Thermal degradation of polybrominated diphenyl ethers over as-prepared Fe₃O₄ micro/nano-material and hypothesized mechanism

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Abstract The thermal degradation of decabromodiphenyl ether (BDE-209) featuring fully substituted bromines was investigated over an as-prepared Fe₃O₄ micro/nano-material at 300 °C. Degradation followed pseudo-first-order kinetics with $k_{\text{obs}}=0.15 \text{ min}^{-1}$ higher than that for decachlorobiphenyl (CB-209). Twenty-six newly produced polybrominated diphenyl ether (PBDE) congeners were identified using the available PBDE standards, while four PBDE congener products were predicted using third-order polynomial regression equation. Analysis of the products indicated that BDE-209 underwent stepwise hydrodebromination over as-prepared Fe₃O₄. Similar to the case for CB-209, two initial hydrodebromination steps are favored at the BDE-209 meta-positions, giving the major products BDE-207 and BDE-197. However, the variance about the preferred products began to emerge from the start of heptabromodiphenyl ethers (hepta-BDEs). The majorly produced hepta-BDE isomer with BDE-183 is unbrominated at one *ortho*-position. However, this is different from the reported degradation of CB-209, which always produced the products chlorinated at all four *ortho*-positions until the *ortho*-position had to be removed for the formation of trichlorobiphenyls and dichlorobiphenyl still

majorly chlorinated at three or two *ortho*-positions. The early BDE-209 hydrodebromination steps appear to be strongly influenced by steric effects, whereas subsequent hydrodebromination steps, as more bromine atoms are removed, will be gradually governed more by thermodynamics.

Keywords Polybrominated diphenyl ether · Fe₃O₄ micro/nano-material · Hydrodebromination products · Degradation pathway · Steric effect · Thermodynamics

Introduction

Polybrominated diphenyl ethers (PBDEs), which have been used as brominated flame retardants, are ubiquitous environmental contaminants. They have two benzene rings joined by an ether linkage, and there are ten positions that can have a bromine substituent, meaning that there are 209 possible PBDE congeners. As a new type of persistent organic pollutants (POPs), tetrabromodiphenyl ethers (tetra-BDEs), pentabromodiphenyl ethers (penta-BDEs), hexabromodiphenyl ethers (hexa-BDEs), and heptabromodiphenyl ethers (hepta-BDEs) have been included in Annex A of the Stockholm Convention since 2009 (UNEP 2009). Furthermore, the technical guidelines for the environmentally sound management of wastes with those PBDEs have been consulted at the seventh meeting of the Conference of the Parties to the Stockholm Convention in May 2015 (Seventh meeting of the conference of the parties to the Stockholm Convention 2015). PBDEs have been used widely in airplanes and other vehicles, building materials, carpets, electronic circuit boards, furniture, and textiles (Alaee 2003). Measures to limit PBDE emissions have been issued in many countries, but large amounts of PBDEs have been released into the environment because of their widespread use. It has been

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found that industrial point sources, such as steel-making and other metallurgical plants and municipal solid waste incinerators, have contributed to PBDE emissions to the environment (Odabasi et al. 2009; Wang et al. 2010a, b). PBDE contents in the flue gases (26.1–109 ng/Nm³) and bottom ash (20.4–186 ng/g) in municipal solid waste incinerators can be three orders of magnitude higher than contents in the atmosphere and reference soils, respectively. It has been established that PBDEs have toxic effects on the endocrine, nervous, and reproductive systems of mammals (Domingo et al. 2008). Therefore, the reduction of PBDEs contents is a matter of public concern in the context of environmental protection.

Numerous methods have been used to degrade PBDEs, including photolytic degradation (Wei et al. 2013), anaerobic microbial debromination (Gerecke et al. 2005; Huang et al. 2014; Tokarz Iii et al. 2008), and biological metabolism (Stapleton et al. 2004). However, these methods have many disadvantages, such as harsh reaction conditions, high equipment costs, and poor efficiencies. Much attention has been paid to the degradation of persistent organic pollutants at relatively low temperatures using various metal oxides as catalysts due to their high catalytic activity, thermal stability, the low costs, and ease of preparation (Ma et al. 2012, 2013a, b, 2014). Nevertheless, to the best of our knowledge, the studies investigating the thermal decomposition of PBDEs by metal oxides are rare in the literatures, and the involved degradation mechanism is unclear.

Of the metal oxides, Fe₃O₄ with the reverse spinel structure has been found to offer promise owing to its non-toxicity, low cost, ferromagnetic property, and recycling performance. In particular, the use of three-dimensional Fe₃O₄ micro/nano-materials for environmental remediation has attracted much attention because these materials have high specific surface areas and do not aggregate strongly due to their microstructures. In the former studies, Fe₃O₄ micro/nano-material exhibited much higher activity toward the degradation of polychlorinated biphenyls (PCBs), and the degradation mechanism reactions were proposed (Huang et al. 2013). PBDEs are structurally composed of two phenyl rings connected by an ether linkage carbon–oxygen bridge, whereas PCBs consist of two phenyl rings connected by a carbon–carbon bridge. It is therefore important to investigate the decomposition of PBDEs by Fe₃O₄ micro/nano-material and the associated degradation pathway as compared to that of PCBs.

In this study, the thermal degradation of decabromodiphenyl ether (BDE-209) featuring ten fully substituted bromines was investigated at 300 °C over as-prepared Fe₃O₄ micro/nano-material. The degradation products were comprehensively determined by GC-MS using 57 kinds of chemical standards and third-order polynomial regression equation. The possible degradation pathways were traced based on the identification of intermediates. Compared to those of decachlorobiphenyl (CB-209), the

effects of the linkage bond between two benzene rings and halogen substituents to the degradation pathway were discussed.

Experimental

Materials

A total of 57 PBDEs were in the standards that were used. Standard solution BDE-AAP-A15X was purchased from AccuStandard (New Haven, CT, USA) and contained 39 PBDE congeners, which were the monobromodiphenyl ethers (BDEs-1, -2, and -3; the dibromodiphenyl ethers (di-BDEs) BDEs-7, -8, -10, -11, -12, -13, and -15; the tribromodiphenyl ethers (tri-BDEs) BDEs-17, -25, -28, -30, -32, -33, -35, and -37; the tetra-BDEs BDEs-47, -49, -66, -71, -75, and -77; the penta-BDEs BDEs-85, -99, -100, -116, -118, -119, and -126; the hexa-BDEs BDEs-138, -153, -154, -155, and -166; and the hepta-BDEs BDEs-181, -183, and -190. Another 15 PBDE standards—the hexa-BDEs BDEs-139, -140, -156, and -169; the hepta-BDEs BDEs-171, -180, -184, and -191; the octabromodiphenyl ethers (octa-BDEs) BDEs-196, -197, -201, -203, and -204; and the nonabromodiphenyl ethers (nona-BDEs) BDEs-207 and -208—were purchased from Wellington Laboratories (Guelph, Canada). BDEs-205 and -206 were purchased from Cambridge Isotope Laboratories (Andover, MA, USA). A BDE-209 standard was purchased from Dr. Ehrenstorfer (Augsburg, Germany). The BDE-209 used in the degradation tests was purchased from Dr. Ehrenstorfer. Dichloromethane and hexane, both of pesticide grade, were purchased from Dika Technologies (Lake Forest, CA, USA).

Fe₃O₄ micro/nano-material was prepared using a simple and cheap process mediated with ethylene glycol, following a previously described procedure (Jia et al. 2011; Zhong et al. 2006). About 1.9 g of ferric nitrate (Fe(NO₃)₃·9H₂O), 4.5 g of polyethylene glycol with a mean molecular weight of 10,000, and 2.7 g of urea were added to 180 mL of ethylene glycol, and the mixture was heated to 230 °C. The resulting precursor material was then calcined at 350 °C in a flowing nitrogen atmosphere. The obtained Fe₃O₄ micro/nano-material was characterized by scanning electron microscopy (SEM; Hitachi S-3000N), transmission electron microscopy (TEM; Hitachi-7500), and x-ray powder diffraction (XRD; Rigaku D/max 2500 diffractometer, Cu Kα radiation, λ=0.154056 nm, 40 kV, 200 mA) (Fig. S1, Online Resource 1). These results indicate that a three-dimensional hierarchical, flower-like Fe₃O₄ micro/nano-material was successfully prepared which was consistent with that reported in our former study (Jia et al. 2011).

All theoretical calculations were carried out using the Gaussian 09 program. The C1...C1' and C_(aromatic)–Br

distances and the ether linkage angle of BDE-209 and the C1...Cl' and C_(aromatic)-Cl distances of CB-209 were calculated by DFT method at the B3LYP, 6-311++G (d, p) theory level.

Degradation of BDE-209

The catalytic activity of the test material was determined by performing tests in sealed glass ampoules. A BDE-209 solution in an approximately 95:5 v/v mixture of dichloromethane and hexane was prepared, and a 0.5-mL aliquot of the solution (521 nmol BDE-209) was added to each ampoule and then allowed to evaporate to dryness at the ambient temperature. A 50-mg aliquot of the Fe₃O₄ micro/nano-material was then added to each ampoule, and sealed in atmosphere and heated to 300 °C for an appropriate time. After the heating reaction, the sealed ampoules were cooled down to room temperature, and were crushed and extracted for the products analysis. All experiments were performed in triplicate to ensure the repeatability of the results.

Analysis of the degradation products

The unreacted BDE-209 and newly formed PBDEs in the treated samples were determined using an Agilent 6890N GC instrument equipped with a DB-5 MS capillary column (15 m×250 μm i.d., 0.25 μm film thickness) and an Agilent 5973 mass selective detector (MSD). The mass spectrometry instrument used a negative chemical ionization source in selected ion monitoring mode (MS-NCI). The high-purity helium carrier gas was used at a flow rate of 1.5 mL/min. The ion source temperature was set at 150 °C. A 1-μL aliquot of a sample was injected into the GC instrument inlet, which was used in splitless mode at 265 °C. The oven temperature program started at 80 °C, which was held for 1 min, increased at 10 °C/min to 220 °C, then increased at 20 °C/min to 300 °C, which was held for 15 min. The ions that were monitored were *m/z* 79 and 81 (for all of the PBDE congeners except for BDE-209) and *m/z* 486.7 and 488.7 (for BDE-209).

Results and discussion

Kinetics study

The time dependence of the degradation of 521 nmol of BDE-209 over the as-prepared Fe₃O₄ micro/nano-material at 300 °C was investigated. The black squares in Fig. 1 represent the changes in the residual BDE-209 amount dependent on the heating time at 300 °C via a quasi-exponential-type decay. The amount of BDE-209 rapidly decreased from 521.3 to 139.7 nmol in 5 min with the degradation efficiency (DgE) of 73 %, and then further decreased to 0.6 nmol in 100 min

with DgE at almost 100 %. However, the estimated photodegradation efficiency of BDE-209 in a sodium pyruvate solution reached only around 75 % after 3 h (Jiang et al. 2014). This illustrates that the Fe₃O₄ micro/nano-material had a high reactive activity for the degradation of BDE-209.

The initial rate at which BDE-209 degraded could be described using a pseudo-first-order kinetics law with respect to the BDE-209 content, as is shown in Eq. 1,

$$\ln \left[(R_{\text{BDE-209}}) / (I_{\text{BDE-209}}) \right] = -k_{\text{obs}} t \quad (1)$$

where *I*_{BDE-209} is the initial mole amount of BDE-209, *R*_{BDE-209} is the mole amount of the BDE-209 remaining after heat had been applied for a given period, and *k*_{obs} is the initial pseudo-first-order rate constant (min⁻¹), calculated from the experimental data.

Plotting ln[(*R*_{BDE-209})/(*I*_{BDE-209})] against time gave a line with a good correlation coefficient (*R*²=0.93) and a slope indicating that the pseudo-first-order rate constant was 0.15 min⁻¹ (see the inset in Fig. 1). The debromination of BDE-209 in the presence of zerovalent iron microparticles (Zhuang et al. 2010) and resin-bound iron nanoparticles (Li et al. 2007) also followed pseudo-first-order kinetics, with rate constants of 9.79×10⁻⁵ min⁻¹ (0.14 day⁻¹) and 4.7×10⁻³ min⁻¹ (0.28 h⁻¹), respectively. However, both of them are smaller than that of BDE-209 degradation over as-prepared Fe₃O₄ micro/nano-material. These comparisons further suggested that catalytic degradation, especially over Fe₃O₄ micro/nano-materials, could be a very promising way for the disposal of PBDEs. Furthermore, the pseudo-first-order rate constant for BDE-209 degradation was slightly higher than that for CB-209 degradation (0.14 min⁻¹, *R*²=0.97) over the same type of Fe₃O₄ (Su et al. 2014). The degradation behaviors of different halogenated compounds might vary in ways that are strongly dependent on the halogen substituents and chemical properties of the compounds. The PBDEs have comparatively labile C-Br bonds, which are weaker than the C-Cl bonds in PCBs. Cleavage of such Br-C bonds is expected to be an easier route for energy decay than corresponding cleavage in their chlorinated analogues (Hu et al. 2005a).

Analysis of the degradation products

The nona- to di-BDEs formed sequentially as the BDE-209 degraded, as illustrated in Fig. 2. The amount of BDE-209 present rapidly decreased and all three nona-BDEs appeared within the first 5 min of the tests. There are 12 possible octa-BDEs, but only five major octa-BDE peaks were observed and confirmed using octa-BDE standards after the tests had been performed for 20 min. Small amounts of hepta-BDEs were found after 40 min. More than 90 % of the BDE-209 had been decomposed after 60 min, and hexa-BDEs, penta-BDEs, and tetra-BDEs were observed after that time. The

Fig. 1 Residual BDE-209 content as a function of reaction time. *Inset* shows the pseudo-first-order kinetic plot of the reaction

amounts of tetra- to hepta-BDEs gradually increased and tri-BDEs appeared after 80 min. BDE-209 almost disappeared after 100 min, and the tetra-BDEs, penta-BDEs, and hexa-

Fig. 2 GC-MS chromatograms obtained at different reaction time (5–100 min) from the degradation of BDE-209 over Fe_3O_4 micro/nano-material

BDEs became the dominant products. The amounts of highly brominated PBDE homologs present gradually decreased and the amounts of the lower brominated homologs gradually increased as the reaction time increased. This demonstrates that the degradation process involved successive reductive hydrodebromination reactions. It has been reported that successive reductive hydrodebromination reactions occur during the degradation of BDE-209 in hexane exposed to sunlight (Wei et al. 2013) and the nZVI-mediated reductive debromination of BDE-209 (Kim et al. 2012). Similar successive reductive hydrodehalogenation reactions have also been observed in the degradation of CB-209 (Huang et al. 2013), hexachlorobenzene (Jia et al. 2011), and octachloronaphthalene (Su et al. 2014) in the presence of as-prepared Fe_3O_4 micro/nano-materials.

Identification of reaction products is extremely challenging, mainly owing to the lack of PBDE standards at the time of experiments. We identified 57 kinds of PBDE chemical standards from mono- to deca-BDEs based on retention time (RT) and GC elution order. However, there were some peaks in the degraded samples with their retention times that did not match any of the 57 chemical standards available. A third-order polynomial regression equation was obtained by plotting the observed GC relative retention time (RRT) against reference RRT determined experimentally using a DB-5 stationary phase which are available in a database (Korytár et al. 2005). The equation (shown in Fig. 3) allowed us to increase the number of possibly identifiable tri- to octa-BDE congeners. We also referred to previously developed quantitative structure–retention relationships (Rayne and Ikonomou 2003; Wang et al. 2006) to help identify PBDE congeners.

Fig. 3 Regression of the experimental relative retention time (RRT) obtained in this work against the reference RRT reported in Korytár et al. (2005) for DB-5 column. Only tri-through octa-BDEs are included. RRT is defined as the retention time normalized by the sum of retention times of BDE-47 and BDE-183

Three nona-BDE peaks were confidently identified as BDEs-208, -207, and -206 according to the RT of the nona-BDE standards. Five octa-BDE peaks were found, and they were identified as BDEs-196, -203, -197, -204, and -201, again from the available standards. It has been reported that more than five major octa-BDE congeners are rarely detected by GC after BDE-209 has been degraded, regardless of which medium the reaction has been performed in (Li et al. 2007). Indeed, the same conclusion could be drawn in the present study. Four hepta-BDEs peaks were observed in this work, identified as BDEs-184, -183, -181, and 190, respectively, according to their well-established GC elution order by chemical standards.

At least five hexa-BDE congeners were formed, and, of them, BDEs-154, -139, and -140 were identified from the retention times of the available standards. A major peak that eluted after BDE-154 was predicted to be possibly BDE-144 on the basis of third-order polynomial regression equation. A peak with a slightly lower RT than BDE-184 was identified as probably being BDE-128 from the reported retention times (EPA 2007) and the application of third-order polynomial regression equation. Three penta-BDE peaks, BDEs-85, -99, and -100, were accurately identified using the available chemical standards. Another major penta-BDE peak eluted before BDE-100 was the closest match to BDE-103 when third-order polynomial regression equation was used. Of the tetra-BDEs that were found, BDE-75 was identified using the available chemical standards. The next peak after BDE-75 was predicted to be BDE-42 from third-order polynomial regression equation. However, the peak that eluted before BDE-75 could not be identified using the equation. For the tri-BDE, BDE-30 was identified using the available chemical standards, but the next eluting peak could not be identified using the third-order polynomial regression equation. Homoplastically, BDEs-10 and -7, assigned to be di-BDEs, were also identified using available chemical standards. We considerably concentrated the samples from the degradation experiments at 60 min so that more reaction intermediates could be identified. The

chromatogram of the reaction products is shown in Fig. 4, and a list of the identifiable peaks is given in Table 1. Three more peaks were observed in the concentrated samples, and their retention times matched BDEs-171, -180, and -138/166. In total, 30 PBDE congeners produced in the degradation process were identified, 26 of which were identified using the available chemical standards and 4 of which were predicted using the third-order polynomial regression. In contrast, only 14 of newly produced PBDE congeners were identified when BDE-209 was photocatalytically debrominated by TiO_2 (Sun et al. 2009). Only 12 of newly produced PBDE congeners were identified when BDE-209 was debrominated by resin-bound iron nanoparticles (Li et al. 2007).

Although PBDEs also possess dioxin-like potency, their relative potencies (REPs) were several orders of magnitude lower than that of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD) (Venkatesan and Halden 2014). Moreover, the reactivities of metal oxides during the degradation of halogenated aromatic compounds usually increase with increasing reaction temperature and time. It is believed that the application of higher temperatures and longer reaction times can result in further transformation of the generated PBDE into non-toxic micromolecular inorganic products (Ma et al. 2007).

Proposed degradation mechanism

Relative distribution of the reaction products is crucial to identifying the mechanisms involved in the degradation of BDE-209. As is shown in Fig. 5a, the BDE-207 content was markedly higher than those of the BDEs-208 and -206. BDE-207 contributed approximately 50 % of the total amount of the three nona-BDE congeners produced when the maximum yield reached. This demonstrated that the bromine at the *meta*-positions were more prone to be removed, compared to the *para*- and *ortho*-positions. A similar conclusion was drawn for the degradation of CB-209 mediated by the same Fe_3O_4 material in the former study (Huang et al. 2013), with more CB-207 than CBs-208 and -206 being produced. Zhuang et al.

Fig. 4 GC-MS chromatogram of concentrated sample at 60 min from the degradation of BDE-209 over Fe₃O₄ micro/nano-material. Inset shows the magnified chromatogram for retention time from 10 to 15 min

(2010) also found that the *meta*-position is more vulnerable than the *ortho*- and *para*-positions to be attacked. Steric effects at the *ortho*-positions might make it difficult for halogen atoms at the *ortho*-positions to be removed during the formation of nona-halogenated compounds from deca-halogenated compounds. The enthalpy (ΔH_f^0) and Gibbs free energy (ΔG_f^0) are lower for CB-207 than for the other nonachlorobiphenyls (Zhai et al. 2005), suggesting that these thermodynamic parameters also contribute to the preferential formation of CB-207. However, higher ΔH_f^0 and ΔG_f^0 values have been reported by Grabda et al. (2007) for BDE-207 than for BDEs-208 and -206. Therefore, the initial hydrodebromination step in the degradation of BDE-209 might be dominated by steric effects.

As observed in Fig. 5b, BDE-197 with fully *ortho*-position bromine substituents contributed approximately 44 % of the total octa-BDE content when the maximum yield was reached. The ΔH_f^0 and ΔG_f^0 values have been found to be lower for BDE-197 than for the other octa-BDEs except for BDE-203 (Grabda et al. 2007). The slightly higher ΔH_f^0 and ΔG_f^0 values for BDE-197 than for BDE-203 indicate that steric effects at the *ortho*-positions also affect the formation of the preferred octa-BDE isomers. The maximum content of CB-197 was also found when CB-209 degraded over the as-prepared Fe₃O₄ micro/nano-material (Huang et al. 2013).

As can be seen from Fig. 5c, BDE-183 contributed approximately 45 % of the total hepta-BDE content when the maximum yield was reached. This indicates that the hydrodebromination at the *ortho*-position favorably occurred in the process to generate major hepta-BDEs

isomers. The ΔH_f^0 and ΔG_f^0 values were calculated to be lower for BDE-183 than for the other detected hepta-BDEs (Grabda et al. 2007). It has been reported that BDE-183 was also a relatively abundant isomer product, when BDE-209 in a mixture of tetrahydrofuran and water (Fang et al. 2011) or spiked soil (Xie et al. 2014) degraded in the presence of Ni and Fe bimetallic nanoparticles. In contrast, the major heptachlorobiphenyl product retained all the chlorine atoms at the *ortho*-positions when CB-209 degraded over the as-prepared Fe₃O₄ micro/nano-material (Huang et al. 2013).

The ΔH_f^0 and ΔG_f^0 values are lower for BDE-144 (Grabda et al. 2007) than for the other hexa-BDEs that were produced when BDE-209 degraded. As observed in Fig. 5d, the thermodynamically stable BDE-144 contributed approximately 60.5 % of the total hexa-BDE content after the reaction had been performed for 80 min. None of the detected hexa-BDEs products retained all of the bromine atoms at the *ortho*-positions. In contrast, the major hexachlorobiphenyl products continuously retained all of the chlorine atoms at the *ortho*-positions when CB-209 degraded over the as-prepared Fe₃O₄ micro/nano-material (Huang et al. 2013).

As can be seen from Fig. 5e, BDE-103 with the removal of one bromine atom at *ortho*-position contributed approximately 75.4 % of the total penta-BDE content when the maximum yield was reached. BDE-103 has been found to have lower ΔH_f^0 and ΔG_f^0 values (Grabda et al. 2007) than the other penta-BDEs that were detected. Figure 5f shows that an unidentified compound and BDE-42 with two bromine atoms at *ortho*-position contributed approximately 64.4 and 24.6 %, respectively, of the total

Table 1 The products from the reaction of BDE-209 with Fe₃O₄ micro/nano-material (PBDEs of retention time with “*” are the predicted products)

Peak number	Retention time (min)	Compound name
1	11.245	BDE-10
2	11.890	BDE-7
3	13.539	BDE-30
4	13.902*	BDE-Unknown*
5	15.721*	BDE-Unknown*
6	16.338	BDE-75
7	17.648*	BDE-42*
8	18.147*	BDE-103*
9	18.271	BDE-100
10	18.773	BDE-99
11	19.518	BDE-85
12	19.865	BDE-154
13	20.286*	BDE-144*
14	20.970	BDE-139
15	21.060	BDE-140
16	21.344	BDE-138/166
17	21.870*	BDE-128*
18	21.929	BDE-184
19	22.127	BDE-183
20	22.449	BDE-180
21	22.868	BDE-171
22	22.986	BDE-181
23	23.180	BDE-190
24	23.790	BDE-201
25	23.894	BDE-204
26	24.098	BDE-197
27	24.496	BDE-203
28	24.656	BDE-196
29	27.486	BDE-208
30	27.885	BDE-207
31	28.955	BDE-206
32	35.163	BDE-209

tetra-BDE content when the tetra-BDE yield reached a maximum. However, the dominant pentachlorobiphenyl and tetrachlorobiphenyl (tetra-CB) produced when CB-209 degraded were CB-104 and CB-54, respectively, still having chlorine atoms at all *ortho*-positions (Huang et al. 2013).

As shown in Fig. 5g and h, the amounts of all the tri-BDEs and di-BDEs that were found continued to rise throughout the experimental period. One unidentified tri-BDE isomer product and BDE-30 with two bromine atoms at *ortho*-position contributed 87.3 and 12.7 %, respectively, of the total tri-BDE content when BDE-209 had been heated for 120 min. BDE-7 only with one bromine atom at *ortho*-position

contributed 80.3 % of the total di-BDE content after 120 min. BDE-7 has been found to have lower ΔH_f^0 and ΔG_f^0 values (Grabda et al. 2007) than the other BDE-10 that were detected. In comparison, the main trichlorobiphenyl (tri-CB) product of the CB-209 degradation was CB-19, which retained chlorine atoms at three of the *ortho*-positions (Huang et al. 2013) (one Cl atom obviously had to be removed). CB-4, detected as the dichlorobiphenyl (di-CB) product, distributes the total two chlorine atoms at *ortho*-positions.

Identifying the intermediate products allowed us to deduce the main hydrodebromination pathways involved in the degradation of BDE-209. BDE-209 produced a range of products, from nona- to di-BDEs, through the successive elimination of bromine atoms. The major hydrodebromination pathways, shown in Scheme 1a, were proposed by determining the major intermediates at each stage of the degradation process. From the relative amounts of the different PBDE congeners, we were able to predict that the major degradation pathway which likely involved BDE-209→BDE-207→BDE-197→BDE-183→BDE-144*, BDE-154→BDE-103*→→→BDE-7. For penta-, hexa-, and hepta-homologs as the products, there were few PBDE congeners with one fully brominated phenyl ring (only minor BDEs-190, -181 and possible BDE-166). This may attribute to that the effect of intramolecular Br–Br repulsion on one phenyl ring is much larger than the repulsion between the two rings, causing the least stability of those fully brominated PBDEs among isomers (Zeng et al. 2005). The hydrodebromination pathway that was identified led us to conclude that the processes involved in the formation of the major nona-BDE products were mainly governed by steric effects. The influence of steric effects gradually decreased when the octa-BDE and less brominated products were formed. The processes involved in the formation of the major hepta- to di-BDE degradation products were more dominated by thermodynamics.

The degradation of BDE-209 in contact with the Fe₃O₄ micro/nano-material initially followed a similar pattern to that of CB-209 in which the halogens at the *ortho*-positions than *meta*- and *para*-positions were more resistant to elimination. However, the preferred debromination pattern for the less brominated PBDEs from the hepta- to di-BDEs was different from the preferred dechlorination pattern for the less chlorinated PCBs. Basically, the major hepta- to di-BDE congeners that were subsequently generated lacked one bromine atom or more at the *ortho*-positions. In contrast, the major PCB congeners up to tetra-CBs contained chlorine atoms at all of the *ortho*-positions, until chlorine atoms at these positions have to be gradually removed to allow the formation of correspondingly major tri- and di-CB congeners. The theoretical structure–activity relationships

Fig. 5 Distribution of the hydrodebromination products **a** nona-BDEs, **b** octa-BDEs, **c** hepta-BDEs, **d** hexa-BDEs, **e** penta-BDEs, **f** tetra-BDEs, **g** tri-BDEs, and **h** di-BDEs following the degradation of BDE-209 over as-prepared Fe_3O_4 at 300 °C as a function of heating time

may strongly affect the degradation pathways of PBDEs and PCBs.

Three-dimensional structures in PBDEs are caused by the ether linkage and the location and number of bromine atoms (Hardy 2002). The PBDE ether linkage generally allows the positions of the phenyl rings with regard to each other to be relatively flexible. The conformation of a PBDE can be described using two torsion angles, ϕ_1 ($\text{C1}'\text{--O--C1--C2}(6)$) and ϕ_2 ($\text{C2}'(6')\text{--C1}'\text{--O--C1}$), between the $\text{C1--O--C1}'$ plane, and the planes of phenyl ring and the angle of the ether bond $\text{C1--O--C1}'$ (Luthe et al. 2008). Theoretically, four diphenyl ether conformations are possible, planar ($\phi_1=\phi_2=0^\circ$), butterflyed ($\phi_1=\phi_2=90^\circ$), skewed ($\phi_1=0^\circ$, $\phi_2=90^\circ$), and twisted ($\phi_1, \phi_2>0^\circ$) (Klosener et al. 2008). PBDEs prefer to be in the skewed or twisted conformations (Klosener et al. 2008). The bromine substituents in the *ortho*-positions will force the aromatic rings to be orthogonal to each other (Hardy 2002), resulting in PBDEs that do not have conformations approaching coplanarity. As can be seen in Scheme 1b, the calculated ether linkage angle in BDE-209 was 127.5° , which resulted in the $\text{C1}\dots\text{C1}'$ distance being $2.46\text{ \AA}$, as comparable to that of the literature reported $2.39\text{ \AA}$ (Klosener et al. 2008). The average $\text{C}_{(\text{aromatic})}\text{--Br}$ distance is $1.900\text{ \AA}$, which is approximately equal to the reported $1.899\text{ \AA}$ (Luthe et al. 2008). There are important differences in the structures of PCBs compared with PBDEs owing to the lack of an ether linkage. The conformation of a PCB can be described using the dihedral angle between the benzene rings, which seems to be the most important determinant of the structure (Luthe et al. 2007). This angle depends on the PCB's substitution pattern, particularly at the *ortho*-positions. The dihedral angles of PCBs have been determined to be $35\text{--}45^\circ$ for non-*ortho*-chlorine substitution, $47\text{--}51^\circ$ for mono-*ortho*-chlorine substitution, $58\text{--}68^\circ$ for di-*ortho*-chlorine substitution, and $86\text{--}87^\circ$ for tetra-*ortho*-chlorine substitution (Luthe et al. 2007). The stability of a PCB congener will increase as the angle increases, so the generation of multiple-*ortho*-chlorine-substituted congeners is preferred. As shown in Scheme 1c, the $\text{C1}\dots\text{C1}'$ and $\text{C}_{(\text{aromatic})}\text{--Cl}$ distances for CB-209 have been calculated to be 1.495 and $1.741\text{ \AA}$, respectively, as comparable to that of the reported 1.48 and $1.747\text{ \AA}$ (Luthe et al. 2007, 2008).

All PBDE congeners have relatively flexible conformations except for those with bromine atoms at all four *ortho*-positions, which have a degree of somewhat conformational rigidity caused by steric effects (Hu et al.

2005b). In contrast, the presence of one or more chlorine atoms at *ortho*-positions will significantly affect the conformation of a PCB molecule, resulting in non-coplanar phenyl rings and restricting the free spinning of the biphenyl-bridge bond (Yak et al. 2000). These conformational and steric effects explain why the major hydrodehalogenation pathways for the degradation of BDE-209 and CB-209 over Fe_3O_4 micro/nano-material were similar at the initial steps, with the formation of the major nona- and octa-substituted isomers. The $\text{C1}\dots\text{C1}'$ distance is $0.965\text{ \AA}$ longer in BDE-209 than in CB-209, and the $\text{C}_{(\text{aromatic})}\text{--Br}$ distance is $0.159\text{ \AA}$ larger than the $\text{C}_{(\text{aromatic})}\text{--Cl}$ distance. This means that steric interactions between *ortho*-substituents are weaker in BDE-209 than CB-209. The ether bond and the $\text{C1--O--C1}'$ angle both contribute to the flexibility of substituted diphenyl ethers, helping to minimize steric interactions between the phenyl rings (Klosener et al. 2008). The conformation of CB-209 forces the electron cloud of the *ortho*-chlorine on one phenyl ring to be above the other phenyl ring, which is likely to hinder the ability of the molecule to be reduced (Yak et al. 2000). Therefore, the bromine atoms at the *ortho*-positions of BDE-209 are relatively vulnerable to being removed compared with the chlorine atoms at the *ortho*-positions of CB-209. This is the reason that debromination in the BDE-209 occurred relatively early at one *ortho*-position than the dechlorination in CB-209.

Conclusions

Successive hydrodebromination reactions occurred when BDE-209 degraded over the Fe_3O_4 micro/nano-material at 300 °C. The hydrodebromination products were comprehensively determined by GC-MS using 57 kinds of chemical standards and third-order polynomial regression equation. The major reaction pathway was $\text{BDE-209} \rightarrow \text{BDE-207} \rightarrow \text{BDE-197} \rightarrow \text{BDE-183} \rightarrow \text{BDE-144}^* \rightarrow \text{BDE-154} \rightarrow \text{BDE-103}^* \rightarrow \dots \rightarrow \text{BDE-7}$. The initial steps in the reaction pathway appeared to be dominated by steric effects, whereas thermodynamics were dominant in later steps as more bromine atoms had been removed. The initial degradation of BDE-209 retained the full tetra-bromine substituents at the *ortho*-position with the formation of the major nona- and octa-brominated products, as comparable to that of CB-209. However, the preferred debromination pattern for the less brominated PBDEs from the hepta- to di-BDEs was different from the preferred dechlorination pattern for the less chlorinated PCBs. Basically, the major hepta- to di-BDE congeners subsequently generated lacked one bromine atom or more at the *ortho*-positions. In contrast, the major PCB congeners up to tetra-CBs contained chlorine atoms at all of the

Scheme 1 **a** Hydrodehalogenation pathways proposed for the degradation of BDE-209 over Fe_3O_4 micro/nano-material; **b** ball-and-stick model of BDE-209; **c** ball-and-stick model of CB-209

ortho-positions, until chlorine atoms at these positions have to be gradually removed to allow the formation of correspondingly major tri- and di-CB congeners. The

difference might be attributed to the flexibility of the linkage bond between two benzene rings and halogen substituents.

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