

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) (Braekvelt 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 (δ -MnO₂) 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 (D₂O) 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 m² 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 KMnO₄ 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 4000–1000 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/H₂O (0:10–10:0). The reactivity of the dissolved BDE-209 (0.1044 μ mol) was investigated in another series of experiments by adding different amounts of birnessite

(0–50 mg ml⁻¹) into 5 ml THF/H₂O (7:3) in 15 ml test tubes. The reaction mixtures for both series of experiments were placed in a shaker for various lengths of time (0–24 h). At designated times, samples were centrifuged. The pellets were extracted three times with THF and extracts were combined with the supernatants for further analysis. To investigate the production of succinic acid from THF by birnessite, 20 mg ml⁻¹ of birnessite in 5 ml THF/H₂O (5:5, 7:3, and 9:1) in the presence or absence of BDE-209 (0.1044 μmol) was reacted for 24 h under dark conditions. Succinic acid production was quantified by an ion chromatography.

Additional experiments were also completed to investigate the role of 1,2-dihydroxyl benzene, catechol as a naturally occurring reductant. Catechol (0.003, 0.045 or 46.135 mmol) was added to 5 ml of water in the presence of 50 mg of birnessite onto which BDE-209 (0.104 μmol) was adsorbed, and the reaction proceeded for 23 d. At designated times (0–23 d), samples were centrifuged, and the pellets were extracted three times with THF. The supernatants were extracted three times with toluene (2 ml) and toluene was completely removed using a N₂ gas stream and then re-dissolved in THF. All triplicate test tubes were covered with aluminum foil during reactions at room temperature.

2.3. Analysis

The combined THF extracts were analyzed for remaining BDE-209 by a high performance liquid chromatography (HPLC) and reaction products were analyzed by a gas chromatography (GC) equipped with an electron capture detector (ECD) and GC–mass spectrometer (MS). Released Br⁻ and succinic acid (a THF oxidation product) were analyzed by ion chromatography. Inhibitor-free THF was used for all experiments except to investigate the inhibitor effect on the debromination of BDE-209.

BDE-209 in THF extracts was quantified with a Varian 9050 HPLC system monitoring at 240 nm, using the Supelcosil LC-18 DB column (length = 10 cm, i.d. = 4.6 mm, film thickness = 5 μm, pore size = 120 Å, surface area = 170 m² g⁻¹, matrix active group = octadecyl phase; Supelco, Bellefonte, PA) after the filtration through a 0.2 μm nylon membrane. The mobile phase was 2% water in acetonitrile delivered isocratically (flow rate = 1.0 ml min⁻¹).

To identify debrominated congeners after the reaction with birnessite, samples were analyzed by GC–ECD, and product identification was based on matching retention times of PBDE standards to retention times of product peaks. Subsamples filtrated for HPLC analysis were passed through a glass pipette (4 mm × 14.6 cm) packed with glass wool, anhydrous Na₂SO₄ and florisil. The column was washed with 3 ml of THF. THF in the collected samples was removed by a N₂ gas stream. Filtrates were re-dissolved in 2 ml hexane, and an internal standard, hexachlorobenzene, was added into the samples before analysis on a Hewlett Packard 5890 II GC–ECD using a DB5-MS

capillary column (length = 30 m, i.d. = 0.25 mm, film thickness = 0.25 μm). The initial oven temperature was 100 °C maintained for 2 min and increased 5 °C min⁻¹ up to 150 °C (maintained for 20 min). The temperature was increased from 150 °C to 290 °C at 5 °C min⁻¹ and maintained for 52 min followed by increasing temperature from 290 °C to 330 °C at 10 °C min⁻¹; the final temperature was maintained for 5 min.

The molecular masses and comparison of debrominated products from the reaction in the presence of H₂O or D₂O were determined with a Thermo Finnigan Polaris Q GC–MS. Electron impact ionization was utilized in the mass spectrometer. The column was a DB5-MS (Agilent J&W; length = 25 m, i.d. = 0.25 mm, film thickness = 0.25 μm). The oven temperature program was identical to that of the GC–ECD system. The injector/inlet temperature program followed the oven temperature program. One micro-liter injections were made under positive electron impact ionization utilizing full scan mode from 50 to 1000 atomic mass units.

Ion chromatography with a Ionpac AS 14 column (i.d. = 4 mm; length = 250 mm) was used to quantify succinic acid produced. The mobile phase was a mixture of 2 mM NaHCO₃ and 2 mM Na₂CO₃ delivered at 1.5 ml min⁻¹.

3. Results and discussion

3.1. Debromination of BDE-209

The rate of degradation (debromination) of BDE-209 was studied in the presence of birnessite in various ratios of a THF and water mixture. Fig. 1 shows that up to 100% of the dissolved BDE-209 (0.1044 μmol) in THF/H₂O (7:3) was debrominated when mixed with birnessite. In the presence of more than 1.4 mg ml⁻¹ birnessite, dissolved BDE-209 was below detectable level (0.52 nmol) in the solution at the end of the reaction. Bromide ion released from BDE-209 was observed in the solution after the reaction was terminated as shown in Figs. 1 and 2. In THF/H₂O (6:4–9:1), over 75% of the initially adsorbed

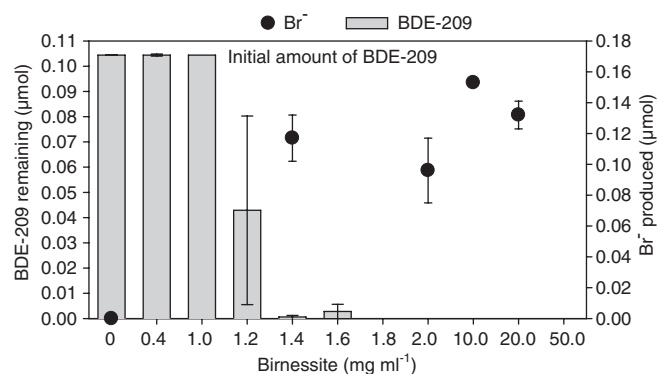


Fig. 1. BDE-209 remaining and Br⁻ released after the 24-h reaction with birnessite (0–50 mg ml⁻¹) in THF/H₂O (7:3); BDE-209 was dissolved.

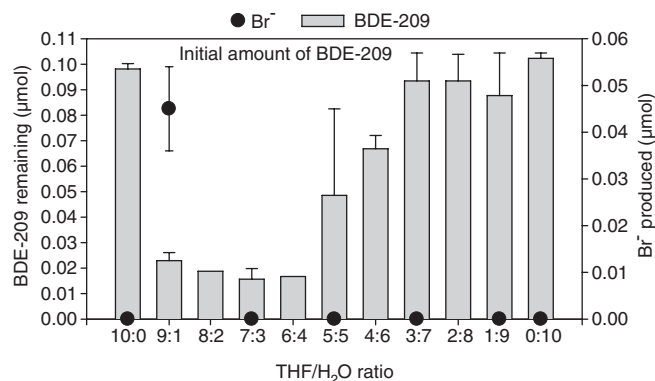


Fig. 2. BDE-209 remaining and Br⁻ released after the 24-h reaction with birnessite (10 mg ml⁻¹) in THF/H₂O (0:10–10:0).

BDE-209 reacted, whereas negligible changes in BDE-209 mass were observed in THF/H₂O with 10:0 and 0:10–3:7 ratios (Fig. 2).

Debromination was confirmed by determining Br⁻ release from BDE-209 after the reaction was terminated. However, even after all BDE-209 disappeared, less than 16% (0.1670 μmol) of the maximum possible release of Br⁻ (1.044 μmol) was found. This indicates approximately 1.7 Br–C bonds on average were reduced per BDE-209 molecule and that some of the bromine still remains in the degradation product structures (Fig. 3 and Table 1). Debromination products were identified based on matching retention times with known standard PBDEs. Debromination products with GC–ECD retention times similar

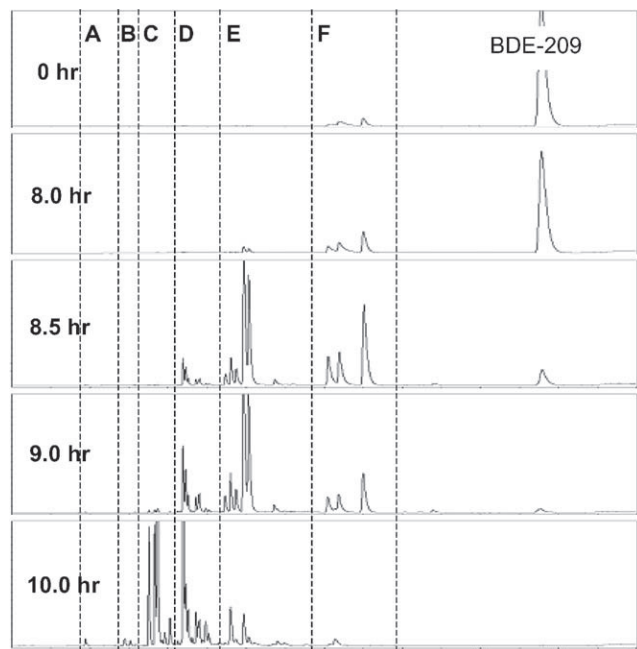


Fig. 3. GC–ECD chromatograms of samples reacted with birnessite in THF/H₂O (7:3) for 0–10 h; BDE-209 was added in the mixture after an adsorption on birnessite surface. Ranges A–F correspond approximately to retention times of: tetra-(A), penta-(B), hexa-(C), hepta-(D), octa-(E), nona-(F) congeners.

Table 1
PBDE congeners (no.^a) with identical RTs^b as reaction products

Reaction time	Reaction products	Br atoms	Number of congeners
0	209	10	4
8.0	206/207/208	9	10
	209	10	
	206/207/208	9	
	196/197	8	
8.5	183/three unknowns	7	15
	209	10	
	206/207/208	9	
	196/197	8	
	183/four unknowns	7	
	153/154	6	
	118	5	
9.0	66	4	17
	209	10	
	206/207/208	9	
	196/197	8	
	183/five unknowns	7	
	138/153/154	6	
	118	5	
10.0	66	4	17
	207/208	9	
	196/197	8	
	183/six unknowns	7	
	138/153/154	6	
	118/one unknown	5	
	66	4	
12.0	207/208	9	17
	196/197	8	
	183/five unknowns	7	
	138/153/154	6	
	118/two unknowns	5	
	66	4	
	24.0	207/208	
196/197		8	
183/ 190/eight unknowns		7	
138/153/154/five unknowns		6	
99/100/118/one unknown		5	
49/47/66		4	

^a 209: 2,2',3,3',4,4',5,5',6,6'-decaBDE, 208: 2,2',3,3',4,5,5',6,6'-nonaBDE, 207: 2,2',3,3',4,4',5,6,6'-nonaBDE, 206: 2,2',3,3',4,4',5,5',6-nonaBDE, 196: 2,2',3,3',4,4',5,6'-octaBDE, 197: 2,2',3,3',4,4',6,6'-octaBDE, 183: 2,2',3,4,4',5',6-heptaBDE, 190: 2,3,3',4,4',5,6-heptaBDE, 153: 2,2',4,4',5,5'-hexaBDE, 154: 2,2',4,4',5,6'-hexaBDE, 118: 2,3',4,4',5-pentaBDE, 66: 2,3',4,4'-tetraBDE, 138: 2,2',3,4,4',5'-hexaBDE, 99: 2,2',4,4',5-pentaBDE, 100: 2,2',4,4',6-pentaBDE, 49: 2,2',4,5'-tetraBDE, 47: 2,2',4,4'-BDE.

^b RT is relative retention time, normalized to retention time of hexachlorobenzene.

to those of tetra- to nona-bromodiphenyl ethers were observed (Fig. 3 and Table 1). The rapid disappearance of BDE-209 occurred between 8 and 9 h after the initiation of the reaction. This lag-time may be due to the time needed to accumulate the THF degradation products to accelerate the BDE-209 degradation. Fig. 3 illustrates the congener profile of degradation products, observed over time. It appears that the first step of degradation of BDE-209 is the loss of one bromine atom followed by the formation of octabromodiphenyl ether (Table 1). Most of BDE-209 and nonabromodiphenyl ethers disappeared

from the chromatograms, and tetrabromodiphenyl ethers appeared on the chromatogram after 8.5 h of reaction. The cumulative number of congeners increased from 3 to 29 over time. It is noteworthy that tetra- (BDE-47, -49, -66) and penta-bromodiphenyl ethers (BDE-99, -100, -118) were identified as products in this study, because the most predominant PBDEs in environmental samples are tetra- and penta-bromodiphenyl ethers (especially BDE-47 and -99) (Hites, 2004). In other previous studies of abiotic (photolytic) debromination, BDE-209 degrades to less brominated PBDEs in various organic solvents and adsorbed on solid supports (Bezares-Cruz et al., 2004; Eriksson et al., 2004; Söderström et al., 2004; Ahn et al., 2006). Additionally, BDE-209 was also converted to lower congeners by a metal (Keum and Li, 2005).

3.2. The role of THF for debromination of BDE-209

THF was initially employed, in this study, to enhance solvation of BDE-209. However, THF has been used as a hydrogen donor for the reductive dehalogenation of octa-fluoronaphthalene (Kiplinger and Richmond, 1996a,b). Our study using THF containing an inhibitor, butylated hydroxytoluene, shows that 100% of initially added BDE-209 in THF/H₂O (7:3) solution was recovered after a 24 h reaction with birnessite, while BDE-209 completely disappeared in THF containing no inhibitor (data not shown). This indicates that THF oxidation in the presence of birnessite is a critical process in debromination as evidenced by the experiment with THF that contained the radical inhibitor, butylated hydroxytoluene. The THF oxidation in the absence of inhibitor by birnessite was indicated by detection of succinic acid, which is an oxidation product of THF. Fig. 4 shows that up to 0.87 μmol of succinic acid was produced by birnessite in the presence of BDE-209 dissolved in THF and water mixture, and the amount of succinic acid produced was greater than in the absence of BDE-209. It indicates approximately 8.4 mole of succinic acid was produced concomitant to BDE-209 transformation. Chemical oxidation of THF has been widely studied using different oxidants (Ogata et al., 1980; Horányi and Rizmayer, 1985; Shi, 1998; Svetlakov et al., 2002; Salavati-Niasari and Najafian, 2003; Yoshimitsu et al., 2003). In those studies, the main products in the oxidation of THF were 2-hydroxytetrahydrofuran, γ -butyrolactone, lactol, 4-hydroxybutyraldehyde, and succinic acid. THF appeared to be oxidized by birnessite to succinic acid. Detection of succinic acid indicates that this oxidation path includes THF ring cleavage (Avgousti et al., 1999; Svetlakov et al., 2002).

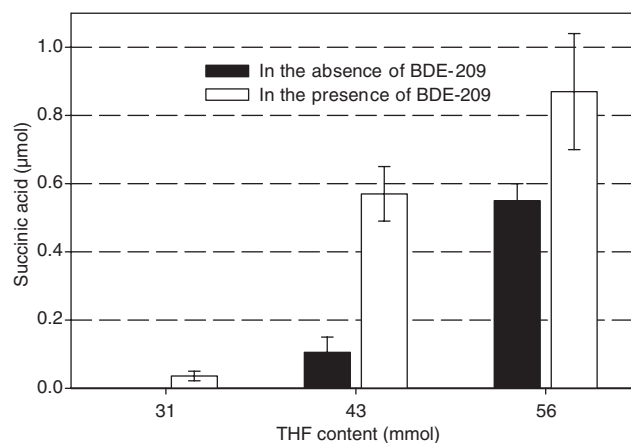


Fig. 4. Succinic acid produced by a 24-h reaction of birnessite (20 mg ml⁻¹) with or without BDE-209 in THF/H₂O (5:5, 7:3, and 9:1).

Water is involved in the reaction to complete the oxidation of THF to form succinic acid (Avgousti et al., 1999). Thus, BDE-209 could not convert in a 100% THF solution in the presence of birnessite due to the fact that THF cannot serve as an electron or hydrogen donor in the absence of water (Fig. 2). To confirm that the hydrogen donor for the debromination reactions is THF, BDE-209 was incubated with birnessite in THF/D₂O (7:3) and the GC-MS data was compared to that of a THF/H₂O mixture (7:3). Various products with different degrees of debromination showed nearly identical mass-spectrometry data between the system with D₂O and those of H₂O (data not all shown). For example, Fig. 5 shows that mass spectra are nearly identical for octabromodiphenyl ether produced in

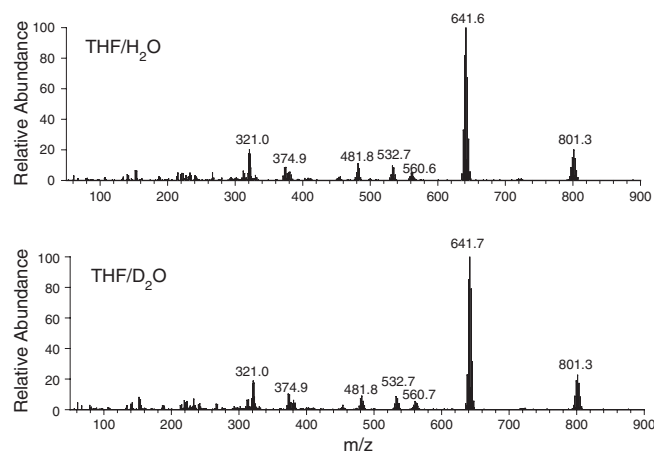
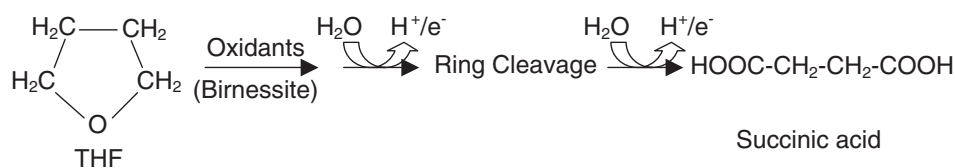


Fig. 5. GC-MS spectrum of one of debrominated product of BDE-209 after the reactions with birnessite in THF/H₂O (7:3) or THF/D₂O (7:3).



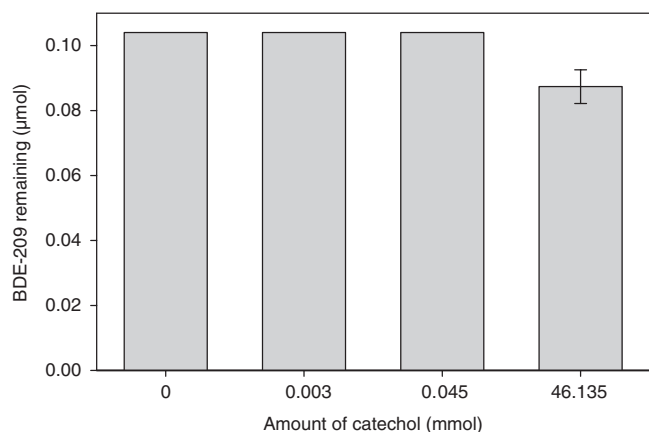


Fig. 6. BDE-209 remaining after a 23-d reaction with birnessite in the presence of catechol as a natural reductant in water.

the system with D₂O and H₂O. The results (Figs. 4 and 5) show that THF was oxidized by birnessite, and H₂O was not a hydrogen donor in our study system.

3.3. Degradation of BDE-209 in the presence of catechol

To examine the possible abiotic debromination of BDE-209 by birnessite in the presence of natural electron and hydrogen donors, experiments were conducted in the presence of catechol, as a natural reductant, rather than THF. Catechol, a soil humic precursor and tannin component, can be easily oxidized by birnessite (Naidja et al., 1998), and may act as hydrogen and electron donor.

Fig. 6 indicates that there is no significant degradation of BDE-209 in the presence of 0.003–0.045 mmol of catechol, however, degradation of BDE-209 (0.104 µmol) was detected when 46 mmol of catechol was added into this system. This shows that BDE-209 may be debrominated by birnessite in the presence of natural electron and hydrogen donors such as soil organic compounds. The amount of BDE-209 that was reductively debrominated with catechol appears to be small, however, this may be a function of the reaction period. The 23 d lab experiment is a short time frame for many reactions occurring in the environment, particularly those involving “persistent” organic compounds like PBDEs. Therefore, considerable debromination of BDE-209 by birnessite might occur in the natural environment. To address this issue in future studies, experimental conditions with a longer incubation time and lower concentrations of natural reductants will be applied to examine BDE-209 debromination.

In conclusion, debromination of BDE-209 occurs in aqueous THF solutions in the presence of birnessite and produces less brominated congeners which are commonly found in biota and other environmental matrices. Manganese oxide-mediated debromination of BDE-209 in the presence of natural electron and hydrogen donors is likely to occur in the environment. Future research into the fate of BDE-209 in birnessite-rich environments is justified.

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