



# Mechanistic insight into reactivity of sulfate radical with aromatic contaminants through single-electron transfer pathway



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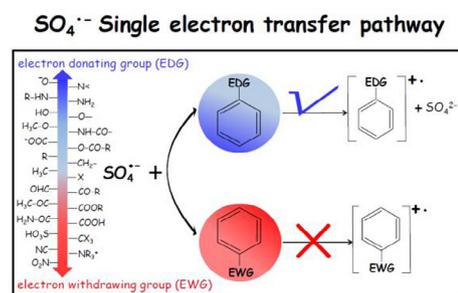
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## HIGHLIGHTS

- We systematically investigated the first step of SET reactions for 76 ACs with  $\text{SO}_4^{\cdot-}$ .
- $\Delta G_{\text{SET}}^\circ$  decreases with an increase of electron donating character of substituents.
- The calculated  $k_{\text{SET}}$  for the ACs were compared with their experimental  $k$  values.
- We proposed two fundamental SET reaction mechanisms for 76 ACs with  $\text{SO}_4^{\cdot-}$ .

## GRAPHICAL ABSTRACT



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## ABSTRACT

Removal of aromatic contaminants (ACs) in waters by sulfate radical anion ( $\text{SO}_4^{\cdot-}$ ) based advanced oxidation technology has been extensively studied. Three main mechanisms have frequently been used to account for the first step of radical oxidation of ACs: radical adduct formation, hydrogen atom abstraction, and single electron transfer (SET), among which the SET pathway is the least understood. In this study, we investigated the first step of SET reactions for 76 ACs with  $\text{SO}_4^{\cdot-}$ . The result shows that the Gibbs free energy ( $\Delta G_{\text{SET}}^\circ$ ) of the reaction increases with a decrease of the electron donating character of the substituents on the ACs. The trend was then quantitatively corroborated by a Hammett type plot, indicating that the electrostatic interaction is the driving force for the SET pathway. Further, we compared the calculated second-order rate constants ( $k_{\text{SET}}$ ) for the ACs via the SET pathway with their experimental  $k$  values, and proposed two fundamental SET reaction mechanisms based on the identified intermediates. The thermodynamic and kinetic results obtained advance the mechanistic understanding of the SET pathway of radical and non-radical bimolecular reactions, and shed light on the applicability of  $\text{SO}_4^{\cdot-}$  in ACs removal during water treatment processes.

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## 1. Introduction

Advanced oxidation technologies (AOTs) producing radical species at ambient temperature and pressure have been widely used

to remove aromatic contaminants (ACs) in groundwater, wastewater, and drinking water treatments [1,2]. Hydroxyl radical ( $\cdot\text{OH}$ ) generated by ozonation, ultraviolet/hydrogen peroxide, or Fenton/photo-Fenton processes, is the most common oxidant species produced in AOTs [3,4]. However, due to its high reactivity toward the ubiquitously present natural organic matters (NOMs),  $\cdot\text{OH}$  usually exhibits low removal efficiency of target contaminants in a complex environmental matrix during the AOT process [5,6]. On the contrary, sulfate radical anion-based AOT that produces sulfate radical ( $\text{SO}_4^{\cdot-}$ ) is less affected by the presence of background NOMs due to the selective reactivity of  $\text{SO}_4^{\cdot-}$ . Consequently, such AOT has received increasing attention for the removal of ACs in the presence of background NOMs in waters [7,8]. In addition, the  $\text{SO}_4^{\cdot-}$  based *in situ* chemical oxidation (ISCO) technologies also exhibit more practical advantages over other ISCO systems, since the radical precursor salt (*i.e.*, persulfate) are relatively stable and can be delivered for long distances in a subsurface system.

Three main mechanisms have been proposed for the first step of  $\text{SO}_4^{\cdot-}$  oxidation of ACs: (1) radical adduct formation (RAF), (2) hydrogen atom abstraction (HAA), and (3) single electron transfer (SET) [9–11]. Mounting experimental evidence has confirmed the occurrence of RAF and HAA pathways in  $\text{SO}_4^{\cdot-}$  oxidation reactions by using electron spin resonance (ESR) spectroscopy [9,12], transient absorption spectroscopy [13], and mass spectrometry [11,14]. In addition, substantial theoretical evidence has been presented to support the radical and non-radical bimolecular reactions via the RAF and HAA pathways on the molecular level. For example, with density functional theory (DFT)-based methods, Caregnato et al. [11] has reported  $\text{SO}_4^{\cdot-}$  oxidation of gallic acid in RAF and HAA pathways, and experimentally verified the predicted products. They concluded that their DFT calculations in aqueous solution support the formation of phenoxyl radicals via the HAA route for the reactions between phenols and  $\text{SO}_4^{\cdot-}$ .

Recognizing that the SET reaction is the simplest and fastest of all chemical reactions, experimental identification and description of the SET pathway is, unfortunately, very limited for  $\text{SO}_4^{\cdot-}$  oxidation reactions [9,15]. The extremely short lifetime of radical cations generated in SET reactions makes it difficult to characterize these reaction intermediates in the presence of other radicals and species [15–17]. For example, Zemel and Fessenden [15] examined the intermediate oxidation products formed within 0.1 and 1  $\mu\text{s}$  for the reactions of  $\text{SO}_4^{\cdot-}$  with benzene and benzoate derivatives using ESR spectroscopy. By analyzing the phenyl (70%) and hydroxycyclohexadienyl radical (30%) intermediates from the SET reaction products of benzoate radical cation, they concluded that the SET route was the main reaction channel. However, capturing and identifying transient species in the RAF and SET pathways for ACs remains quite an analytical challenge. Tripathi [16] reported that the adduct radicals produced through the RAF route and radical cation via the SET pathway have overlapping absorption signals, resulting in conflicting evidence between the two pathways. More importantly, many questions regarding the mechanisms of the SET reactions of ACs with  $\text{SO}_4^{\cdot-}$  still remain unanswered. For example, how does one verify the SET pathway and distinguish it from others? How fast does a radical and non-radical bimolecular reaction take place via the SET route? Do the  $\text{SO}_4^{\cdot-}$  based SET reactions follow certain degradation patterns? The fundamental thermodynamic and kinetic information can be used to predict the byproducts that may be oxidized by  $\text{SO}_4^{\cdot-}$ . As a reaction proceeds, different degradation pathways lead to different byproducts depending on the reaction mechanisms. With this information available, one can predict the potential byproducts for compounds whose kinetics and thermodynamics have not been experimentally investigated before. Therefore, in addition to further development of analytical techniques, an improved mechanistic understanding of the SET reaction of ACs with  $\text{SO}_4^{\cdot-}$  is desired.

Quantum mechanics-based calculation offers an alternative way to provide mechanistic insights into radical oxidation, especially when the experimental identification is technically challenging. For instance, Madhavan et al. [18] investigated the  $\cdot\text{OH}$ -mediated degradation byproducts for ibuprofen with electrospray ionization mass spectrometry, and mono and dihydroxylated intermediates, such as 2-(4-(1-hydroxy-2-methylpropyl) phenyl) propanoic acid, were identified as secondary and tertiary byproducts. However, their evidence was insufficient to identify the reaction pathways on the molecular level. Upon the Madhavan et al. [18] study, Xiao et al. [19] investigated  $\cdot\text{OH}$  oxidation of ibuprofen in a variety of pathways, and constructed the energy profiles for these reaction channels with DFT calculation. They elucidated the reaction mechanisms and confirmed that the first and dominant step of ibuprofen oxidation with  $\cdot\text{OH}$  is to undergo the HAA channel, which is followed by an additional  $\cdot\text{OH}$  attack with the resulting ibuprofen radical, forming the observed mono and dihydroxylated intermediates. Their quantum mechanics-based calculations supported the experimental evidence obtained by Madhavan et al. [19]. Further, previous studies have revealed that the overall reactivity for  $\text{SO}_4^{\cdot-}$  is strongly dependent on electron donating/withdrawing character of functional groups on the organic compounds [20]. Xiao et al. [8] reported that the overall  $\text{SO}_4^{\cdot-}$  reactivity dependence can be quantitatively described by quantum mechanics-based descriptors such as energies of the highest/lowest occupied molecular orbitals. Our previous study points to a necessity to investigate the electronic effect of functional groups on  $\text{SO}_4^{\cdot-}$  based SET reactions.

In the present study, we selected 76 ACs covering a wide variety of structural diversities and reactivities with  $\text{SO}_4^{\cdot-}$ . We performed a quantum mechanical study on the feasibility of these contaminants taking the SET pathway in  $\text{SO}_4^{\cdot-}$  oxidation reactions. We tested the hypothesis that, the electron donating/withdrawing character of the functional groups affects the thermodynamic viability of the SET reaction. In addition, the kinetics of the ACs that are thermodynamically feasible to react with  $\text{SO}_4^{\cdot-}$  via the SET channel were also investigated with the emphasis on the connection between the calculation results and experimental measurements. Specifically, we compared the calculated SET rate constants ( $k_{\text{SET}}$ ) with the observed second-order values ( $k_{\text{obs}}$ ), and proposed two fundamental SET reaction mechanisms based on the identified intermediates.

## 2. Materials and methods

### 2.1. Aromatic contaminants

In the present study, 40 benzene and 36 benzoate derivatives, totaling 76 ACs, were investigated, and their structures are listed in Table A1 in Appendix A. The selection of these ACs is based on the environmental relevance, existing studies, structural diversity in functional groups, and data for both conjugate acid–base pairs for acidic/basic species. The singly charged states were also considered for compounds containing hydroxyl group ( $-\text{OH}$ ), carboxyl group ( $-\text{COOH}$ ), secondary ( $-\text{NH}-$ ) and tertiary amine ( $-\text{N}<$ ) group. Their  $\text{pK}_a$  values are listed in Table A2.

### 2.2. Electronic structure calculations

Due to the intractable amount of time required for *ab initio* conformational searching, the global minimum was sought using Spartan'10 with the Merck Molecular Force Field (MMFF) [21]. The MMFF was designed for modeling organic molecules so is well suited for this task [21]. The lowest energy conformer of a compound from Spartan was then optimized at the DFT level using Gaussian

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