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Rapid debromination of polybrominated diphenyl ethers (PBDEs) by zero valent metal and bimetals: Mechanisms and pathways assisted by density function theory calculation[☆]

Rui Wang^a, Ting Tang^a, Guining Lu^{a, b, c, *}, Kaibo Huang^a, Hua Yin^{a, b}, Zhang Lin^{a, b, e}, Fengchang Wu^d, Zhi Dang^{a, b, c}

^a School of Environment and Energy, South China University of Technology, Guangzhou 510006, China

^b The Key Lab of Pollution Control and Ecosystem Restoration in Industry Clusters, Ministry of Education, Guangzhou 510006, China

^c Guangdong Provincial Engineering and Technology Research Center for Environmental Risk Prevention and Emergency Disposal, Guangzhou 510006, China

^d State Key Laboratory of Environmental Criteria and Risk Assessment, Chinese Research Academy of Environmental Sciences, Beijing 100012, China

^e Guangdong Engineering and Technology Research Center for Environmental Nanomaterials, China

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ABSTRACT

Polybrominated diphenyl ethers (PBDEs) undergo debromination when they were exposed in zerovalent metal or bimetallic systems. Yet their debromination pathways and mechanisms in these systems were not well understood. Here we reported the debromination pathways of three BDE congeners (BDE-21, 25 and 29) by nano-zerovalent iron (n-ZVI). All these BDE congeners have three bromine substituents that were located in *ortho*-, *meta*- and *para*-positions. Results demonstrated that BDE-21, 25 and 29 preferentially debrominate *meta*-, *ortho*- and *para*-bromines, respectively, suggesting that bromine substituent at each position (i.e. *ortho*-, *meta*- or *para*-) of PBDEs can be preferentially removed. Singly occupied molecular orbitals of BDE anions are well correlated with their actual debromination pathways, which successfully explain why these BDE congeners exhibit certain debromination pathways in n-ZVI system. In addition, microscale zerovalent zinc (m-ZVZ), iron-based bimetals (Fe/Ag and Fe/Pd) were also used to debrominate PBDEs, with BDE-21 as target pollutant. We found that the debromination pathways of BDE-21 in m-ZVZ and Fe/Ag systems are the same to those in n-ZVI system, but were partially different from those in Fe/Pd systems. The debromination of BDE-21 in Pd-H₂ system as well as the solvent kinetic isotope effect in single metal and bimetallic systems suggests that H atom transfer is the dominant mechanism in Fe/Pd system, while e⁻ transfer is still the dominant mechanism in Fe/Ag system.

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1. Introduction

Persistent organic pollutants (POPs) are notorious for their persistence and bioaccumulation in the environment. As one kind of POPs, polybrominated diphenyl ethers (PBDEs) have aroused significant concern in this field due to their widely use as flame retardant and consequently global distribution (Rahman et al., 2001). Unlike other flame retardants that are usually incorporated into the materials through covalent bonding (i.e. reactive type),

PBDEs are simply dissolved in the polymers without any chemical bonding (i.e. additive type) (de Wit, 2002; Rahman et al., 2001). Therefore, PBDEs can be easily migrated from electronic products to the environment (Alaee et al., 2003). Accordingly, recent studies have reported their existence in soil (Dong et al., 2014; Parolini et al., 2013; Zhang et al., 2014), sediments (Wang et al., 2016; Wu et al., 2013), sewage sludge (Kim et al., 2013), fish (Zeng et al., 2013), and breast milk (Tang and Zhai, 2017). PBDEs are one kind of endocrine disrupting pollutant which pose a great risk to human health (Akortia et al., 2016). Efforts are necessary to develop effective technologies to remove them from environment.

Nanoscale zero-valent iron (n-ZVI) is one kind of well-known strong reducing agents which can degrade various contaminants (Stefaniuk et al., 2016). Even though recent studies have shown that

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* Corresponding author. School of Environment and Energy, South China University of Technology, Guangzhou 510006, China.

E-mail address: luta@scut.edu.cn (G. Lu).

n-ZVI can reduce various halogenated solvent through dehalogenation process (Cwiertny et al., 2006, 2007; Liu et al., 2005; Xie and Cwiertny, 2013), the dehalogenation of chlorinated or brominated aromatic compounds such as polychlorinated biphenyls (PCBs), polybrominated biphenyls (PBBs) and PBDEs by n-ZVI have received relatively less attention. Currently, the information related to debromination of PBDEs by n-ZVI is limited, and most of these studies focused on the deca-BDE (BDE-209) (Fang et al., 2011; Keum and Li, 2005; Li et al., 2007; Shih and Tai, 2010). The large amount of debromination products of BDE-209 makes it difficult to definitely confirm the debromination pathways of PBDEs. Although previous studies try to summarize the debromination sequence of PBDEs by n-ZVI as *meta*->*ortho*->*para*- (Li et al., 2007; Shih and Tai, 2010; Zhuang et al., 2010), this is just the case for specific BDE congeners. Whether this rule of thumb is suitable for all PBDEs still remains in question.

The debromination pathways of PBDEs by zerovalent metal are not always consistent. When a metal additive (such as palladium) was plated on the surface of n-ZVI, the debromination pathways can be changed (Wang et al., 2017; Zhuang et al., 2012). This raised another interesting scientific question that why metal additive can greatly improve the degradation rates and change the pathways of halogenated pollutants. For recent decades, this question has not been answered with certainty. Generally, there are two dominant viewpoints to explain this phenomenon. First, the metal additive can accelerate the iron corrosion through the formation of galvanic couple, which consequently enhance the electron transfer (e-transfer) from iron to pollutants (Elliott and Zhang, 2001; Schrick et al., 2002a; Xu and Zhang, 2000; Yan et al., 2010). Second, the metal additive can act as a hydrogenation catalyst where the adsorbed atomic hydrogen species can promote the pollutant degradation by hydrogen transfer (H-transfer) (Kim et al., 2008; Wang et al., 2017; Zhuang et al., 2011, 2012). Great efforts have been made to explore this question. Kim et al. (2008) have found that the palladization changed the dechlorination pathways of 1,2,3,4-tetrachlorodibenzo-*p*-dioxins by n-ZVI, which suggest that palladization shifts the mechanism toward a greater role of H-transfer rather than e-transfer. Zhuang et al. (2011) have found that kinetics constants of PBDEs by palladized n-ZVI did not correlate with the energy of lowest unoccupied molecular orbitals (E_{LUMO}), indicating this is not an e-transfer process. Our previous studies have found that the debromination pathway of 2,2',4,4'-tetrabromodiphenyl ether (BDE-47) in Fe/Pd system is the same to that in Pd-H₂ systems, which suggest that the H-transfer is dominant mechanism (Wang et al., 2017). In addition, Xie et al. explored the solvent kinetic isotope effects on the degradation of chlorinated solvent by Fe/Pd and claimed that H-transfer is also the dominant mechanism (Xie and Cwiertny, 2013). However, all these studies only focused on n-ZVI and Fe/Pd, and different studies focused on different pollutants. To comprehensively elucidate this question, more efforts are desperately needed.

Here, we explore the debromination of BDE-21, BDE-25 and BDE-29 by n-ZVI to elucidate the debromination sequence of PBDEs. These three BDE congeners were selected because they all have *ortho*-, *meta*- and *para*-bromine substituents but with different arrangement pattern, so that we can explore whether the debromination sequence of these BDE congeners by n-ZVI are the same or not. In addition, the debromination of BDE-21 was investigated in six systems (i.e. zinc, n-ZVI, Fe/Pd, Fe/Ag, Pd-H₂ and Ag-H₂) to compare its debromination pathways. The reaction rates of BDE-21 in D₂O- and H₂O-based systems were compared when the reducing agent is zinc, n-ZVI, Fe/Pd and Fe/Ag, separately, to explore the solvent kinetic isotope effects. This can help us to gain further insight about the relative roles of H-transfer and e-transfer in the debromination of PBDEs by bimetallic systems.

2. Experimental

2.1. n-ZVI and bimetallic particles synthesis and characterization

n-ZVI and bimetallic particles were prepared by aqueous reduction of ferrous sulfate by the excess of sodium borohydride. Detailed information of the synthesis method is available in the supplementary data. The zinc powder was purchased from Sigma company, USA. All these metal particles were characterized by scanning electron microscopy (SEM), and two iron-based bimetallics (Fe/Ag and Fe/Pd) were characterized by Energy Dispersive Spectrometer (EDS) to confirm that the noble metal additive was successfully plated on the surface of n-ZVI. As shown in Fig. S1, the n-ZVI particles and two iron-based bimetallic particles (i.e. Fe/Ag and Fe/Pd) have the similar particles size, which are all around 50–150 nm, indicating that the metal additive plating did not affect the particles size. In addition, the particle size of m-ZVZ is around 3–8 μm, which is much larger than those of n-ZVI, Fe/Ag and Fe/Pd. The EDS images in Fig. S2 indicate that the Ag and Pd were successfully plated on the n-ZVI surface. Note that the loading amount of both Ag and Pd on n-ZVI was 1% by weight, since we only focus on the debromination of PBDEs in Fe/Ag and Fe/Pd systems, the effect of loading amount of metal additive is beyond the scope of this work.

2.2. Debromination experiment

2,4,5-tribromodiphenyl ether (BDE-29), 2,3',4-tribromodiphenyl ether (BDE-25), 2,3,4-tribromodiphenyl ether (BDE-21), 3,4'-dibromodiphenyl ether (BDE-13), 3,4-dibromodiphenyl ether (BDE-9), 2,4-dibromodiphenyl ether (BDE-7), 2,3'-dibromodiphenyl ether (BDE-6), 2,3-dibromodiphenyl ether (BDE-5), 4-monobromodiphenyl ether (BDE-3), 3-monobromodiphenyl ether (BDE-2), 2-monobromodiphenyl ether (BDE-1) and diphenyl ether (DE) were purchased from Accustandard company, USA. The structures of these PBDEs were listed in Table S1. 100 μL of the individual PBDE stock solution (In acetone) at the 100 mg L⁻¹ was added into 8 mL serum vial. After the solvent were evaporated, 10 mg of metal materials (i.e. n-ZVI, m-ZVZ, Fe/Ag or Fe/Pd) was added to each vial. Then 2 mL H₂O or D₂O was added into the vials. The final concentrations of PBDEs in this system were all present at 5 mg L⁻¹. The vials were capped and then placed on a rotary shaker at a speed of 250 rpm and covered by aluminized paper to avoid any photodegradation. At selected time intervals, the vials were sacrificed to extract the parent BDEs and the potential products. Detailed extraction process was described as follows: 1 mL concentrated hydrochloric acid was added into each vial to completely dissolve the metal particles, which can avoid the adsorption of PBDEs by these particles during the extraction process. Then 2 mL iso-octane was added into each vial, the vials were capped and placed on a vortex mixer to fiercely mix for 15 min. After mixture, the upper organic layer was dehydrated by anhydrous sodium sulfate and then transferred into a 2 mL GC sample vial for analysis. All samples were prepared in triplicate.

2.3. Instrumental analysis

PBDE congeners were identified and quantified by Thermo scientific Gas Chromatography-Mass Spectrometer (GC-MS). The injection volume was 1 μL with splitless mode. The temperature of injection inlet was set at 280 °C. A TG-5DILMS column (30 m × 0.25 mm × 0.25 μm) was used for the separation. The oven temperature was held initially at 120 °C for 1 min, then increased at the rate of 20 °C min⁻¹ to 190 °C, and decreased at the rate of 25 °C min⁻¹ to 170 °C, then increased at the rate of 25 °C min⁻¹ to the final temperature of 250 °C. The samples were analyzed by selective

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