

A PRELIMINARY STUDY FOR COMBUSTION OF HEXABROMOCYCLODODECANE (HBCD) AND ITS BY-PRODUCTS

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Introduction

Hexabromocyclododecane (HBCD) is a group of additive brominated flame retardants (BFRs) that are widely used in expandable polystyrene (EPS), extruded polystyrene (XPS), high impact polystyrene (HIPS), and polymer dispersion for textiles¹. The major commercial preparations of HBCD are composed of the three diastereomers, termed α - β - and γ -HBCD². Approximately 3,200 metric tons of HBCD technical preparations were used in Japan in 2007³. The main use of HBCD (80%) is in polystyrene (EPS and XPS), and approximately 20% of the total use of HBCD is in textiles in Japan³. The rapid increase in the use of BFRs such as HBCD has also raised the level of environmental concern about brominated chemicals such as polybrominated dibenzo-p-dioxins/furans (PBDDs/DFs) and brominated polycyclic aromatic hydrocarbons (BrPAHs)^{4,5}, which are produced upon their combustion. There are many papers in which PBDDs/DFs formation from combustion of BFRs alone or the influence of BFRs as a bromine source in municipal solid waste (MSW) incinerators have been studied^{6,7}. However, BrPAHs formation from combustion of BFRs still remains unclear.

In this study, we determined decomposition rates of HBCD by combustion of powdery HBCD and plastics containing HBCD at a electric furnace. The individual concentrations of 16 BrPAHs produced as by-product in flue gas were also determined.

Materials and methods

Incineration. The combustion chamber is a cylindrical furnace with a diameter of 28 mm and a length of 405 mm. The furnace has a stable temperature control (set temperature $\pm 5^\circ\text{C}$) and maximum temperature is 1000°C (QF-02; Dia Instruments Co., Ltd., Japan) (Figure 1). Combustion experiments were conducted with powdery HBCD and extruded polystyrene containing HBCD (1.1 wt%) at two different temperatures (500 and 800°C). Mixture gas of pure oxygen (20%) and pure nitrogen (80%) was used in combustion. The residence time of gases in the furnace was set to be 2 s by adjustment of gas flow at each temperature. A particular type of silica boat for sample introduction to the furnace was used to stabilize the burning rate of the sample, which is $5 \text{ kg/h/m}^3_{\text{N}}$ (Figure 2).

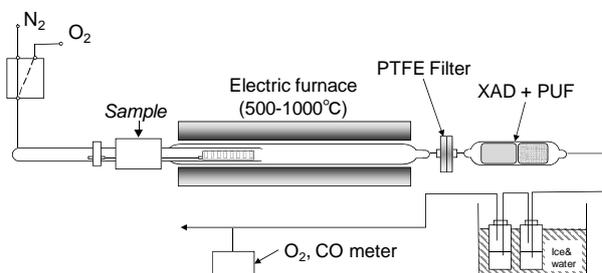


Figure 1. Experimental apparatus.

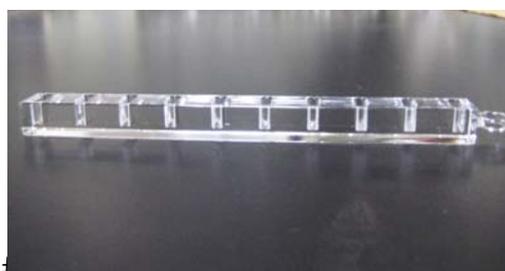


Figure 2. Silica boat for sample introduction.

Samples and chemicals. Flue gas samples were collected from exits of the furnace in order to determine concentrations of HBCD and BrPAHs. Sampling method of the samples was based on a modified standard method for PCDDs, PCDFs, and Co-PCBs, which comprised of a Teflon-coated filter for collecting particle matter and a “PUF/XAD-2/PUF” cartridge (ORBO-1500, Supelco, USA) for collecting gas-phase BrPAHs. Sixteen individual BrPAHs (mono- and di-bromoPAHs) determined in this study were bromonaphthalen (BrNap), dibromonaphthalene (Br₂Nap), bromofluorene (BrFle), dibromofluorene (Br₂Fle), bromophenanthrene (BrPhe), bromoanthracene (BrAnt), dibromoanthracene (Br₂Ant), bromopyrene (BrPyr), dibromopyrene (Br₂Pyr), and bromobenz[a]anthracene (BrBaA).

Analytical procedures. The determinations of HBCD and BrPAHs were performed according to an established method with some modifications⁴. Briefly, samples were extracted using a soxhlet extraction method for the filter and cartridge. An aliquot of the extracts was spiked with internal standards (fluoranthene-*d*₁₀), and then cleaned with a silica gel cartridge column (Supelclean LC-Si, 1 g, Supelco, USA). The cartridge column were eluted with 10 mL of 10% dichloromethane/hexane. The determination of the HBCD and BrPAHs was performed using gas chromatography–mass spectrometry with tandem quadrupole detectors (GC/MS/MS) with the Agilent 7683B GC interfaced with a Waters Quattro Micro MS. The MS was operated in electron impact mode (70 eV energy and 200 mA ion current) and in the selected ion monitoring (SIM) mode. The separation of individual BrPAHs and HBCD was achieved using a DB-5 capillary column (0.32 mm i.d. × 60 m length and 0.25 μm film thickness; J&W Scientific). The column oven temperature was programmed from 100°C (1 min) to 300°C at a rate of 10°C/min with a final hold time of 10 min. QA/QC protocols included the analysis of matrix spikes and procedural blanks. Peaks were identified by comparison of the retention times of samples to standards if the signal-to-noise (S/N) ratio was >3, and were quantified if target/qualifier ion ratios were within 15% of the theoretical values. Any sample with recovery below 50% was discarded and reanalyzed.

Results and discussion

Decomposition rate of HBCD. Combustions of HBCD were performed using powdery pure HBCD (> 95 wt%) and extruded polystyrene containing HBCD (1.1 wt%) at two different temperatures (500 and 800°C). Concentrations of HBCD in flue gas collected from combustions of pure HBCD (500°C, 2s), pure HBCD (800°C, 2s), and HBCD in PS (800°C, 2s) were 120, 0.83, and 0.011 μg/m³_N, respectively. The decomposition rates calculated from these results and feed rate of HBCD were 99.9966% for pure HBCD (500°C, 2s), 99.999983% for pure HBCD (800°C, 2s), and 99.999979% for HBCD in PS (800°C, 2s) (Figure 3). The concentration in combustion of pure HBCD at 500°C was 100-fold higher than that in combustion of pure HBCD at 800°C, whereas the difference in pure HBCD and HBCD in PS have no discernible impact on the decomposition rates.

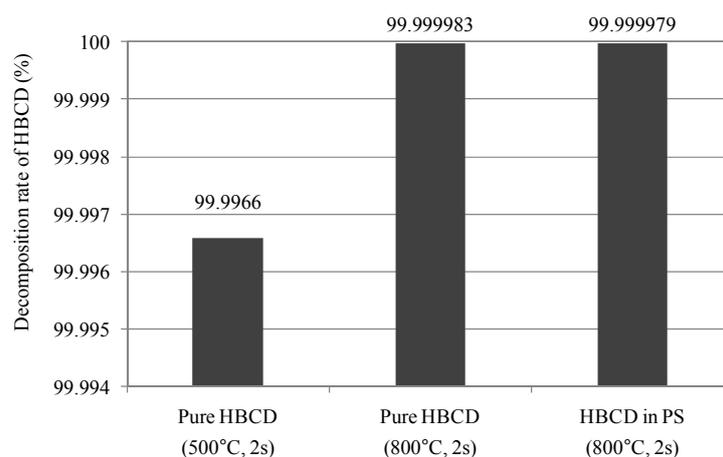


Figure 3. Decomposition rates of HBCD with changing temperature of furnace (500 and 800°C) and sample (powdery pure HBCD and extruded polystyrene containing HBCD).

Concentrations of BrPAHs. Concentrations of sixteen individual BrPAHs in flue gas collected from the exit of furnace were determined in order to analyze generation behaviors of by-products from combustions of HBCD (Figure 4). The Concentrations of BrPAHs in combustion of pure HBCD at 500°C were 9100 $\mu\text{g}/\text{m}^3_{\text{N}}$ for BrNap and 140 $\mu\text{g}/\text{m}^3_{\text{N}}$ for Br₂Nap. The Concentrations of BrPAHs in combustion of pure HBCD at 800°C were 85 $\mu\text{g}/\text{m}^3_{\text{N}}$ for BrNap, 47 $\mu\text{g}/\text{m}^3_{\text{N}}$ for Br₂Nap, 3.2 $\mu\text{g}/\text{m}^3_{\text{N}}$ for 3-BrPhe, 3.0 $\mu\text{g}/\text{m}^3_{\text{N}}$ for 9-BrPhe, 2.4 $\mu\text{g}/\text{m}^3_{\text{N}}$ for 1-BrAnt, and 9.3 $\mu\text{g}/\text{m}^3_{\text{N}}$ for 1,5-Br₂Ant. The Concentrations of BrPAHs in combustion of HBCD in PS at 800°C were 1.2 $\mu\text{g}/\text{m}^3_{\text{N}}$ for BrNap. Concentrations of the other target analytes were lower than the limits of quantification (LOQs) ($< 1 \mu\text{g}/\text{m}^3_{\text{N}}$).

The highest BrNap and Br₂Nap concentrations were measured in sample from combustion of pure HBCD at 500°C, which were 100- and 3-fold higher than those at 800°C, respectively, whereas 3-BrPhe, 9-BrPhe, 1-BrAnt, and 1,5-Br₂Ant were detected only in sample from combustion of pure HBCD at 800°C. Aracil *et al.* found trends on 16 main PAHs yields that most had a maximum at 850°C in pyrolysis, but naphthalene at 700°C⁸. Kim *et al.* also found an increase of the 16 main PAH yields with temperature during combustion of 0.5 g PVC with 2 L/min air in a downstream vertical tubular furnace at temperatures of 300, 600 and 900°C: about 800, 3500 and 5000 ppm, respectively⁹. Furthermore, Horii *et al.* showed a high correlation between

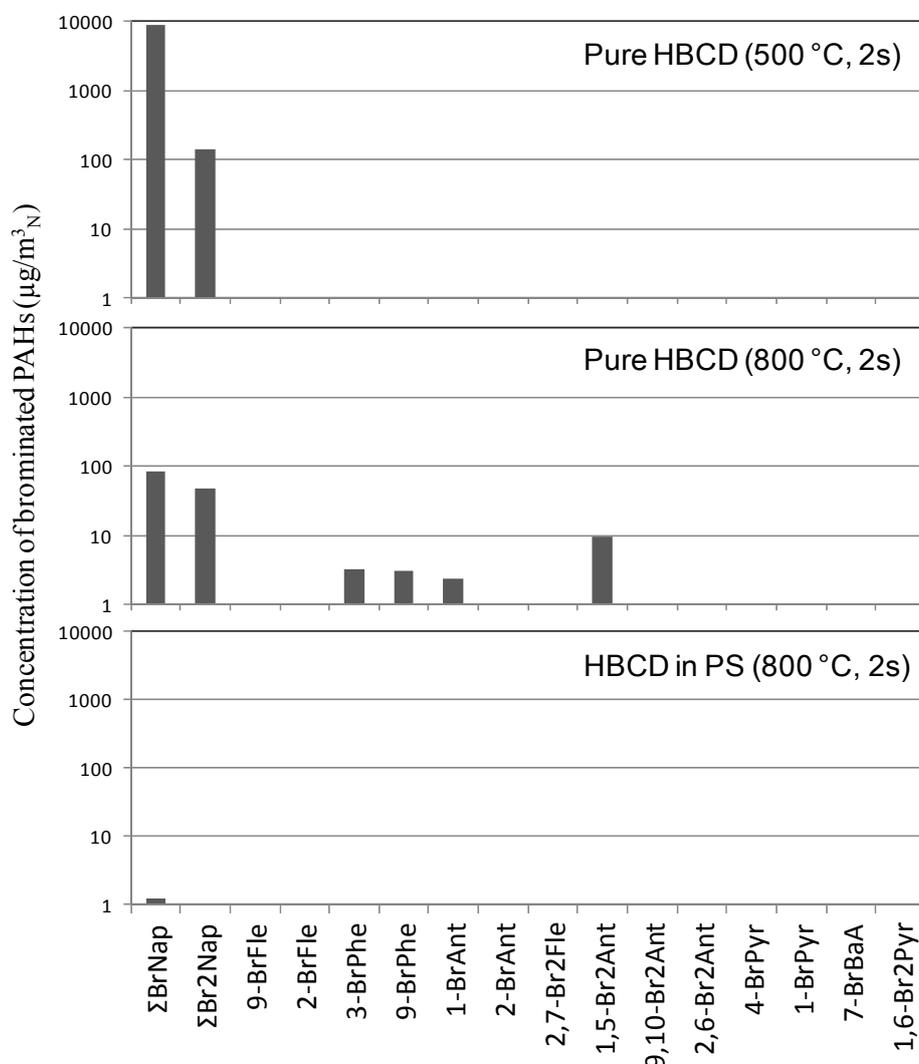


Figure 4. Concentrations of BrPAHs produced by combustion of HBCD samples

Cl-/BrPAHs and its parent homologue emitted from waste incinerators, which means that the direct chlorination and bromination of the parent PAHs can be the major mechanism of formation of Cl-/BrPAHs in waste incinerators⁴. Therefore, the maximum of halogenated PAHs yields may appear between 800 to 1000°C, which are general temperatures in MSW and industrial waste incinerators. Further studies are needed to clarify behaviors of halogenated PAHs regarding temperature and atmosphere of the reaction.

Acknowledgements

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