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Photochemical reactions between bromophenols and hydroxyl radical generated in aqueous solution: A laser flash photolysis study



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ABSTRACT

Bromophenols (BPs) have been reported as precursor compounds to form some more toxic pollutants such as hydroxylated polybrominated diphenyl ethers (OH-PBDEs), polybrominated dibenzo-*p*-dioxin/dibenzofurans (PBDD/Fs), but only limited data about environmental fate of BPs is available to assess their ecological risks. In this study, the photochemical reactions of eight BPs and hydroxyl radical ($\cdot\text{OH}$) generated from NaNO_2 were investigated using laser flash photolysis (LFP) in aqueous solution. Two transient intermediates, OH adducts and bromophenoxy radicals, were identified after irradiation, and the possible reaction pathways were proposed. Both numbers and positions of bromine atoms significantly affected their formation by different mechanisms. Lifetimes of all eight bromophenoxy radicals were also determined to be longer than 100 μs . More OH adducts were generated at lower pH values and higher Fe (III) concentrations, while the relative amounts of bromophenoxy radicals were bigger at higher pH values and Fe (III) concentrations. In addition, fulvic acid (FA) showed promoting effects for the formation of the two transient species in low concentration, while inhibitive effects in high concentration. These results will provide vital insights into the photochemical process of BPs in natural water environments.

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1. Introduction

Brominated phenols (BPs) are widely used in many industrial products such as polymer intermediates, flame retardant intermediates and wood preservatives [1–3]. At present, BPs have been globally detected in a variety of abiotic and biotic matrices including waters, air, sediments, fish, birds [3–5], as well as human milk and serum [6]. For example, the total concentrations of 2,4-DBP and 2,4,6-TBP in the rivers and seawater from Korea were up to 118 and 52.9 ng/L, respectively [1]. The total concentration of bromophenols detected in sea food (*i.e.* clam and oyster) in Hong Kong was up to 321.8 ng/g [7].

Toxicologic studies indicate that BPs has possible adverse effects on aquatic organisms and human bodies including embryo toxicity [8], reproduction toxicity [4] and potential carcinogenicity [9]. It is also noted that BPs are potential precursor compounds that transform into some more toxic pollutants such as hydroxylated polybrominated diphenyl ethers (OH-PBDEs) and polybrominated dibenzo-*p*-dioxin/dibenzofurans (PBDD/Fs) under certain

conditions [10–13]. Recently, Jiang and coworkers [10] have reported that BPs could be oxidized to OH-PBDEs by potassium permanganate in wastewater treatment plants (WWTP). Our previous studies have demonstrated that 2,4-DBP and 2,6-DBP could dimerize to form OH-PBDEs and hydroxylated polybrominated biphenyls (OH-PBBs) under simulated sunlight, in which bromophenoxy radicals were an important intermediates [11,12]. Yu et al. have found that BPs could form PBDD/Fs by the dimerization of bromophenoxy radicals in homogeneous gas phase [13]. Therefore, to study the environmental transformation behaviors of BPs, particularly involving reaction intermediates, is very important to assess the ecological risks of this class of organic pollutants.

The photochemical reaction plays important role in the transformation behaviors of organic pollutants (OPs) in natural water environments, in which reactive oxygen species (ROS) are often involved such as the hydroxyl radical ($\cdot\text{OH}$), singlet oxygen, superoxide, hydrogen peroxide and triplet excited states [14]. Among them, $\cdot\text{OH}$ has been considered to be a very powerful oxidant with the redox potential of 2.8 eV [15]. Major photochemical $\cdot\text{OH}$ sources have been identified as nitrate, nitrite, and dissolved organic matters (DOM) in previous studies [16,17]. The steady-state concentration of $\cdot\text{OH}$ in the surface water generally

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ranges from 10^{-17} M to 10^{-15} M [18,19]. Higher concentration of $\bullet\text{OH}$ (10^{-14} – 10^{-12} M) has been observed in the surface water contaminated by acidic mine drainage [20]. Thus, there is a big possibility for $\bullet\text{OH}$ to react with contaminants due to its higher oxidability and concentration in natural waters. For example, $\bullet\text{OH}$ has been reported to be the key reactive intermediate in the photo-transformation process of pesticides and pharmaceuticals in the aqueous environments [21]. Therefore, in order to understand the photo-transformation of BPs in natural waters, it is very necessary to investigate the photochemical reactions of BPs and $\bullet\text{OH}$.

In this study, the major objective was to investigate the photochemical reaction of all eight BPs with $\bullet\text{OH}$ in aqueous solutions using laser flash photolysis (LFP) technique, which is a powerful tool for spectroscopic and kinetic determination of both primary photophysical transformations and rapid chemical reactions. The influences of numbers and substituted positions of bromine atoms on the photochemical reaction were also studied. In addition, the effects of environmental factors such as pH values, Fe (III), and fulvic acid (FA) on the formation of reaction intermediates were explored. These findings advanced our understanding of environmental fate of BPs, and their ecological risk in sunlit water bodies.

2. Materials and methods

2.1. Chemicals

All eight bromophenols (>99% purity) including 2-bromophenol (2-BP), 3-bromophenol (3-BP), 4-bromophenol (4-BP), 2,4-dibromophenol (2,4-DBP), 2,6-dibromophenol (2,6-DBP), 3,5-dibromophenol (3,5-DBP), 2,4,6-tribromophenol (2,4,6-TBP) and pentabromophenol (PBP) were purchased from Acros Organics (New Jersey, USA). The structures of eight BPs are shown in Fig. S1, and the ground-state spectra of eight BPs and NaNO_2 are presented in Fig. S2. Acetonitrile and ethanol were of HPLC grade and from Tedia (Fairfield, Ohio, USA). Sodium azide (98%) was purchased from J&K Scientific Ltd. (Beijing, China). $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, H_2SO_4 , NaOH , NaNO_2 were reagent grade and used without further purification. All aqueous solutions were prepared using ultrapure water (18 M Ω cm, 25 °C) obtained from an OKPURE water system (Laikie Instrument Co., Ltd., Shanghai, China).

2.2. Laser flash photolysis (LFP) experiments

A LP920 LFP spectrometer (Edinburgh Instruments Ltd., UK) equipped with a frequency tripled Q-switched Nd: YAG laser (Brilliant) was employed. The third harmonic (266 nm, 355 nm) oscillation of laser (25 mJ/pulse, HRFM 4 ns) was used for excitation. The irradiation light quanta were 3.34×10^{16} and the absorbed light quanta of all the species were calculated (Table S1). The samples were bubbled with nitrogen gas (N_2) for 15 min, transferred into a 1 cm quartz cuvette, and then sealed from the atmosphere. A xenon lamp (450 W) was used as the probe light to monitor the formation and subsequent decay of transient species. The temporal profiles were recorded using a monochromator (TMS300) equipped with a photomultiplier (Hamamatsu R928) and a digital oscilloscope (Tektronix, TDS3012C). The transient absorption spectra were measured by an intensified charged-coupled device (ICCD) with a gate time of 1.5 μs (width of the oscilloscope trigger pulse), and a 0.2 μs time delay (the delay between the laser flashlamp pulse and the oscilloscope trigger pulse) (Andor, DH 720). All LFP experiments were performed at 20 ± 1 °C.

2.3. Source of OH radical

Nitrous acid (HNO_2) exists widely in atmosphere, rivers, lakes, and oceans (Reisinger, 2000; Okafor and Ogbonna, 2003). In this study, NaNO_2 was used to generate $\bullet\text{OH}$ by photolysis and each sample (1 mM) was added with 0.5 mM NaNO_2 at pH=6 unless otherwise specified. H_2SO_4 (1 M) and NaOH (1 M) was used to adjust the pH by pH meter.

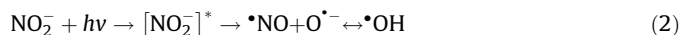
2.4. Density functional theory (DFT) calculation

The DFT calculation was performed with Gaussian 09 suite of programs Frisch et al. [22]. All geometries were fully optimized at the B3LYP/6-31+G (d,p) Lee et al. [23]. The bulk solvent effect of water was considered by using the integral equation formalism polarized continuum model (IEFPCM) based on the self-consistent-reaction-field (SCRF) method [24].

3. Results and discussion

3.1. Photochemical reactions between BPs and NaNO_2 induced by laser flash photolysis

Transient absorption spectra of N_2 -saturated 1 mM BPs and 0.5 mM NaNO_2 mixed aqueous solutions in the 266 nm laser flash photolysis are shown in Fig. 1. The main absorption bands of transient species for eight BPs were observed in the region of 290–350 nm and 380–450 nm, respectively, which suggested that two kinds of different transient species were generated during the process. $\bullet\text{OH}$ can be generated using NaNO_2 under irradiation and further react with BPs. Mvula et al. and Land et al. reported that the prominent product from the reaction between aromatic compound and $\bullet\text{OH}$ was OH adduct which exhibited a broad absorption in 275–375 nm with peak at 330 nm [25,26]. The transient absorption spectra observed in this study were of 290 nm–350 nm with peak centered around 300 nm (2-BP, 4-BP), 310 nm (3-BP, 2,6-DBP, 2,4-DBP, 3,5-DBP, 2,4,6-TBP) and 330 nm (PBP), which were similar to the above absorbance spectrum. When efficient $\bullet\text{OH}$ scavengers such as ethanol and iso-propanol were added to the reaction solution, the formation of the absorption band peak at 310 nm was observed to be strongly suppressed immediately (Fig. S3). Based on the experiments results and literatures, the transient absorption band ranging from 290 nm to 350 nm with peak around 310 nm was assigned to BP-OH adducts which may be formed through the following reactions [27,28]:



Various phenoxy radicals showed characteristic double absorbance peaks around 400 nm [26,29]. The transient species with absorbance ranging from 380 nm to 450 nm with double peaks centered around 400 nm for 2-BP, 4-BP, 2,4-DBP, 2,6-DBP in this work were assigned as bromophenoxy radicals. Compared with mono- and di- substituted BPs, the wider absorption bands of bromophenoxy radicals were formed by TBP and PBP at the range of 400–480 nm with the maximum absorption wavelength at 440 nm and 470 nm. The results were in accordance with that of Terzian et al's. [30] which reported that pentabromophenoxy radicals had the maximum absorption wavelength of 470 nm.

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