# Photodecomposition of bromophenols

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HIGHLIGHTS

- Photodecomposition serves as a potent elimination corridor for BPs in the environment.
- PBs decompose more effectively in the gaseous phase than in the aqueous phase.
- Photoreactivity of BPs decreases along the following sequence *ortho* > *meta* > *para*.
- TDDFT calculations reveal that higher brominated congeners display lower excitations energies, and are more labile to photodebrominate.

GRAPHICAL ABSTRACT
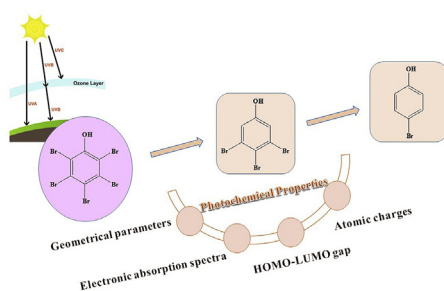
ABSTRACT

Photodecomposition of bromophenols (BPs) represents a potent channel of debromination and elimination of these species in the environment. From this perspective, the present contribution reports geometrical parameters, electronic absorption spectra and excited states of the complete series of BPs in their ground state (S_0), as well as their first singlet exited state (S_1). We calculate excitation energies for $S_0 \rightarrow S_1$ transition within the framework of the time-dependent density functional theory (TDDFT). We estimate and discuss charges on bromine atoms and HOMO-LUMO energy gaps (E^{H-L}) as molecular descriptors for the photoreactivity of BPs and photo-induced debromination mechanism of BPs. Spectral patterns reveal that, as the degree of bromination increases, peaks of absorption spectra red-shift toward wavelengths near 300 nm, for the pentabrominated phenol. Based on the analysis of optimised geometries and Hirshfeld's atomic charges, photodebromination of BPs commences via the loss of an *ortho* Br atom. The excitation energies decrease linearly with increasing number of bromine atoms. This indicates that, higher brominated congeners of BPs photodecompose more readily than lower brominated congeners.

1. Introduction

Bromophenols (BPs) constitute principal components and intermediates in the production of a wide range of brominated flame retardants (BFRs). Structural entities of several BFRs such as tetrabromobisphenol A (TBBA) and polybrominated diphenyl ethers (PBDEs) incorporate BP-like moieties. As a result, thermal decomposition of materials laden with BFRs often produce appreciable amounts of BPs (Weber and Kuch, 2003; Barontini et al., 2004; Barontini and Cozzani, 2006; Grause et al., 2008; Terakado et al., 2011). When non-bonded chemically to the polymeric matrix of treated objects, BFRs can leach out under ambient conditions (Kim et al., 2006; Choi et al., 2009; Zhou et al., 2013). Photodecomposition of desorbed BFRs into BPs represents a chief route for

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Table 1
Comparison of C—Br bond lengths, for all 19 congeners of bromophenols, in ground (S_0) and excited (S_1) states in the gaseous phase. Bond lengths are in Å.

BPs congener	Number of Br atoms	S_0	S_1
2-MBP	1	1.934	2.174
3-MBP	1	1.926	1.906
4-MBP	1	1.926	1.896
2,3-DBP	2(2,3)	1.922; 1.916	2.082; 2.014
2,4-DBP	2(2,4)	1.930; 1.923	2.126; 1.959
2,5-DBP	2(2,5)	1.929; 1.922	2.088; 1.932
2,6-DBP	2(2,6)	1.933; 1.916	2.135; 1.963
3,4-DBP	2(3,4)	1.915; 1.914	2.069; 1.998
3,5-DBP	2(3,5)	1.922; 1.922	2.019; 2.030
2,3,4-TriBP	3(2,3,4)	1.922; 1.907; 1.914	2.045; 2.004; 1.942
2,3,5-TriBP	3(2,3,5)	1.919; 1.913; 1.919	2.030; 2.036; 1.929
2,3,6-TriBP	3(2,3,6)	1.922; 1.913; 1.913	2.092; 1.976; 1.914
2,4,5-TriBP	3(2,4,5)	1.926; 1.912; 1.912	2.027; 1.985; 1.969
2,4,6-TriBP	3(2,4,6)	1.929; 1.920; 1.913	2.086; 1.954; 1.969
3,4,5-TriBP	3(3,4,5)	1.915; 1.905; 1.915	2.015; 1.967; 2.004
2,3,4,5-TBP	4(2,3,4,5)	1.920; 1.907; 1.906; 1.913	1.996; 2.006; 1.944; 1.942
2,3,4,6-TBP	4(2,3,4,6)	1.922; 1.905; 1.913; 1.911	2.051; 1.971; 1.948; 1.919
2,3,5,6-TBP	4(2,3,5,6)	1.920; 1.911; 1.911; 1.904	2.043; 1.972; 1.948; 1.920
2,3,4,5,6-PBP	4(2,3,4,5,6)	1.921; 1.906; 1.907; 1.906; 1.905	1.997; 1.966; 1.948; 1.948; 1.925

Table 2
Comparison of C—Br bond lengths, for all 19 congeners of bromophenols ,in ground (S_0) and excited (S_1) states in the aqueous phase. Bond lengths are in Å.

BPs congener	Number of Br atoms	S_0	S_1
2-MBP	1	1.953	2.209
3-MBP	1	1.952	2.232
4-MBP	1	1.953	1.898
2,3-DBP	2(2,3)	1.940; 1.939	2.091; 2.054
2,4-DBP	2(2,4)	1.946; 1.947	2.133; 1.988
2,5-DBP	2(2,5)	1.946; 1.946	2.130; 1.986
2,6-DBP	2(2,6)	1.950; 1.941	2.125; 2.029
3,4-DBP	2(3,4)	1.938; 1.938	2.103; 2.027
3,5-DBP	2(3,5)	1.946; 1.945	2.081; 2.080
2,3,4-TriBP	3(2,3,4)	1.939; 1.928; 1.937	2.039; 2.039; 1.963
2,3,5-TriBP	3(2,3,5)	1.935; 1.934; 1.941	2.028; 2.071; 1.944
2,4,5-TriBP	3(2,4,5)	1.941; 1.934; 1.934	1.977; 2.029; 2.022
2,4,6-TriBP	3(2,4,6)	1.944; 1.942; 1.936	2.072; 1.972; 2.014
3,4,5-TriBP	3(3,4,5)	1.937; 1.927; 1.937	2.031; 1.992; 2.030
2,3,4,5-TBP	4(2,3,4,5)	1.935; 1.927; 1.927; 1.934	1.980; 2.030; 1.969; 1.960
2,3,4,6-TBP	4(2,3,4,6)	1.937; 1.924; 1.933; 1.932	2.047; 1.996; 1.966; 1.930
2,3,5,6-TBP	4(2,3,5,6)	1.934; 1.930; 1.931; 1.926	2.022; 1.986; 1.977; 1.953
2,3,4,5,6-PBP	4(2,3,4,5,6)	1.934; 1.925; 1.928; 1.926; 1.926	1.978; 1.978; 1.966; 1.971; 1.943

diminishing the overall environmental burden of BPs. For instance, de Wit (2000) found that, 2,4,6-tribromophenol evolves as a major product from exposure of TBBA to strong UV light. In addition to their well-established role as building blocks for the notorious polybrominated dibenzo-*p*-dioxin and polybrominated dibenzofuran (PBDD/F) pollutants (Evans and Dellinger, 2003, 2005; Schüler and Jager, 2004; Arnoldsson et al., 2012; Altarawneh and Dlugogorski, 2013; Altarawneh et al., 2009a,b), bromophenols exhibit strong toxicological effects (Lau et al., 1984; Olsen et al., 2002), depending primarily on the pattern and degree of bromination (Eljarrat and Barceló, 2011).

Beside the oxidation of BPs by atmospherically-persistent OH radicals (Evans and Dellinger, 2006), the photodecomposition process induced by sun radiation affords another potent elimination pathway of these chemicals in the environment (Komiya et al., 1974). Using theoretical and experimental approaches, great deal of research has revealed fundamental understanding pertinent to photodissociation of halogenated aromatics in aqueous media (Chen et al., 2009; Loeff et al., 1970; Tang et al., 2003; Fang et al., 2008; Wang et al., 2012; Xie et al., 2009; Zeng et al., 2008). Depending on the type and position of halogens, fission of the halogen—carbon bond proceeds via multiple electronic states. A

detailed dynamic analysis by the first principle calculations attributes the photodecomposition of aryl halides to non-adiabatic phenomena in which intersystem crossing occurs at 266 nm and involves a transition from singlet excited state to triplet excited state (Freedman et al., 1980; Gu et al., 2001; Borg et al., 2006; Han and He, 2007).

Studies on photodecomposition of brominated aromatics have mainly focused on PBDEs (Fang et al., 2008; Zeng et al., 2008) and bromobenzenes (Loeff et al., 1970; Tang et al., 2003). Relatively, few enquiries investigated photo-induced decomposition of monobromophenols by flash spectroscopy and photo fragment translational spectroscopy techniques (Joschek and Miller, 1966; Lipczynska-Kochany, 1992). These studies reported a monobromophenol molecule releasing a bromine atom from breaking the C—Br bond and a hydrogen atom originating from the fission of the hydroxyl O—H bond, under the UV radiation. Joschek and Miller (1966) suggested that, the photodecomposition of the C—Br bond in the monobromophenols proceeds via absorption of 472.7 kJ mol^{-1}. This considerable amount of energy engenders the excitation of the molecule and fission of the C—Br bond. During the photolysis process, fission of the C—Br bond in the ground state and the formation of the first lying singlet excited state require 343.0 kJ mol^{-1}