PHOTOTRANSFORMATION OF BROMOPHENOLS IN THE SIMULATED SEAWATER

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Introduction

In recent years, brominated aromatic compounds such as bromophenols (BPs) are the subjects of many studies due to their environmental significance as persistent and potentially hazardous substances[1]. BPs are widely used as flame retardants and intermediates for the yield of other retardants[2], thus they are universally distributed in the effluents of waste water treatment plants[3] and surface water[4]. It should be noticed that BPs have been demonstrated to convert to PBDDs by high-temperature homogeneous gas-phase reaction in waste incinerators[5] or bromoperoxidase-catalyzed dimerization in some marine organisms[6], indicating that more toxic compounds generated by transformation of BPs.

The photochemical process plays an important role in the transfer and transformation of organic pollutants in abiotic environment[7]. In marine environment, several methoxylated and hydroxylated polybrominated biphenyl ethers (MeO-PBDEs, OH-PBDEs) have been structurally identified as natural products[8,9]. Both phenol and chlorophenols (CPs) have been observed to produce halogenated hydroxydiphenyl ethers during the photochemical process[10]. Considering the structural similarity between bromophenols and chlorophenols, it is rational to hypothesize the possibility for the formation of more toxic compounds through the photopolymerization of bromophenols.

In this work, 2,4-dibromophenol (2,4-diBP) was used as precursor to investigate the phototransformation process of BPs in simulated seawater. Some crucial factors in seawater, such as inorganic ion (Cl^-/Br^-) and photoactive components (Fe(III)), which could markedly influence the photochemical process of organic compounds[11], were selected to investigate their influence on the phototransformation of 2,4-diBP. Photopolymerization products of 2,4-diBP were also identified. It is helpful for better understanding of the natural transformation fate of brominated organic compounds and its potential impacts on the ecosystem.

Materials and methods

2,4-diBP was purchased from Acros Organics (New Jersey, USA). The photochemical experiments were performed in a “merry-go-round” photoreactor equipped with a 350 W Xenon lamp and 290 nm cut-off filters to simulate sunlight. Simulated seawater used in the experiment was prepared using Milli-Q water, NaCl and NaBr to get the concentration of 0.5 M Cl^- and 0.8 mM Br^-, and the pH was adjusted to 8.0, similar as natural seawater. Solutions for photolysis were put in quartz tubes. Photolysis products were extracted by dichloromethane. The quantification of 2,4-diBP was performed by HPLC (2695-2996, Waters, USA). Dimer products of 2,4-diBP phototransformation were analyzed by GC-MS (6890/5973, Agilent, USA) equipped with the DB-5MS (30 m × 0.25 mm i.d. × 0.25 µm film, J&W Scientific, Folsom, CA).

Results and discussion

Fig.1 shows the 2,4-diBP transformation of different initial concentrations in simulated seawater with 1µM Fe(III) under simulated sunlight. It was clear that the transformation of 2,4-diBP was quite fast in the first 60 minutes, and was transformed completely in 180 minutes. Interestingly, 2,4-diBP degraded faster with initial concentration of 100 μgL^{-1} than that of 10 μgL^{-1}.

Simultaneously, the effect of Cl^-/Br^- and Fe(III) on the phototransformation of 2,4-diBP was also studied, as shown in Fig. 2. It was obvious that less than 40% 2,4-diBP was degraded in the Milli-Q water, lower than that in the presence of individual Cl^-/Br^- or Fe(III). By contrast, 80% 2,4-diBP was degraded in the coexistence of Cl^-/Br^- and Fe(III), which was twice as much as that in the Milli-Q water, indicating that Cl^-/Br^- and Fe(III) are beneficial for 2,4-diBP phototransformation.

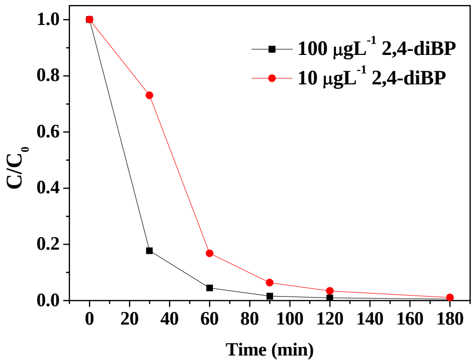


Fig. 1 2,4-diBP transformation as a function of irradiation time in the presence of different 2,4-diBP concentrations in the simulated seawater with 1µM Fe(III) .

With the addition of photosensitive Cl^-/Br^- or Fe(III), light absorbance of solutions may be enhanced, resulting in the faster transformation of 2,4-diBP in the coexistence of Cl^-/Br^- and Fe(III). Therefore, experiments about the UV-Visible absorbance of the solutions used in above experiments were carried out. Fig. 3 shows that all the solutions display broad absorbance bands with a maximum near 287 nm. However, absorbance bands tailed off to approximately zero absorbance around 305 nm in solutions without Fe(III), while broadened to 370 nm and 390 nm with the addition of Fe(III) in Milli-Q water and simulated seawater, respectively. Thus, solutions with Cl^-/Br^- and Fe(III) could absorbed more radiation under simulated sunlight ($\lambda > 290$ nm), leading to faster transformation of 2,4-diBP.

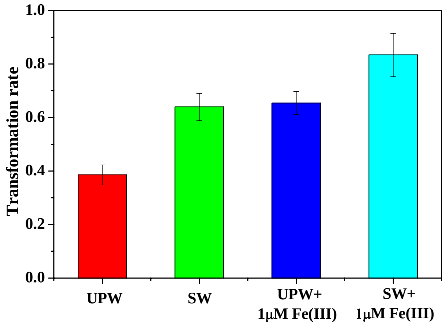


Fig. 2 2,4-diBP (10 μgL^{-1}) degradation irradiated for 60 minutes under different conditions. UPW: Milli-Q water, SW: simulated seawater.

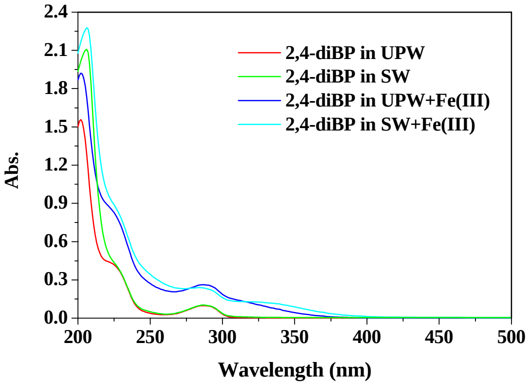


Fig. 3 UV-Visible spectrums of different solutions. UPW: Milli-Q water, SW: simulated seawater.

As shown in Fig. 4, the GC-MS chromatograms of 2,4-diBP phototransformation indicate that the product at the retention time of 20.74 min with mass cluster of 500, 502 and 504 was probably the dimer of 2,4-diBP such as hydroxylated tetrabrominated diphenyl ether (tetrabromo OH-BDE) or dihydroxylated tetrabrominated biphenyl (diOH-TeBB) (Scheme 1).

Possible photopolymerization process of 2,4-diBP in the simulated seawater was illustrated in Scheme 1. 2,4-diBP could photodimerize to form tetrabromo OH-BDE or diOH-TeBB. It could be proposed that phototransformation of BPs in the marine environment could form OH-PBDEs or diOH-PBBs. This work is helpful for better understanding the fate of brominated organic compounds in nature and its potential impacts on the ecosystem.

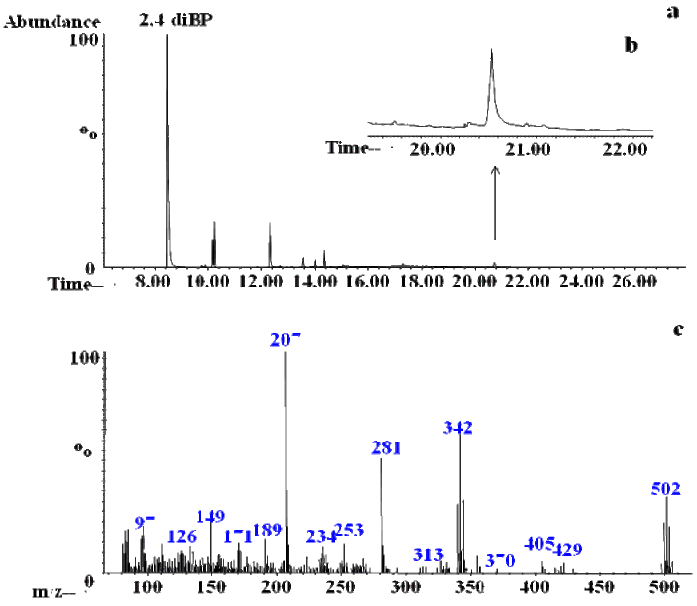
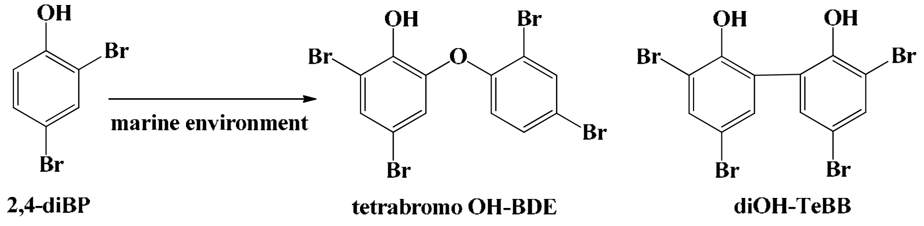


Fig. 4 GC-MS chromatograms of (a) the products of 2,4-diBP phototransformation, (b) zoom region between 20.00 and 22.00 minutes, and (c) the peak corresponding to 2,4-diBP dimer (retention time of 20.74 min).

Scheme 1 Possible photopolymerization process of 2,4-diBP in the marine environment.



Acknowledgements

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