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Quantum chemical study of the photolysis mechanisms of sulfachloropyridazine and the influence of selected divalent metal ions

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HIGHLIGHTS

- Sulfur dioxide extrusion product confirmed by two paths in photolysis of SCP.
- Step 2 of Path-II, estimated as RDS for triplet-sensitized photolysis of SCP.
- Cu^{2+} and Ca^{2+} promoted the triplet-sensitized Photolysis of SCP but Zn^{2+} inhibits.
- Increase ASD and ΔNBO of N1–C5 decrease E_a of RDS.

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ABSTRACT

Sulfonamides have been found in aquatic environments. Degradation of sulfachloropyridazine (SCP) mainly proceeds through direct and indirect photolysis in the aquatic environment. However, the mechanisms underlying the triplet photolysis of SCP and the influence of metal ions on the photolysis mechanism have not yet been fully explained. In this study, we elucidated the triplet photolysis mechanisms of SCP and the effects of three selected metal ions (Zn^{2+}, Ca^{2+}, and Cu^{2+}) on the SCP photolysis mechanisms using quantum chemical calculation. Optimization of molecular structures and reaction pathways analysis of SCP were carried out at the B3LYP/6-31+G(d,p) level of theory. Two minimum energy pathways were investigated in the triplet photolysis of SCP. In Step 2 of Path-I, the photolysis product of SCP is a sulfur dioxide extrusion product, (4-(3-chloro-6-iminopyridazine-1(6H)-yl)aniline). The estimated activation energies of Step 2 and Step 3 of Path-I were much higher than in Path-II. Therefore, Path-II was found as the lowest energy pathway to obtain the SCP photoproducts, and Step 2 of Path-II was confirmed as the rate-determining step (RDS) in the photolysis mechanism of SCP. For the RDS of Path-II, computations with the three metal ions complexes (IM1–Cu^{2+}, IM1–Ca^{2+}, and IM1–Zn^{2+}) show that the metal ions Cu^{2+} and Ca^{2+} promote triplet-sensitized photolysis of SCP by reducing the activation energy of RDS of Path-II, whereas Zn^{2+} showed an inhibitory effect in photolysis of SCP by increasing the activation energy.

1. Introduction

As a subclass of antibiotics, sulfonamides are widely used in aquaculture, animal husbandry (Could, 1999; Kummerer, 2009; Sarmah et al., 2006), and agriculture (Hirsch et al., 1999), as well as in the treatment of human respiratory and urinary tract infections (Huovinen, 2001). Because of their high activity and low cost, the worldwide consumption of antibiotics continues to increase and antibiotics are frequently detected in the aquatic environment (Iglesias et al., 2012; Angela et al., 2006; Kummerer, 2009). Currently, antibiotics are considered emerging pollutants of particular attention because of potential adverse effects such as the development of bacterial resistance (Garcia-Galan et al., 2009; Yu et al., 2013) and toxicity to aquatic organisms (Kim et al., 2007; Luo et al., 2010; Stoll et al., 2012; Barana et al., 2011).

Sulfachloropyridazine (SCP) is an effective antibiotic that can be applied over a broad spectrum of health problems and it was found to be one of the most frequently detected antibiotics in surface water (Choi et al., 2008; Miao et al., 2004; Baran et al., 2012). SCP is also commonly detected in soil, particularly at those areas where manure is used as fertilizer for crops (Blackwell et al., 2007, 2009; Leal et al., 2013; Schmitt et al., 2004). To date, much study has been given to the behavior and fate of sulfonamides in the aquatic environment, including SCP (Dirany et al., 2012; Bonvin et al., 2012; Yang et al., 2010; Zessel et al., 2014; Wang and Gardinali, 2014). Furthermore, photolysis is found to be an important factor to determine the fate and behavior of organic

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pollutants and antibiotics (Batchu et al., 2014a,b; Kovacevic and Sabljic, 2013; Li et al., 2011; Sarmah et al., 2006; Wammer et al., 2011; Wang et al., 2014a, 2014b, 2015; Wei et al., 2011; Zhao et al., 2008).

Boreen et al. (2005) identified a sulfur dioxide extrusion product, 4-(2-iminopyrimidine-1(2H)-yl) aniline, upon triplet-sensitized photolysis of sulfadiazine in water by both direct and indirect photolysis, and they also proposed photo-products for SCP. However, the mechanisms underlying the triplet-sensitized photolysis of SCP and its possible photoproducts have not yet been fully elucidated. This study employs quantum chemical computations to investigate the triplet-sensitized photolysis mechanisms of SCP and elucidate those photoproducts with minimum energy reactive pathways.

Another important goal of this study was to investigate the effects of metal ions on the triplet-sensitized photolysis mechanism of SCP. Kamiya and Kameyama (2001) have studied the inhibitory effects of Cu^{2+}, Mn^{2+}, Co^{2+}, and Cr^{3+} on photolysis of organophosphorus compounds, Hubicka et al. (2012) observed that Cu^{2+}, Zn^{2+}, and Al^{3+} promote photodegradation of moxifloxacin. Werner et al. (2006) also found that the direct photolysis rate constant of tetracycline in the presence of Ca^{2+} and Mg^{2+} is greater than when these ions are absent. In light of these previous studies, we realize that, within those issues being addressed by the contemporary environmental community, there is an urgent need to study the interactions between SCP and metal ions to fully characterize their photolysis properties.

2. Computational details

In this study, SCP was selected as a model compound (Fig. 1). Geometry optimizations of all structures were carried out using density functional theory methods (Zhao et al., 2008) with Gaussian-09 software package (Frisch et al., 2009). Becke's Three Parameter hybrid exchange functional with the Lee–Yang–Parr gradient corrected correlation function (B3LYP) (Becke, 1993) was used with the 6-31+G(d,p) basis set (Ditchfield et al., 1971; Hariharan and Pople, 1973, 1974; Francl et al., 1982; Rassolov et al., 1998; Clark et al., 1983) throughout the studies. The integral equation formalism polarized continuum model with water selected as the solvent was used to simulate the photolysis of SCP in water. Frequency calculations of each reactant and product were carried out at the same level to confirm the local minimum of all the stationary points. Transition states were confirmed as such by the observation of a single imaginary vibrational frequency for each elementary reaction. The progression of molecular structure of reactants toward the transition states and products was performed by following the intrinsic reaction coordinates. Zero-point energies corrections were considered for the calculated activation energy (E_a). The ultraviolet absorbance spectra of SCP in water was computed using time-dependent density function theory at the B3LYP/6-31+G(d,p) level (Burke et al., 2005; Zhao and Han, 2009, 2012). Atomic charges were obtained based on the natural bond orbital (NBO) scheme at the same level of theory.

3. Results and discussion

3.1. Geometries optimization of the SCP triplet state in water

As shown in Fig. 1, good agreement between the computed optimized molecular structure of SCP and available experimental data (Tan et al., 2005) lends confidence that the selected level of theory is suitable for further study. The largest difference in bond lengths of between the experimental and computed molecular structures was a difference of 0.08 Å for the S–N1 bond, and the largest difference in bond angles N1–S–C5, O1–S–C5, C1–N1–S, and N2–C1–N1 between the structures was 4.0°. Additionally, the wavelength of the maximum intensity in the computed absorption spectrum was 263 nm, which was in good agreement with the experimentally observed maximum at 260 nm in research conducted by Boreen et al. (2005). These results indicate that the B3LYP/G-31+G(d,p) level of theory is a suitable method for further detailed study of the photolysis mechanisms of SCP.

3.2. Triplet-sensitized photolysis mechanisms of SCP

Boreen et al. (2005). identified the extrusion product as (4-(2-iminopyrimidine-1(2H)-yl) aniline) in photolysis of sulfamethazine (SMZ) and they also proposed the formation of the sulfur dioxide extrusion product (4-(3-chloro-6-iminopyridazine-1(6H)-yl)aniline for SCP photolysis. This may be because of the SCP and SMZ species being in the same family and having some structural similarities. In this study, the formation of the sulfur dioxide extrusion product was studied with two minimum energy paths (Path-I and Path-II) in the triplet photolysis of SCP. As depicted in Fig. 2, Path-I was computed according to proposed photoproducts of SCP by Boreen et al. (2005). There were four steps in

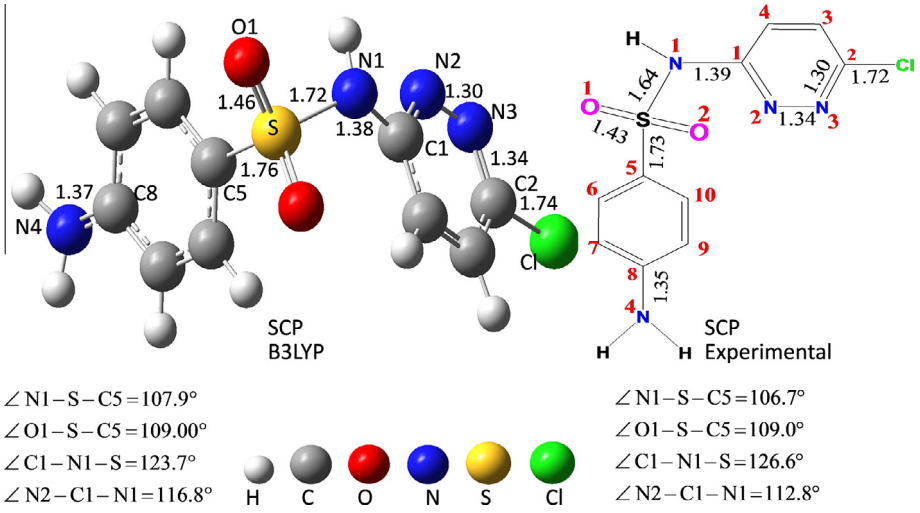

Fig. 1. Comparison of experimental and theoretical optimized parameter values of SCP by selected bond length (Å) and angles (°).