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Direct and dissolved oxygen involved photodegradation of MeO-PBDEs in water

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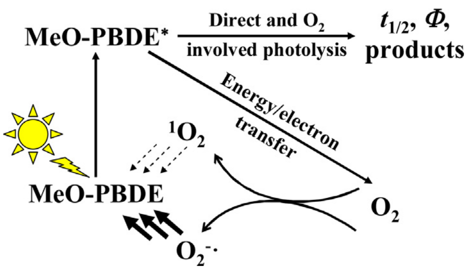
HIGHLIGHTS

- Photodegradation of MeO-PBDEs in pure water is susceptible to their structures.
- $^1O_2$ and $O_2^{-\bullet}$ are photo-generated in the aerated MeO-PBDEs solutions.
- $^1O_2$ can not oxidize MeO-PBDEs; while $O_2^{-\bullet}$ behaves contrarily.
- Hydrodebromination is the major elimination pathway for MeO-PBDEs.
- Direct photolysis half-lives of MeO-PBDEs in the surface waters are evaluated.

GRAPHICAL ABSTRACT



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ABSTRACT

Photodegradation has been proved to be a crucial way of elimination for polybrominated diphenyl ethers (PBDEs) and hydroxylated PBDEs (HO-PBDEs). However, it is still unknown whether methoxylated PBDEs (MeO-PBDEs) can also undergo photodegradation. In this study, 4′-MeO-BDE-17, 5-MeO-BDE-47, 5′-MeO-BDE-99, 6-MeO-BDE-47 and 6-MeO-BDE-85 were selected as targets to investigate their photodegradation in water. Meanwhile, the effects of dissolved oxygen on the photoreactions of MeO-PBDEs were also unveiled. Simulated sunlight experiments indicate that 6-MeO-BDE-47 resisted photodegradation for 20 h, while other MeO-PBDEs underwent relatively fast photodegradation, which was greatly susceptible to the substitution patterns of methoxyl and bromine. Photo-excited MeO-PBDEs (except 6-MeO-BDE-47) can sensitize dissolved oxygen to generate singlet oxygen ($^1O_2$) and superoxide anion radical ($O_2^{-\bullet}$). The generated $^1O_2$ cannot degrade the MeO-PBDEs, whereas $O_2^{-\bullet}$ was reactive with MeO-PBDEs. The contribution of dissolved oxygen to the photodegradation of 4′-MeO-BDE-17 and 6-MeO-BDE-85 was negligible; while the negative contribution was observed for 5-MeO-BDE-47 and 5′-MeO-BDE-99. Hydrodebromination was a crucial photodegradation pathway for MeO-PBDEs (excluding 4′-MeO-BDE-17 and 6-MeO-BDE-47). Eventually, direct photolysis half-lives of MeO-PBDEs except 6-MeO-BDE-47 in the surface waters at 40 N latitude were calculated to be 1.35–3.46 d in midsummer and 6.39–17.47 d in midwinter.

1. Introduction

In recent years, methoxylated polybrominated diphenyl ethers (MeO-PBDEs) have received increasing concern due to their presence in biota [1–5] and toxicological effects [6–11]. To date, many *ortho*-, *meta*- and *para*-MeO-PBDEs have been detected in

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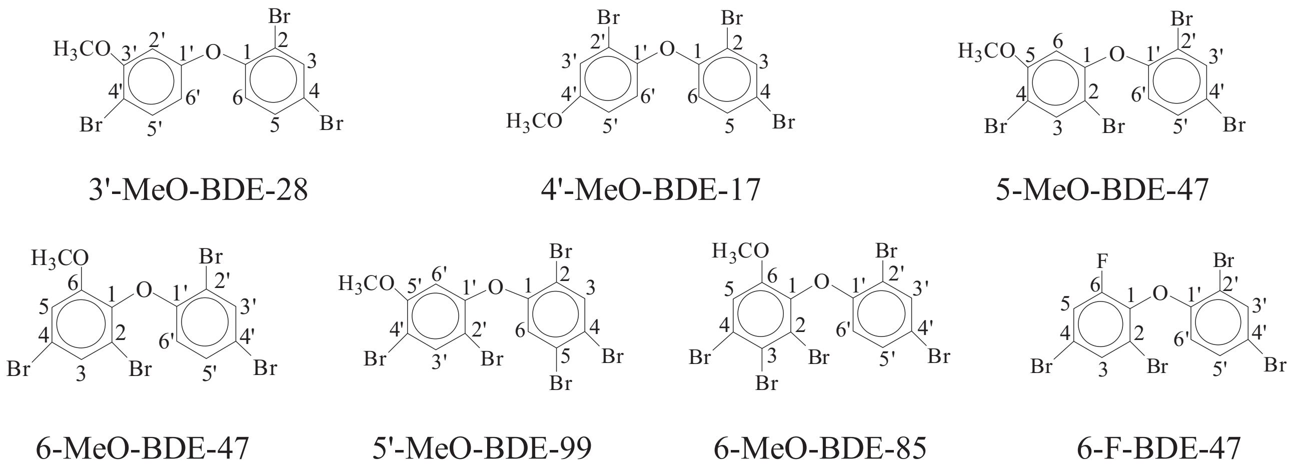

Fig. 1. Molecular structures of the MeO-PBDEs and 6-F-BDE-47 under study. The serial number of carbon atoms follows IUPAC chemical nomenclature.

various environmental matrices, e.g., air, river water, seawater, soil and sediments [12–18]. It is known that some *ortho*-MeO-PBDEs (e.g., 6-MeO-BDE-47 and 2′-MeO-BDE-68) in the environmental media mainly derive from natural sources [19]. As MeO-PBDEs structural analogues, polybrominated diphenyl ethers (PBDEs) and hydroxylated PBDEs (HO-PBDEs) display distinguishable sources from MeO-PBDEs. As the only source of PBDEs, human activities cause the release of industrial PBDEs products into the environment [20]. Some studies [21–23] have proved that HO-PBDEs can be produced in the reactions between PBDEs and hydroxyl radical, besides their natural sources [24,25]. In addition, Wan et al. [1] proposed the evidence for the metabolic transformation between HO-PBDEs and MeO-PBDEs in marine organisms. Some MeO-PBDEs with relatively high $\log K_{OW}$ (>5) [26] can be bioaccumulated and biomagnified in the human bodies [3,4,27] through seawater and freshwater food webs [27,28]. Due to the impact of toxicological effects, MeO-PBDEs posed the exposure risks to organisms. To understand the fate and transport of MeO-PBDEs in the environment, it is important to understand the transformation kinetics and mechanisms of MeO-PBDEs.

PBDEs and HO-PBDEs have been proved to undergo photodegradation [29–36], which is susceptible to the compound structures [30,32,34,35] and surrounding media [29–31,33–36]. Many studies on the photodegradation of PBDEs were performed in organic solvents instead of a water environment, due to the low solubility of PBDEs in water [37]. It is known that organic solvents have different physicochemical properties from water, such as hydrogen-donating ability and reactive oxygen species (ROS) quenching capabilities [30,38]. Thus, the photodegradation behavior of PBDEs in organic solvents can be distinctive with that in water or mixed organic solvent/water [30,39]. For example, Leal et al. [39] determined the quantum yield (Φ) of BDE-209 in water to be 0.010 ± 0.001, which is about 20-fold smaller than that in ethanol. Eriksson et al. [30] observed almost 2-fold faster photodegradation for PBDEs in methanol than that in mixed methanol/water (80:20, v:v) solution.

From the previous studies, we hypothesized that some MeO-PBDEs can also be photodegradable, and the different Br- and MeO-substitution patterns may cause different photodegradation kinetics. Meanwhile, we employed water instead of organic solvents as the medium, so as to give an estimation of MeO-PBDEs photodegradation kinetics in the aquatic environment. Hydrodebromination has been proved to be a crucial photodegradation pathway for PBDEs, resulting in products with less brominated PBDEs [29–32]. In this study, we managed to identify debrominated products and discern whether hydrodebromination is also the main photodegradation pathway for MeO-PBDEs in water.

Most photochemical reactions occur at the lowest excited singlet states (S_1) or triplet states (T_1). Dissolved oxygen may quench the excited states (S_1 or T_1) via energy/electron transfer [40,41]. The electron configuration of ground state O_2 is triplet ($^3\sum_g{}^-$) [42]. Thus, O_2 can effectively quench the photo-excited triplet state compounds [43,44] and lead to the formation of singlet oxygen ($^1O_2$). $^1O_2$ has two electron configurations, which are $^1\sum_g{}^+$ and $^1\Delta_g$. $^1\sum_g{}^+$ is highly energetic, unstable and easily transforms into $^1\Delta_g$. Thus, $^1\Delta_g$ is the most common electron configuration of $^1O_2$ [42]. Zhang et al. [41] employed simulated sunlight experiments supported by density functional theory calculation to elucidate the generation pathways of $^1O_2$ and $O_2{}^{-\bullet}$ in a 2-phenylbenzimidazole-5-sulfonic acid solution. However, it is not clear whether the excited states of MeO-PBDEs can induce O_2 to generate $^1O_2$ and $O_2{}^{-\bullet}$, and how these ROS react with MeO-PBDEs.

In this study, five MeO-PBDEs that are frequently detected in the aquatic environment were selected as target compounds, which are 4′-MeO-BDE-17, 5-MeO-BDE-47, 5′-MeO-BDE-99, 6-MeO-BDE-47 and 6-MeO-BDE-85 (Fig. 1). The objectives of this study are to determine the photolytic half-lives ($t_{1/2}$), Φ and products of MeO-PBDEs in water. In addition, the role of O_2 in the photoreactions of MeO-PBDEs was also examined.

2. Materials and methods

2.1. Materials

Sources of the chemicals used in this study are described in Supplementary materials.

2.2. Photodegradation experiments

MeO-PBDEs water solutions (5 μg/L) were prepared with acetonitrile as co-solvent (0.5% by volume) [45]. which is detailed in Supplementary materials. To investigate the role of dissolved oxygen in the photodegradation of MeO-PBDEs, both aerated and deaerated water solutions were prepared. The latter was obtained through deaeration with N_2.

All the photochemical experiments were performed with an XPA-1 merry-go-around photochemical reactor (Xujiang Technology Co., Ltd.). A monochromator (SP-300, Acton Research Corporation) and a spectrophotometer (UV2800, Hitachi) were employed to measure the emission spectra of two light sources (300 and 500 W high-pressure Hg lamps) and the transmittance of