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THE ROLE OF BROMINE IN THE *DE NOVO* SYNTHESIS IN A MODEL FLY ASH SYSTEM

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ABSTRACT

The role of bromine in the *de novo* synthesis in a model fly ash system has been evaluated. A silica-alumina carrier was impregnated with a CuX_2 catalyst system ($\text{X}=\text{Cl}$, 0.5 wt%; $\text{X}=\text{Br}$, 0.8 wt%). A flow of air with 5 vol. % HX ($\text{X}=\text{Cl}$ or Br) was passed over a fixed bed at 300°C.

Several processes have been investigated concerning the role of bromine and chlorine in the formation of polyhalogenated dibenzo-p-dioxins and -dibenzofurans in municipal waste incinerator fly ash under conditions observed in an electrostatic precipitator:

- (i) The exchange of bromine and chlorine in 2,3,7,8-tetrabromodibenzo-p-dioxin;
- (ii) The reactivity and selectivity of bromine and chlorine in the halogenation of the parent structures dibenzo-p-dioxin and dibenzofuran;
- (iii) The competition of bromine and chlorine in the *de novo* synthesis.

INTRODUCTION

The last decade several studies about the formation of polybrominated dibenzo-p-dioxins and -dibenzofurans (PBDDs and PBDFs) during thermal degradation of polymers containing brominated flame retardants have been published [1,2]. Also the presence of mixed brominated/chlorinated dibenzo-p-dioxins and -dibenzofurans (PXDDs and PXDFs with $\text{X}=\text{Cl}$, Br) in municipal waste incinerator fly ash has been shown [3,4]. However, the analysis of PBDD/PBDFs and the mixed halogenated PXDD/PXDFs ($\text{X}=\text{Cl}$, Br) is accompanied with difficulties. The physico-chemical properties of polybrominated compounds, *i.e.* high molecular weight, high melting point, low vapour pressure and low thermal stability requires a sophisticated GC/MS analysis.

Due to the lack of standard materials, the isomer specific analysis of PBDD/PBDFs has not been developed yet. Although some attempts have been made to use QSAR methods to predict the GC retention behaviour from molecular structure, no adequate method has been developed to separate all PBDD/PBDF isomers [5,6]. The complete isomer specific GC analysis of PXDD/PXDFs ($\text{X}=\text{Cl}$, Br) even seems to be an impossibility in view of the fact that there are 5020 possible congeners.

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Therefore, a selective conversion of PBDD/PBDFs and PXDD/PXDFs into the fully chlorinated compounds would solve the analytical problems described above. A selective conversion of PBDD/PBDFs and PXDD/PXDFs into PCDDs and PCDFs would require maintenance of isomer distribution and implies a bromine/chlorine exchange reaction occurring at a much faster rate than halogenation or dehalogenation reactions. The first part of this study presents the copper catalyzed bromine/chlorine exchange in 2,3,7,8-tetrabromodibenzo-p-dioxin.

During municipal waste incineration polychlorinated dibenzo-p-dioxins (PCDDs) and -dibenzofurans (PCDFs) are formed predominantly on the electrostatic precipitators at temperatures between 300–400°C [7]. Recently, it became clear that the input of bromine in a municipal waste incinerator may possibly enhance the formation of chlorinated compounds [8]. 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.* the *de novo* synthesis [9]. The second part of this study describes the reactivity and selectivity of chlorine and bromine in the heterogeneously catalyzed halogenation of the unsubstituted parent compounds dibenzo-p-dioxin (DD) and dibenzofuran (DF). The third part of this study deals with the competition of bromine and chlorine in the *de novo* synthesis in a model fly ash system.

EXPERIMENTAL

Exchange experiments

A Al_2O_3 - SiO_2 supported catalyst system of CuCl_2 (0.5 wt. %) was impregnated with 450 ng/g 2,3,7,8- Br_4DD from a solution of n-hexane. The hexane was evaporated and batches of 0.5 g matrix were heated at $T = 200$, 250 and 300°C. The gas flow composition consisted of N_2 (10 ml/min) and HCl (5 ml/min). Reaction time was 5 and 15 min. A cold trap ($T = -10^\circ\text{C}$) was used to collect possible evaporated species. Before soxhlet extraction with toluene the samples were spiked with a mixture of ^{13}C labeled PCDD/PCDFs and PBDD/PBDFs. Further clean-up was performed according to standard procedures which have been described previously [10]. GC/MS analysis was performed on a HP 5980/5970B (MSD, SIM, 70 eV), cold on-column injection, DB-5 column (30 m, 0.32 mm i.d., 0.25 μm film density), temperature program (140°C/min (40°C/min) $\rightarrow$ 200°C (6°C/min) $\rightarrow$ 300°C (isotherm)).

The assumptions for quantification of PXDD/PXDFs (X=Cl and/or Br) were:

- (i) response factors and recoveries of ^{12}C - and ^{13}C -labelled congeners are equal;
- (ii) response factors and recoveries within a certain isomer group are equal;
- (iii) response factors and recoveries of mixed brominated/chlorinated dibenzo-p-dioxins are equal to those of their fully chlorinated analogues.

Halogenation experiments

Halogenation experiments of DD and DF have been carried out at 250 and 300°C on a Al_2O_3 - SiO_2 supported CuCl_2 (0.5 wt. %) or CuBr_2 (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 nebulized into the gas flow by a motor-driven syringe (0.48 ml/h) from a solution of n-hexane; DD (250°C; 3.4 μmole) and (300°C; 0.5 μmole), DF (250°C; 3.2 μmole) and (300°C; 0.6 μmole). All experiments at 250°C were conducted in triplicate. The experiments at 300°C were performed as single experiments or in duplicate. A cold trap ($T = -10^\circ\text{C}$) was used to collect possible evaporated compounds. Before soxhlet extraction with

toluene, the samples were spiked with a mixture of ^{13}C -labelled PCDD/PCDFs and PBDD/PBDFs. Further clean-up was performed according to standard procedures [10]. The GC/MS analysis of PCDD/PCDFs was performed on a HP 5980/5970B (MSD, SIM, 70 eV EI), 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) $\rightarrow$ 200°C (4°C/min) $\rightarrow$ 250°C (isotherm)). PBDD/PBDFs were analyzed on a DB-5 column (30 m, 0.32 mm i.d., 0.25 μm film density), temperature program (140°C (40°C/min) $\rightarrow$ 200°C (8°C/min) $\rightarrow$ 320°C (isotherm)).

Competition experiments

Two series of combustion experiments were conducted in triplicate with a physical mixture of $\text{SiO}_2\text{-Al}_2\text{O}_3$, loaded with 0.5 wt% CuCl_2 by pore volume impregnation, and activated carbon in the ratio of 25:1 by weight in a flow of air containing either 5 vol. % HCl or 5 vol. % HCl/HBr (9:1) at 300°C. The sample size was 2 g, the reaction time 2 h, and the gas flow rate was 100 ml min⁻¹. One additional experiment was conducted under the same conditions without HCl in the gas flow, as a blank test.

The combustion experiments were performed in a horizontal Pyrex tube reactor. After preheating of the reactor, an inlet tube with a cylindrical sample basket was introduced into the centre of the reactor. The gas flow through the fixed bed was controlled by mass flow controllers and mixed in a chamber containing ceramic pellets. A cold trap (toluene, 0°C) was used to collect possibly evaporated species. Before soxhlet extraction with toluene, the samples were spiked with a mixture of ^{13}C -labelled PCDD/PCDFs and PBDD/PBDFs. Further clean-up was performed according to standard procedures [10]. The GC/MS analysis is described previous sections.

RESULTS AND DISCUSSION

Bromine-chlorine exchange in 2,3,7,8-tetrabromodibenzo-p-dioxin

The results of the bromine/chlorine exchange reactions in 2,3,7,8- Br_4DD are shown in Figs. 1-3. Yields of exchange products are given in molar fractions, in percentages relative to the amount of parent compound 2,3,7,8- Br_4DD . In neither of the experiments products were detected in the cold valve. At 200°C, 5 min. (data not shown) no exchange reactions were observed.

At 250°C, 5 min. only a negligible exchange of 2,3,7,8- Br_4DD into 2,3,7,8- Cl_4DD was observed. The most important exchange products were monochlorotribromo- to monobromotrichlorodibenzo-p-dioxins. The structural formula of the tetrasubstituted bromochlorodibenzo-p-dioxin isomers are shown in Scheme I. In addition to exchange reactions also halogenation reactions into predominantly hexasubstituted dibenzo-p-dioxins and dehalogenation reactions into trisubstituted dibenzo-p-dioxins were observed. The overall recovery of tri- to hexabromochlorodibenzo-p-dioxins based on the amount of 2,3,7,8 Br_4DD was 54%.

When the exchange reaction time was increased to 15 min. a shift towards the chlorinated species was observed. The yield of 2,3,7,8- Cl_4DD was about 10%. The overall recovery of tri- to hexasubstituted bromochlorodibenzo-p-dioxins was only 38%. Again side reactions such as halogenation and dehalogenation reactions take place. It is remarkable that only hexa- and no pentasubstituted dibenzo-p-dioxins were observed.

Figure 1. The exchange products of 2,3,7,8-Br₄DD + HCl (T=250°C, t=5 min.).

Figure 2. The exchange products of 2,3,7,8-Br₄DD + HCl (T=250°C, t=15 min.).

Figure 3. The exchange products of 2,3,7,8-Br₄DD + HCl (T=300°C, t=5 min.).

Because there was one GC peak detected within the hexasubstituted isomers, the copper catalyzed halogenation reaction must be very selective at 250°C. This is in agreement with the selective halogenation of unsubstituted dibenzo-p-dioxin [11].

At 300°C, 5 min. the main exchange products are bromochloro dibenzo-p-dioxins. No 2,3,7,8-Cl₄DD was observed. The overall recovery was 85%. Again side reactions such as (de)halogenation reactions were observed. In contrast to the halogenation reactions at 250°C, halogenation at 300°C yields pentasubstituted dibenzo-p-dioxins. The selectivity of halogenation which was observed at 250°C is lost at 300°C, for several pentasubstituted isomers were detected.

Scheme I. The route of Br/Cl exchange in 2,3,7,8-Br₄DD.

Halogenation ($X = \text{Cl}, \text{Br}$) of DD and DF

Table I shows the total conversion of DD and DF into tetra- to octahalogenated compounds at 250 and 300°C. The product distribution of halogenation at 250°C, *i.e.* the degree of halogenation and the distribution over surface and cold trap, is shown in Figs. 4-6. At 250°C the chlorination of DD shows a higher conversion than the chlorination of DF. Chlorination of DD also shows a higher conversion than bromination. However, the product distribution over surface and cold trap, shows that the major part of the chlorinated

Table I. Total conversion of DD and DF into tetra- to octahalogenated compounds

	Temperature (°C)	HCl (%)	HBr (%)
DD	250	1.6	0.2
DF	250	0.3	-
DD	300	0.5	1.5
DF	300	1	4

compounds is found in the cold trap, whereas brominated compounds remain adsorbed on the surface. Two processes, *i.e.* catalytic halogenation at the active sites and (de)sorption interfer. Therefore, no clear conclusions can be drawn about the reactivity of chlorine *versus* bromine in the halogenation of DD at 250°C. Within the chlorinated as well as within the brominated compounds a maximum is found at the tetrahalogenated compounds.

Figure 4. Chlorination of DD and DF (surface, 250°C).

Figure 5. Chlorination of DD and DF (cold trap, 250°C).

Figure 6. Bromination of DD (surface and cold trap, 250°C).

Figure 7. Halogenation of DD (X=Cl, Br) at 300°C.

Figure 8. Halogenation (X=Cl, Br) of DF at 300°C.

E_A increases with increasing number of substituents

Figure 9. Electrophilic aromatic substitution of DD.

For the chlorination of DD a selectivity towards the lateral 2,3,7,8-positions was observed. On the surface 75% of the Cl_4DD consisted of 2,3,7,8- Cl_4DD , and in the cold trap even 95 %. The selectivity towards 2,3,7,8-substitution was much less pronounced within the PCDFs, namely 30% on the surface and 15% in the cold trap. The bromination of DD at 250°C was also very selective because 85% of the Br_4DDs consisted of 2,3,7,8- Br_4DD on the surface and in the cold trap.

In Figs. 7 and 8 the halogenation of DD and DF at 300°C is shown. Only the surface has been analyzed. A maximum is observed for octachlorinated dibenzo-p-dioxin and -dibenzofuran. Again a selectivity towards 2,3,7,8-substitution was observed. Bromination of DD and DF resulted in a maximum at the penta- and hexabrominated dibenzofurans and hexa- to octabrominated dibenzo-p-dioxins. Within the PBDDs a selective bromination pattern was observed, but the PBDFs showed no selectivity at all. The GC patterns of the PBDF isomers were comparable to those of pyrolysis samples of polymers containing polybrominated fire retardants [12]. Table I shows a higher conversion for bromination of DD and DF than for chlorination at 300°C. At this temperature, hydrogen bromide is about three times more reactive in the halogenation of DD and DF than hydrogen chloride on a molar base. However, in order to get more reliable quantitative data further investigation is necessary.

Scheme II. Sequence of halogenation of dibenzo-p-dioxin.

The sequence of halogenation of positions 2 → 8 → 3 → 7 → 1 → 4 → 6 → 9 is comparable with an electrophilic aromatic substitution pattern [13]. The copper catalyzed 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. Based upon the halogenation pattern, it is supposed that the halogenation of DD and DF in the copper catalyzed model fly ash system is an electrophilic aromatic substitution process. The relatively high selectivity and reactivity of DD towards halogenation are then explained by the charge density distribution in the aromatic rings in DD with relatively negative charged lateral positions due to the presence of two ether bonds shown in Fig. 9.

Comparison of the results of halogenation at 250 and 300°C shows that the degree of halogenation is temperature dependent. The observed maximum at the tetrahalogenated compounds at 250°C is explained by the increasing activation energy with increasing number of o/p directing and deactivating halogen substituents. At 300°C there is enough thermal energy available to take the activation energy barrier for complete chlorination. Bromination of DD and DF is not completed. This indicates a higher activation energy barrier for bromination than for chlorination. In addition, the bromination of DF is sterically hindered.

The main sequence of halogenation of DD is shown in Scheme II. Despite the high reactivity of hydrogen bromide at 300°C, the bromination of DD is a selective process. 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 behaviour [14], we were able to assign 17 PBDD isomers [15].

Competition of HCl and HBr in the de novo synthesis

Table II and Fig. 10 present the results of the competition experiment. The results of the halogenation with HCl *versus* a 9:1 mixture of HCl and HBr, a ratio comparable to the conditions in Wilken's study [8], showed no significant difference in the yield of PXDDs and PXDFs (X=Cl or Cl and Br). From the distribution of PXDDs and PXDFs shown in Figs. 11 and 12, it can be seen that the mixed halogenated PXDDs and PXDFs arising from the halogenation with HCl/HBr are mono- and dibrominated compounds, but over 70% of the total yield of PXDDs and PXDFs consists of PCDDs and PCDFs. These results indicate that bromine has no enhancing effect on the formation of PCDDs and PCDFs in a heterogeneous catalyzed mechanism of formation of PCDDs and PCDFs from carbon by the *de novo* synthesis. The presumed catalytic effect of hydrogen bromide in the formation of PCDDs and PCDFs [8], does not occur under conditions applied in the model fly ash system. The hypothesis that (i) bromine is a more effective halogenation agent, and (ii) exchange of bromine and chlorine might increase the yield of chlorinated species is therefore not confirmed by this study.

However it can not be excluded that bromine plays a key role in the gas phase for the fire retardant activity of brominated compounds is based upon their effectiveness in radical scavenging processes in the gas phase. If

Table II. Yield of PXDDs and PXDFs (X=Cl, Br) in the *de novo* synthesis

Yield	PXDD (pmole/g C)	PXDF (pmole/g C)	ratio
HCl	293(±163)	2290(±1038)	0.12(±0.02)
HCl/HBr	493(±132)	3115(±415)	0.16(±0.05)

Figure 10. Formation of PXDD/Fs (X=Cl, Br) by *de novo* synthesis HCl and HCl/HBr (9:1).

Figure 11. Formation of PXDDs (X=Cl, Br) from HCl/HBr (9:1) in the *de novo* synthesis.

Figure 12. Formation of PXDFs (X=Cl, Br) from HCl/HBr (9:1) in the *de novo* synthesis.

Wilken's results hold true, bromine would enhance the formation of halogenated (aromatic) compound in the post combustion zone of an incinerator by a gas phase mechanism.

CONCLUSIONS

Although the bromine/chlorine exchange reaction of 2,3,7,8-Br₄DD into 2,3,7,8-Cl₄DD has been shown to occur in a heterogeneous catalyzed system, this method is, under chosen test conditions, not selective enough to get a complete conversion without side reactions as halogenation and dehalogenation.

The halogenation of DD and DF in a model fly ash system displays an electrophilic aromatic substitution pattern. The chlorination of DD and DF is a selective process with preference for the lateral 2,3,7,8 positions. DD is more selective than DF. Despite higher reactivity at 300°C, the bromination of DD shows the same selectivity. Bromination of DF at 300°C is not selective. At 300°C hydrogen bromide is more reactive in the halogenation of DD and DF than hydrogen chloride. The degree of halogenation is temperature dependent.

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, it can be concluded that unsubstituted DD and DF 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.

The input of bromine in waste incineration processes may increase the emission of chlorinated species including PCDDs and PCDFs by a gas phase formation of brominated compounds followed by a bromine-chlorine exchange reaction in the gas phase or on the fly ash surface. An increased surface catalyzed formation of PCDDs and PCDFs due to the presence of HCl and HBr (9:1) could not be detected.

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