



Effects of metals on the transformation of hexabromocyclododecane (HBCD) in solvents: Implications for solvent-based recycling of brominated flame retardants

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ABSTRACT

The management of electronic wastes (e-wastes) has become a global issue as it may release large quantities of hazardous materials such as heavy metals and brominated flame retardants (BFRs) to the environment. Solvent-based recycling is a newly developed, efficient and environmentally beneficial technology for the removal or recovery of BFRs from e-wastes. However, little is known about the behavior of BFRs in the solvents and to what extent they may be affected by co-existing heavy metals. This study quantified the rates of transformation of hexabromocyclododecane (HBCD), a widely used BFR, in the presence of different solvents (i.e. acetone, methanol or toluene) and metals (i.e. Ni, Cu, Zn, Fe or Al). Our experimental results showed that less than 20% of HBCD was transformed in all pure solvent systems within 24 h at 50 °C. The presence of Ni greatly increased the transformation of HBCD (45–99%) in these solvent systems, whereas other metals had little or no effect on extraction process. The kinetics study showed that transformation of HBCD in Ni-containing systems followed pseudo-first-order kinetics and that the highest transformation rate constant ($1.2 \pm 0.1 \text{ h}^{-1}$) of HBCD was recorded in the Ni + acetone system. The formation of HBr and pentabromocyclododecene in the acetone + Ni system suggested that transformation of HBCD proceeded via dehydrobromination. Collectively, these results indicated that acetone should not be applied in the recycling or extraction of HBCD from Ni-rich e-wastes, as debromination of HBCD may occur during these processes, even at mild extraction temperatures.

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1. Introduction

Due to advances in technology and decreasing costs, an increasing number of electronic products rapidly reach obsolescence, resulting in a fast-growing surplus of waste electrical and electronic equipment (WEEE) around the world. Electronic waste (e-waste) has become the fastest growing section of the world's municipal solid waste. It is estimated that approximately 20–50 Mt of e-wastes are generated worldwide every year (Herat, 2008). Furthermore, the volume of e-wastes is expected to increase by 3–5% per year in developed countries and will triple in developing countries by 2010 (Basel Conference Addresses Electronic Wastes Challenge, 2006). The continuously growing amount of WEEE has raised worldwide concern regarding the fate and management of e-wastes as this waste may release large quantities of hazardous materials such as heavy metals and brominated flame

retardants (BFRs) which can have serious adverse environmental impacts (Morf et al., 2005; Gullett et al., 2007).

The majority of e-wastes are either dumped in landfills or combusted without recovery of energy and material, whereas a small portion undergoes recycling (Zhang et al., 2000). To date, disposal in landfills or incinerators is not a recommended management option for e-wastes in many countries largely because it causes secondary environmental pollution for toxic substances to leach to groundwater from landfills or formation of toxic by-products during combustion (Soderstrom and Marklund, 2002; Weber and Kuch, 2003; Spalvins et al., 2008). Unlike landfills and incineration, recycling of e-wastes can minimize landfill space and reduce energy consumption as well as conserve and protect valuable resources such as base and precious metals (Veit et al., 2005; Nnorom and Osibanjo, 2008). Therefore, recycling is currently considered the preferred option. The WEEE Directive aims to protect the environment through promoting the reuse, recycling and recovery of electronic trash and was established in the EU.

Despite its advantages, recycling may still result in serious environmental pollution if the hazardous materials in e-wastes (such as BFRs) are not disposed of properly (Ni and Zeng, 2009). BFRs

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are widely used in electronic products to reduce flammability. Some BFRs have been assigned as having persistent, bioaccumulative and toxic properties. The mechanical recycling of BFRs-containing e-wastes for recovery of metals can result in the release of BFRs and polybrominated dioxins and furans (PBDDs/Fs) when exposed to hot shredding and crushing (Morf et al., 2005; Schlummer et al., 2007). Thermal processing, such as smelting and energy recovery of e-waste, not only contributes to emissions of PBDDs/Fs but also causes additional equipment corrosion due to the formation of HBr (Ebert and Bahadir, 2003; Tange and Drohmann, 2005). Therefore, BFRs have to be removed or recovered from e-wastes so that the valuable metals can be easily and safely processed and recycled.

Solvent-based recycling technology was identified as the most commercially viable and environmentally beneficial treatment option for the removal or recovery of BFRs (Schlummer et al., 2007; Nnorom and Osibanjo, 2008). The Fraunhofer IVV and the United Kingdom's Waste & Resources Action Programme have developed a solvent-based recycling process (Creasolv) that can successfully and effectively remove BFRs from WEEE polymers using safe solvent formulation and produce recycled polymers (Freegard et al., 2006; Schlummer et al., 2006). Altwaiq et al. (2003) investigated the extraction efficiencies of BFRs from polymers using supercritical fluid CO₂. It was found that the extraction efficiency of BFRs varied according to the applied extraction solvents and procedures. High extraction efficiencies of BFRs could be achieved by using supercritical fluid CO₂ in the presence of toluene, acetonitrile and tetrahydrofuran as a modifier or by using 1-propanol as a solvent during Soxhlet extraction (Altwaiq et al., 2003). These studies mainly focused on the separation of BFRs from pure plastics and polymers by solvent-based recycling technology. However, e-waste is a mixture of various materials which contains about 40% metals and 30% plastics. Little information is available concerning the effects of solvent-based recycling technology on the removal of BFRs from e-wastes. BFRs always co-exist with heavy metals, such as Ni, Cu, Zn, Fe and Al in electronic products. Whether these high-concentration metals influence the behavior of BFRs in extractive recycling processes is unclear. To understand the behavior of BFRs in solvents and to what extent they may be affected by co-existing heavy metals may be of fundamental importance in the correct choice of solvent for the separation BFRs from e-wastes, and in the prediction of toxic products that may be derived from the solvent-based recycling of e-wastes.

Hexabromocyclododecane (HBCD) is a commonly used BFR found in extruded and expanded polystyrene for thermal insulation in building, although it also is used in upholstery furniture, automobile interior textiles, and electric and electronic equipment (Covaci et al., 2006). In addition, the use of HBCD in these applications is increasing when other BFRs were banned or withdrawn such as penta- and octabrominated diphenyl ether mixtures. However, there is a lot of evidence to suggest that HBCD exhibits the typical properties of persistent organic pollutants such as persistence and bioaccumulation, and can cause a thyroid hormone effect and endocrine disrupting effect (Covaci et al., 2006; Saegusa et al., 2009; van der Ven et al., 2009). The European Chemicals Agency has included it in the Substances of Very High Concern list under the framework of the Registration, Evaluation, Authorisation and Restriction of Chemicals. Although the use of HBCD has not been restricted by the Restriction of Hazardous Substances (RoHS) directive, HBCD has been included in the list of substances added to a proposal to revise the RoHS directive. A global ban on HBCD is currently being considered. It will be required to remove or extract HBCD from e-wastes once it is listed in the RoHS directive in the future. However, prior study only focused on the extraction of other frequently used BFRs such as polybrominated diphenyl ethers and tetrabromobisphenol A (Altwaiq et al., 2003). Little

information was available on the extraction of HBCD using solvent-based recycling technology.

The present study aims to investigate the behavior of HBCD in different solvents (i.e. acetone, methanol and toluene) as well as the effects of metals (i.e. Ni, Cu, Zn, Fe and Al) on the transformation of HBCD and the formation of products in solvent systems. Acetone, methanol and toluene were chosen as model solvents as they are good for dissolution of BFRs and are widely used for the extraction and analysis of BFRs. The results may be valuable for environmental engineers in selecting solvents in the extractive recycling of HBCD-containing e-wastes.

2. Materials and methods

2.1. Chemicals

The technical HBCD mixture was purchased from Tokyo Chemical Industry (Tokyo, Japan). This mixture contained α (~20%), β (~10%), and γ (~70%) diastereomers of HBCD. Acetone and toluene were ACS certified grade from Honeywell Burdick & Jackson (Morristown, NJ, USA). Methanol and hexane were ACS certified grade from Merck (Whitehouse Station, NJ, USA). The Ni, Cu, Zn, Fe and Al powders (<100 mesh; 0.05 mm) were purchased from Tianjin Fuchen Chemical Reagents Factory (Tianjin, China). 4,4'-dibromo-octafluorobiphenyl (98.8%) was supplied by AccuStandard (New Haven, CT, USA). All chemicals were used as received without further purification.

2.2. Batch experiments

Four batch experiments were conducted in 10-mL amber ampoules under ambient O₂ conditions in the absence of direct sunlight. The first set of experiments investigated the transformation of HBCD in different solvents (i.e. acetone, methanol and toluene) at 50 °C. The second set examined the effect of metals (i.e. Ni, Cu, Zn, Fe and Al) on the transformation of HBCD in different solvents at 50 °C. The third set examined the effect of low temperature conditions on HBCD transformation in different solvents with Ni. The fourth set investigated the effect of different Ni dosages on the transformation of HBCD in acetone.

Before initiating the batch experiments, fresh solutions containing 7 μ M of HBCD were prepared by dissolving 4.5 mg HBCD in 1000 mL solvent (acetone, methanol or toluene). The reaction was initiated by adding 2 mL fresh solution containing HBCD into the ampoules in the first batch experiment. For the second batch experiment, 2 mL fresh solution and 1 g metal powder were simultaneously added into the ampoules. The use of this high metal-to-solvent (1:2; g mL⁻¹) ratio was due to the facts that some e-wastes such as printed circuit boards scrap contain high level of metals and that the volume of solvents used is relatively small in the solvent-based recycling process. After addition of solutions and metals, the ampoules were immediately sealed in a methane-oxygen flame and placed on a rotary shaker (365° rotation in the vertical direction) at 50 °C. Similar procedures were performed in the third batch experiment, except that the ampoules were placed on a rotary shaker at 30 or 10 °C. In the fourth batch experiment, 2 mL fresh HBCD solution (dissolved in acetone) and 0.01 g Ni were added into the ampoules which were placed on a rotary shaker at 50 °C.

The reaction times were recorded at the start of mixing. At a predetermined time, two ampoules were taken from the shaker for analysis of HBCD and products. Duplicate ampoules were centrifuged at 3000g for 5 min at 10 °C, and the ampoules were then broken. A 1-mL aliquot of suspension was transferred into a 2 mL vial for the analysis of HBCD and transformation products by gas

chromatography–electron capture detector (GC–ECD) and gas chromatography–mass spectrometry (GC–MS), respectively. In addition, to evaluate whether debromination of HBCD occurred in all the reaction systems, concentrations of the liberated bromide ion were determined. The solvent in duplicate ampoules was evaporated under a gentle N_2 flow until dryness, and then 2 mL of Milli Q water was added into the ampoules to extract the bromide ion. The concentration of bromide ion in the extracts was analyzed by ion chromatography (IC). To study the mechanisms of HBCD transformation in the presence of Ni, the surface element composition of Ni was analyzed by X-ray photoelectron spectroscopy (XPS). The reproducibility of the method (i.e. sampling, extraction and measurements) was evaluated by the relative standard deviations of the triplicate samples from all metal + solvent systems following reaction for 24 h. The relative standard deviations were less than 3%.

2.3. Chemical analysis

The HBCD diastereomers were analyzed using an Agilent 1100 high performance liquid chromatography system (Agilent Technologies, Palo Alto, CA, USA), equipped with a vacuum degasser, a quaternary pump and autosampler, and an Applied Biosystems–Sciex API 4000 triple quadrupole mass spectrometer (Applied Biosystems, Foster City, CA, USA) equipped with a TurbolonSpray ionization interface according to the method described by Yu et al. (2008).

Concentrations of HBCD were analyzed using a Shimadzu 2010 GC (Shimadzu, Kyoto, Japan), equipped with an Rtx-1 fused silica capillary column (30 m length; 0.25 mm id; 0.25 μ m film thickness) and ECD. The oven temperature program for HBCD analysis was from 70 °C (initial time, 1 min) to 260 °C holding for 8 min at a rate of 20 °C min^{-1} , from 260 to 300 °C holding for 10 min at a rate of 20 °C min^{-1} . The injector and ECD temperatures were

280 and 310 °C, respectively. Nitrogen was used as the carrier gas. Quantification of HBCD was performed by internal calibration. The peak area and the concentration of the internal standard (4,4'-dibromooctafluorobiphenyl) were also referred for HBCD quantification in addition to evaluating the stability of the instruments.

Identification of potential products of HBCD was attempted using a Shimadzu QP2010 plus GC–MS (Shimadzu, Kyoto, Japan). The Rxi-5 ms fused silica capillary column (30 m length; 0.25 mm id; 0.25 μ m film thickness) was used. The oven temperature program for the analysis of HBCD products was the same as that for HBCD analysis. Helium was used as the carrier gas at a flow rate of 1 mL min^{-1} . The inlet was in the splitless mode and was held isothermally at 280 °C. The ion source and MS interface temperature was maintained at 250 and 280 °C, respectively. The MS was operated in electron-impact ionization mode with electron energy of 70 eV, and the scan ranged from 45 to 700 amu.

The identification and quantification of bromide ions was performed by a Dionex ICS900 IC (Dionex, Sunnyvale, CA, USA), equipped with a RFIC IonPacAS19 analytical column (250 mm \times 4 mm id), a RFIC IonPacAG19 guard column (50 mm \times 4 mm id) and a conductivity detector. The mobile phase, containing 20 mM KOH was pumped at a flow rate of 1.0 mL min^{-1} . The injection volume was 200 μ L. Quantification of Br^- was performed by external calibration.

The surface characterization of Ni before and after reaction was analyzed by an ESCALAB 250 XPS (Thermo Fisher Scientific, MA, USA) equipped with a dual X-ray source (Mg/Al). We used an aluminum anode ($K\alpha$, 1486.6 eV). The pressure in the sample cell was about 2×10^{-7} Pa. The energy resolution of the spectrometer was 1.5 eV at pass energy of 20 eV. The Ni 2p and C 1s lines were systematically recorded. The C 1s line (284.8 eV) is traditionally used as a reference for correcting charge shift.

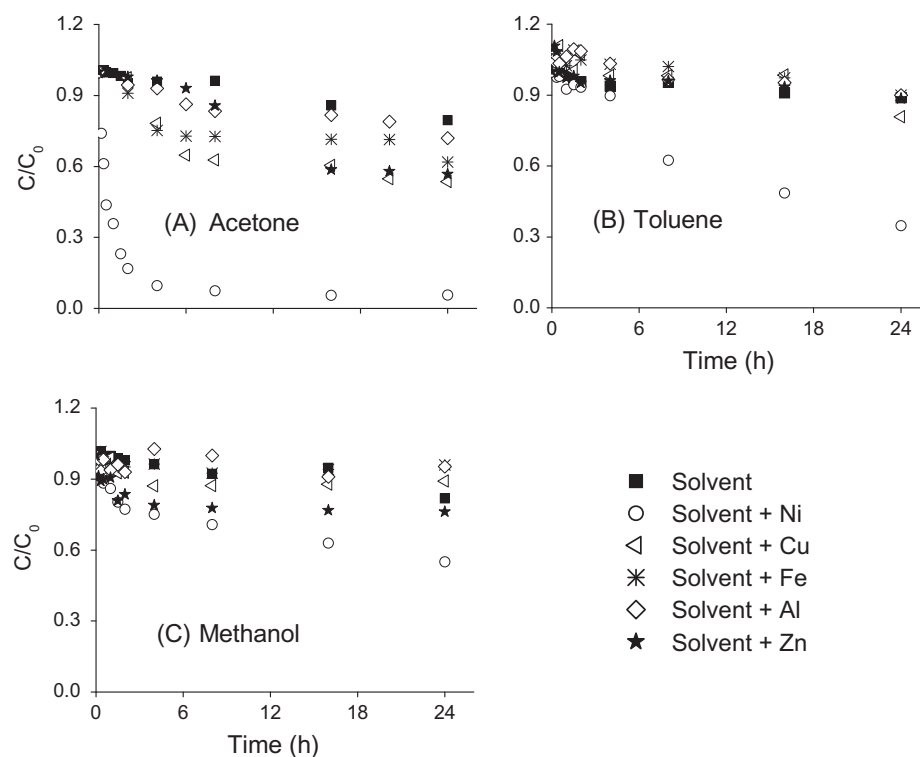


Fig. 1. Transformation of HBCD in different solvent and solvent + metal systems at 50 °C within 24 h. (A): acetone; (B): toluene; (C) methanol. C_0 is the initial concentration of HBCD (7 μ M) in the solvent; C is the concentration of HBCD in the solvent at a given time. Symbols represented the mean values of duplicate experimental data.

3. Results and discussion

3.1. Stability of HBCD in the presence of solvent

Fig. 1 shows that there is a 20%, 18% and 11% loss of HBCD in acetone, methanol and toluene, respectively, at 50 °C within 24 h. This suggested that HBCD was not stable in these solvents, particularly in acetone. Previous studies have reported loss of HBCD in other solvents. Tomy et al. (2005) observed that technical HBCD almost disappeared completely in acetonitrile solution within 4 d under ambient laboratory conditions; Hiebl and Vetter (2007) noted that the storage of HBCD standards in *n*-hexane and iso-octane resulted in loss of HBCD. All of these authors speculated that the loss of HBCD in solvent was attributed to glass absorbance due to low solubility of HBCD in these solvents. In the present study, however, the fact that transformation products of HBCD were detected and identified in solvent (see below) suggested that chemical transformation rather than absorbance was expected to play an important role in the loss of HBCD in solvents. As the instability of HBCD in solvent may lead to the formation of other toxic products, a solvent that can completely recover and extract HBCD from e-wastes in the solvent-based recycling process is preferred.

3.2. Transformation of HBCD in the presence of solvent and metal

It was noted that there was a 19–46%, 12–43%, 10–38%, and 5–28% loss of HBCD in the presence of Cu, Zn, Fe or Al, respectively, in all solvent systems at 50 °C within 24 h (Fig. 1). The addition of these metals seemed to slightly or negligibly increase the transformation of HBCD in the solvent. However, previous studies have reported that these metals could significantly promote the degradation of HBCD under thermal conditions (Larsen and Ecker, 1986; Barontini et al., 2003; Sakai et al., 2007). This discrepancy indicates that HBCD has more resistance to transformation during solvent-based recycling than during thermal processing in the presence of Cu, Zn, Fe or Al. In contrast to these metals, the addition of Ni significantly enhanced the disappearance of HBCD in all solvent systems (Fig. 1). More than 99% of HBCD was transformed in the acetone + Ni system. In the toluene + Ni and methanol + Ni systems, the concentration of HBCD decreased by approximately 65% and 45% of the initial concentration, respectively. Therefore, Ni mediated the transformation of HBCD to a larger extent than the other metals in the solvent. In addition, it is worth noting that the standard procedure for analysis of HBCD in e-waste also involves extraction of the matrix with organic solvent. As Ni is always present in e-waste, transformation of HBCD should be an important process during solvent extraction. As a result, HBCD may be significantly underestimated. Depending upon the

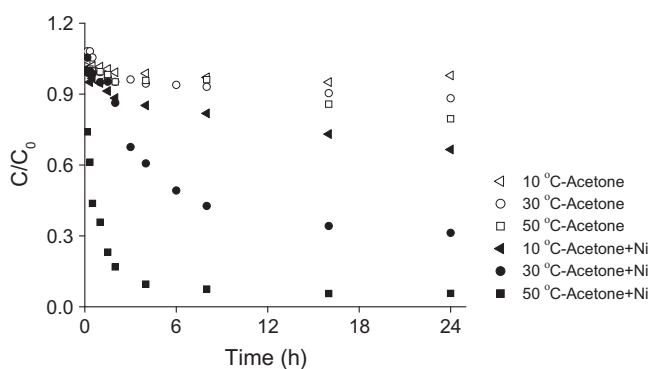


Fig. 2. Transformation of HBCD in acetone and acetone + Ni systems at different temperatures. The definition of C_0 and C are the same as in Fig. 1. Symbols represented the mean values of duplicate experimental data.

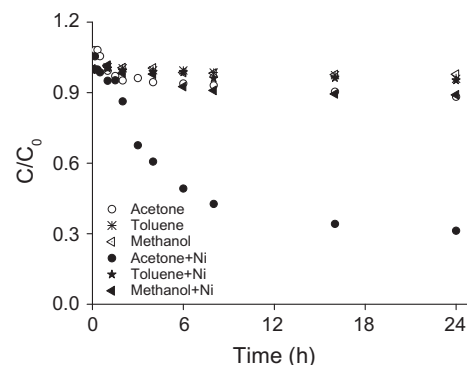


Fig. 3. Transformation of HBCD in solvent and solvent + Ni systems at 30 °C. The definition of C_0 and C are the same as in Fig. 1. Symbols represented the mean values of duplicate experimental data.

type of solvents, the reduction percentages of HBCD within 24 h in the presence of 5 g L^{-1} of Ni can be more than 40%.

Nevertheless, the transformation of HBCD in the solvent + Ni system was decreased with decreasing temperature (Figs. 2 and 3). In the toluene + Ni and methanol + Ni systems, the transformation of HBCD was less than 10% of the initial concentration at 30 °C within 24 h (Fig. 3), suggesting that HBCD was difficult to transform in toluene or methanol at room temperature even when Ni was present. This result was consistent with the observation reported by Tomy et al. (2005), where HBCD was found to be stable in methanol solutions at ambient environment. However, in the acetone + Ni system, more than 60% of HBCD was transformed at 30 °C (Fig. 2). Therefore, methanol or toluene is a better choice than acetone for the complete recovery of HBCD from Ni-rich e-waste during solvent-based recycling at room temperature.

3.3. Kinetics of HBCD transformation

A pseudo-first-order kinetic model was applied to quantitatively describe the transformation of HBCD. Table 1 summarizes the observed first-order rate constant (k_{obs}) and the half lives ($t_{1/2}$) of HBCD transformation in the solvent and solvent + Ni systems. The highest k_{obs} ($1.2 \pm 0.1 \text{ h}^{-1}$) of HBCD was recorded in the acetone + Ni system at 50 °C (Table 1). Moreover, the $t_{1/2}$ of HBCD decreased as the amount of Ni increased, and ranged from 5.0 h (5 mg L^{-1} of Ni) to 0.58 h (5 g L^{-1} of Ni).

It was observed that k_{obs} strongly depended on reaction temperature conditions in the acetone and acetone + Ni systems. The dependence of the reaction rate on temperature can be delineated

Table 1

Pseudo-first-order rate constants and half lives of HBCD transformation in the presence of solvent and Ni.

| Temperature (°C) | Solvent | Metal (5 g L^{-1}) | k_{obs} (h^{-1}) | $t_{1/2}$ (h) | R^2 |
|------------------|----------|--------------------------------|--------------------------------------|---------------|-------|
| 50 | Acetone | – ^b | 0.0093 ± 0.00079 | 75 | 0.95 |
| 50 | Acetone | Ni | 1.2 ± 0.14 | 0.58 | 0.93 |
| 50 | Acetone | Ni ^a | 0.14 ± 0.018 | 5.0 | 0.89 |
| 30 | Acetone | – | 0.0063 ± 0.0019 | 110 | 0.55 |
| 30 | Acetone | Ni | 0.11 ± 0.0090 | 6.3 | 0.94 |
| 10 | Acetone | – | 0.0023 ± 0.00077 | 301 | 0.51 |
| 10 | Acetone | Ni | 0.017 ± 0.0017 | 41 | 0.93 |
| 50 | Toluene | – | 0.0057 ± 0.0012 | 122 | 0.68 |
| 50 | Toluene | Ni | 0.046 ± 0.0020 | 15 | 0.98 |
| 50 | Methanol | – | 0.0071 ± 0.0011 | 98 | 0.84 |
| 50 | Methanol | Ni | 0.024 ± 0.0045 | 29 | 0.80 |

^a The concentration of Ni was 5 mg L^{-1} .

^b No addition of Ni.

by the Arrhenius equation. A linear regression of the transformation rate constant of HBCD against temperature [see [Supplementary Material \(SM\)](#), Fig. SM-1] yielded an E_a value of 32 ± 9 and 78 ± 11 kJ mol^{-1} for the transformation of HBCD in acetone and the acetone + Ni system, respectively. It is common sense that E_a was higher and k_{obs} was slower. However, k_{obs} for the transformation of HBCD in the acetone + Ni system was higher than that in the acetone system. This discrepancy may be explained by speculating that the reaction mechanism of HBCD in the acetone + Ni system is different from that in the acetone system. As the transformation of HBCD in acetone and the acetone + Ni system involved homogeneous and heterogeneous reaction systems, respectively, a difference in the reaction mechanism between the two systems would be expected.

3.4. HBCD debromination and reaction mechanism

Due to the rapid transformation of HBCD in the acetone + Ni system, the transformation mechanism of HBCD in this system

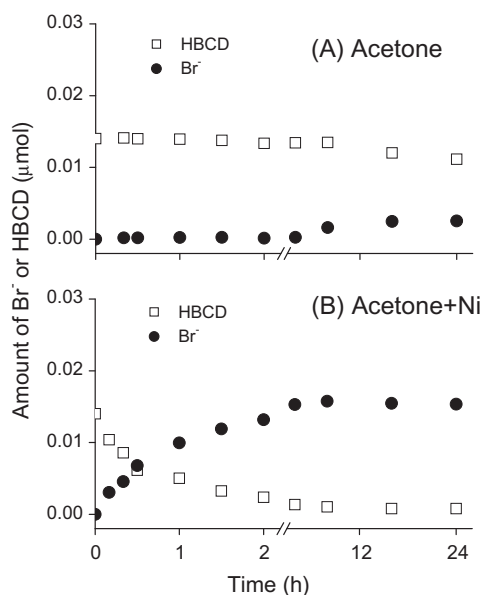


Fig. 4. Disappearance of HBCD and production of bromine ions in acetone (A) and acetone + Ni (B) systems within 24 h at 50 °C. Symbols represented the mean values of duplicate experimental data.

was studied in detail. The technical HBCD mixture consisted of three diastereoisomers (α -, β -, and γ -HBCD), in which γ -HBCD ($\sim 70\%$) was the predominant diastereomer. After a reaction period of 20 h in the acetone + Ni system at 50 °C, the concentration of γ -HBCD decreased rapidly and was much lower than that of α - and β -HBCD (Fig. SM-2). This suggests that γ -HBCD is more susceptible to transformation than α - and β -HBCD, and transformation of γ -HBCD may account for the decrease in technical HBCD. However, transformation of α - and β -HBCD also occurred since there was an almost complete loss of technical HBCD over 20 h ($\sim 99\%$). Davis et al. (2006) also reported simultaneous transformation of three HBCD diastereoisomers in wastewater sludge and freshwater aquatic sediment.

To evaluate the extent of debromination of HBCD, the concentration of bromide ions was determined. Fig. 4 shows that the production of bromide ions increased with increasing transformation of HBCD in acetone or the acetone + Ni system. It was found that the transformation of 0.0028 μmol of HBCD resulted in the release of 0.0026 μmol of bromide ions after 24 h of incubation in the acetone system. After the addition of Ni, the transformation of HBCD increased to 0.013 μmol , leading to the production of 0.015 μmol of bromide ions. According to the mass-balance analysis, approximately one bromine atom was eliminated per HBCD molecule and another five bromine atoms still remained in the debromination product structure in both the acetone and acetone + Ni systems.

Another debromination product of HBCD, with a GC retention time of 23.42 min, was detected in both the acetone and acetone + Ni systems (Fig. 5). This product had a mass spectrum similar to that of pentabromocyclododecene (PBCDe) reported by Hiebl and Vetter (2007), with high-mass fragment ions at m/z 401 $[\text{M}-\text{Br}-\text{HBr}]^+$, 319 $[\text{M}-\text{Br}-2\text{HBr}]^+$, 239 $[\text{M}-\text{Br}-3\text{HBr}]^+$, 159 $[\text{M}-\text{Br}-4\text{HBr}]^+$, and low-mass fragment ions at m/z 117, 105, 79, 67 and 54 which indicated an aliphatic backbone of PBCDe (Fig. 5). Moreover, the characteristics of the mass spectrum of this product were very similar to that of HBCD standards (data not shown), and was also observed for PBCDe described by Hiebl and Vetter (2007). Therefore, we tentatively identified this product as PBCDe due to lack of an authentic standard. PBCDe has been reported previously in biotic and abiotic compartments including indoor dust, chicken eggs, fish, sludge, and sediments (Davis et al., 2006; Hiebl and Vetter, 2007; Abdallah and Harrad, 2009). On the basis of the identification of products, HBCD may be debrominated *via* dehydrobromination (β -elimination) to form PBCDe and HBr in both the acetone and acetone + Ni systems. This debromination pathway is inconsistent with the results of Davis et al. (2006), who proposed that HBCD is sequentially debrominated *via*

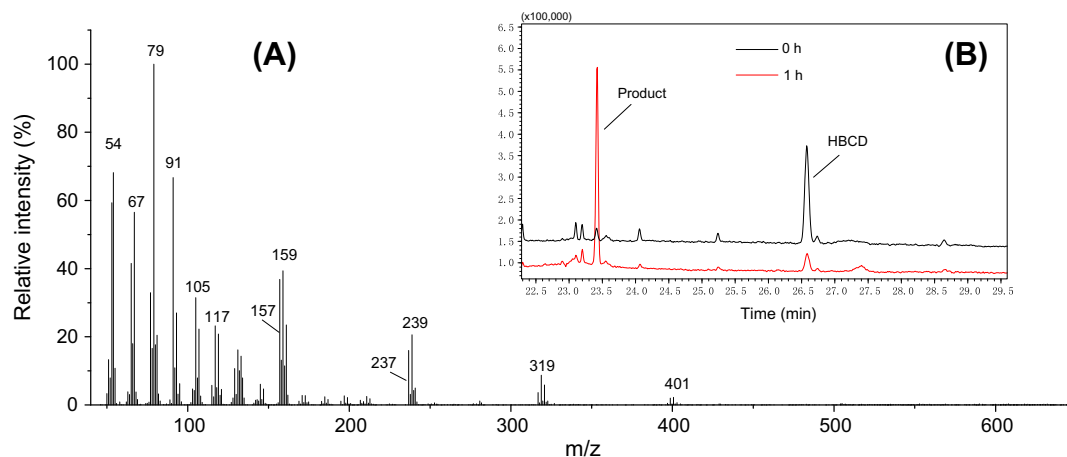


Fig. 5. Mass spectrum (A) and GC chromatograms (B) of the product of HBCD isolated in the acetone + Ni system following reaction for 1 h at 50 °C.

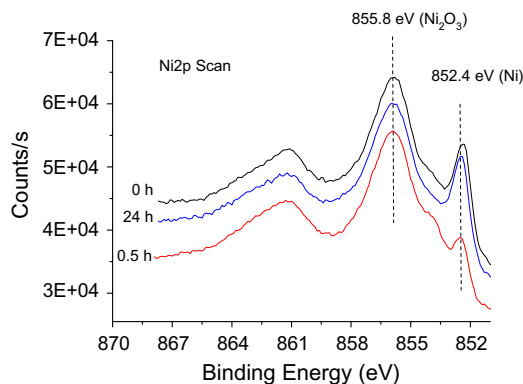


Fig. 6. Ni 2p regions of the XPS spectra of Ni during the transformation of HBCD in the acetone + Ni system at different reaction times.

dihaloelimination as a major pathway for the degradation of HBCD in the environment.

From an organic chemistry standpoint, there are two mechanisms involving in β -elimination of HBCD. One is unimolecular (E1) elimination, the other is bimolecular (E2) elimination. We can rule out the possibility of E1 elimination since acetone as an aprotic solvent does not favor the ionization of the leaving group. E2 elimination appears to be the more likely route in the dehydrobromination of HBCD in the acetone system. Acetone may act as a Lewis base pulling a hydrogen ion away from carbon and simultaneously the bromine separates, resulting in the formation of PBCDe and HBr. As the difference in the transformation mechanism of HBCD between the acetone and acetone + Ni systems has been mentioned above, HBCD was possibly transformed via E1 elimination in the acetone + Ni system. Tavoularis and Keane (1999) demonstrated the gas phase catalytic dehydrochlorination of halogenated aliphatic compounds using a silica-supported Ni catalyst. They proposed that the conversion of an alkyl halide to an alkene proceeded via the E1 elimination route. Additional work has been initiated to examine the role Ni plays in the dehydrobromination of HBCD.

Fig. 6 presents the XPS analysis of the Ni surface for different reaction times. The intensity of Ni decreased as the reaction progressed, indicating that Ni may interact with the reactants absorbed on the surface of Ni. After a reaction period of 24 h, the intensity of Ni was back to the level of the initial reaction time. This suggests that Ni may play a catalytic role in the dehydrobromination of HBCD. A number of studies have investigated the debromination of brominated compounds using Ni as a catalyst. For example, Menini et al. (2000) reported debromination of bromobenzene using a Ni/SiO₂ catalyst in the presence of hydrogen; Murthy et al. (2005) also demonstrated the catalytic debromination of bromobenzene, 1,3-dibromobenzene and 1,3-bromochlorobenzene over silica-supported Ni; Liu et al. (2006) reported the debromination of tetrabromobisphenol A in a dilute alkaline aqueous solution by Raney Ni–Al alloy. However, the debromination mechanism in these studies was hydrodebromination, different from the dehydrobromination of HBCD mentioned in our study.

In conclusion, HBCD is susceptible to dehydrobromination in the acetone/acetone + Ni system, resulting in the formation of HBr and PBCDe. The release of HBr not only influences the feedback recovery of bromine but also has the potential to cause equipment corrosion. In addition, the effects of PBCDe on human and environmental health are unclear. Therefore, caution should be used in the application of acetone in the solvent-based recycling of plastics. On the other hand, more attention should be paid to the extractive recycling of Ni-rich e-waste, as Ni has strong catalytic activity on

the dehydrobromination of HBCD in other solvent systems at elevated temperature.

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Appendix A. Supplementary material

Supplementary materials illustrating the correlation of pseudo-first-order rate constant of HBCD transformation with temperature (Fig. SM-1) and change in the concentration of three diastereoisomers of HBCD (Fig. SM-2) are provided. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.chemosphere.2010.06.061.

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