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Comparison of the reactivity of ibuprofen with sulfate and hydroxyl radicals: An experimental and theoretical study

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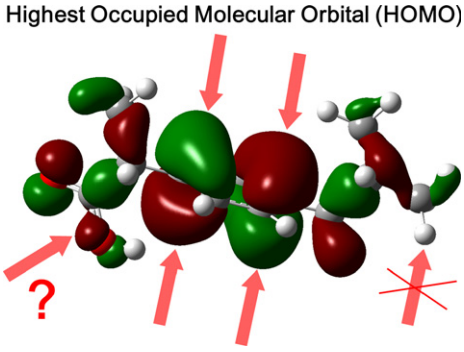
HIGHLIGHTS

- Oxidation of ibuprofen by $^{\bullet}OH/SO_4^{\bullet-}$ is experimentally and theoretically studied.
- The second–order rate constants (k) of ibuprofen with $^{\bullet}OH$ is higher than $SO_4^{\bullet-}$.
- $SO_4^{\bullet-}$ exhibits higher energy barriers than $^{\bullet}OH$, resulting in a smaller $k_{SO_4^{\bullet-}}$.
- H–atom abstraction is the most favorable pathway for both $^{\bullet}OH$ and $SO_4^{\bullet-}$.

GRAPHICAL ABSTRACT



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ABSTRACT

Hydroxyl radical ($^{\bullet}OH$) and sulfate radical anion ($SO_4^{\bullet-}$) based advanced oxidation technologies (AOTs) are effective methods to treat trace organic contaminants (TrOCs) in engineered waters. Although both technologies result in the same overall removal of TrOCs, the mechanistic differences between these two radicals involved in the oxidation of TrOCs remain unclear. In this study, we experimentally examined the degradation kinetics of neutral ibuprofen (IBU), a representative TrOC, by $^{\bullet}OH$ and $SO_4^{\bullet-}$ at pH 3 in UV/H_2O_2 and UV/persulfate systems, respectively. The second–order rate constants (k) of IBU with $^{\bullet}OH$ and $SO_4^{\bullet-}$ were determined to be $3.43 \pm 0.06 \times 10^9$ and $1.66 \pm 0.12 \times 10^9$ M^{-1} s^{-1}, respectively. We also theoretically calculated the thermodynamic and kinetic behaviors for reactions of IBU with $^{\bullet}OH$ and $SO_4^{\bullet-}$ using the density functional theory (DFT) M06–2X method with 6–311++G** basis set. The results revealed that H–atom abstraction is the most favorable pathway for both $^{\bullet}OH$ and $SO_4^{\bullet-}$, but due to the steric hindrance $SO_4^{\bullet-}$ exhibits significantly higher energy barriers than $^{\bullet}OH$. The theoretical calculations corroborate our experimental observation that $SO_4^{\bullet-}$ has a smaller k value than $^{\bullet}OH$ in reacting with IBU. These comparative results are of fundamental and practical importance in understanding the electrophilic interactions between radicals and IBU molecules, and to help select preferred radical oxidation processes for optimal TrOCs removal in engineered waters.

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1. Introduction

Advanced oxidation technologies (AOTs) involving production of hydroxyl radical ($^{\bullet}OH$) and sulfate radical anion ($SO_4^{\bullet-}$) at ambient temperature and pressure, exhibit high efficiency for removal of trace organic contaminants (TrOCs) such as pharmaceuticals, plasticizers, and personal care products in engineered waters (Vogna et al., 2004; Xiao et al., 2014a; Ye et al., 2017). $^{\bullet}OH$ based AOTs, including H_2O_2/UV, Fenton, ozonation, and sonication, oxidize target contaminants by attacking electron–rich sites on molecules (Crittenden et al., 2005). However, as a strong and non–selective oxidant, $^{\bullet}OH$ oxidation is significantly affected by matrix components, such as ubiquitously present effluent organic matters (EfOMs) and alkalinity in wastewater (Dong et al., 2010; Rosario-Ortiz et al., 2010). $SO_4^{\bullet-}$, on the other hand, is more inert to the water matrices, leading to intensive scientific investigation and industrial exploration as an alternative oxidant in water engineering (Gau et al., 2010; Zhang et al., 2015a). Generally, $SO_4^{\bullet-}$ can be produced in a persulfate (PS)/peroxymonosulfate (PMS) system activated by heat, base or catalyzers (*e.g.*, Co^{2+} and Fe^{2+}) (Furman et al., 2010; He et al., 2013; Liang et al., 2004). Further, the high solubility and nontoxic properties of PS/PMS are beneficial to typical water treatment processes (Mora et al., 2009).

The intrinsic differences between $SO_4^{\bullet-}$ and $^{\bullet}OH$ yield different reactivities and reaction pathways with organic contaminants. Two most common degradation mechanisms proposed to account for the first step of $^{\bullet}OH$ oxidation of TrOCs are H–atom abstraction and radical addition to unsaturated/aromatic structures. But for $SO_4^{\bullet-}$, single electron transfer (SET) reaction is also possible due to a higher electron affinity of $SO_4^{\bullet-}$ (2.43 eV) compared to $^{\bullet}OH$ (1.83 eV) (Avetta et al., 2015; Chu and Hopke, 1988). Although $^{\bullet}OH$ and $SO_4^{\bullet-}$ are both oxidizing radicals and result in the same overall chemistry for certain reactions, the dissimilarities in reaction mechanism on the molecular level are unclear. Particularly, $SO_4^{\bullet-}$ and $^{\bullet}OH$ co–exist in the PS/PMS system in circumneutral pH leading to competing pathways in the oxidation of target TrOCs (Liang et al., 2007). In such dual–radical system, the existing uncertainty and obscuration lead to a number of questions: 1) What factors control the difference in reaction kinetics for these two radicals? 2) Is there any relationship that can correlate the physiochemical properties of TrOCs molecules (*e.g.*, electrophilicity, size, and structure) to the kinetic difference? 3) How to verify and distinguish one reaction pathway from others in the presence of competing radicals? Therefore, a better understanding of the mechanistic differences between these two radicals involved in the oxidation of TrOCs is highly desired.

Density functional theory (DFT) is considered to be a powerful tool to study radical oxidation kinetics, mechanisms, and byproduct formation on the molecular level (DeMatteo et al., 2005; Luo et al., 2017; Villamena et al., 2007). For example, Minakata and Crittenden (2011) calculated the rate constants using DFT method for $^{\bullet}OH$ and eight organic contaminants to be within one order of magnitude of experimental measurements. In our previous study, DFT calculation results between neutral form of ibuprofen (IBU) and $^{\bullet}OH$ showed H–atom abstraction is the favored pathway over $^{\bullet}OH$ addition reactions due to their lower activation barriers (Xiao et al., 2014c). Our results also indicated that more thermodynamically stable byproducts are generated in the abstraction reactions. The calculated rate constant ($6.72 \times 10^9\ M^{-1}\ s^{-1}$) between neutral IBU and $^{\bullet}OH$ was in excellent agreement with the experimental value ($6.5 \pm 0.2 \times 10^9\ M^{-1}\ s^{-1}$) (Packer et al., 2003).

In this study, we experimentally measured k values of IBU reacting with $^{\bullet}OH$ and $SO_4^{\bullet-}$ using the relative rate method and steady–state approximation. In addition, we theoretically investigated the thermodynamic and kinetic behavior of the reactions of IBU with $^{\bullet}OH$ and $SO_4^{\bullet-}$ using a DFT method. IBU is selected as an example of TrOCs in this study due to its environmental relevance and computational tractability for the DFT method (Prasanthkumar and Alvarez-Idaboy, 2014; Wang et al., 2008). More importantly, there is experimental evidence regarding $^{\bullet}OH/SO_4^{\bullet-}$ oxidation of IBU and identified byproducts, which can be used to confirm our experimental and theoretical results (Vimal and Stevens, 2006; Wang et al., 2008; Xiao et al., 2014b). The comparative evaluation of oxidative degradation of TrOCs by $^{\bullet}OH$ and $SO_4^{\bullet-}$ is of scientific and practical importance, as selection of oxidants during water treatment processes determines the removal efficiency of TrOCs where results can vary from partial remediation to complete mineralization.

2. Methodology

2.1. Experimental method

2.1.1. Materials

IBU (99%), $Na_2S_2O_8$ (99%), H_3PO_4 (85–90%), Na_2HPO_4 (99%), NaH_2PO_4 (99%), acetophenone (ACP, 99%), and *t*-butanol (99.7%) were purchased from Sigma Aldrich. H_2O_2 (30% by weight), H_2SO_4 (guaranteed reagent), $KMnO_4$ (analytical grade), and $Na_2C_2O_4$ (analytical grade) were purchased from Sinopharm Chemical Reagent, China. Deionized (DI) water used to prepare solutions was from a Molecular water system (Molresearc 1010A). Solution pH was measured by a S220 pH meter (Mettler Toledo).

Stock solutions of IBU and ACP were prepared in DI water and stored at 4 °C in dark. For the kinetic studies, the initial concentrations of IBU and ACP in the working solutions were 10 μM. Solution pH was adjusted to pH 3 with 10 mM phosphate buffer system. We did not observe pH change in any of our experiments. The selection of pH 3 is based on two factors: 1) at pH 3 the dominant radical species in a UV/$S_2O_8^{2-}$ system is $SO_4^{\bullet-}$ (Fang et al., 2012; Liang et al., 2007), and 2) IBU is a weak acid with pK_a 4.9, thus at pH 3 the majority (*i.e.*, 98.5%) of IBU is in its neutral form. The solution was continuously stirred by a magnetic bar, and solution temperature was maintained at 20 ± 1 °C with a Neslab chiller (SC150-A25B, Thermo Fisher Scientific). During experiments, 1 mL samples were taken from the reactor for chemical analysis at scheduled times using a 2.5 mL glass syringe (Gastight 1001, Hamilton). All experiments were carried out in triplicate.

2.1.2. UV irradiation

Fig. 1 shows the schematic diagram of the UV photochemical reactor used in this study. A low pressure UV lamp (GPH212T5L/4, 10 W, Heraeus) in a quartz sleeve was placed in the centerline of a 450 mL cylindrical photochemical reactor. A water circulating system (SC150–A25B, Thermo Fisher Scientific) kept the quartz cold trap temperature at 20 ± 0.1 °C. The average light intensity per volume (I_0) in the UV reactor was estimated to be 6.16×10^{-6} Einstein $L^{-1}\ s^{-1}$ with potassium ferrioxalate as a standard chemical actinometry (Hatchard and Parker, 1956; Parker, 1953). The effective optical path length (b) was 1.32 cm measured by H_2O_2 actinometry (Beltran et al., 1995; Xiao et al., 2015b). Zhang et al. (2015b) measured I_0 to be 3.19×10^{-6} Einstein $L^{-1}\ s^{-1}$ for a 4 W low pressure UV lamp with the same method. Xiao et al. (2015b) reported b to be 2.6 cm in their UV/H_2O_2 system with a 5 W low pressure UV lamp. Our I_0 and b values are in agreement with reported values. The molar extinction coefficient (ε) at 254 nm and the quantum yield (φ) values for H_2O_2 and $S_2O_8^{2-}$ were from previous studies ($\varepsilon_{H_2O_2}$ = 19.6 $M^{-1}\ cm^{-1}$, $\varepsilon_{S_2O_8^{2-}}$ = 21.1 $M^{-1}\ cm^{-1}$, $\varphi_{H_2O_2}$ = 0.5 mol Einstein^{-1}, and $\varphi_{S_2O_8^{2-}}$ = 0.7 mol Einstein^{-1}) (Baxendale and Wilson, 1957; Crittenden et al., 1999; Legrini et al., 1993). The emission wavelength and intensity of the UV lamp were determined using a fiber optic spectrometer (USB 2000+, Ocean Optics). Background degradation experiments in the dark suggest that there is no need to quench the reaction efficiency before IBU analysis.

2.1.3. Analytical methods

The concentration of $Na_2S_2O_8$ and H_2O_2 was measured by the $KMnO_4$ titration method (Ojani et al., 2010; Razmi and Mohammad-Rezaei, 2010). Analysis of IBU and ACP was performed