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## FORMATION OF PBDD/F PRECURSORS IN GAS-PHASE DECOMPOSITION OF TETRABROMOBISPHENOL A (TBBA)

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### Introduction

Tetrabromobisphenol A (TBBA) belongs to a well-known group of bromine bearing hydrocarbons collectively termed as brominated flame retardants (BFRs) added extensively to consumer products, especially plastics used in electrical and electronic equipment, textiles and furniture to increase their fire retardancy behaviour.<sup>1-3</sup> At the end of their life cycle, the consumer products are discharged into the waste stream. Based on the infrastructure, energy demands and regulations in different countries, the waste streams are subjected to either open burnings<sup>4</sup> or other thermal treatments,<sup>5-7</sup> such as incineration and recycling processes for the purpose of their safe disposal, including energy and metal recovery. Therefore, it is essential to gain an understanding of the decomposition chemistry of BFRs at elevated temperature.

Previous laboratory and pilot-scale contributions have addressed thermal breakdown of polymeric materials laden with TBBA, under both oxidative and inert atmosphere, in the temperature range of 180 to 850 °C.<sup>8-12</sup> These studies reported overall decay of TBBA, its evaporation and decomposition corridors, weight loss curves, the formation of HBr as the major bromine product, selective qualitative and quantitative analyses of brominated and non-brominated products, and proposed the mechanism based on temperature profiles of the product species. Owing to the high boiling point of TBBA, all pertinent investigations have targeted its thermal decomposition in the condensed medium. To the best of our knowledge, literature offers no analogous account for the gas phase degradation of TBBA.

The current contribution assesses yields of the precursor species for formation of polybrominated dibenzo-p-dioxins and polybrominated dibenzofurans (PBDD/Fs),<sup>13-18</sup> arising during thermal degradation of TBBA in the gas phase. In particular, we focus our attention on the yields of brominated congeners of benzene and phenol that arise during the pyrolysis and oxidation of TBBA between 500 and 800 °C, with a reaction time of 2 s. In the current study, we also develop multiple reaction monitoring (MRM) methods for the precise analysis of the PBDD/Fs precursors and propose plausible reaction pathways that govern the initial decomposition of TBBA.

### Materials and Methods

All experiments were conducted in a setup that comprises three sections: (i) feed preparation unit; (ii) isothermal tubular reactor; and, (iii) product collection assembly. Feed preparation section incorporates a vapouriser made from a vertical quartz tube containing TBBA (97 % purity) housed in an oven operating at 177 °C, introduced TBBA vapour with a flow rate of 0.06 mg min<sup>-1</sup> into the reactor inlet. The outlet from the vapouriser leads to the horizontal tubular reactor (12.7 mm o.d., 10.0 mm i.d., 235.0 mm<sup>3</sup> volume), made from ultra-pure quartz, installed along the centre line of a 3-zone temperature-controlled furnace. The exhaust of the reactor connects to the product collection line that encompasses two consecutive impingers; i.e., an alkaline trap filled with a solution of NaOH and a solvent trap loaded with dichloromethane (DCM) and cooled by a sodium chloride/ice bath to capture volatile (VOC) and semi-volatile (SVOC) organic compounds. We coated the inner surfaces of reactor tube with B<sub>2</sub>O<sub>3</sub> layer<sup>19-20</sup> in order to eliminate small (but not negligible!) oxidation effects of quartz surfaces. Prior to each experiment, including procedural blanks, reactor tube underwent baking at 500 °C for 3 h in flowing air, to burn off condensed contaminants remaining from a preceding trial. Deuterated biphenyl (D10) served to spike the solvent in the solvent trap, prior to each experiment, to estimate the percentage recovery of the products (typical recovery >74 %). Then, after each experiment, before concentrating the solvent solution using a rotary evaporator, we dissolved <sup>13</sup>C-benzene (typical recovery >97 %) in the solution to evaluate the percentage recovery of light organic compounds, and then reduced the volume of the solvent solution to about 1 mL for the analysis.

Typically, a volume of 1  $\mu\text{L}$  of the concentrated sample was injected into the gas chromatograph (GC) operated in a splitless mode, with the capillary column leading to the source of a triple quadrupole mass spectrometer (QQQMS). The QQQMS worked in positive electron impact (EI) ionisation, at the ionisation voltage of 70 eV. The GC oven housed a DB5-MS column (15 m length, 0.25 mm i.d., 0.25  $\mu\text{m}$  film thickness) for the analysis of brominated species. Helium served as the carrier gas with its flow rate maintained at 1.5  $\text{mL min}^{-1}$  at a pressure of 25.1 kPa. The injector, interface, and ion source temperatures were set at 250  $^{\circ}\text{C}$ , 300  $^{\circ}\text{C}$  and 200  $^{\circ}\text{C}$ , respectively. The GC oven temperature involved a constant temperature period of 30  $^{\circ}\text{C}$ , retained for 3 min, then a temperature ramp of 8  $^{\circ}\text{C min}^{-1}$  to reach 100  $^{\circ}\text{C}$ , held for 2 min, then another temperature ramp of 4  $^{\circ}\text{C min}^{-1}$  to attain 290  $^{\circ}\text{C}$ , held for 2 min. We developed an MRM acquisition method, equivalent to MS/MS method, for accurate identification and quantitation of each species. To achieve this, we optimised the abundance of daughter ions of each species as a function of collision energy. The identification of each brominated phenol and benzene (dioxin/furan precursors) involved comparing their mass spectra with the spectra of genuine standards. Finally, the development of the calibration curves for species quantitation entailed injecting genuine standards at 10 levels of concentration.

## Results and Discussion

Thermal decomposition of TBBA under inert and oxidative environment involved experiments performed at 500  $^{\circ}\text{C}$ , 600  $^{\circ}\text{C}$ , 700  $^{\circ}\text{C}$  and 800  $^{\circ}\text{C}$  with the products analysed in GC-QQQMS in full scan and MRM modes. We detected a range of VOCs and SVOCs. Herein, we present detailed results of MRM scan mode for the active precursors of PBDD/Fs including phenol, and brominated congeners of phenol (2/4-monobromophenol (2/4-MBPh), 2,4/2,6-dibromophenol (2,4/2,6-DBPh), 2,4,6-tribromophenol (2,4,6-TriBPh)), benzene and brominated benzenes (monobromobenzene (MBBz), 1,4/1,3/1,2-dibromobenzene (1,4/1,3/1,2-DBBz) and 1,3,5/1,2,4/1,2,3-tribromobenzene (1,3,5/1,2,4/1,2,3-TriBBz)). Figure 1 depicts an example of the GC-MS MRM chromatogram for the dioxin/furan precursors collected for the reactor operated at 600  $^{\circ}\text{C}$ . The caption to Figure 1 presents the combined elution order for the oxidation and pyrolysis experiments.

Figure 2 depicts the comparison of integrated yields of phenol and congeners of mono-tri bromophenols arising in the gas phase pyrolysis and oxidation of TBBA. The formation of the PBDD/Fs precursors initiates at a temperature of 450  $^{\circ}\text{C}$  with a maximum yield occurring at around 600  $^{\circ}\text{C}$  and 700  $^{\circ}\text{C}$ . The yields of 2,6-DBPh and 2,4,6-TriBPh exceed those of other phenolic products at all operating temperatures. This dominant formation of 2,6-DBPh and 2,4,6-TriBPh accords with the results of previous studies documented in the literature that have addressed the thermal decomposition of pure TBBA and TBBA dispersed in polymeric materials.<sup>8-9</sup> Note that above 600  $^{\circ}\text{C}$ , the yields of brominated phenols decrease as the temperature increases. Under oxidation condition, at above 750  $^{\circ}\text{C}$ , no 2-MBPh, 4-MBPh, 2,4-DBPh and 2,4,6-TriBPh elute from the reactor. The presence of oxygen has no significant influence on the yields of brominated phenolic compounds.

Figure 3 presents histograms illustrating the yields of congeners of brominated benzenes. We observed these species at all reaction temperatures, and also identified benzene appearing at all operating temperatures using the Rxi-5Sil MS column (30 m length, 0.25 mm i.d., 0.25  $\mu\text{m}$  film thickness) to avoid the co-elution of benzene peak with the solvent. Among the bromobenzene congeners, the MBBz appears in maximum yields of 270  $\text{mg kg}^{-1}$  and 360  $\text{mg kg}^{-1}$  at 700  $^{\circ}\text{C}$  in pyrolysis and oxidation experiments, respectively.

Scheme 1 suggests pathways for the formation of selected congeners of brominated phenols and brominated benzenes. In our recent theoretical investigation,<sup>21</sup> we have proposed the mechanistic pathways to explain the initial species arising in the pyrolysis of TBBA. The self-expulsion of a methyl group from TBBA molecule constitutes the most preferred channel in an initial unimolecular decomposition of TBBA, with a rate constant of  $2.09 \times \text{T}^{1.93} \exp(-37000/\text{T}) \text{ s}^{-1}$ .<sup>21</sup> The other important pathways mark the cleavage of isopropylidene linkage and fission of aromatic C-Br bond. The IM1 intermediate forms upon unimolecular fission of the C-Br bond in TBBA followed by H abstraction from any RH species present in the reacting system. In a typical combustion environment, a TBBA molecule reacts readily with the H/O radical pool.<sup>21</sup> An H atom can displace the OH group in TBBA and IM1, IM2, IM3 molecules in bimolecular reactions. The formation of benzene and phenolic compounds implies the fission of isopropylidene linkage in TBBA, IM1- IM3, IM7, IM8, IM12 and

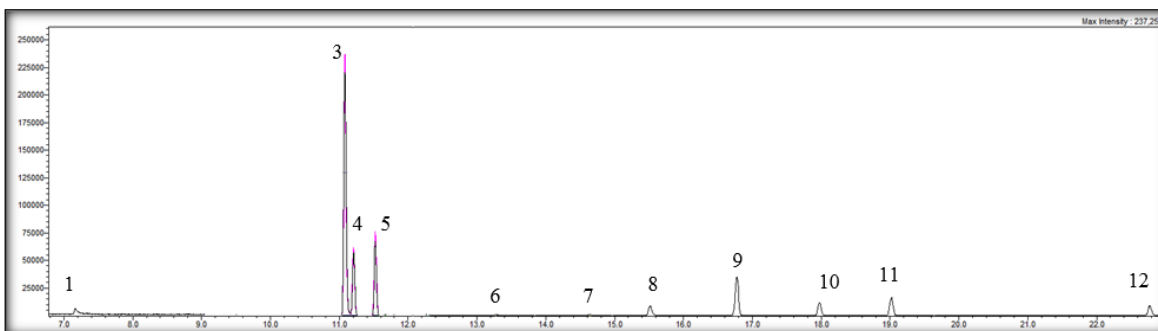
IM13 adducts, generating numerous radical species (i.e., IM4 and IM6, IM9, IM10, IM14, IM15). Subsequent bromination/hydrogenation reactions of radical species with Br or H atoms lead to the formation of brominated phenols and brominated benzenes. However, the experimentally measured yields of brominated benzenes are lower than the brominated phenols owing to the slow displacement of the hydroxyl group with H or Br radical.<sup>15</sup> The high yields of 2,6-diBPh, 2,4,6-triBPh reflect the presence of bromine at 2,6-positions in the parent TBBA molecule. The observed higher yield of brominated compounds, under oxidative conditions than in pyrolysis at all reaction temperatures, reflects the appearance of the OH radicals. These radicals are abundant in the oxidative environment, react with H to form H<sub>2</sub>O, and reduce the concentration of H atoms that replace the Br atoms.

### Acknowledgment

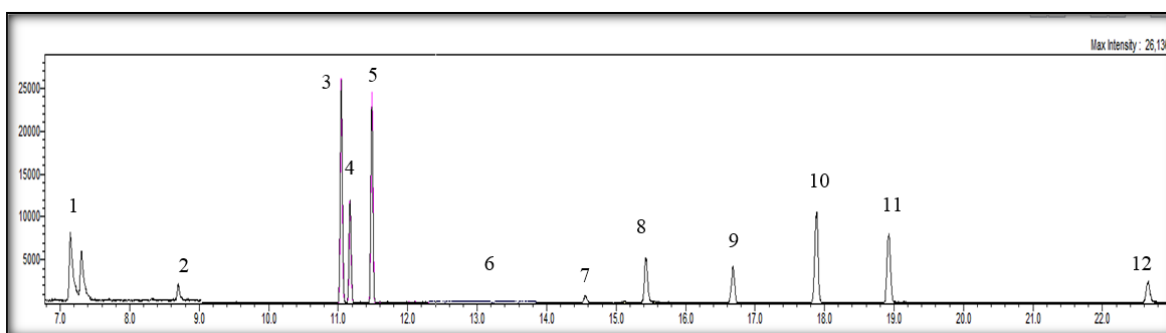
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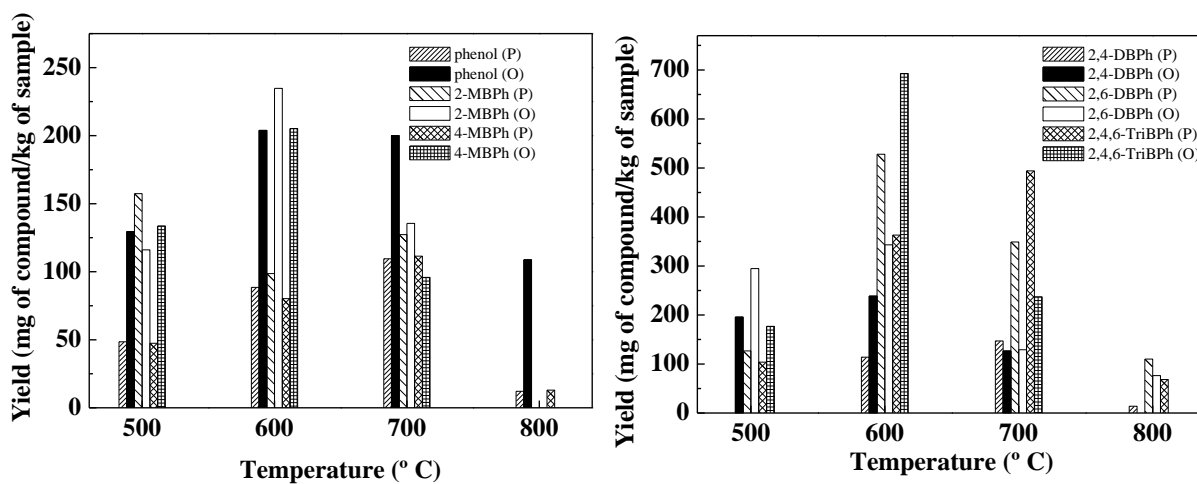


(a) oxidation

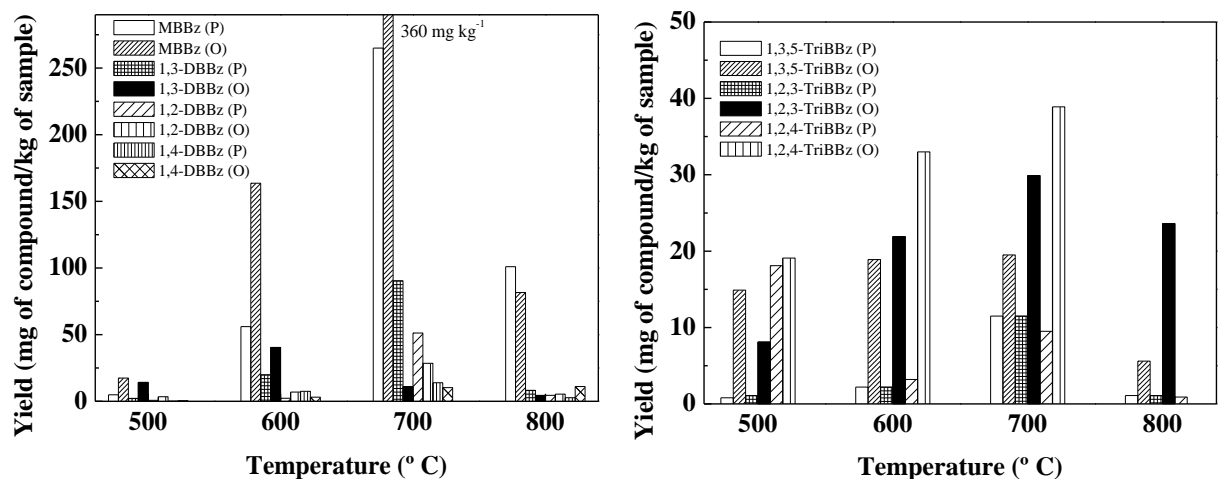


(b) pyrolysis

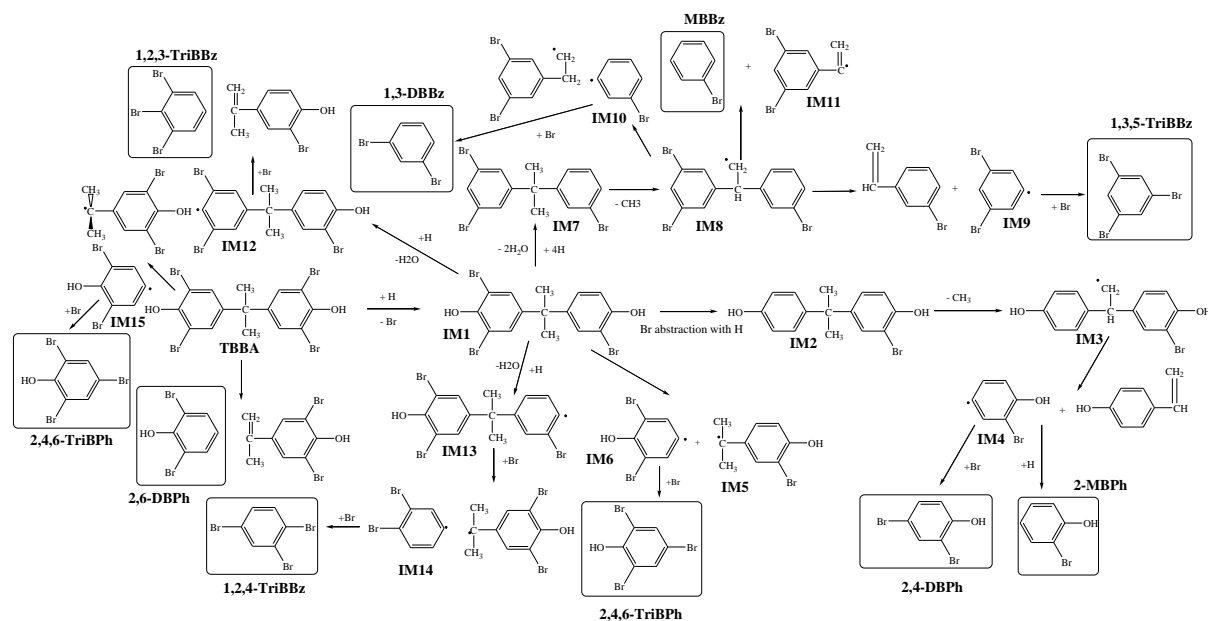
**Figure 1.** An example of MRM traces for the condensable product evolved during the gas-phase oxidation ( $6.0 \pm 0.5\%$   $O_2$ ) (a) and pyrolysis (b) of pure TBBA experiment performed at  $600\text{ }^\circ\text{C}$  for residence time of 2 s (1: phenol, 2: 2-MBPh, 3:1,3-DBBz, 4: 1,4-DBBz, 5: 1,2-DBBz, 6: 4-MBPh, 7: 2,4-DBPh, 8: 2,6-DBPh, 9: 1,3,5-TriBBz, 10: 1,2,3-TriBBz, 11: 1,2,4-TriBBz, 12: 2,4,6-TriBPh).



**Figure 2.** Comparison of yields of the phenol and its brominated congeners from the gas phase pyrolysis (P) and oxidation (O) of TBBA at various decomposition temperatures and at 2 s residence time.



**Figure 3.** Comparison of yields of congeners of brominated benzene appearing in the gas phase pyrolysis (P) and oxidation (O) of TBBA at various decomposition temperatures and at 2 s residence time.



**Scheme 1.** Plausible pathways leading to the formation of brominated benzenes and phenols from decomposition of TBBA.