EFFECT OF BROMINE SUBSTITUENTS IN THE FORMATION OF PXDD FROM POLYHALOGENATED PHENOLS

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Introduction

The condensation of chlorophenols has been studied extensively in the last two decades and was discussed as one mechanism in particular for the formation of PCDD in thermal processes.

Brominated flame retardants and brominated and brominated-chlorinated dibenzodioxins and dibenzofurans have received increased attention recently due to the growing use of brominated flame retardants during the last decade. This is resulting in an increase of brominated compounds in waste (e.g. electric and electronic shredder waste), containing a considerable amount of bromine, in the form of brominated flame retardants.

Many studies reported on the formation of PBDD/PBDF from brominated diphenylethers.[1-6)] or bromophenols [5-7)]. However with the exception of Sidhu et al.[7)], a comparison of the condensation behaviour of bromophenols and chlorophenols was not done. The condensation of brominated phenols is interesting from several aspects. Bromophenols are used as flame retardants and might be a source of PBDD/F during thermal stress. Bromophenols can also be generated during the combustion/pyrolysis of bromodiphenylether or tetrabromobisphenolA[8)] containing material, serving as potential precursors for the formation of PBDD/PBDF. Further, in municipal waste incinerators with sufficient secondary combustion, the largest amount of chlorinated aromatic compounds (PCDD, PCDF, PCBs, PCNs, and chlorophenols) are formed in the cooling section (boiler, duct, dust filtration). Therefore in combustion processes involving high concentrations of brominated flame retardants, mixed PXDD/PXDF might be formed by condensation reactions of precursors or de novo synthesis in the cooling zone.

Therefore we investigated the condensation of a brominated phenol in more detail and compare it to the condensation reaction of the analogous chlorophenol.

Materials and Methods

2,4-dichlorophenol (2,4-Cl_2P) and 2,4-dibromophenol (2,4-Br_2P) were chosen as compounds for the experiments (Alrich, Steinheim Germany). These isomers are major phenolic compounds formed by electrophilic halogenation (e.g. in thermal processes)[8)] and they possess a halogen and a hydrogen substituent in ortho-position, allowing the assessment of formation mechanisms during the condensation steps.

Equimolar amounts of the phenols were sealed in a pyrex ampoule and heated for the respective time in an GC oven. After the experiment, the ampoules were carefully crushed and rinsed with toluene. The clean-up is reported elsewhere.[9)]

Analysis was carried out by high resolution gas chromatography on a HP 6890 gas chromatograph coupled to a HP 5973 mass selective detector (low resolution mass spectrometry). The GC columns used was a DB-5 fused silica column (30 m, 0.32 mm i.d., 0.25 µm film thickness, J&W Scientific, Folsom/USA).

The quantification was carried out by chlorinated ^{13}C-labelled standards. The brominated compounds were quantified with respective response factors. For the quantification of phenoxyphenols, the higher fragmentation was considered in the quantification.

Results and discussions

Formation of halogenated dibenzodioxins

Figure 1 shows the brominated, chlorinated and mixed brominated-chlorinated dibenzodioxins formed during the experiments at 300 °C with a residence time of 10 and 30 minutes respectively. The Br_1Cl_1DD and Br_2DD were the main polyhalogenated dibenzodioxins formed followed by the trihalogenated congeners. Cl_2DD were detected only as a minor product (Figure 1). Halogenated dibenzofurans were not formed at 300 °C in agreement with the temperature dependence observed in the formation of PCDD and PCDF from chlorinated phenols.[10)]

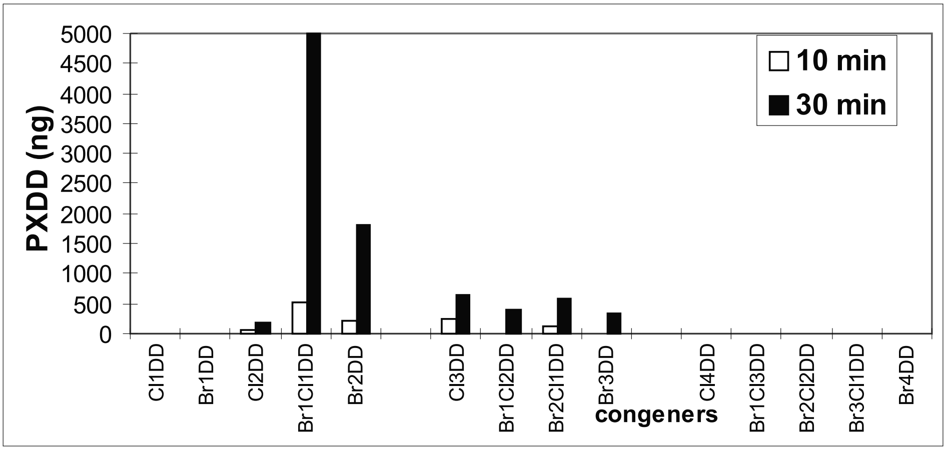

Figure 1. Formation of polyhalogenated dibenzodioxins during the condensation of equimolar amounts of 2,4-Cl_2P and 2,4-Br_2P at 300 °C in the presence of air.

Formation of halogenated phenoxyphenols (predioxins)

Figure 2 shows the distribution of halogenated phenoxyphenols (PXPP) formed as products of the first condensation step. The main product was Br_1Cl_2PP followed by Br_3PP. The analogous phenoxyphenols resulting from chlorine substitution (Cl_1Br_2PP and Cl_3PP) were only minor compounds. The ratio of the substitution of bromine:chlorine derived from the phenoxyphenols formed (at 10 minutes) was approximately 10:1. This demonstrates the high potential of bromine to be substituted during condensation reactions of halogenated phenols compared to chlorine substituents. The results are in agreement with the study of Sidhu et al. who reported a rapid dimerisation of 2,4,6-Br_3P in comparison to the chlorinated 2,4,6-Cl_3P in thermal gas phase reaction[7)].

In addition considerable amounts of Cl_4PP and Br_2Cl_2PP were formed demonstrating that in the first condensation step hydrogen can also be easily substituted. However, the minute amount of tetrahalogenated dibenzodioxins formed (Figure 1) indicates that in the second condensation step the hydrogen elimination is only a minor step if taking place at all (see below).

Additionally, small amounts of Br$_2$PP (38 ng) were detected while no Cl$_2$PP was found. This demonstrates that partial debromination/hydrogenation takes place under the applied conditions while dechlorination/hydrogenation did not occur.

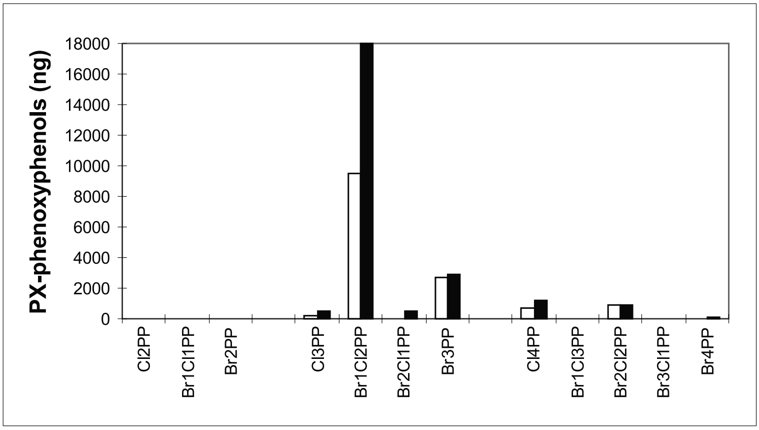

Figure 2. Formation of halogenated phenoxyphenols during the condensation of equimolar amounts of 2,4-Cl$_2$P and 2,4-Br$_2$P at 300°C in the presence of air.

We also analysed the halogenated phenols in the reaction mixture (Figure 3). In addition to the starting compounds, we detected trihalogenated phenols and bromo-chlorphenol. Br$_3$P and Br$_2$Cl$_1$P were formed in approximately the same concentration (ca. 3% of starting phenols) while Br$_2$Cl$_1$P and Cl$_3$P were detected in minute amounts or were not detected respectively. Therefore only bromination and no chlorination occurred under the applied conditions. The comparable amount of Br$_2$Cl$_1$P and Br$_1$Cl$_2$P imply that no preference existed in the bromination of the 2,4-Cl$_2$P and 2,4-Br$_2$P. In addition C$_1$B$_1$P was formed in the same concentration range as the X$_3$P (Figure 3) indicating that in addition to the bromination of a hydrogen position, chlorine can be substituted by bromine[1] . However, we did not detect other Cl$_2$P or Br$_2$P isomers suggesting that no isomerisation reaction occurred under the applied conditions.

Conclusions

Bromine is eliminated easily from bromophenols during thermal condensation reactions. This increases the condensation rate of brominated phenols or brominated+chlorinated phenols in comparison to reactions of only chlorinated phenols. This should be considered and evaluated for technical application of bromophenols involving thermal stress.

It cannot be evaluated from small scale laboratory experiments if the increased condensation of partially brominated phenolic compounds could have an effect on total amount of PXDD/PXDF formed in combustion processes when the bromine concentration is increased. It is interesting in this respect that Wilken et al.11) observed an increased formation of chlorinated DD/DF (in addition to the expected formation of mixed brominated-chlorinated DD/DF) in a municipal waste incinerator after the addition of 5 kg tetrabromomethane into the feed material.

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[1] The B1C1P could theoretically be formed als via Br1Cl2 by a dechlorination step or from DBP by a chlorination. However since we did not detect any chlorination or dechlorination in other reaction products, we can exclude this pathway.

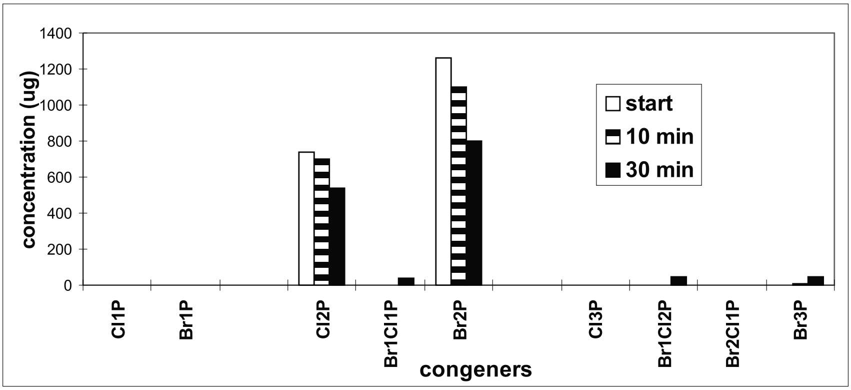

Figure 3. Halogenated phenols detected before and after the condensation experiment

Bromination (hydrogen- and chlorine-positions) and debromination reactions of phenols occur even without the addition of metal catalysts in parallel to the condensation reactions. These side reactions have to be considered in the interpretation of mechanistic studies involving brominated aromatics. One indicator for a first assessment of side reactions is the analysis of bromination and debromination of starting compounds. Furthermore, these side reactions, in our estimation, make it difficult to form isomer specific PBDD and PBDF by thermal condensation.

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