Available online at www.sciencedirect.com
ScienceDirect
Chemosphere 71 (2008) 656–662
CHEMOSPHERE
www.elsevier.com/locate/chemosphere

On the thermally induced isomerisation of hexabromocyclododecane stereoisomers

Robert Köppen, Roland Becker *, Christian Jung, Irene Nehls

Department of Analytical Chemistry, Reference Materials, Federal Institute for Materials Research and Testing (BAM), Richard-Willstätter-Strasse 11, D-12489 Berlin, Germany

Received 26 July 2007; received in revised form 30 October 2007; accepted 4 November 2007

Abstract

The interconversion of the stereoisomers contained in technical 1,2,5,6,9,10-hexabromocyclododecane, a major brominated flame retardant increasingly found in the environment and in biota, was investigated at elevated temperatures. The application of pure enantiomers of the three constituents α-, β-, and γ-HBCD enabled the unambiguous elucidation of the individual isomerisation reactions as well as the quantification of all respective rate constants. At 160 °C the rate constants range over two orders of magnitude from 1.50×10^{-3} to 1.88×10^{-5} mol(%) s^{-1}. A preliminary mechanistic explanation for the differences of the rate constants which govern the composition of HBCD diastereomers at equilibrium is given.

Keywords: Flame retardant; Diastereomers; Enantiomers; Rearrangement; Kinetics; HBCD

1. Introduction

1,2,5,6,9,10-Hexabromocyclododecane (HBCD) is applied as additive flame retardant to plastic materials, such as expanded polystyrene foams, upholstery textiles, adhesives, and styrene–acrylonitrile resins (Barda et al., 1985; de Wit, 2002; BSEF, 2005) with an estimated global market demand of about 22 000 metric tons in 2003 (BSEF, 2007). HBCD is persistent in the environment and increasingly found in the biosphere and is potentially bioactive (Vos et al., 2003; Covaci et al., 2006; BSEF, 2007).

Technical HBCD consists of a mixture of three diastereomeric pairs of enantiomers, termed (±)α-, β-, and γ-HBCD with the γ-isomers as main component (Groweiss et al., 1991; Becher, 2005). HBCD diastereomers were found in sewage sludges and sediments with increasing levels (de Wit et al., 2006; Hale et al., 2006; Law et al., 2006a; Marvin et al., 2006), in both terrestrial and aquatic organisms (Tomy et al., 2004; Janak et al., 2005; Law et al., 2006b) and in humans (Covaci et al., 2006). In case of fish a dominance of the α- over the γ-diastereomer (Tomy et al., 2004; Janak et al., 2005) and enantioselective accumulation (Tomy et al., 2004) was observed. The respective ratio of HBCD stereoisomers in different biological matrices may be due to the concomitant variability in physicochemical properties (Hunziker et al., 2004) or caused by stereoselective uptake and metabolism. There is strong evidence for a biologically induced interconversion of HBCD stereoisomers (Law et al., 2006b).

Previous investigations have shown that HBCD decomposes at temperatures above 220 °C (Peled et al., 1995; Barontini et al., 2001) and that alteration of the HBCD isomer ratio takes place between 160 and 200 °C (Peled et al., 1995; Janak et al., 2005). These findings obtained with technical HBCD prove the transformation of γ-HBCD to α-HBCD. However, no attempt was undertaken to elucidate the reaction mechanism or possible pathways. During the processing of polymer materials containing HBCD the temperature may exceed 160 °C. This would lead to a thermal isomerisation of HBCD and as a direct consequence to

* Corresponding author. Tel.: +49 30 8104 1121; fax: +49 30 8104 1127.
E-mail address: roland.becker@bam.de (R. Becker).

0045-6535/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.chemosphere.2007.11.009

environmental HBCD contamination with increased amount of α-diastereomer.

A recent investigation revealed that (+)-α-HBCD arises as main product from (+)-γ-HBCD under thermal stress and that the (−)-γ-enantiomer gave predominantly the (−)-α-enantiomer. In both cases minor amounts of the other four HBCD stereoisomers were found (Köppen et al., 2006). It should be noted that any individual isomerisation steps actually taking place and their kinetics can only be elucidated with the help of a time series with enantiomerically pure starting material. Recently, the characterisation of all six individual HBCD stereoisomers contained in the technical HBCD mixture was reported (Koeppen et al., 2007) and enabled a detailed investigation of their isomerisation. The intention of this work was to analyse the isomerisation of HBCD under thermal stress in detail. A mechanism and a kinetic model for the interpretation of the observed generation of all six stereoisomers starting from purified (+)-γ-HBCD is presented.

2. Materials and methods

2.1. Chemicals

Native α-, β- and γ-HBCD were provided by Wellington Laboratories, Inc. (Ontario, Canada) as racemic solutions in toluene (chemical purity > 98%). Technical HBCD was purchased from Fluka (Buchs, Switzerland). Pure HBCD enantiomers were obtained by enantiospecific separation from the technical HBCD mixture using preparative HPLC as reported elsewhere (Koeppen et al., 2007). HPLC grade solvents 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).

2.2. High performance liquid chromatography

Enantioselective determinations of HBCD isomers were performed using a HPLC system (Agilent 1100 series, Agilent Technologies, Waldbronn, Germany) consisting of a vacuum degasser, binary pump, column thermostat, thermostatted autosampler and a diode array detector (DAD) run at a fixed wavelength of 208 nm. The HPLC system was equipped with a combination of a Zorbax XBD-C18 (double end-capped, pore size: 80 Å; Agilent Technologies, Waldbronn, Germany) and a chiral NUCLEODEX β-PM (pore size: 100 Å; Macherey–Nagel GmbH & Co, Düren, Germany) analytical column (both columns: 5 μm, 200 × 4.6 mm, ID). 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 min, followed by linear gradient to 100% in 35 min and held at 100% for 3 min with a constant flow rate of 0.3 ml min^{-1}. HBCD samples were injected as solutions in tetrahydrofuran (10 μl, 5 mg ml^{-1}) and the concentrations of all six stereoisomers were in the linear range of the detector. The relative response factors of the HBCD diastereomers (α:β:γ = 0.82:1:0.83) were determined from nine injections of the pure racemic standard substances and used to calculate molar fractions of the stereoisomers from the measured detector responses. Concentrations of HBCD stereoisomers were reported as molar fractions of the total HBCD amount at the respective point in the times series.

2.3. Thermal isomerisation

The thermal rearrangement of pure HBCD enantiomers was investigated using a chamber kiln oven (N 11/H, Nabertherm GmbH, Bremen, Germany) equipped with the program controller B 150 and thermostatted within ±0.5 °C of the set value. HBCD enantiomers (5 mg) were weighed in glass vials (32 × 11.6 mm) and placed on a preheated aluminium rack in the oven. In case of (+)-γ-HBCD, the samples were kept at 160 °C and over a period of 60 min vials were withdrawn at 2 min intervals, placed on a cold flagstone outside the oven to reach ambient temperature immediately. Then, each sample was dissolved in 1 ml of tetrahydrofuran and the HBCD composition was analysed by HPLC-DAD as described above. (+)-α-HBCD was thermostatted at 200 °C (60 min) and four samples of (+)-β-HBCD were thermostatted at 170 °C (10, 20, 30, 40 min) for reasons outlined below. Each time series was conducted in duplicate.

2.4. Treatment of data

The sum concentration of the six HBCD stereoisomers measured at a particular time was set 100% in each case. Then, the molar fraction of each diastereomer was calculated as mol(%). The Mathematica 4.0 software package from Wolfram Research, Inc. (USA) was used for numerical evaluation of kinetic data.

3. Results and discussion

γ-HBCD was chosen as starting material to study the isomerisation pathways because its rapid turnover allows to monitor the formation of the other isomers during a reasonable time series. The investigations were carried out in the liquid phase shortly above the melting point of the γ-enantiomers. Fig. 1a depicts the behaviour of neat (+)-γ-HBCD at 160 °C monitored by HPLC-DAD.

The initial generation of (+)-α-HBCD is followed by the formation of (+)-β-HBCD and then the remaining four HBCD stereoisomers. The sum of all stereoisomers totals to the original amount of the starting (+)-γ-HBCD at any time during the exposition period. A closer analysis of this time series suggests a cascade of consecutive interconversions that is consistent with the circuit mechanism shown in Fig. 2. Obviously, the reciprocal inversion of the configurations at two vicinal carbons takes place not