



A mechanistic kinetic model for singlet oxygen mediated self-sensitized photo-oxidation of organic pollutants in water

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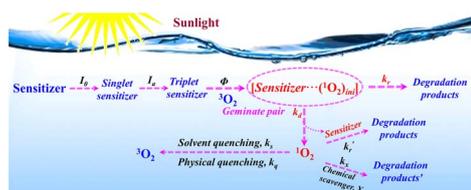
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GRAPHICAL ABSTRACT



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ABSTRACT

Singlet oxygen ($^1\text{O}_2$) mediated self-sensitized photo-oxidation in aqueous solution is a relatively uncommon photo-degradation pathway that has been reported for some organic pollutants. Such reactions have been modeled by the empirical first-order kinetics, but significant deviation occurs at high substrate concentrations and in the presence of $^1\text{O}_2$ scavengers and in D_2O matrices. A mechanistically based kinetic model was developed for $^1\text{O}_2$ mediated self-sensitized photo-oxidation by accounting for the sensitized generation of $^1\text{O}_2$ and the heterogeneous reaction between the substrate/sensitizer and $^1\text{O}_2$ in the photochemical system. The initially formed $^1\text{O}_2$ is treated in the model to be spatially correlated with its sensitizer, which could simultaneously undergo reaction and dissociation, instead of being evenly distributed in the solution instantaneously once formed. The oxidation of the substrate/sensitizer by $^1\text{O}_2$ occurs in both the geminate pairs and in solution, while the $^1\text{O}_2$ in solution is also quenched by the solvent and scavengers present. The model could well describe the solar photodegradation of *p*-arsanilic acid (*p*-ASA) under various initial concentrations, and predict the effect of $^1\text{O}_2$ scavenger NaN_3 , and D_2O matrices on degradation rate. The performance of the model was also validated by the kinetics of $^1\text{O}_2$ mediated self-sensitized photo-oxidation of *p*-aminobenzoic acid (PABA), 1-benzyl-3,4-dihydroisoquinoline, and 3,4-dihydropapaverine reported in the literature. Overall, this kinetic model could help better understand the fundamental processes involved in $^1\text{O}_2$ mediated self-sensitized photo-oxidation and predict the photochemical fate of organic pollutants that undergo such photochemical transformation in sunlight surface water.

1. Introduction

Solar photochemical transformation is an important process for the degradation and elimination of a range of organic pollutants in sunlight

surface water, such as sulfa drugs [1–3], tetracyclines [4], cyclophosphamide [5], nitrofurans [6], cephalosporins [7,8], and chemotherapeutic drugs [8,9]. Specifically, photo-reactive pollutants could either undergo direct photolysis or degrade via indirect photochemical

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pathways, which may involve reactions with reactive species commonly present in sunlit natural waters [1], such as singlet oxygen ($^1\text{O}_2$) [10], hydroxyl radical ($\cdot\text{OH}$) [11,12], superoxide anion radical ($\text{O}_2^{\cdot-}$) [13], photo-excited organic matter [10,14,15], and carbonate radical ($\text{CO}_3^{\cdot-}$) [7,16]. In addition to the above two common mechanisms, self-sensitized photolysis is a relatively uncommon pathway that is responsible for the decomposition of a number of organic pollutants in surface water [10,17–20].

In self-sensitized photolysis, sensitizer (S), which is also the substrate of the subsequently generated reactive species, is first activated from its ground state (S_0) to the lowest excited singlet state (S_1) by absorbing photons, then it is transformed to the lowest triplet state sensitizer (T_1) through inter-system crossing [21]. Since the lifetime of T_1 -state is much longer than that of S_1 -state, sensitizer in T_1 -state may further transform via two processes [22–25]. One process involves electron transfer or hydrogen abstraction between the triplet excited sensitizer and externally added substrate, which initiates radical reactions [22–25]. In the other process, dissolved oxygen (DO) acts as the only electron and energy acceptor in solution [24,25]. The electron is transferred from the T_1 -state sensitizer to ground-state oxygen ($^3\text{O}_2$), yielding sensitizer cation radical ($S^{\cdot+}$) and $\text{O}_2^{\cdot-}$: $T_1 + ^3\text{O}_2 \rightarrow S^{\cdot+} + \text{O}_2^{\cdot-}$ [24,25]. In the parallel reaction, only energy transfer occurs during the collision of the excited sensitizer with ground-state oxygen ($^3\text{O}_2$), producing $^1\text{O}_2$: $T_1 + ^3\text{O}_2 \rightarrow S_0 + ^1\text{O}_2$ [18,22]. In general, electron transfer from the T_1 -state sensitizer to ground-state oxygen occurs much less frequently compared to energy transfer in the second process [24,25]. Meanwhile, $^1\text{O}_2$, due to its high electrophilicity, is capable of oxidizing a wide variety of pollutants, such as polycyclic aromatic hydrocarbons, phenols, sulfides, and amines [26,27]. Therefore, $^1\text{O}_2$ could function as the predominant reactive species responsible for the self-sensitized photo-oxidation of organic pollutants in aqueous solution in the absence of other externally added sensitizers [10,17–19].

Photochemical transformation of a limited number of organic pollutants have been found to occur through self-sensitized photo-oxidation involving $^1\text{O}_2$, and the degradation products, degradation pathways, interference factors, and degradation rates have been characterized in details [15,19,28]. The self-sensitized photodegradation rates of organic compounds are commonly fitted by pseudo-first-order kinetics, which appears to be consistent with the common hypothesis in the case of direct photolysis, that is, the rate of the photodegradation depends only on the solar irradiance [10,29,30]. However, in self-sensitized photodegradation, it has been observed that the degradation rate often increased with the initial concentrations of the substrates at their environmental concentrations ($\sim\mu\text{M}$) [4,28], but decreased when their concentrations reached much higher levels ($\sim\text{mM}$) [30,31]. Partial removal of DO from the solution phase was also found to significantly reduce the rate of photodegradation [17]. Both phenomena cannot be explained by true first-order degradation kinetics. On the other hand, since the degradation of the substrate was initiated with the self-sensitized formation of $^1\text{O}_2$, degradation could be approximated as a bimolecular reaction between the substrate and self-sensitized $^1\text{O}_2$, thus the overall degradation should follow pseudo-second-order kinetics. Nonetheless, the self-sensitized photodegradation of substrates at environmental concentrations ($< 1\text{ mM}$) could be well fitted by pseudo-first-order kinetics in most cases [17,30,32,33]. Overall, despite the fact that the kinetics of self-sensitized photodegradation has been treated empirically as pseudo-first-order, significant deviation from such a kinetic model has been observed, particularly at high substrate concentrations, in D_2O matrices, and in the presence of $^1\text{O}_2$ scavengers [17]. Therefore, models fully accounting for the fundamental processes involved in self-sensitized photo-oxidation are needed to reliably predict the degradation kinetics of pollutants that undergo such photochemical transformation.

p-Arsanilic acid (*p*-ASA) is a phenylarsenic feed additive that has been used extensively in swine and poultry farming to promote growth

and combat intestinal parasitic diseases for several decades [17,34,35]. Although the use of *p*-ASA and other phenylarsenic compounds in food animal production has been phased out in the European Union and the U.S., they are still used heavily in many countries around the world, including China [17,29,34]. Most of the *p*-ASA fed to animals is excreted chemically unchanged into urine and feces, which are often applied (with and without composting) as a fertilizer on agricultural soils [17,34,35]. Being highly water soluble ($\sim 11\text{ g/L}$), *p*-ASA can leach out from manure and soil easily with rainfall and irrigation water, and subsequently enter surrounding surface water [17,34,35]. In sunlit surface water, *p*-ASA quickly undergoes $^1\text{O}_2$ mediated self-sensitized photodegradation, releasing arsenite and arsenate [17,29]. As inorganic arsenic species (arsenite and arsenate) have much greater toxicity than phenylarsenic compounds, photodegradation of *p*-ASA could significantly increase the ecotoxicity, and consequently, the risk to aquatic organisms. Thus it is important to understand the kinetics of *p*-ASA photodegradation in sunlit surface water, as well as predict the effect of environmental factors (e.g., DO and $^1\text{O}_2$ scavengers) on its rate of photochemical transformation.

In this work, a mechanistic model fully accounting for the formation and depletion of $^1\text{O}_2$, as well as the reaction between the substrate/sensitizer and $^1\text{O}_2$ in self-sensitized photo-oxidation was developed. It could well describe the dependence of photodegradation rate on the substrate concentration and the influence of solution chemistry (e.g., the presence of $^1\text{O}_2$ scavengers and D_2O matrices). The performance of this model was evaluated with the experimental data of *p*-ASA photodegradation obtained in our laboratory, and further validated by results reported in the literature. Compared to the empirical pseudo-first- and pseudo-second-order kinetics treatment for $^1\text{O}_2$ mediated self-sensitized photo-oxidation, the mechanistically based model developed hereby is based on the fundamental processes involved in the sensitized generation of $^1\text{O}_2$ and the reaction between $^1\text{O}_2$ and the substrate, and thus is capable of accurately predicting the effect of initial concentration on the substrate's photodegradation rate under all relevant conditions, as well as the effect of environmental factors, such as DO and $^1\text{O}_2$ scavengers. It could serve as a valuable tool for understanding the fundamental processes in $^1\text{O}_2$ mediated self-sensitized photo-oxidation and predicting the photochemical fate of organic pollutants that undergo such photodegradation in sunlit surface water.

2. Materials and methods

2.1. Photodegradation experiments

p-ASA of $> 98\%$ purity (TCI Chemicals, Shanghai, China), rose bengal (RB) (Kemio Chemical Reagent, Tianjin, China) and furfuryl alcohol (FFA) (Sinopharm Chemical Reagent, Beijing, China) of analytical grade, and D_2O of $> 99.8\%$ purity (J & K Scientific, Beijing, China) were used as received. Stock solution of *p*-ASA (2.67 mM) was prepared by dissolving *p*-ASA in triple-distilled water. Solar irradiation of *p*-ASA solutions was performed using a Suntest CPS+ solar simulator (Atlas, Mount Prospect, Illinois, USA) in the wavelength range of 280–800 nm. The intensity of simulated sunlight was fixed at 765 W m^{-2} . Photon irradiance of the solar simulator and UV-vis absorption spectra of *p*-ASA are shown on Fig. S1.

To study the effect of substrate concentration on photodegradation rate of *p*-ASA, experiments were conducted at various initial concentrations (0.7, 1.3, 6.7, and 13.3 μM). To eliminate the effect of DO on *p*-ASA photolysis, the reaction system was sparged by a stream of high purity oxygen ($> 99.99\%$) for 30 min prior to simulated solar irradiation and throughout the photodegradation experiments. The pH of *p*-ASA solutions was adjusted to that of triple-distilled water (~ 5.7) using 0.1 and 0.5 M NaOH, unless noted otherwise. During simulated solar irradiation experiments, 200 mL of *p*-ASA solutions were placed in customer-made beakers (60 mm in diameter, height of 100 mm) made of optical grade fused quartz. Unless specified otherwise, all

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