

FORMATION OF PBDFs AND PBBs FROM BROMOBENZENES

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Introduction

Halogenated benzenes and phenols constitute the most discussed gas-phase precursors for the formation of the notorious halogenated dioxin compounds, especially, polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs)¹⁻⁴ and their analogous brominated counterparts (PBDD/Fs).⁵⁻⁷ Distinct emission profiles of PCDD/Fs with respect to PBDD/Fs in industrial effluents have suggested different governing mechanisms. It is generally accepted that, the majority of PCDD/Fs form via the burn off of the carbon matrix in the so-called de novo synthesis.⁸⁻⁹ Consistency in homologue profiles of PCDD/Fs among the various emission sources indicate a global governing mechanism that is independent of the chlorination pattern of gas-phase chlorinated benzenes and phenols. On the contrary, profiles of PBDD/Fs display considerable sensitivity to the input feed.^{5, 10} It follows that, the precursor pathway is more prevalent in the formation of PBDD/Fs than the de novo synthesis.^{7,11-12} Another salient difference is that, chlorine in PCDD/Fs displays inorganic origins (i.e. from municipal waste), whereas bromine constituents in PBDD/Fs stem from organic materials. Emission of PBDD/Fs from thermal systems is often linked with thermal decomposition of brominated flame retardants (BFRs).¹³⁻¹⁴

Structural entities of nearly all BFRs, such as tetrabromobisphenol A (TBBA),¹⁵ brominated diphenyl ethers (PBDEs)¹⁶⁻¹⁷ and 1,2-bis(tribromophenoxy) ethane (BTBPE)⁵, encompass brominated benzene and phenol rings. Certain BFRs, such as PBDEs¹⁸ and brominated biphenyls (PBBs)¹⁹, act as direct building blocks for PBDD/Fs in their own right. However, degradation of BFRs to brominated benzene and phenol rings provides further seeds to the production of PBDD/Fs.²⁰ Experimental²¹ and theoretical⁷ studies have thoroughly investigated the generation of PBDD/Fs from brominated phenols. Nonetheless, the analogous role of brominated benzenes has not been fully elucidated so far. Surprisingly, there is a considerable paucity of studies on the anticipated production of PBDD/Fs from oxidation and pyrolysis of bromobenzenes. In a previous theoretical investigation,²² we presented a mechanistic account for initial steps encountered in the formation of PCDFs from oxidation of chlorobenzenes. Suggested pathways comprise: (i) initial coupling of chlorobenzenes and chlorophenoxy radicals; (ii) cyclisation of intermediate species into PCDFs; and, (iii) unimolecular loss of H/Cl from pre-PCDF intermediates. To this end, our aim in this paper is two-fold. Firstly, to describe initial oxidative decomposition pathways of a monobromobenzene (MBB) molecule leading to the generation of bromophenoxy radicals. Secondly, to acquire reaction and activation enthalpies for steps leading to the production of PBDEs, PBBs and pre-PBDF intermediates.

Computational Methodology

We use the hybrid density functional theory (DFT) at M062X²³ level along with the basis set of 6-311+G(d,p)²⁴ to carry out structural optimisations, energy calculations and estimation of vibrational frequencies. It has been shown that, the M062X functional offers reliable performance in estimating kinetic and thermochemical parameters for general application in organic reactions. Gaussian09 package executes all computations.²⁵ All transition structures contain one and only one negative vibrational frequency along the specified reaction coordinate. The latter has been confirmed by performing intrinsic reaction coordinate calculations (IRC).

Results and Discussion

Formation of bromophenoxy radicals

In Figure 1, we present reaction enthalpies for initial decomposition pathways in a MBB molecule. We calculate bond dissociation enthalpy (BDH) for a C-Br bond to be 337.4 kJ/mol, significantly lower than the aromatic C-H bonds (412.5 kJ/mol). Thus, unimolecular decomposition of MBB most likely commences with the loss of a Br atom. Due to the relatively weak C-Br bonds, decomposition of brominated hydrocarbons often establishes a bromine-rich environment. Likewise, C_xH_y entities in polymeric materials serve as a source of H atoms. Thus, we compute enthalpy differences for bimolecular reactions of Br and H radicals with the MBB molecule. Br radicals preferentially abstract hydrogen atoms whereas H radicals selectively abstract Br atoms.¹⁸ Reaction enthalpies for abstraction of an H atom from the three distinct sites in MBB reside in the very narrow range of 106.9 – 111.6 kJ/mol. On the other hand, the formation of HBr via abstraction of Br atom by H atom is slightly exothermic by 20.5 kJ/mol.

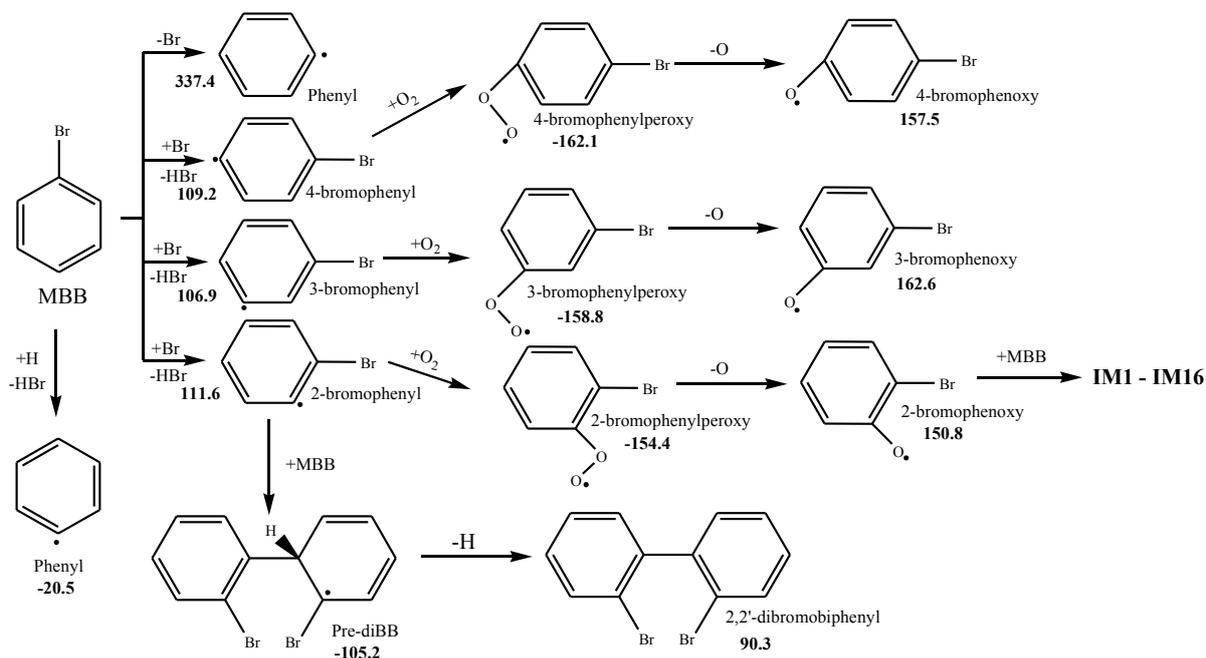


Figure 1: Reaction pathways for the formation of bromophenyl and bromophenoxy radicals from MBB molecule and 2,2'-dibromobiphenyl from the dimerisation reaction of MBB and a 2-bromophenyl radical. Values denote reaction enthalpies in kJ/mol, calculated at 298.15 K.

Initial decomposition of MBB and its bimolecular reactions with H and Br atoms yield three bromophenyl/phenyl radicals. The introduction of oxygen molecule to the vacant radical sites in bromophenyl radicals produces their peroxy adducts through considerably exothermic reactions of 154.3 – 162.1 kJ/mol. Fission of the O-O bonds in the three bromophenylperoxy adducts generates the corresponding bromophenoxy radicals. These reactions are endothermic by 150.8 – 162.6 kJ/mol.

Formation of pre-intermediates for PBBs and PBDFs

The lowermost part of Figure 1 shows that, the addition of a MBB molecule to a 2-bromophenyl radical forms a 2,2'-dibromobiphenyl molecule in a two-step mechanism. In the first step, the reaction of the MBB molecule with the 2-bromophenyl radical is exothermic by 105.2 kJ/mol and produces the intermediate structure of pre-diBB. Loss of the out-of-plane H atom in pre-diBB incurs modest endothermicity of 90.3 kJ/mol and affords the 2,2'-dibromobiphenyl molecule. We have shown recently that, the oxidative transformation of 2,2'-dibromobiphenyl evolves in very complex, yet considerably exothermic mechanism to form dibenzofuran (DF), 1-bromodibenzofuran (1-MBDF) and 4-bromodibenzofuran (4-MBDF).¹⁹

Herein, we only consider products from bimolecular reactions of the MBB molecule with one bromophenoxy radical, the 2-bromophenoxy (2-BPxy) radical. Figure 2 depicts structures for all products arising from bimolecular reactions of MBB with the 2-BPxy radical. Owing to its resonance-stabilised structure, spin density in the 2-BPxy radical appears on the phenoxy O atom as well as on *ortho* C(Br), *ortho* C(H) and *para* C(H) sites. As a result, 16 different structures can potentially form from bimolecular reactions of the MBB molecule and the 2-BPxy radical. The addition of phenoxy O atom in the 2-bromophenoxy radical at the C(Br) position in the MBB molecule expels the Br atom in MBB molecule and yields the 2-bromodiphenyl ether molecule. Intermediates IM2 – IM4 form upon coupling of the phenoxy O atom in the 2-bromophenoxy radical at the three C(H) sites in the MBB molecule. Formation of IM1 – IM4 requires very similar activation enthalpies (78.3 – 84.9 kJ/mol). Loss of H atoms from the ether bridge in the IM2-IM4 structures forms dibromodiphenyl ethers molecules. As we have demonstrated recently, PBDD/Fs are synthesised from PBDEs through a very facile mechanism.¹⁸ Generation of PBDFs from IM2-IM4 occurs via trivial barriers through direct C-C ring-closure reactions. The insertion of an oxygen molecule at an *ortho* position in IM2-IM4 intermediates leads to the production of PBDDs.¹⁸

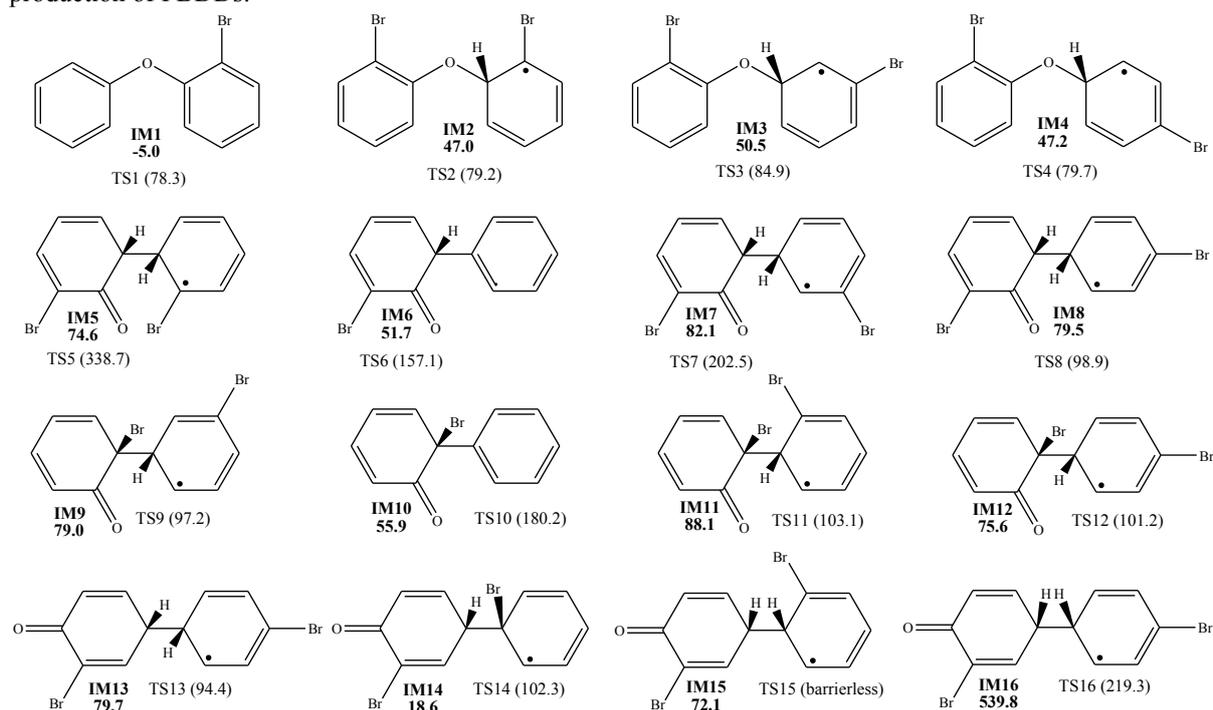
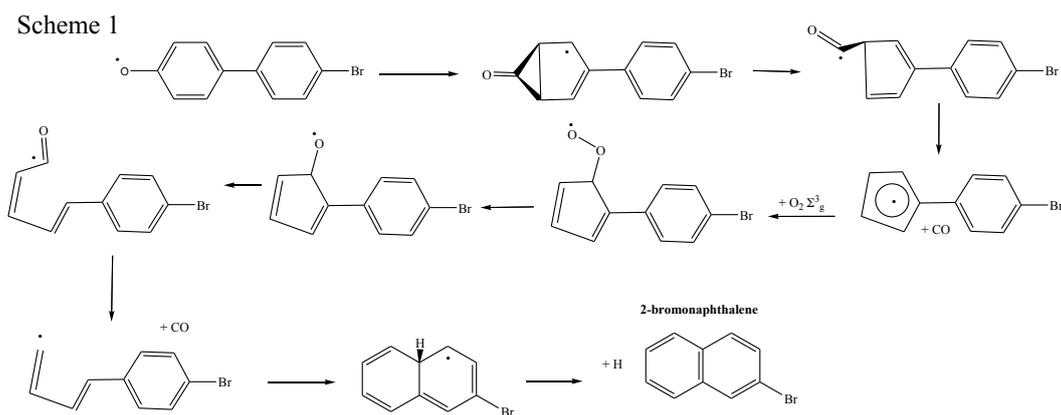


Figure 2: Structures of products from bimolecular reactions of MBB with 2-BPxy radical. All values are in kJ/mol, calculated at 298.15 K.

Structures IM5-IM8 arise in linking of *ortho* C(H) sites in the 2-BPxy radicals to the four different positions in the MBB molecule. Formation of these intermediates requires endothermicity in the range of 51.7 – 82.1 kJ/mol through comparable activation enthalpies. Pairing at the C(Br) site in the MBB molecule releases the Br atom and gives the structure of IM6. Similarly, coupling of the MBB molecule at the *ortho* C(Br) site results in the formation of IM9 – IM12 pre-structures. The presence of the phenoxy O atom in the IM5-IM12 structures at the *ortho* position (with respect to the C-C linkage) enables these moieties to act as direct intermediates for the generation of PBDFs. Ring-cyclisation of the phenoxy O in IM5-IM12 adducts toward an *ortho* site (with respect to the C-C linkage) produces isomers of PBDFs.¹⁹ Condensation reaction of MBB and 2-BPxy into the pre-PBDF IM9-IM12 intermediates takes place through activation enthalpies in the range of 97.2 – 180.2 kJ/mol. All Br and H atoms at the C-C bridges in IM10-IM12 intermediates are very weakly bounded. As a consequence, bimolecular reactions of MBB and 2-BPxy constitute a source for the emission of Br atoms.

Coupling of the MBB molecule at the *para* site of the 2-BPxy radical produces the IM13-IM16 moieties. With the presence of the phenoxy O atom at the *para* position, these intermediates could not act as precursors for PBDFs. Upon the facile loss of Br and H atoms from the C-C bridge, unimolecular decomposition of IM13-IM16 occurs through the so-called ring contraction/CO elimination mechanism. Subsequent attachment of an oxygen molecule to the radical site initiates the formation of bromonaphthalenes as depicted in Scheme 1:



In conclusion, the current study presents mechanistic pathways for the formation of pre-PBDD/F intermediates from oxidation of a MBB molecule. Initial oxidative decomposition of MBB affords bromophenoxy radicals. Bimolecular coupling reactions of MBB and bromophenoxy radicals produce stable molecules such as PBDEs and PBBs. We have shown previously that, the oxidative conversion of PBDEs and PBBs produces PBDD/Fs through a series of reactions marked with low activation enthalpies. Direct ring-cyclisation of several MBB/*ortho* 2-BPxy products generates isomers of PBDFs. Overall, there is a paucity of experimental investigations on the potential of bromobenzenes to form PBDD/Fs. Outcomes of this theoretical study call for a more rigorous experimental investigation into the role of bromobenzenes in the synthesis of PBDD/Fs.

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