Reductive debromination of nonabrominated diphenyl ethers

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Introduction

Brominated flame retardants (BFRs) have been widely used in a broad range of products, e.g. plastics, electronic equipment, textiles and vehicles, since the 1960s. Commercial polybrominated diphenyl ether (PBDE) products (PentaBDE, OctaBDE and DecaBDE) have been used in a wide variety of applications (Alaee et al., 2003). Penta- and OctaBDE were banned in the EU in 2004, and voluntarily phased out by the only US producer at approximately the same time (Cox and Efthymiou, 2003; Great Lakes Flame Retardants, 2005). The use of DecaBDE was restricted from July 1st 2008 according to the RoHS directive, i.e. applications in electric and electronic equipment/products (EU, 2008). In December 2009 it was announced that DecaBDE will be voluntarily phased out in the US within the coming years (BSEF, 2009). Commercial DecaBDE products contains, apart from the fully brominated congener (BDE-209), a small fraction (up to 3%) of the three nonaBDEs; BDE-206, BDE-207 and BDE-208 (La Guardia et al., 2006). The extensive use of DecaBDE will lead to release into the environment long after they are phased out of production since the compounds are not only released into the environment as a result of synthesis and incorporation into material but also during use and final disposal of the flame retarded products and articles. PBDEs are now ubiquitous environmental contaminants, found in all abiotic compartments and in wildlife and humans (de Wit, 2002; Law et al., 2003; Hites, 2004).

The properties of the PBDEs suggest that they, and in particular the more highly brominated ones, will end up in either sediments or soils (Hites, 2004; Shoeib et al., 2004). Because of this, their potential for chemical transformations in any of the abiotic compartments is of interest. Sediments are often anaerobic and it is well known that persistent organohalogen compounds such as PCBs may undergo reductive dehalogenation in this compartment (Suflita et al., 1982). La Guardia and coworkers has presented sediment levels of nonaBDEs of 3-10% of ΣPBDE-content (La Guardia et al., 2007), significantly higher than the percentage of nonaBDEs in the technical decaBDE mixtures. Gerecke et al. have shown reductive debromination of BDE-209 to nona- and octaBDEs after incubation in anaerobic sewage sludge for 238 days (Gerecke et al., 2005). In another study it was similarly shown that decaBDE and an octaBDE mixture underwent debromination under anaerobic conditions (He et al., 2006).

This work focuses on identification of transformation products from reductive debromination of the three nonabrominated DEs, to add knowledge of PBDE transformation product patterns in the environment.

Materials and methods

Authentic reference standards BDE-196, BDE-197, BDE-198, BDE-201, BDE-204 and BDE-205, were purchased as standard solutions from Campro Scientific (Veenendaal, The Netherlands), while

the BDE-153, BDE-154, BDE-155, BDE-169, BDE-180, BDE-181, BDE-182, BDE-183, BDE-184, BDE-191, BDE-194, BDE-202, BDE-203, BDE-206, BDE-207 and BDE-208 were synthesised in house (Marsh et al., 1999; Christiansson et al., 2006; Teclechiel et al., 2007). Chemicals and solvents were of *pro analysis* quality. BDE-206 and BDE-208 were of ≥98% purity and BDE-207 of ≥95% purity.

Gas chromatography-mass spectrometry (GC-MS) was performed on a GCQ instrument from Finnigan Mat (San Jose, USA). The gas chromatograph was equipped with a DB-5 capillary column (15 m x 0.25 mm, 0.1 µm film) from J&W Scientific (Folsom, USA). The column temperature programme was: 80°C for 1 minute increased 15 °C/min to 300 °C and thereafter 2 °C/minute to 320 °C. The injector temperature was 250 °C. Carrier gas was helium. Mass spectra were recorded in electron ionisation mode at an ion source temperature of 180 °C and electron energy of 70 eV. The scan range was 50 to 950 amu.

Solutions of BDE-206, BDE-207 and BDE-208 were prepared by dissolving the compound in a mixture of THF and ethanol (2:1) to a final concentration of 11 µmol/L (BDE-206 and BDE-207) and 7.7 µmol/L (BDE-208) utilising an ultrasound bath. Reagent solutions of sodium borohydride were prepared by dissolving 1.5 g of the hydride in 150 mL ethanol (99.5%). The reduction reactions were repeated three times per compound and were performed as follows: To a round bottomed flask covered in aluminium foil, a volume of 36 mL of the sodium borohydride solution was transferred and stirred at room temperature. Reaction was initiated by addition of a PBDE congener solution (4 mL) and the reaction vessel was plugged with a glass stopper. After one hour, 20 mL of the reaction mixture was withdrawn with a measuring pipette and quenched with acetic acid solution pH 3 (10 mL) in a glass beaker. After one additional hour (two hours in total) the remaining reaction mixture (20 mL) was quenched with the same acidic solution (10 mL) as above. Solid potassium hydroxide was added to the quenched reaction samples to acquire a pH above 10. The samples were then individually extracted in separation funnels (100 mL) with cyclohexane (three times, 10 mL). The pooled cyclohexane phases were washed with water twice (10 mL) and thereafter the solvent was evaporated under a gentle stream of nitrogen. The samples were finally dissolved in *n*-hexane (1 mL) and injected on a GCQ for analysis. The reduction kinetics were studied at two time points, i.e. at one and two hours, respectively, for each of the three compounds studied.

Results

The reduction reactions of the three nonaBDEs (BDE-206, BDE-207, BDE-208) formed primarily debrominated products, proceeding from mainly octa- to heptaBDEs after one hour to include further debrominated DEs after two hours. The octaBDEs formed in the reductive transformations of BDE-206, BDE-207 and BDE-208 are presented in Figure 1. Unidentified transformation products are assumed to be PBDEs not available among the authentic reference standards and corresponding to other brominated compounds.

When studying experimental or abiotic chemical and metabolic transformations of highly brominated diphenyl ethers, the pattern of debromination is naturally of interest. In this study the three nonabrominated diphenyl ethers showed a propensity for *ortho*-debromination in the initial transformation step. An overview of all identified congeners gives an indication of resistance to debromination in the *para*-position.

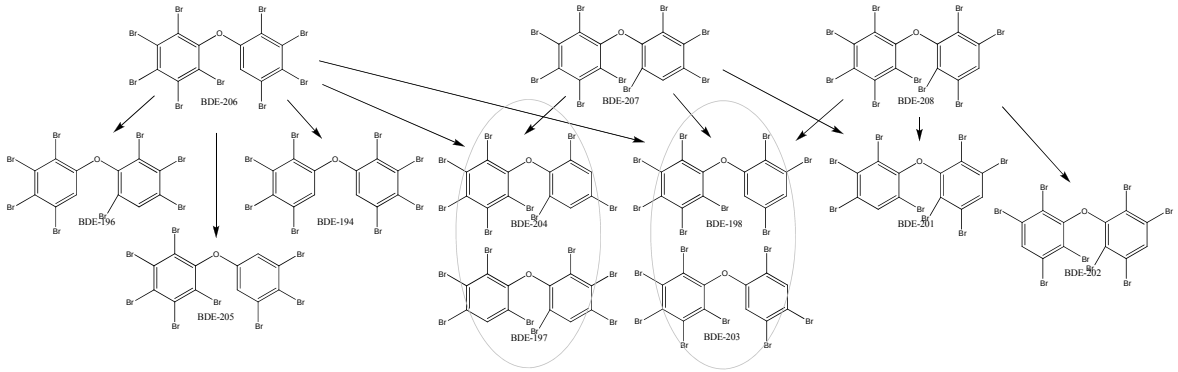

Figure 1. Octabrominated diphenyl ether congeners formed through reductive debromination of BDE-206, BDE-207, and BDE-208. The octaBDEs within the grey circles indicate coeluting compounds.

BDE-206, the nonaBDE isomer lacking a bromine atom in the *ortho*-position, produces two major transformation products (BDE-194 and BDE-205) that have undergone *ortho*-debromination. Three major *ortho*-debrominated products emerge through reduction of BDE-207; BDE-196, BDE-198 and/or BDE-203. The latter also being potential products also from hydride treatment of BDE-208. The reductive debromination of BDE-207 gave primarily one octaBDE product, BDE-196, with an additional few congeners at lower levels. The product spectrum was further simplified for BDE-208 showing one or two PBDE congeners as octaBDE transformation products. The majority contribution to this octaBDE product peak can perhaps be assumed to be BDE-198, with hydrogens in the *ortho*- and *para*-positions, since BDE-208 lacks a bromine in the *para*-position and the compound coeluting with BDE-198, BDE-204, lacks bromines in the *ortho*- and *meta*-positions.

La Guardia and coworkers has reported a detailed account for the congener composition of PentaBDE, OctaBDE and DecaBDE (La Guardia et al., 2006). Amongst the non-detected congeners, BDE-182 was found in the transformation of BDE-206 and BDE-207, BDE-181 in the transformation of BDE-206 and BDE-208, and BDE-205 in the transformation of BDE-206 in the present study. BDE-204 was possibly formed in the transformation of BDE-206 and BDE-207. These results show how compounds not present in the commercial technical mixtures can originate from transformation of higher brominated DE congeners.

The study of reductive debromination of the three nonaBDEs using sodium borohydride as reductive agent has not, to the best of our knowledge, been presented before. The results give extensive information about the transformation paths of the nonaBDEs.

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