due to small PFDD concentrations in water a large standard deviation of **H** resulted (6).

Vapour pressure P: **P** was calculated from the determined **H** values: **P = S · H** .

Thermal analysis: The thermal properties of 2,3,7,8-TeFDD were determined by using thermogravimetry / differential thermal analysis mass spectrometry (TG/ DTA 220/ MS) of Seiko Instruments/ Balzers QMG 421; temperature program: 35-300°C 5°/min, flow rate: 200 ml/min

GC/MS: The identification and quantification were carried out with FISONS Instruments MD800/ GC 8000 series EI (70 eV); DB5 MS-fused silica column (30 m; 0,25 id, 0,25 µm d_F); temperature program: 2 min 60°C; 20°/min 180°C; 2,4°/min 220°C; 20°/min 280°C; 2min 280°C. The selected masses were the M^+, M^+-47 (-COF) and M^+-56 (-C_2O_2) signals for the PFDD and the M^+, M^+-47 (-COF) and M^+-29 (-CHO) signals for the PFDF.

Results and Discussion

Aqueous solubility S :

For the 11 investigated fluorinated dioxins/furans the solubility **S** (table 1) is slightly until four orders of magnitude higher than the chlorinated dioxins/furans (7, 8) with the same degree of substitution, except for the difluorinated dioxins/furans. A dependency of **S** from the degree of substitution is almost not found for the PFDD in contrast to the PCDD. 1,2,4,6,7,9- and 1,2,4,6,8,9-HxFDD were formed together (1:1) in the synthesis and could not be separated.

Table 1: Determined physical-chemical properties of PFDD/F at 25°C compared with PCDD/F

PXDD/F	S (Mol/L)		log K_{OW}		H (Pa m^3/Mol)		P (Pa)	
X =	F	Cl	F	Cl	F	Cl	F	Cl
1,2,3,4,8,9-HxXDF	1.5E-8	2.2E-11	*4,4*	*8,5*				
1,2,3,4,7,8-HxXDF	1.0E-8	2.2E-11	4,0	8,5				
2,3,4-TrXDF	2.3E-7	-	3,4	6,4				
1,2-DiXDF	2.1E-9	6.1E-8	-	5,6				
OcXDD	5.5E-7	7.8E-13	3,0	8,2	5,3	0,7	2,9E-3	E-7 - E-10
1,2,3,4,7,8-HxXDD	1.1E-6	4.1E-12	3,8	7,8				
1,2,4,6,7,9-HxXDD + 1,2,4,6,8,9-HxXDD	1.7E-7	4.1E-12	3,1	7,8	3,8	4,5	6,6E-4	1,4E-6
1,2,3,4,7-PeXDD	5.5E-7	4.3E-11	3,6	7,4	15,2	0,3	8,3E-3	4,3E-6
1,2,6,7-TeXDD	7.3E-10	6.1E-10	-	-				
2,3,7,8-TeXDD	5.8E-8	6.1E-10	3,5	6,8	3,9	0,7	2,3E-4	E-4 – E-8
2,7-DiXDD	7.2E-8	5.1E-7	3,3	5,7	4,9	8,1	3,5E-4	8,1E-3

S: aqueous solubility; K_{OW} :octanol water partition constant, **H**: henry's law constant, **P**: vapour pressure

Octanol water partition constant K_{OW} :
The relative standard deviation of the K_{OW} determination varied between 18.2 and 35.3 %. The K_{OW} were determined for 10 PFDD/F (table 1). No evidence for a dependency of substitution degree was found in contrast to the PCDD/F. Comparing with chlorinated dioxins/furans (8) the PFDD/F have 2 until 5 orders of magnitude lower K_{OW}.

Henry's law constant H :
Like the PCDD the investigated **H** levels of PFDD varying strong but they are significantly higher exceptonal 2,7-DiXDD and the mixed HxXDD (table 1).

Vapour pressure P :
The investigated PFDD show very similar **P** and no evident dependency of the fluorination degree. The tetra to octa PFDD have 2 until 6 orders of magnitude higher **P** as the comparable PCDD (9). Exceptional the dihalogenated compounds are similar (table 1).

Thermal analysis :
The experiments were carried out exemplary under N_2 and Air. As figure 1 shows, the decrease of the weight of the 2,3,7,8-TeFDD begins at 104°C (TG curve) already. The loss of the total amount of 2,3,7,8-TeFDD is finished at 177°C before reaching the melting point of 183°C (10). The same results were found in both experiments. No decomposition in the observed temperature range for the 2,3,7,8-TeFDD was detected with the coupled MS. We conclude from these results, that the 2,3,7,8-TeFDD starts to sublimate without any decomposition at 104°C. This sublimation has to be noticed and is very important for the analysis of PFDD/F include sampling and clean up.
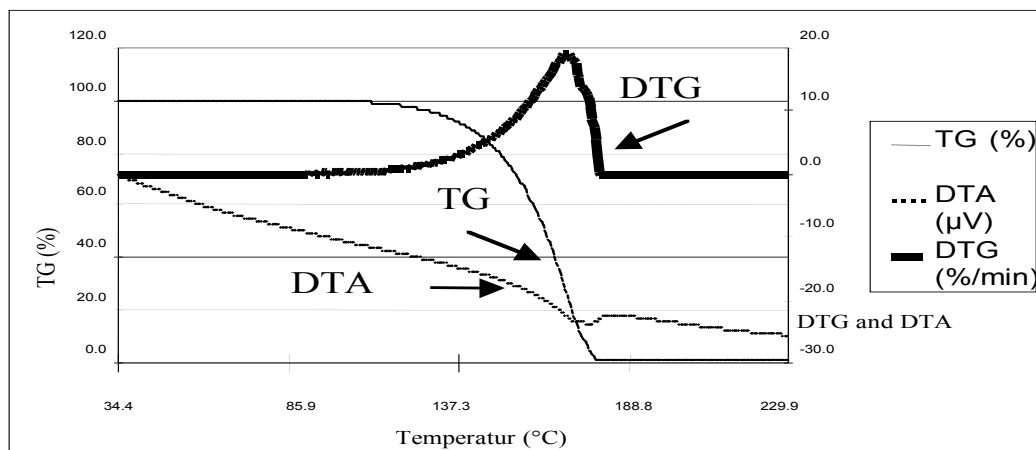

Figure 1: Thermal analysis (TG, DTG, DTA) of 2,3,7,8-TeFDD

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