

# TOXIC SPECIES FROM OXIDATION OF TETRABROMOBISPHENOL A

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## Introduction

This study investigates formation of a wide spectrum of brominated compounds from oxidative thermal decomposition of tetrabromobisphenol A (TBBA); a commonly used brominated flame retardant (BFR).<sup>1</sup> The high content of TBBA in municipal, industrial and commercial waste streams triggers emission of toxic brominated pollutants during uncontrolled recycling and open burnings of objects laden with TBBA.<sup>2-3</sup> Prior investigations, focused on the thermal breakdown of TBBA and TBBA-treated polymeric materials using TGA-FTIR and DSC-FTIR analyses, yielded qualitative and semi-quantitative measurements of the degradation products of TBBA.<sup>4-7</sup> In particular, the study of Ortunõ et al. presented comprehensive quantitative measurements of decomposition of TBBA.<sup>8</sup> In spite of these efforts, the combustion chemistry underpinning degradation of TBBA in the presence of oxygen remains incompletely understood. This is because the previous research did not differentiate satisfactorily between the chemical reactions occurring in condensed media and those taking place in the gas phase. It seems that, the high boiling point of TBBA (i.e., 250 °C) made it difficult to design studies that decouple the contribution of the decomposition pathways working in the gas phase from corridors operating in the condensed medium prior to its evaporation.

Bimolecular isomerisation reactions govern the decomposition pathways of TBBA in the condensed media in comparison to unimolecular reactions that commonly prevail in the gas phase. To the best of our knowledge, literature offers no experimental account of the gas phase oxidation of TBBA, unobscured by processes arising in the condensed phase. Our recent theoretical study<sup>9</sup> has mapped out major decomposition pathways operating in the unimolecular decomposition of TBBA and its bimolecular reactions with H/O/Br radicals. However, products arising from the theoretically-developed pathways remain without an experimental verification. From this perspective, the present contribution reports temperature-profiles of volatile organic compounds (VOCs) with a focus on precursors of polybrominated dibenzo-*p*-dioxins and dibenzofurans (PBDD/F) that evolve in the gas-phase oxidation of TBBA over a temperature range of 300 °C – 850 °C and for the reaction time set to 2.0 s. We have thoroughly presented potential pathways for the formation of the major observed products based on our previous contributions on pyrolysis of TBBA.<sup>9-10</sup> The present article identifies and quantitates several oxygenated compounds that arise in the presence of oxygen but were not detected under pyrolytic conditions.

## Materials and Methods

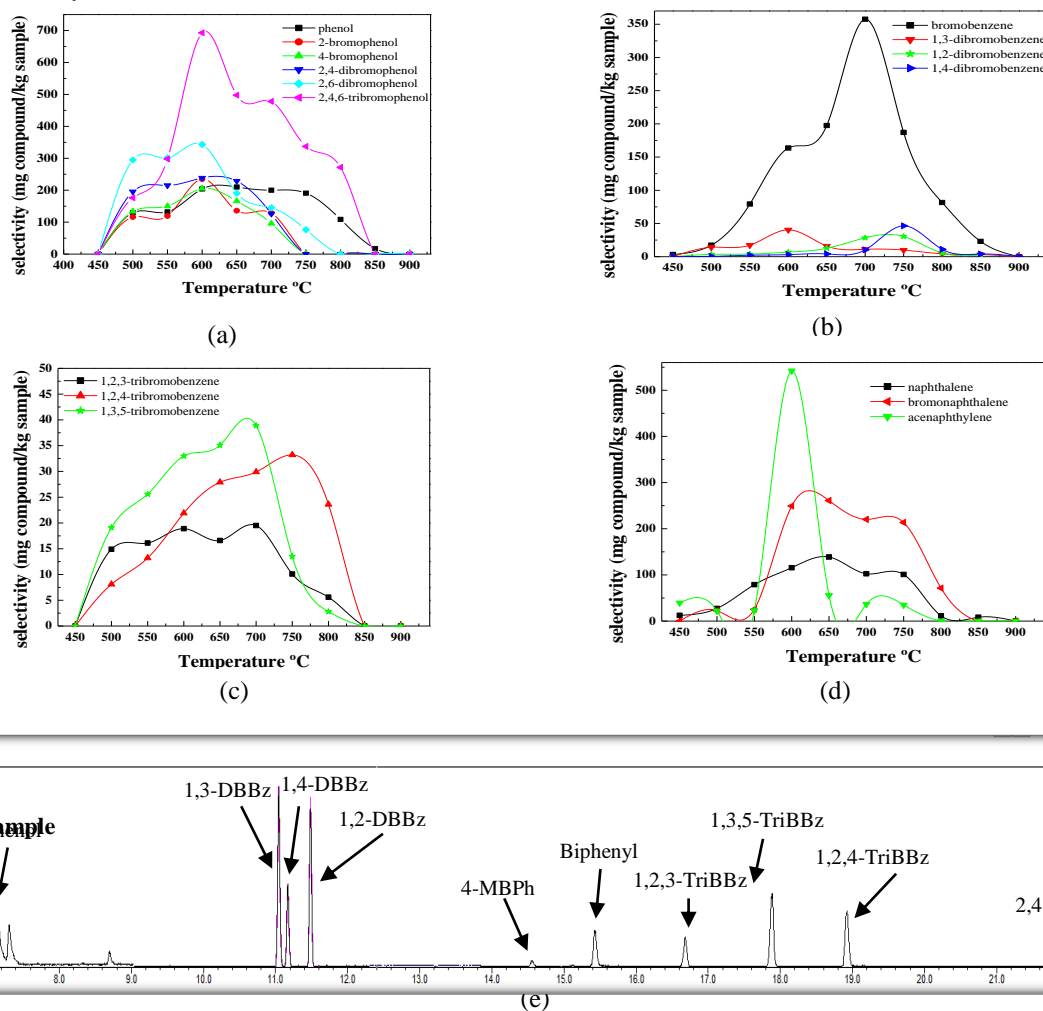
A laboratory-scale bench-type apparatus consisted of ultra-high purity quartz tube reactor (12.7 mm o.d., 10.0 mm i.d., 235.0 mm<sup>3</sup> volume) equipped with fuel vaporiser to supply a controlled rate of TBBA vapour into the reaction system along with a sampling train for intercepting the volatile and condensable products. A gas mixture, consisting of nitrogen (99.998 %) supplemented with controlled amounts of air (6.0 ± 0.5 % O<sub>2</sub>, 99.999 %) and TBBA vapours, flowed into the preheated high-purity quartz-tube (99.995 %) reactor. The product sampling train incorporated two succeeding absorption traps that captured HBr (in 0.1 N NaOH solution) and condensable products (in dichloromethane (DCM), trap placed in the ice bath) from the exhaust gases leaving the reactor. We coated the reactor walls with a B<sub>2</sub>O<sub>3</sub> layer<sup>11</sup> to minimise further their catalytic effects. Before each experiment, we purged the reactor tube with the stream of nitrogen and air; and baked the reactor tube at 500 °C for at least 3 h, to remove organic residuals that might have remained in the reactor from the preceding runs. We run the procedural blanks and repeats in order to monitor the quality and reproducibility of our experimental measurements. Deuterated (D-10) biphenyl was introduced in the DCM solvent trap prior to each experiment to inspect the percentage recovery of products during the experimental run (> 78 %). To estimate losses of light VOCs during sample preparation, we spiked the DCM solvent with <sup>13</sup>C<sub>6</sub>-benzene (typical recovery > 97 %) at the conclusion of each experiment and before concentrating the samples to a volume of 1 mL using a rotary evaporator.

We injected the concentrated product sample (1 µL; in splitless mode) into the gas chromatograph triple quadrupole mass spectrometer (GC-QQQMS) equipped with a Rxi-5SilMS capillary column (15 m × 0.25 mm i.d. × 0.25 µm), with the length of the column selected to afford the analysis of semi-volatile brominated compounds. The MS electron impact source operated with an ionisation energy of 70 eV, in the positive ionisation mode. The quadrupoles worked both in multiple reaction monitoring (MRM) and total ion current (TIC) modes. Helium served as carrier gas with a constant flow rate maintained at 1.5 mL min<sup>-1</sup> through the column. The injector, ion source and the transfer line functioned at 250 °C, 200 °C and 300 °C, respectively. The GC oven was programmed to start at 30 °C, held this temperature for 3 min, then to increase the temperature to 100 °C with a heating ramp of 8 °C min<sup>-1</sup> keeping 100 °C for 2 min and then to raise this temperature at a rate of 4 °C min<sup>-1</sup> to reach 290 °C, held for 2 min. We generated multiple-reaction monitoring (MRM) acquisition methods to acquire the quantitative measurements for the key species. For the MRM method development, we obtained the response of each daughter ion for all target

compounds for the collision energy (CE) range of 3 – 54 V, sampled at intervals of 3 V. We optimised the CE responses between 3 and 54 V, depending on the chemical species, and carried these values across to our MRM method. Genuine standards afforded identification of each target compound, in terms of its retention time on column and ratios of the dominant  $m/z$  signals in its spectrum, and its quantification by calibration curves based on 10 levels of concentration.

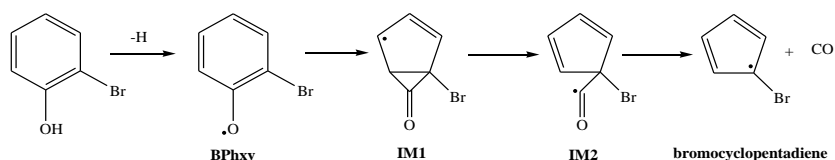
## Results and Discussion

Oxidative thermal decomposition of TBBA yields a number of volatile and semi-volatile organic pollutants. We estimate the quantitative profiles of key species as function of temperature, including phenol, 2/4-bromophenol, 2,4/2,6-dibromophenol, 2,4,6-tribromophenol, bromobenzene, 1,3/1,2/1,4-dibromobenzene, 1,3,5/1,2,4/1,2,3-tribromobenzene, naphthalene, bromonaphthalene, acenaphthylene, 2,6-dibromo-4-methylphenol, 3,5-dibromo-4-hydroxybenzaldehyde, benzofurans and dibenzofurans. Among these compounds, brominated phenols (BPh) and brominated benzenes (BBz) function as direct potent gas-phase precursors of PBDD/Fs. BBz in the presence of oxygen produce brominated phenoxy radicals that readily synthesise into PBDF and polybrominated biphenyls (PBB) through bimolecular reactions of BBz and BPhxy radicals.<sup>12</sup> We found that, BBz evolve in the oxidative environment by the displacement of OH group in the parent TBBA molecule by Br atom followed by the cleavage of isopropylidene linkage. Figure 1 presents selectivity of products as a function of reaction temperature. Our previous theoretical study revealed the mechanistic details of the formation of BPh and BBz from TBBA.<sup>9-10</sup> The present experimental investigation confirms the formation of BPh and BBz in excess of 550 °C, with 2,4,6-tribromophenol and monobromobenzene as the most abundant congeners with their peak emission recorded at around 600 °C and 700 °C, respectively. The overall concentration of BPh exceeds that of BBz, owing to the oxidative decomposition of BBz that generates brominated phenoxy radicals. The latter readily convert into BPh by H abstraction from any species present in the system.



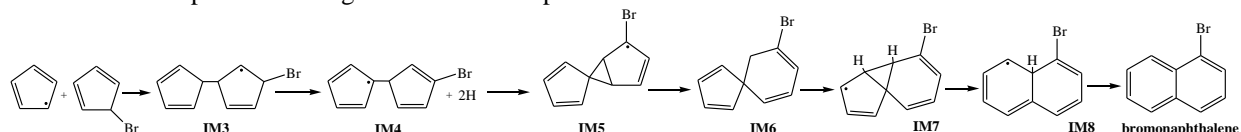
**Figure 1.** (a–d) Selectivity of species obtained from the gas-phase oxidation of TBBA as function of temperature. Lines were drawn as guide to the eye. (e) An example of MRM chromatogram for the selected VOC. Selectivity of product species  $i$  is defined as mass of species  $i$  produced/mass of feed converted.

Oxidative thermal degradation of TBBA generates several PAH such as naphthalene, bromonaphthalene, acenaphthylene, biphenylene, acetophenone (Figure 1d depicts the quantitative profiles for naphthalene, bromonaphthalene and acenaphthylene). Naphthalenes and brominated naphthalenes arise due to the formation of brominated phenolic-type moieties by a direct cleavage of the isopropylidene linkage in TBBA. These phenolic structures decompose into bromocyclopentadiene radicals via the well-documented ring contraction/CO elimination mechanism; see Scheme 1 for the formation of bromocyclopentadiene radical from a 2-MBPh molecule. The emergence of a non-brominated cyclopentadiene radical follows a similar mechanistic pathway to that of the brominated cyclopentadiene radical.<sup>13</sup>



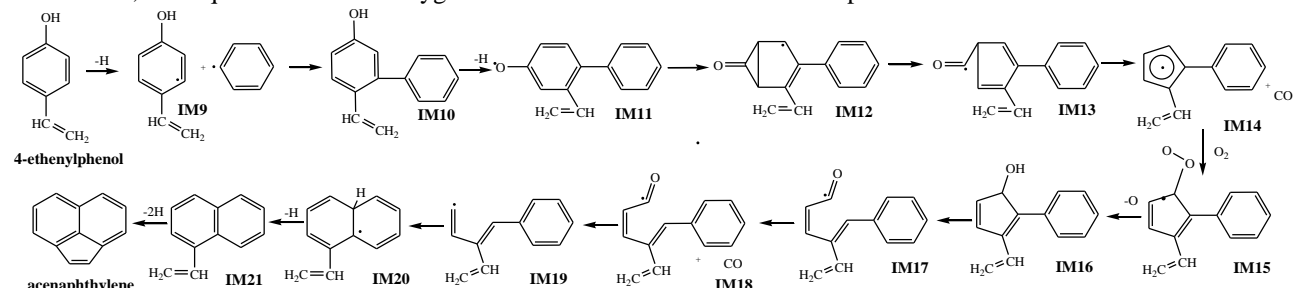
**Scheme 1.** An example of the bromocyclopentadiene radical generation from 2-monobromophenol.

Cyclopentadiene radicals produce several experimentally-important products, such as naphthalene and benzofuran. Scheme 2 illustrates the mechanistic pathways for the formation of bromonaphthalene from the coupling reaction of cyclopentadiene and bromocyclopentadiene. The initial synthetic moiety (IM3) forms via the bimolecular reaction of cyclopentadiene radical and bromocyclopentadiene. The product from the first coupling undergoes 2H elimination to afford the IM4 structure that isomerises into a tricyclic species (IM5) through a three-membered ring-closure step. The unimolecular rearrangement of IM5 produces the bicyclic mesomer, IM6, by ring isomerisation. IM6 passes through a three-membered ring-closure arrangement to yield tricyclic specie, IM7 that converts into IM8. Finally, the loss of the out-of-plane H atom generates bromonaphthalene.



**Scheme 2.** Pathways for the formation of naphthalene from the coupling of bromocyclopentadiene and cyclopentadiene radical.

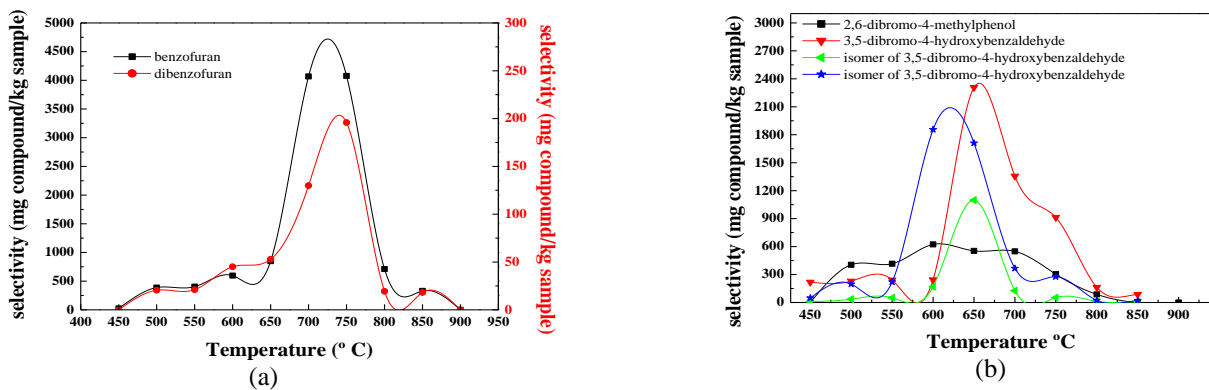
As explained earlier, the direct fission of isopropylidene structure in TBBA bears BPh as the main product and generates several congeners of alkylated phenols as minor species.<sup>9-10</sup> The alkylated phenols constitute active precursors for the formation of acenaphthylene. For example, 4-ethenylphenol loses an H atom to produce 2-ethenyl-5-hydroxybenzen-1-ylum (IM9) radical. The condensation reaction of IM9 with a phenyl radical produces acenaphthylene through a series of steps as portrayed in Scheme 3. Major steps include the ring contraction/CO elimination, subsequent addition of oxygen molecule to the radical site and stepwise elimination of H atoms.



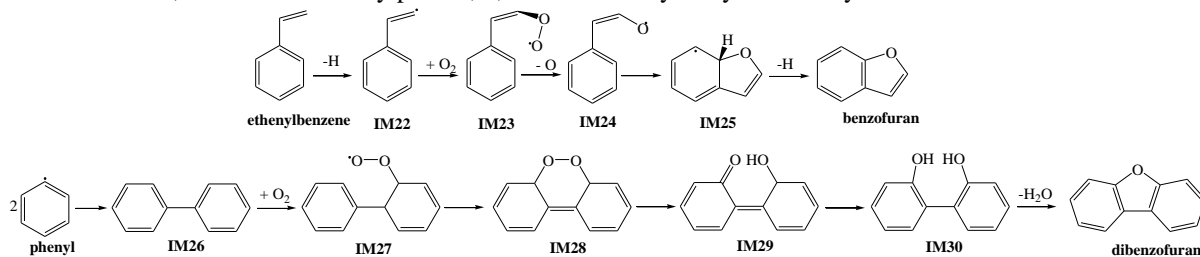
**Scheme 3.** Mechanistic pathways for the generation of acenaphthylene from 4-ethenylphenol.

Oxidative decomposition of TBBA produces benzofuran and dibenzofuran in appreciable amounts (as evident in Figure 2a). In addition to benzofuran, we also identified its brominated congeners. The formation of benzofuran increases three fold under oxidative environment in comparison to pyrolysis.<sup>10,14</sup> Benzofuran and dibenzofuran reach their peak values in the temperature window of 700 – 750 °C. Various intermediate species that evolve by the decomposition of the TBBA molecule serve as a potential source for the generation of benzofuran and dibenzofuran. For instance, mono and dibrominated ethenylbenzenes may form via the cleavage of isopropylidene linkage in 1,3-dibromo-5-[1-(3-bromophenyl)ethyl]benzene. Addition of oxygen to ethenylbenzene initiates its conversion into benzofuran (refer to the upper part in Scheme 4). Under pyrolytic conditions, observed higher quantities of brominated and non-brominated biphenyls most likely stem from the self-coupling reactions of phenyl radicals. Under oxidative atmosphere, addition of oxygen to the radical site in phenyl radicals prompts their rapid decomposition, and hence

oxidative conditions result in low selectivity to biphenyls. Formation of dibenzofuran from biphenyl proceeds via a complex, yet very exothermic mechanism, as pictured in the lower part of Scheme 4. A recent theoretical study provides a complete energy profiles.<sup>14</sup>



**Figure 2.** Selectivity of species formed in the gas-phase oxidation of TBBA: (a) benzofuran and dibenzofuran, (b) 2,6-dibromo-4-methylphenol, 3,5-dibromo-4-hydroxybenzaldehyde and its two isomers.



**Scheme 4.** Mechanistic pathways for the generation of benzofuran and dibenzofuran.

Thermal degradation of TBBA also produces 2,6-dibromo-4-methylphenol, 3,5-dibromo-4-hydroxybenzaldehyde, butylated hydroxytoluene, ethyl-3-hydroxybenzoate, 1-bromo-2-ethynyl benzene, 1-bromo-4-ethynyl benzene, 1-bromo-2-vinylbenzene, tribromo acetic acid, benzoic acid, benzyl alcohol, benzoic acid ethyl ester, bromo-2-methylbenzoic acid, 3,5-dimethylbenzaldehyde, 4-bromo-1,1'-biphenyl and ethyl ethoxybenzoate. Figure 2b presents the selectivity of 3,5-dibromo-4-hydroxybenzaldehyde and its isomers along with 2,6-dibromo-4-methylphenol as function of temperature. The selectivity of 3,5-dibromo-4-hydroxybenzaldehyde from oxidation of TBBA surpasses that from pyrolysis<sup>14</sup> of TBBA. Formation of this product presumably initiates via oxygen addition at a vacant radical site in the 2,6-dibromo-4-methylenephenol molecule. In conclusion, the present results indicate that, oxygenated products of TBBA evolve in high concentration in combustion environment when compared with the pyrolysis. In the latter, non-oxygenated compounds dominate the product species.<sup>10, 14</sup> Higher temperatures favour the formation of non-brominated moieties in both systems owing to a relatively weak aromatic C-Br bond ( $\sim 330 \text{ kJ mol}^{-1}$ ).

### Acknowledgment

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