

Birnessite mediated debromination of decabromodiphenyl ether

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Abstract

Decabromodiphenyl ether (BDE-209) is a major component of a commercial flame retardant formulation; however, there is limited information on the fate of BDE-209 in the environment, including metal oxide mediated degradation. Laboratory experiments were conducted to investigate the birnessite (δ -MnO₂)-promoted debromination of BDE-209 in tetrahydrofuran (THF)-water systems as well as catechol solutions. Up to 100% (0.1044 μ mol initial charge) of BDE-209 disappeared upon reaction with birnessite in THF/H₂O (4:6–9:1). The formation of aqueous Br⁻ from BDE-209 reduction was determined and up to 16 mole% of initial bromine was released over the course of the reaction indicating approximately 1.7 Br–C bonds were reduced per BDE-209 molecule. The distribution of debrominated congeners, however, indicated a much greater extent of debromination for some products than what was inferred from an average bromine mass balance. The produced congeners varied from tetra- to nona-bromodiphenyl ether, including BDE-47 and -99, during the 24 h reaction. Experiments with deuterated water indicated that water was not the major hydrogen donor in the reduction but rather THF provided the reducing power. This conclusion was supported by the presence of succinic acid, which was produced from oxidation of THF. The reactions with aqueous catechol, rather than THF-water mixtures, were performed to assess the possible role that compounds found in natural environments, such as tannin-like phenols, might have on the chemistry. These experiments indicated that birnessite mediated debromination of BDE-209 might occur in natural settings.

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1. Introduction

Polybrominated diphenyl ethers (PBDEs) have been produced industrially as flame retardants since the early 1960s and the market demand (~70,000 metric tons in 2001) for PBDEs has dramatically increased over the years with ~86% distributed to the Americas and Asia (BSEF, 2003; Hites, 2004). Concern over the environmental risk of PBDEs has increased due to the awareness of their toxicity as endocrine disruptors, their neurodevelopmental toxic effects, and due to the nearly ubiquitous detection

of PBDEs in sediments, sewage sludge, fish, mammals (including humans) and air (de Wit, 2002). The dominant PBDEs detected in the environment are the less brominated congeners, such as tetra- and hexa-bromodiphenyl ethers rather than decabromodiphenyl ether (BDE-209) which account for ~80% of all PBDEs produced (BSEF, 2003; Hites, 2004). Although the lower molecular weight formulations were phased out of production in the US and Europe at the end of 2004 (McPherson et al., 2004), the question remains as to whether the congener distributions typically found in environmental samples are derived from these commercial mixtures or from the environmental degradation of BDE-209.

BDE-209 has a low vapor pressure and is highly hydrophobic (expected log K_{ow} > 8) (Braekevelt et al., 2003),

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therefore, its bioavailability may be kinetically limited. Due to these properties, knowledge of the possible abiotic transformation pathways of BDE-209 is crucial to develop a complete understanding of the fate of BDE-209 in the environment. Some studies have indicated that photolytic debromination of BDE-209 may be the most significant abiotic process leading to the formation of less brominated BDEs (Bezares-Cruz et al., 2004; Eriksson et al., 2004; Söderström et al., 2004; Ahn et al., 2006). Another possible reductive abiotic degradation of BDE-209 by zerovalent iron has been reported by Keum and Li (2005), however, there is a lack of information regarding whether naturally occurring common metal oxides may be involved in the degradation of BDE-209.

Metal oxides present in soils and sediments participate in various reactions of organic compounds including oxidation and reduction (Huang, 2000; Jokic et al., 2001; Zhang and Huang, 2003). Numerous studies have demonstrated degradation of chlorinated organic pollutants by various metal oxides (Stone, 1987; Ulrich and Stone, 1989; Pizzigallo et al., 1995; Huang, 2000; Park et al., 2000). The dissociation energy of the carbon–halogen bond of C–Br (1.15 MJ mol^{-1}) is lower than C–Cl (1.41 MJ mol^{-1}) (Brady and Holum, 1993), therefore, debromination of PBDEs, such as BDE-209, by metal oxides is highly probable given the facile exchange of electrons in the organo-bromide-birnessite systems. Manganese oxides are one of most common metal oxides in soils and sediments and mediate several abiotic transformations of organic compounds (McBride, 1987, 1994). Among manganese oxides, birnessite ($\delta\text{-MnO}_2$) is the most common form, and it is a naturally occurring mineral with layered oxide structures of varying composition that are of low crystallinity (McKenzie, 1971) in a mixed valence (+2/+3/+4) configuration. It is a very reactive metal oxide in soils and sediments (Huang, 2000); therefore, birnessite is likely to play an important role in the debromination of BDE-209 under natural settings.

Reductive debromination of PBDEs, represented by R–Br, requires the transfer of two electrons to R–Br and a proton to complete the reaction ($\text{R–Br} + \text{H}^+ + 2\text{e}^- \rightarrow \text{R–H} + \text{Br}^-$). The protons and electrons, which can be derived from water or other organic reactants, are important to assist debromination of PBDEs. In laboratory debromination experiments, an organic solvent is generally used to increase PBDE solubility as aqueous experiments with BDE-209 are very slow, and experimentally difficult to conduct, due to the low K_{ow} (Braekevelt et al., 2003). Co-solvents may actually participate in the reaction. Overall, the objectives of this study were to determine: (1) the extent of BDE-209 debromination by birnessite in the presence of tetrahydrofuran (THF), a common organic solvent serving as a co-solvent or phase transfer catalyst, and (2) the subsequent chemical role of THF and the naturally occurring reductant catechol as electron and hydrogen donors in debromination by birnessite.

2. Material and methods

2.1. Chemicals

Decabromodiphenyl ether (BDE-209; 98% purity), catechol (1,2-dihydroxybenzene) and succinic acid were obtained from Aldrich Chemical Co. (Milwaukee, WI). Tetrahydrofuran (THF) with inhibitor (butylated hydroxytoluene) or inhibitor-free THF were purchased from Sigma Chemical Co. (St. Louis, MO). Deuterium oxide (D_2O) and a mixture of 39 PBDE congeners (EO-5113) each having from one to seven bromine atoms, was obtained from Cambridge Isotope Lab, Inc., [2-,3-,4-mono-bromodiphenyl ether (BDE); 2,4-, 2,4'-, 2,6-, 3,3'-, 3,4-, 3,4'-, 4,4'-diBDE; 2,2',4-, 2,3',4-, 2,4,4'-, 2,4,6-, 2,4',6-, 2',3,4-, 3,3',4-, 3,4,4'-triBDE; 2,2',4,4'-, 2,2',4,5'-, 2,3',4,4'-, 2,3',4',6-, 2,4,4',6-, 3,3',4,4'-tetraBDE; 2,2',3,4,4'-, 2,2',4,4',5-, 2,2',4,4',6-, 2,3,4,5,6-, 2,3',4,4',5-, 2,3',4,4',6-, 3,3',4,4',5-pentaBDE; 2,2',3,4,4',5-, 2,2',4,4',5,5'-, 2,2',4,4',5,6'-, 2,2',4,4',6,6'-, 2,3,4,4',5,6-hexaBDE; 2,2',3,4,4',5,6-, 2,2',3,4,4',5',6-, 2,3,3',4,4',5',6-heptaBDE] with one to seven bromine substitutions. Standards of five congeners (3,3',4,4'-tetraBDE; 2,2',3,4,4',6,6'-heptaBDE; 2,2',3,3',4,4',5,6'-octaBDE; 2,2',3,3',4,4',5,5',6-, 2,2',3,3',4,4',5,6,6'-nonaBDE), from Wellington Laboratories, were also utilized.

Birnessite (surface area: $27.7 \text{ m}^2 \text{ g}^{-1}$) was prepared according to the method of McKenzie (1971). Briefly, two moles of HCl were added drop-wise to a boiling solution of 1.0 mole of KMnO_4 in 2.5 l of deionized water with vigorous stirring. After boiling for an additional 10 min, the precipitate was filtered and washed several times with deionized water, then freeze-dried. Analysis of birnessite by X-ray diffraction and infrared spectroscopy showed the presence of poorly crystalline minerals, with characteristic peaks matching those reported in the literature (McKenzie, 1971). The X-ray powder diffraction patterns were obtained using a PADV X-ray diffractometer with a Co-K α radiation source (Scintag, Inc., Cupertino, CA). The infrared absorption spectra were obtained using a Nexus 670 Fourier Transform Infrared Spectrophotometer (Thermo Electro Co., Waltham, MA) with 1.0 mg samples of the minerals dispersed in KBr (99.0 mg) pellets analyzed at a range of $4000\text{--}1000 \text{ cm}^{-1}$.

2.2. Experimental setup

A stock solution of 1.0 mg ml^{-1} BDE-209 in THF was used in this study. The reduction of adsorbed and dissolved BDE-209 was explored with two series of experiments.

In the first series of experiments, 0.1 ml BDE-209 stock solution was added to 50 mg birnessite in 15 ml-test tubes, and THF was removed by air-drying in the dark for one day to study the reactivity of adsorbed BDE-209. Birnessite (onto which BDE-209 was adsorbed) was placed in 5 ml THF/ H_2O (0:10–10:0). The reactivity of the dissolved BDE-209 ($0.1044 \text{ } \mu\text{mol}$) was investigated in another series of experiments by adding different amounts of birnessite

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