

The halogenation of dibenzo-p-dioxin and dibenzofuran in a model fly ash system

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Introduction

During municipal waste incineration polychlorinated dibenzo-p-dioxins (PCDDs) and -dibenzofurans (PCDFs) are formed predominantly on the electrostatic precipitators at temperatures between 300-400°C¹. Recently, it became clear that the input of bromine in a municipal waste incinerator may possibly enhance the formation of chlorinated compounds². Therefore, the study of the behaviour of chlorine and bromine in the formation of PXDDs and PXDFs (X=Cl, Br) in a model fly ash system may give more insight in the postulated mechanism of formation, i.e. 'de-novo' synthesis³.

This study deals with the reactivity and selectivity of chlorine and bromine in the heterogeneous catalysed halogenation of the unsubstituted parent compounds dibenzo-p-dioxin (DD) and dibenzofuran (DF).

Experimental

The halogenation experiments of DD and DF have been carried out at 300°C on a Al₂O₃-SiO₂ supported CuCl₂ (0.5 wt.%) or CuBr₂ (0.8 wt.%) catalyst system. The carrier gas flow consisted of 85 ml/min nitrogen, 10 ml/min oxygen and 5 ml/min HX (X=Cl, Br). The reaction time was 30 min. DD and DF were injected and nebulised into the gas flow by a motor-driven syringe (0.48 ml/hr) from a solution of n-hexane ([DD]=0.37 mg/ml and [DF]=0.41 mg/ml). A cold trap (T=-10°C) was used to collect possible evaporated compounds. Before Soxhlet extraction with toluene, the samples were spiked with a mixture of ¹³C labeled PCDD/PCDFs and PBDD/PBDFs. Further clean-up was performed according to standard procedures⁴. The GC/MS analysis of PCDD/PCDFs was performed on a HP 5980/5970B (MSD, SIM, 70 eV EI), carrier gas helium, cold on-column injection, SP 2331, 60 m, 0.32 mm i.d., 0.25 μm film density, temperature program 140°C (40°C/min) → 200°C (4°C/min) → 250°C (isotherm). PBDD/PBDFs were analysed on a DB-5 column, 30 m, 0.32 mm i.d., 0.25 μm film density, temperature program 140°C (40°C/min) → 200°C (8°C/min) → 320°C (isotherm).

Results and discussion

Dibenzo-p-dioxin

Table 1 shows the results of the heterogeneous catalysed halogenation of DD with HBr (single experiment) and HCl (in duplo; experiments I and II) in ng/g and nmole/g. Due to experimental difficulties in handling the introduction of very small volumes of the DD solutions into the gas flow, the uncertainty in the data is large. The chlorination of DD resulted predominantly in the formation of octachlorodibenzo-p-dioxin. The bromination of DD gave high yields of hexa-, hepta- and octabromodibenzo-p-dioxin. On molar base hydrogen bromide is three times more reactive in the halogenation of DD than hydrogen chloride. In order to get more reliable quantitative data further investigation is necessary.

Table 1. The yields of halogenation of DD in ng and nmole per g $Al_2O_3-SiO_2/CuX_2$

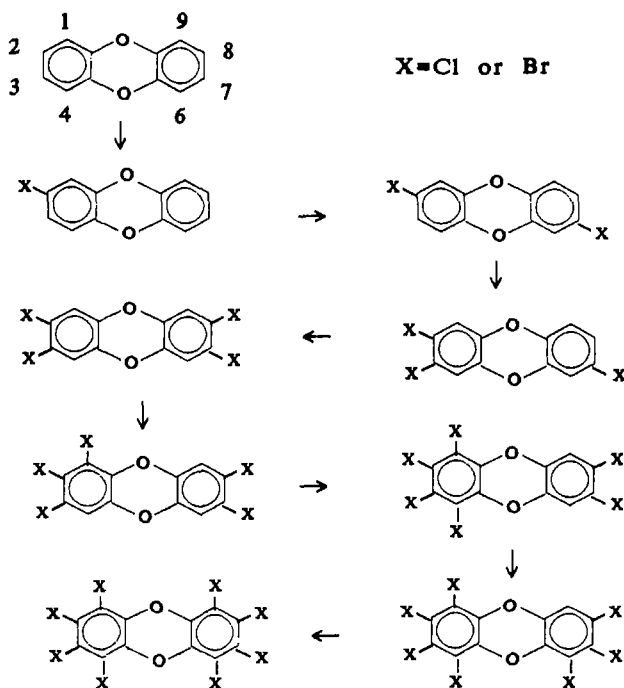
isomer	DD/HBr (I)		isomer	DD/HCl (I)		DD/HCl (II)	
	ng/g	nmole/g		ng/g	nmole/g	ng/g	nmole/g
2,3,7,8-Br ₄ DD	116	0.233	2,3,7,8-Cl ₄ DD	8.0	0.025	59.2	0.184
1,2,3,7,8-Br ₅ DD	139	0.241	1,2,3,7,8-Cl ₅ DD	15.8	0.044	16.2	0.046
1,2,4,7,8-Br ₅ DD	48	0.083	1,2,4,7,8-Cl ₅ DD	6.0	0.017	2.2	0.006
1,2,3,4,7,8/ 1,2,3,6,7,8-Br ₆ DD	508	0.770	1,2,3,4,7,8-Cl ₆ DD	65.8	0.169	36.6	0.094
1,2,4,6,7,9/ 1,2,4,6,7,8-Br ₆ DD	172	0.262	1,2,3,6,7,8-Cl ₆ DD	27.4	0.070	13.2	0.034
1,2,3,6,7,9/ 1,2,3,6,8,9-Br ₆ DD	288	0.440	1,2,3,6,7,9/ 1,2,3,6,8,9-Cl ₆ DD	21.4	0.055	4.7	0.012
1,2,3,7,8,9-Br ₆ DD	113	0.173	1,2,3,7,8,9-Cl ₆ DD	28.8	0.074	10.3	0.026
1,2,3,4,6,7,8-Br ₇ DD	1077	1.465	1,2,3,4,6,7,8-Cl ₇ DD	88.3	0.208	116.7	0.275
1,2,3,4,6,7,9-Br ₇ DD	624	0.846	1,2,3,4,6,7,9-Cl ₇ DD	8.7	0.021	63.0	0.149
Br ₈ DD	1677	2.058	Cl ₈ DD	578.4	1.258	950.9	2.069
Σ Br ₄₋₈ DD	4763	6.571	Σ Cl ₄₋₈ DD	848.6	1.941	1273	2.895

The heterogeneous catalysed halogenation of dibenzo-p-dioxin (X=Cl, Br) is very selective towards the lateral 2,3,7,8 positions. The main sequence of halogenation of DD is shown in fig. 1. The sequence of halogenation of positions 2 → 8 → 3 → 7 → 1 → 4 → 6 → 9 is comparable with an electrophilic aromatic substitution⁵. The copper catalysed halogenation of DD thus involves an attack of an electrophilic halogen on the aromatic ring structure of DD. This may be a positive charged halogen or a radical cation.

Despite the high reactivity of hydrogen bromide, the bromination of DD is a selective proces. Therefore, a mixture of predominantly 2,3,7,8-substituted PBDD isomers was obtained. With the use of a QSAR method relating structural information to retention behaviour⁶, we were able to assign 17 PBDD isomers⁷.

Figure 1. The sequence of halogenation (X=Cl, Br) of dibenzo-p-dioxin

SELECTIVE HALOGENATION OF DIBENZO-p-DIOXIN



Dibenzofuran

Table 2 shows the results of the halogenation of DF with HBr and HCl (both in triplo; experiments I, II and III). The chlorination of DF showed similar trends as were found in the chlorination of DD. Again a preference for the lateral 2,3,7,8 positions was observed. The main product of chlorination was octachlorodibenzofuran. The bromination showed no selectivity at all. The GC patterns of the PBDF isomers were comparable to those of pyrolysis samples of polymers containing polybrominated flame retardants⁸. The bromination of DF showed an optimum yield in penta- and hexabrominated dibenzofurans. On molar base the overall yield of tetra- to octabromodibenzofuran is significant higher than the yield of the analogous chlorinated dibenzofurans.

Conclusions

In a model fly ash system hydrogen bromide is more reactive in the halogenation of DD and DF than hydrogen chloride. The chlorination of DD and DF is a selective process with preference for the lateral 2,3,7,8 positions. Despite higher reactivity the bromination of DD shows the same selectivity. Bromination of DF is not selective.

Because the selective halogenation pattern of DD (X=Cl and Br) and DF (X=Cl) in a model fly ash system shows no resemblance with the typical

PCDD/PCDF incineration pattern, one can conclude that unsubstituted DD and DF probably are no precursors in the 'de-novo' synthesis. The typical isomer distribution of PCDD/PCDFs in incineration processes is supposed to originate from already halogenated precursors.

Table 2. The yields of halogenation of DF in ng and nmole per g Al_2O_3 - SiO_2 / $CuCl_2$

	DF/HCl (I)		DF/HCl (II)		DF/HCl (III)	
isomer	ng/g	nmole/g	ng/g	nmole/g	ng/g	nmole/g
ΣCl_4DF	4	0.013	5	0.016	8	0.026
ΣCl_5DF	3	0.008	11	0.032	6	0.018
ΣCl_6DF	5	0.013	32	0.086	38	0.102
ΣCl_7DF	25	0.061	108	0.265	210	0.515
Cl_8DF	594	1.339	1582	3.565	4736	11.303
$\Sigma Cl_{4-8}DF$	631	1.434	1738	3.964	4999	11.931
	DF/HBr (I)		DF/HBr (II)		DF/HBr (III)	
isomer	ng/g	nmole/g	ng/g	nmole/g	ng/g	nmole/g
ΣBr_4DF	1120	2.3	960	2.0	4710	9.8
ΣBr_5DF	6490	12	4920	8.8	96500	170
ΣBr_6DF	6940	11	8110	12	29800	46
ΣBr_7DF	1540	2.1	3050	4.2	18700	26
Br_8DF	n.d.	n.d.	230	0.16	1750	2.2
$\Sigma Br_{4-8}DF$	16100	27	17200	28	151000	260

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