

## Thermal rearrangement of HBCD enantiomers

Robert Köppen<sup>1,2</sup>, Roland Becker<sup>2</sup>, Christian Jung<sup>2</sup>, Irene Nehls<sup>2</sup>

<sup>1</sup>Humboldt University Berlin, Department of Chemistry, Brook-Taylor-Str. 2, D-12489 Berlin, Germany;

<sup>2</sup>Federal Institute for Materials Research and Testing (BAM), Department of Analytical Chemistry; Reference Materials, Richard-Willstätter-Str. 11, D-12489 Berlin, Germany

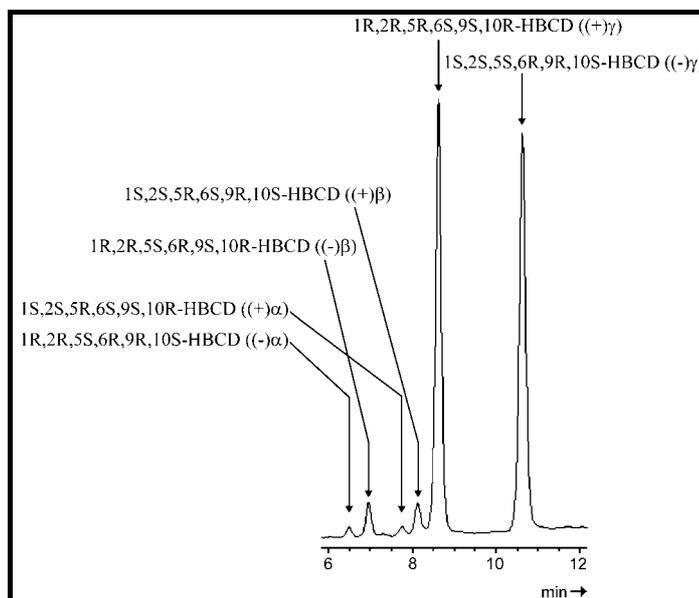
### Introduction.

Brominated flame retardants are a group of chemicals added to combustible polymer materials, which are used in construction, electronic equipment, textiles and many household products, to reduce their flammability. 1,2,5,6,9,10-hexabromocyclododecane (HBCD) is one of the worldwide most used brominated flame retardants. It's main field of application are various plastic materials, upholstery textiles, adhesives, styrene-acrylonitrile resins and expanded polystyrene foams (Barda 1985, deWit 2002, Law et al. 2006). As an additive brominated flame retardant HBCD has the potential to migrate out of products into the environment, because it is not covalently bonded to the material but only mixed with or dissolved in the material.

Technical HBCD consists of a mixture of three diastereomeric pairs of enantiomers, termed ( $\pm$ )  $\alpha$ -,  $\beta$ -, and  $\gamma$ -HBCD with the  $\gamma$ -isomer as main component (Becher 2005, Heeb et al. 2005). The structural differences between these diastereomeric pairs of enantiomers lead to concomitant variability in physicochemical properties such as hydrophobicity and water solubility (Hunziker et al. 2004, Covaci et al. 2006), resulting in variable propensities for biological uptake and metabolism. The physicochemical properties of HBCD make it persistent in the environment and potentially bioactive (de Wit 2002, Vos et al. 2003). In conjunction with their resistance to degradation the HBCD diastereomers are bioaccumulative in both terrestrial and aquatic organisms and were found in humans and consequently challenge scientists and regulators (Law et al. 2005).

### Figure 1

Chromatographic separation of HBCD enantiomers on a chiral NUCLEODEX  $\beta$ -PM analytical column



HBCD decomposes at temperatures above 220 °C (Larsen & Eckert 1988, Barontini et al. 2001) and at temperatures between 160 and 200 °C thermal rearrangement of the HBCD isomers takes place (Peled 1995, Janak et al. 2005). Therefore, a quantification of individual isomers by gas chromatography/mass spectrometry (GC-MS) is not feasible. Diastereoselective analysis of HBCD in environmental samples requires reversed-phase HPLC coupled to a diode array detector (DAD) or a MS detector. Separation of the pairs of enantiomers requires a chiral stationary phase (Figure 1).

Characterisation of the pure HBCD enantiomers and correlation of their absolute configurations with their order of elution and their sense of optical rotation was done in preparation for the investigation of the thermal rearrangement of the HBCD enantiomers (Köppen et al. 2007). Herein, the thermal rearrangement of the pure HBCD stereoisomers, including a kinetic model for their interconversion is described.

### **Materials and Methods.**

Native  $\alpha$ -,  $\beta$ - and  $\gamma$ -HBCD as racemic solutions in toluene (chemical purity >98%) were provided by Wellington Laboratories Inc. (Ontario, Canada). Technical HBCD was purchased from Fluka (Buchs, Switzerland). HPLC grade acetonitrile and tetrahydrofurane were obtained from J.T. Baker (Deventer, Holland). Water was obtained from a demineralising system (DTS Wasser-Abwasser-Technik GmbH, Frankfurt/Main, Germany) consisting of a reverse osmosis plant (RO 1500) and three series-connected softening units (WSD60-800).

Enantioselective determinations were performed using an HPLC system (Agilent 1100series) equipped with a combination of a C18 and a chiral NUCLEODEX  $\beta$ -PM analytical column (both 5  $\mu$ m, 200 mm x 4.6 mm ID). The column outlet was coupled to a UV-detector with a fixed wavelength of 208 nm. Resolution of enantiomers was achieved at a column temperature of 30 °C using an acetonitrile/water gradient (v/v) starting with an initial acetonitrile fraction of 80 %, held for 10.0 min, followed by linear gradient to 100 % in 35 min and held at 100 % for 3 min. For the investigation of the thermal rearrangement of HBCD a chamber kiln N 11/H equipped with a program controller was used. Technical HBCD and pure enantiomers were kept at different temperatures and at different times samples were taken out, cooled and analysed by HPLC.

### **Results and Discussion.**

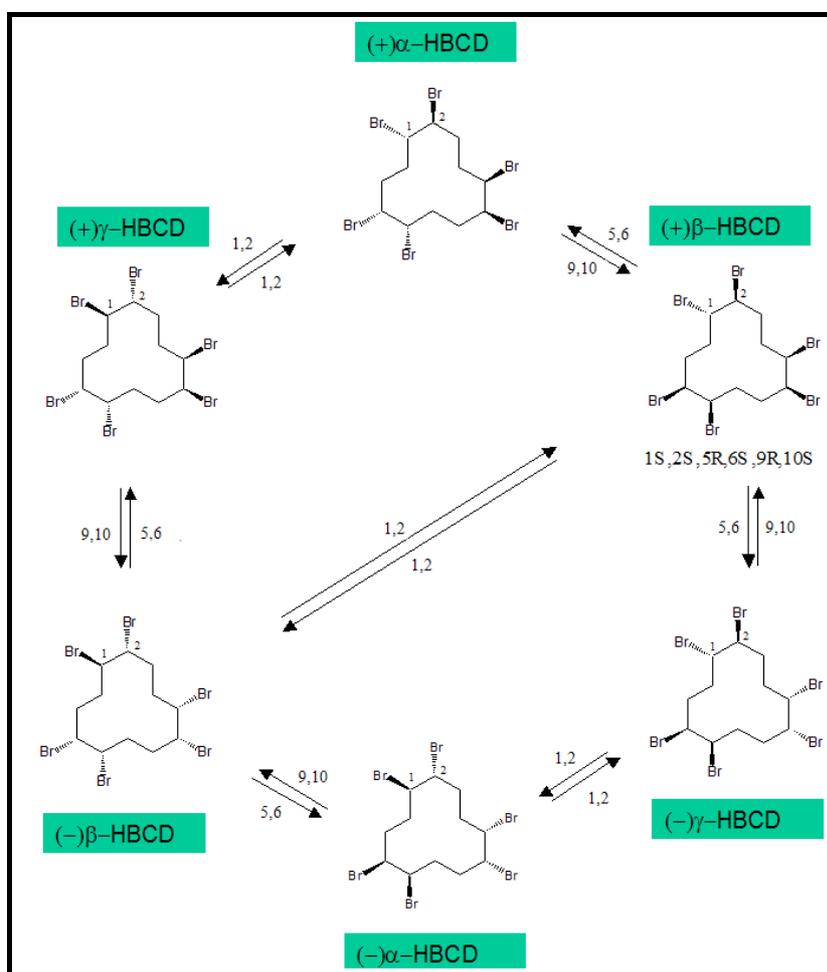
Samples of pure HBCD-enantiomers were weighed into glass vials and stored in a chamber kiln at different temperatures and for different times. The  $\gamma$ -enantiomers were examined at 160 °C. In intervals of two minutes over a period of 60 minutes samples were taken for the enantiomerspecific analysis. The pure heated samples were analysed by reversed-phase HPLC using a combination of a C18 and a permethylated  $\beta$ -cyclodextrin-bonded stationary phase for enantiomeric separation. As a result of these procedure it was possible to evaluate the rate constants for the thermal rearrangement of the pure  $\gamma$ -enantiomers.

Under thermal stress the rearrangement of all six pure HBCD enantiomers can be observed. The  $\beta$ - and  $\gamma$ -enantiomers gave predominantly the  $\alpha$ -enantiomers, whereas the pure  $\alpha$ -enantiomers are widely stable. In Figure 2 the different pathways of the inversion of the HBCD stereocenters are displayed which leads to the  $\alpha$ -enantiomers as end products. It is clearly visible why the formation of  $\alpha$ -enantiomers from the  $\gamma$ -enantiomers, which are the main component of the technical mixture, already occurs at 150 - 160 °C. This transformations requires only the inversion of the stereocenters 1 and 2. Hence, it can be concluded, that the inversion of the stereocenters in positions 1 and 2 proceeds faster than that in positions 5 and 6 or 9 and 10, respectively. In comparison to the thermal rearrangement of the  $\gamma$ -enantiomers the interconversion of the  $\beta$ -enantiomer stereocenters leads to the formation of both

$\alpha$ -enantiomers, because of the fast transformation of the  $\beta$ -enantiomers into each other (stereocenters 1 and 2).

The Thermal rearrangement of the  $\gamma$ -enantiomers begins in the temperature range of 150 - 160 °C. With rising temperatures the process of thermal rearrangement accelerates until at temperatures above 200 °C decomposition of HBCD takes place. If the temperatures reach 170 °C the thermal rearrangement of the  $\beta$ -enantiomers begins and at 200 °C the thermal equilibrium of the  $\alpha$ -enantiomers will be adjusted. An interconversion of the  $\alpha$ -enantiomers will be only observed in correlation with the thermal equilibrium, due to the needed energetically unfavourable inversion of all six stereocenters. Furthermore it seems like the  $\alpha$ -enantiomers are the energetically favourable configuration and so they are the dominant enantiomers in the HBCD composition at thermal equilibrium.

**Figure 2**  
Pathways of the interconversions of HBCD stereoisomers



Regardless of which enantiomer was used as starting point all six enantiomers were formed by thermal rearrangement.

## References.

- Barda HJ. 1985. In: Ullmann's Encyclopedia of industrial Chemistry, Wiley-VCH, Weinheim, 417.
- Barontini F, Cozzani V, Petrc L. 2001. Ind Eng Chem Res 40:3270.
- Becher G. 2005. Chemosphere 58:989.
- Covaci A, Gerecke ASC, Law RJ, Voorspoels S, Köhler M, Heeb NV, Lesile H, Allchin CR, DeBoer J. 2006. Environ Sci Technol 40:3680.
- de Wit CA. 2002. Chemosphere 46:583.
- Heeb NV, Schweizer WB, Kohler M, Gerecke AC. 2005. Chemosphere 61:65.
- Hunziker RW, Gonsior S, MacGregor JA, Desjardins D, Ariano J, Friederich U. 2004. Organohalogen Comp 66:2300.
- Janak K, Covaci A, Voorspoels S, Becher G. 2005. Environ Sci Technol 39:1987.
- Köppen R, Becker R, Emmerling F, Jung C, Nehls I. 2007. Chirality, in press.
- Larsen ER, Eckert EL. 1988. J Fire Sci 4:139.
- Law RJ, Kohler M, Heeb NV, Gerecke AC, Schmid P, Voorspoels S, Covaci A, Becher G, Janak K, Thomsen C. 2005. Environ Sci Technol 39:281a.
- Law RJ, Kohler M, Heeb NV, Gerecke AC, Schmid P, Voorspoels S, Covaci A, Becher G, Janak K, Thomsen C. 2006. Environ Sci Technol 40:2.
- Peled M, Scharia R, Sondack D. 1995. In: Advances in Organobromine Chemistry II, Desmurs JR (ed.). Elsevier, Amsterdam, 92.
- Vos JG, Becher G, van den Berg M, de Boer J, Leonards PEG. 2003. Pure Appl Chem 75:2039.