

The exchange of bromine and chlorine in 2,3,7,8-tetrabromodibenzo-p-dioxin

Luijk, R., Jansen, J., Govers, H.A.J.

Department of Environmental and Toxicological Chemistry, University of Amsterdam, Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands

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 X=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 (X=Cl, Br) is accompanied with difficulties. The physico-chemical properties of polybrominated compounds, i.e. high molecular weight, high melting point, low vapor pressure and low thermostability makes the GC/MS analysis very difficult (or request high demands on the 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 behavior from molecular structure, no adequate method has been developed to separate all PBDD/PBDF isomers^{5,6}. The complete isomer specific analysis of PXDD/PXDFs (X=Cl, Br) even seems to be an impossibility in view of the fact that there are over 5000 possible congeners.

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.

This study presents the copper catalysed bromine/chlorine exchange in 2,3,7,8-tetrabromodibenzo-p-dioxin.

Experimental

A Al₂O₃-SiO₂ supported catalyst system of CuCl₂ (0.5 wt.%) was impregnated with 450 ng/g 2,3,7,8-Br₄DD 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 N₂ (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 procedures⁷. GC/MS analysis was performed on a HP 5980/5970B (MSD, SIM, 70 eV), carrier gas helium, cold on-column injection, DB-5 column, 30 m, 0.32 mm i.d., 0.25 μm film density, temperature program $140^{\circ}\text{C}/\text{min}$ ($40^{\circ}\text{C}/\text{min}$) \rightarrow 200°C ($6^{\circ}\text{C}/\text{min}$) \rightarrow 300°C (isotherm).

The assumptions for quantification of PXDD/PXDFs ($X = \text{Cl}$ and/or Br) were:

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

Results and discussion

The results of the bromine/chlorine exchange reactions in 2,3,7,8- Br_4DD are shown in the figures 1 to 3. The yield 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 monochlorotri-bromo- to monobromotrichloro-dibenzo-p-dioxins. The structural formula of the tetrasubstituted bromochlorodibenzo-p-dioxin isomers are shown in scheme 1. Besides the exchange reactions also halogenation into predominantly hexasubstituted dibenzo-p-dioxins and dehalogenation 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%.

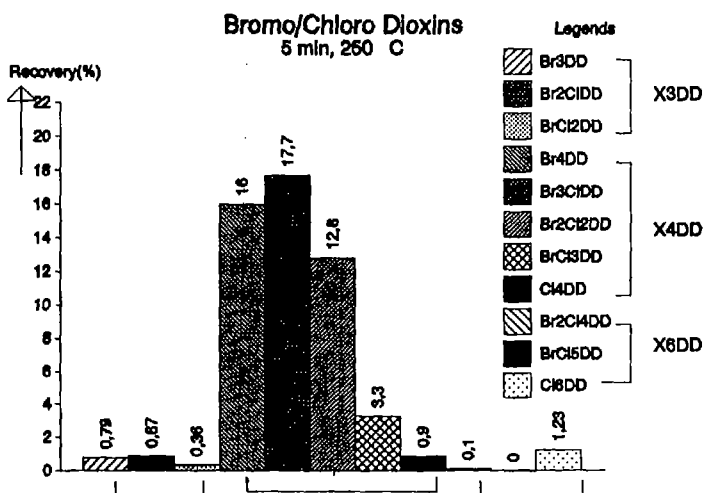


Figure 1. The exchange products of 2,3,7,8- Br_4DD + HCl ($T = 250^{\circ}\text{C}$, $t = 5$ min.)

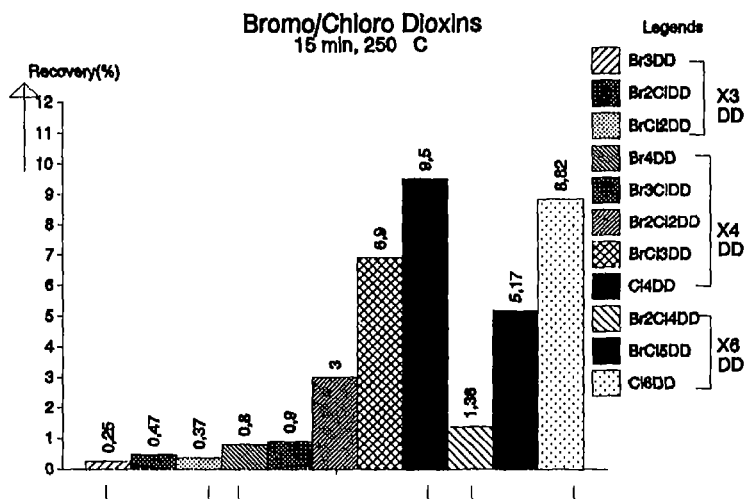


Figure 2. The exchange products of 2,3,7,8-Br₄DD + HCl (T=250°C, t=15 min.)

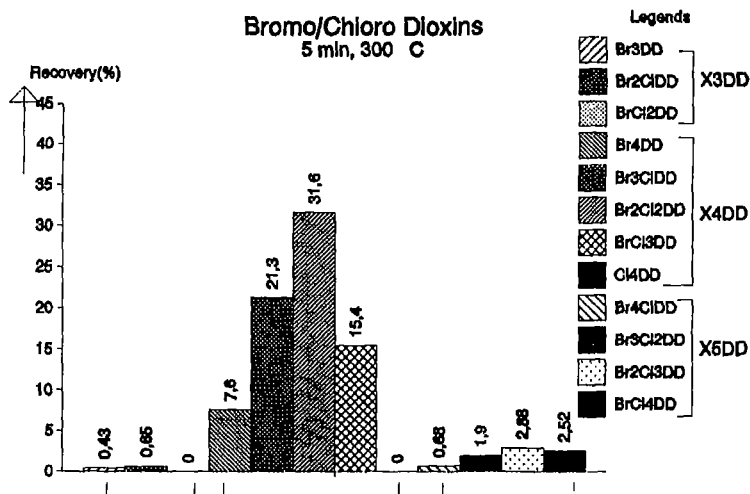
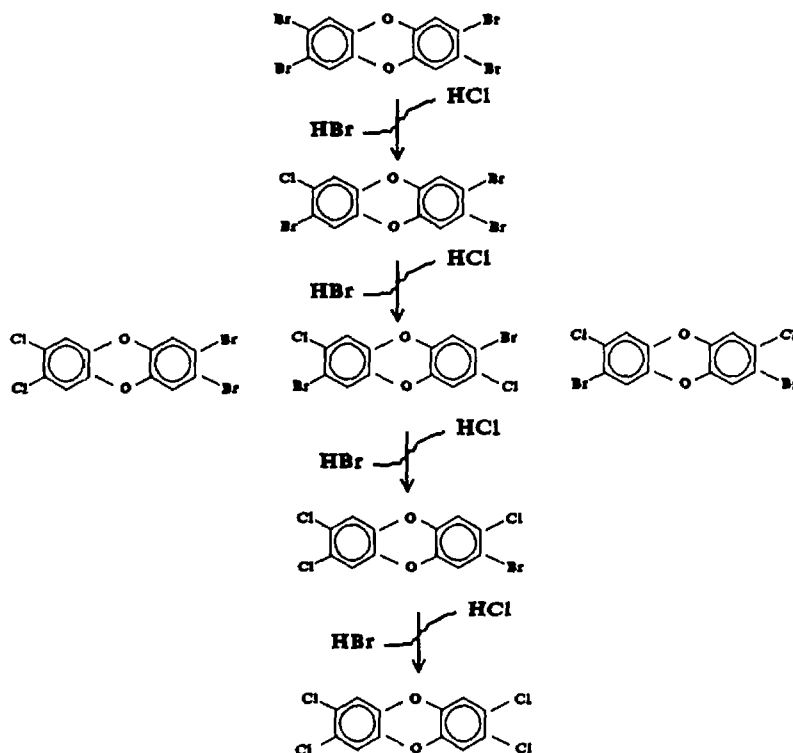


Figure 3. The exchange products of 2,3,7,8-Br₄DD + HCl (T=300°C, t=5 min.)

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-Cl₄DD was about 10%. The overall recovery of tri- to hexasubstituted bromochlorodibenzo-p-dioxins was only 38%. Again side reactions as halogenation and dehalogenation take place. It is remarkable that only hexa- and no pentasubstituted dibenzo-p-dioxins were observed. Because there was one GC peak detected within the hexasubstituted isomers, the copper catalysed halogenation reaction must be very selective at 250°C. This is in agreement with the selective halogenation of unsubstituted dibenzo-p-dioxin⁸.



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

Conclusion

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 catalysed system, this method is, under chosen test conditions, not selective enough to get a complete conversion without side reactions as halogenation and dehalogenation.

References

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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 as (de)halo-genation were observed. In contrast to the halogenation reaction 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, as several pentasubstituted isomers were detected.