



Elucidating triplet-sensitized photolysis mechanisms of sulfadiazine and metal ions effects by quantum chemical calculations



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HIGHLIGHTS

- Triplet-sensitized photolysis mechanism of SDZ was electron transfer or H transfer.
- SDZ⁰ and SDZ⁻ showed different triplet-sensitized photolysis routs.
- Presence of Mg²⁺, Ca²⁺, or Zn²⁺ promoted triplet-sensitized photolysis of SDZ⁰.
- Presence of Mg²⁺, Ca²⁺, or Zn²⁺ inhibited triplet-sensitized photolysis of SDZ⁻.

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ABSTRACT

Sulfadiazine (SDZ) mainly proceeds triplet-sensitized photolysis with dissolved organic matter (DOM) in the aquatic environment. However, the mechanisms underlying the triplet-sensitized photolysis of SDZ with DOM have not been fully worked out. In this study, we investigated the mechanisms of triplet-sensitized photolysis of SDZ⁰ (neutral form) and SDZ⁻ (anionic form) with four DOM analogues, i.e., fluorenone (FL), thioxanthone (TX), 2-acetonaphthone (2-AN), and 4-benzoylbenzoic acid (CBBP), and three metal ions (i.e., Mg²⁺, Ca²⁺, and Zn²⁺) effects using quantum chemical calculations. Results indicated that the triplet-sensitized photolysis mechanism of SDZ⁰ with FL, TX, and 2-AN was hydrogen transfer, and with CBBP was electron transfer along with proton transfer (for complex SDZ⁰-CBBP2) and hydrogen transfer (for complex SDZ⁰-CBBP1). The triplet-sensitized photolysis mechanisms of SDZ⁻ with FL, TX, and CBBP was electron transfer along with proton transfer, and with 2-AN was hydrogen transfer. The triplet-sensitized photolysis product of both SDZ⁰ and SDZ⁻ was a sulfur dioxide extrusion product (4-(2-iminopyrimidine-1(2H)-yl)aniline), but the formation routs of the products for SDZ⁰ and SDZ⁻ were different. In addition, effects of the metal ions on the triplet-sensitized photolysis of SDZ⁰ and SDZ⁻ were different. The metal ions promoted the triplet-sensitized photolysis of SDZ⁰, but inhibited the triplet-sensitized photolysis of SDZ⁻.

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1. Introduction

Antibiotics that fight bacterial infections are widely applied in aquaculture, animal husbandry, and medical treatment (Kümmerer, 2009). Due to their abuse, antibiotics are largely released into and frequently detected in the aquatic environment (Kümmerer, 2009; Zuccato et al., 2010). To date, antibiotics known as emerging pollutants are of particular concern due to their adverse effects such as inducing bacterial resistance (Yu et al., 2013) and the emergence of “superbugs” (Woodward, 2010). Sulfadiazine (SDZ) was found to be one of the most frequently detected

antibiotics in surface water (Wei et al., 2011; Na et al., 2013; Bayen et al., 2014). Recently a lot of attention has also been drawn to the studies on the behavior and fate of SDZ in the aquatic environment (Sukul et al., 2008; Anskjaer et al., 2013; Fang et al., 2014).

Photolysis is found to be an important factor of determining the fate and behavior of organic pollutants including SDZ (Sabljić and Peijnenburg, 2001; Boreen et al., 2004, 2005; Sukul et al., 2008; Ge et al., 2009, 2010; Li et al., 2011; Wammer et al., 2011; Challis et al., 2013; Wei et al., 2013; Batchu et al., 2014). The wavelength at maximum electronic absorbance of SDZ is 263.6 nm in water (Premakumari et al., 2011). SDZ mainly proceeds indirect photolysis in the aquatic environment due to the fact that only sunlight with a wavelength >290 nm reaches the surface of the earth. Indirect photolysis may include reaction with transient

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excited species such as singlet oxygen ($^1\text{O}_2$), hydroxyl radical ($\cdot\text{OH}$), triplet excited state dissolved organic matter (^3DOM), or other reactive species (Boreen et al., 2005). Boreen et al. (2005) reported that SDZ in natural water proceeds triplet-sensitized photolysis with DOM, and the primary product formed in the triplet-sensitized photolysis was identified as a sulfur dioxide extrusion product (4-(2-iminopyrimidine-1(2H)-yl)aniline). However, the mechanisms underlying the triplet-sensitized photolysis of SDZ with DOM have not been fully understood.

In recent years, the issues on the combined pollution of organic pollutants and metal ions has been drawing a lot of attention. Mg^{2+} and Ca^{2+} occur at a high concentration and Zn^{2+} is as a metal ion pollutant in natural water environment (Hafuka et al., 2014). Contemporary studies suggest that metal ions e.g. Mg^{2+} and Ca^{2+} can have an effect on the photochemical behavior of organic pollutants. Werner et al. (2006) found that the direct photolysis rate constant of tetracycline in the presence of Ca^{2+} or Mg^{2+} is greater by a magnitude than that of tetracycline in the absence of Ca^{2+} and Mg^{2+} . Martínez et al. (1996) also found that Ca^{2+} and Mg^{2+} had an impact on the photochemical properties of norfloxacin. Following environmental release there will be interactions between metal ions and SDZ. Therefore, effects of metal ions on the photolysis of SDZ are urgently needed to be investigated.

Obtaining experimental data can be laborious, costly, and time-consuming. Quantum chemistry calculations have been found to be efficient alternatives for predicting the environmental behavior and fate of organic pollutants, and for providing an important information on reaction intermediates or reactive species involved in chemical reactions that are difficult to be detected experimentally (Sabljić, 2001; Wang et al., 2012, 2014a,b; Kovacevic and Sabljic, 2013a,b). It was the purpose of this study to investigate the triplet-sensitized photolysis mechanisms of SDZ in water and three metal ions (Mg^{2+} , Ca^{2+} , and Zn^{2+}) effects. Based on density functional theory (DFT), NBO charge and electron spin densities were calculated to study the triplet-sensitized photolysis mechanisms (electron transfer or hydrogen transfer) of SDZ with four DOM analogues, and the formation routes of photolysis products and the metal ions effects were calculated.

2. Computational methods

SDZ was selected as a model compound (Fig. 1). The geometry optimization of all structures in solvent water was carried out using DFT (Kohn et al., 1996) and Becke's three-parameter hybrid exchange function with Lee–Yang–Parr gradient-corrected correlation functional (B3LYP) (Becke, 1993) with 6-311+G(d,p) basis set. The polarized continuum model (PCM) was employed to consider the solvent effects in water. The UV absorbance spectra of SDZ in water was calculated using the time-dependent density functional

theory (TDDFT) at B3LYP/6-311++G(d,p) level (Burke et al., 2005; Zhao and Han, 2009, 2012). The atom charge was examined based on the natural bond orbital (NBO) scheme at B3LYP/6-311++G(d,p) level.

Sensitizers fluorenone (FL), thioxanthone (TX), 2-acetonaphthone (2-AN), and 4-benzoylbenzoic acid (CBBP) were selected as DOM analogues to investigate the triplet-sensitized photolysis mechanisms of SDZ. The energies of the lowest triplet excited state of FL, TX, 2-AN, and CBBP were calculated at TDDFT/B3LYP/6-311++G(d,p) level. The triplet-sensitized photolysis pathways of SDZ with DOM analogues in solvent water were calculated employing DFT method at B3LYP/6-311+G(d,p) level of theory. Frequency calculations were done at the same level to confirm all the stationary points. Transition states were characterized with one imaginary vibrational frequency. Intrinsic reaction coordinate (IRC) calculations were performed to confirm that transition state do connect with the corresponding reactions and products. Zero-point energy correction was considered for the estimated reaction activation energy. All the calculations were carried out using the Gaussian 09 software package (Frisch et al., 2009).

3. Results and discussion

3.1. Geometries of two dissociation species (SDZ^0 and SDZ^-) of SDZ in water

As depicted in Fig. 1, SDZ has three dissociation species with $\text{p}K_{a1} \sim 1.8$ and $\text{p}K_{a2} \sim 6.5$ (Sanli et al., 2010; Białk-Bielińska et al., 2012). Both the neutral (SDZ^0) and the anionic (SDZ^-) form are present in the natural water environment. The optimized geometries of SDZ^0 and SDZ^- were presented in the Fig. 2. There are some differences between the geometries of SDZ^0 and SDZ^- . For example, the bond length of C1–S in SDZ^0 (1.77 Å) is a little shorter than that in SDZ^- (1.80 Å), and the bond lengths of S–N1 (1.70 Å) and N1–C2 (1.39 Å) in SDZ^0 are a little longer than those (1.61 and 1.36 Å) in SDZ^- . The largest difference of dihedral angles C1–S–N1–C2, C3–C1–S–N1, and S–N1–C2–N4 between SDZ^0 and SDZ^- reaches to 18.3°. The computed wavelengths at maximum electronic absorbance of SDZ^0 and SDZ^- in water are 263.0 nm and 250.0 nm at TDDFT/B3LYP/6-311++G(d,p) level, respectively, which are in good agreement with the experimental data 263.6 nm in water (pH = 6.5) (Premakumari et al., 2011).

3.2. Triplet-sensitized photolysis mechanisms of SDZ^0

Due to the fact that the energy of the lowest triplet excited state of DOM (57.4 kcal mol $^{-1}$) (Zepp et al., 1985)/FL (54.7 kcal mol $^{-1}$)/TX (62.0 kcal mol $^{-1}$)/2-AN (59.4 kcal mol $^{-1}$)/CBBP (68.8 kcal mol $^{-1}$) is lower than that of SDZ (80.0 kcal mol $^{-1}$ for SDZ^0 and 77.7 kcal mol $^{-1}$

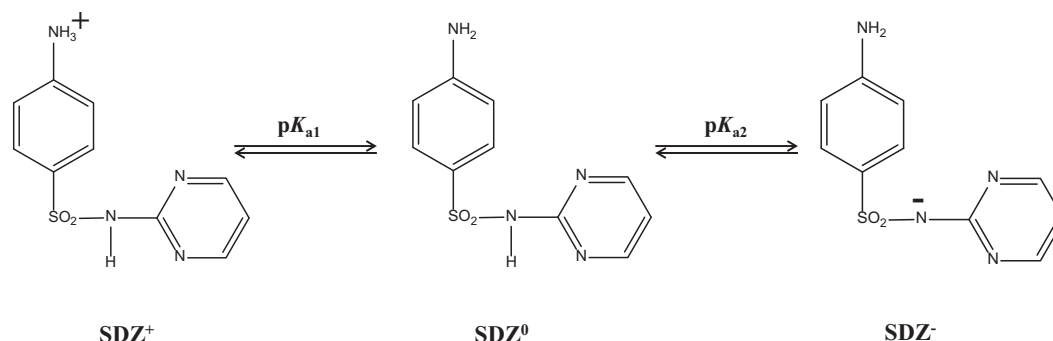


Fig. 1. Dissociation species of sulfadiazine (SDZ) at different pH values.

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