



Effects of halide ions on photodegradation of sulfonamide antibiotics: Formation of halogenated intermediates



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ABSTRACT

The occurrence of sulfonamide antibiotics (SAs) in estuarine waters urges insights into their environmental fate for ecological risk assessment. Although many studies focused on the photochemical behavior of SAs, yet the effects of halide ions relevant to estuarine and marine environments on their photodegradation have been poorly understood. Here, we investigated the effects of halide ions on the photodegradation of SAs with sulfapyridine, sulfamethazine, and sulfamethoxazole as representative compounds. Results showed that halide ions did not significantly impact the photodegradation of sulfapyridine and sulfamethoxazole, while they significantly promoted the photodegradation of sulfamethazine. Further experiments found that ionic strength applied with NaClO₄ significantly enhanced the photodegradation of the SAs, which was attributed to the decreased quenching rate constant of the triplet-excited SAs (³SA^{*}). Compared with ionic strength, specific Cl⁻ effects retarded the photodegradation of the SAs. Our study found that triplet-excited sulfamethazine can oxidize halide ions to produce halogen radicals, subsequently leading to the halogenation of sulfamethazine, which was confirmed by the identification of both chlorinated and brominated intermediates. These results indicate that halide ions play an important role in the photochemical behavior of some SAs in estuarine waters and seawater. The occurrence of halogenation for certain organic pollutants can be predicted by comparing the oxidation potentials of triplet-excited contaminants with those of halogen radicals. Our findings are helpful in understanding the photochemical behavior and assessing the ecological risks of SAs and other organic pollutants in estuarine and marine environment.

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1. Introduction

Antibiotics are widely used in aquaculture, stockbreeding, and human medicine (Sarmah et al., 2006). Antibiotics are of great concern as many of them can induce bacterial resistance and resistant genes even at environmental concentrations (Chen et al., 2013a; Luo et al., 2010; Martínez, 2008; Pruden et al., 2006; Sapkota et al., 2008). It was estimated that in 2013, China consumed 92,700 tons of antibiotics, with approximately 53,800 tons released into the receiving environment (Zhang et al., 2015). Antibiotics have been frequently detected in rivers, lakes, and wastewater effluents (Kümmerer, 2009). Recently, these compounds were also detected in estuarine and coastal waters (Shimizu et al., 2013; Zhang et al., 2013; Zou et al., 2011). For

example, the concentrations of some antibiotics are up to 6.8 µg/L in coastal waters of the China Bohai Bay (Zou et al., 2011). Thus, it is necessary to understand the environmental fate of antibiotics in estuarine and coastal waters for the purpose of ecological risk assessment.

Photochemical degradation has been proved to be a major transformation pathway for organic pollutants in surface waters (García-Galán et al., 2012; Wang and Lin, 2012; Yan and Song, 2014). The photochemical processes can be substantially impacted by the constituents of surface waters (Chen et al., 2013b; Vione et al., 2014). The effects of water constituents relevant to freshwater on photodegradation of antibiotics have been studied extensively (Bahn Müller et al., 2014; Ge et al., 2009; Li et al., 2011, 2014). However, photochemical behavior of antibiotics is poorly investigated in seawater conditions. In seawater, the background constituents differ significantly from those of freshwater, such as halide ions. Previous studies showed that halide ions were important participants in photochemical processes. Zhang et al. (2010)

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observed that halide ions inhibited the photodegradation of 2-phenylbenzimidazole-5-sulfonic acid. Grebel et al. (2012) investigated the effects of halide ions on the photodegradation of 17 β -estradiol, and found that 70% of the decrease was attributed to ionic strength effects. However, Glover and Rosario-Ortiz (2013) referred that halide ions increased the steady state concentration of triplet-excited dissolved organic matter ($^3\text{DOM}^*$) by enhancing the inter-system crossing of DOM from the singlet state to the triplet state. Parker et al. (2013) found that halide ions decreased the quenching rate of $^3\text{DOM}^*$, which led to an increase of steady state concentration of $^3\text{DOM}^*$. Therefore, the underlying mechanisms for the effects of halide ions are intricate, which needs to be further clarified.

Understanding the halogenation mechanisms of organic pollutants is helpful for the risk assessment of halogenated compounds due to their higher toxicity than parent compounds (Beitz et al., 1998; Grebel et al., 2010; Liu et al., 2009; Riu et al., 2011). Previous studies indicated that halide ions can react with $\cdot\text{OH}$ producing halogen radicals, leading to the formation of halogenated products (Grebel et al., 2010; Liu et al., 2009). Liu et al. (2009) observed the formation of chlorinated intermediates in surface saline water mostly due to the formation of $\text{Cl}_2^{\cdot-}$ radical as a consequence of Fe (III) irradiation. Triplet-excited state is an important reactive intermediate in the phototransformation of organic pollutants due to its longer life than that of singlet-excited state (Klán and Wirz, 2009). Jammoul et al. (2009) reported that the triplet-excited state of benzophenone, as a proxy for an aromatic carbonyl compound in the natural sea surface microlayer, could oxidize halide ions to produce halogen radicals. Méndez-Díaz et al. (2014) found that reactions of DOM with photochemically generated reactive halogen species (RHS) may represent an important abiotic natural source of organobromine and organoiodine in seawater. Calza et al. (2008, 2012) observed that photoinduced RHS can react with phenols leading to the halogenation of phenols in seawater. However, to our knowledge, no studies have addressed the photoinduced halogenation processes of antibiotics so far, even though a large number of antibiotics have been detected and reported in estuarine waters and seawater (Bayen et al., 2013; Nödler et al., 2014; Zou et al., 2011). Theoretically, photohalogenation of one organic pollutant may also occur in the presence of halide ions if the triplet-excited state is strong enough to trigger the formation of halogen radicals.

The triplet-excited state was observed to be involved in the photodegradation of some antibiotics (Boreen et al., 2005; Ge et al., 2009; Li et al., 2016; Ryan et al., 2011). It became the purpose of this study to investigate the effects of halide ions on the photodegradation of three sulfonamide antibiotics (SAs), i.e., sulfapyridine, sulfamethazine, and sulfamethoxazole. The three compounds were selected as models because they were frequently detected in estuarine and coastal waters (Nödler et al., 2014; Shimizu et al., 2013; Zhang et al., 2012; Zou et al., 2011). Steady state photochemical experiments were performed to explore the effects of halide ions on the photodegradation of the SAs. The oxidation potential was calculated by density functional theory (DFT) in order to probe the effects of halide ions on the photodegradation. The halogenated products were identified by HPLC coupled with time-of-flight mass spectrometry.

2. Materials and method

2.1. Chemicals

Sulfapyridine, sulfamethoxazole, and sulfamethazine (purity $\geq 99\%$) were purchased from J&K Scientific (China). Sorbic acid (*t,t*-HDA, 99%) was obtained from Tokyo Chemical Industry (Japan). 2,4,6-trimethylphenol (99%) was provided by J&K Scientific

(China). Sodium chloride, sodium bromide, and sodium perchlorate were of analytical grade from Tianjin Kemiou Chemical Reagent (China). Acetonitrile and isopropanol were of HPLC grade from Tedia. Ultra pure water was obtained from a purification system of Shanghai Lakecore Instrument (China). This water was used to prepare photodegradation solutions and HPLC eluent. Other chemical reagents were of analytical grade and were used as received without further purification.

Freshwater (37°45'46.02"N and 119°09'17.37"E) and seawater (37°46'59.26"N and 119°17'11.80"E) were sampled from the Yellow River Estuary located in Dongying (China). Water samples were filtered through 0.45 μm glass filters, and stored at -20°C before use. Concentrations of inorganic ions, TOC, pH and conductivity were measured and listed in Table S1 (for detailed analytical processes see the supplementary material). According to the characterization of the samples, the ionic strength of seawater sample was about 0.5 M.

2.2. Photochemical experiments

An XPA-7 merry-go-round photoreactor (Xujiang Electromechanical Plant, China) with a water-refrigerated 500 W medium-pressure Hg lamp and 290 nm cut-off filters was employed in the photochemical experiments. The light source irradiation spectrum was measured by optical sensors (RAMSES, TriOS) and the main irradiation wavelengths include 313, 334, 365, 405, and 436 nm (Fig. S1). The light intensity in the center of the open quartz tubes (50 mL, inner diameter 2.0 cm) was 5.3 mW/cm^2 . The initial concentration of each SA in the photolytic solutions was 5 μM unless otherwise mentioned. Phosphate buffer 10 mM was used to control pH = 8.3 of the photolytic solutions. Dark controls were performed under the same conditions without light irradiation. With a water-refrigerated equipment, the temperature of solutions with irradiation is about 25–28 $^\circ\text{C}$, which is slightly higher (1–2 $^\circ\text{C}$) than that in dark controls. All the experiments were performed in triplicate.

To test whether triplet-excited state was involved in the direct photodegradation of the SAs, scavenging experiments were carried out using *t,t*-HDA as a quencher of triplet-excited state. The effects of halide ions on the SAs photodegradation were explored. Additionally, NaClO_4 was used to probe the effect of ionic strength on the photodegradation. Furthermore, *t,t*-HDA and 2,4,6-trimethylphenol as probes of triplet-excited state (Grebel et al., 2011; Zeng and Arnold, 2013) were used to explore the effects of ionic strength on the photodegradation. The *t,t*-HDA isomerization rate (R_{HDA}) can be expressed as (Grebel et al., 2011):

$$R_{\text{HDA}} = \frac{F_{\text{T}}k_{t,t\text{-HDA}}[t, t\text{-HDA}]}{k_{t,t\text{-HDA}}[t, t\text{-HDA}] + k_{\text{scavenger}}} \quad (1)$$

where F_{T} is the formation rate of triplet-excited state, $[t, t\text{-HDA}]$ is the initial concentration of *t,t*-HDA (0.2–1.0 mM), $k_{t,t\text{-HDA}}$ is the second-order rate constant for reaction of *t,t*-HDA with triplet-excited state, and $k_{\text{scavenger}}$ is the scavenging rate constant for reaction between scavengers and triplet-excited state. Equation (1) can be re-arranged as:

$$[t, t\text{-HDA}]/R_{\text{HDA}} = [t, t\text{-HDA}]/F_{\text{T}} + k_{\text{scavenger}}/(F_{\text{T}}k_{t,t\text{-HDA}}) \quad (2)$$

Linear regression of $[t, t\text{-HDA}]/R_{\text{HDA}}$ against $[t, t\text{-HDA}]$ can determine F_{T} and $k_{\text{scavenger}}$:

$$F_{\text{T}} = 1/\text{Slope} \quad (3)$$

$$k_{\text{scavenger}} = (k_{t,t\text{-HDA}} \text{ Intercept})/\text{Slope} \quad (4)$$

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