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Mechanistic insight into degradation of endocrine disrupting chemical by hydroxyl radical: An experimental and theoretical approach[☆]

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ABSTRACT

Advanced oxidation processes (AOPs) based on formation of free radicals at ambient temperature and pressure are effective for treating endocrine disrupting chemicals (EDCs) in waters. In this study, we systematically investigated the degradation kinetics of bisphenol A (BPA), a representative EDC by hydroxyl radical (•OH) with a combination of experimental and theoretical approaches. The second–order rate constant (k) of BPA with •OH was experimentally determined to be $7.2 \pm 0.34 \times 10^9$ M^{-1} s^{-1} at pH 7.55. We also calculated the thermodynamic and kinetic behaviors for the bimolecular reactions by density functional theory (DFT) using the M05–2X method with 6–311++G** basis set and solvation model based on density (SMD). The results revealed that H–abstraction on the phenol group is the most favorable pathway for •OH. The theoretical k value corrected by the Collins–Kimball approach was determined to be 1.03×10^{10} M^{-1} s^{-1}, which is in reasonable agreement with the experimental observation. These results are of fundamental and practical importance in understanding the chemical interactions between •OH and BPA, and aid further AOPs design in treating EDCs during wastewater treatment processes.

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1. Introduction

Bisphenol A (BPA), with an annual production of 3.6×10^3 million kg, has received a great deal of attention from regulatory agencies and scientific communities due to its potential endocrine disrupting effect and wide presence in the environment (Le Corre et al., 2015; Staples et al., 1998). For example, BPA has been detected at the level of 0.14–12.0 μg l^{-1} in U.S. river waters, and at much higher level (10 mg L^{-1}) in leachates from hazardous waste landfill sites in Japan (Buxton and Kolpin, 2005; Yamamoto et al., 2001). With a sufficient level of exposure, BPA can exhibit adverse effects on endocrine system by binding to hormone receptors, which govern the physiological development and reproduction for organisms (Meeker et al., 2010; Schug et al., 2011). In addition, the degradation byproducts of BPA still possess estrogenic activity (Hu et al., 2002; Rosenfeldt and Linden, 2004). For example, Tsutsumi et al. (2001) reported 0.22 mM BPA degraded in the reaction with manganese peroxidase after an hour, but the estrogenic activity still remained 40% as compared to the initial concentration.

Advanced oxidation processes (AOPs) based on formation of free radicals at ambient temperature and pressure are effective for treating endocrine disrupting chemicals (EDCs) in waters (Ghernaout, 2013). A variety of AOPs such as ozonation, sonication,

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and UV/H_2O_2, have been investigated and developed to reduce the concentrations of EDCs in wastewater (Xiao et al., 2013). Among AOPs, UV/H_2O_2 is a mature and widely used method in water engineering process, because it has a relatively low operation cost, short contact time, and safe use. In addition to direct photolysis of the EDCs, hydroxyl radical (•OH), a strong oxidant in nature with oxidation potential ranging from 1.77 to 2.74 V, is also accounted for their degradation (Oturan and Aaron, 2014; Xu et al., 2007).

The degradation kinetics of BPA from waters by AOPs has been reported in many studies (Katsumata et al., 2004; Rivas et al., 2009; Rosenfeldt and Linden, 2004). For example, Rosenfeldt and Linden (2004) reported the second–order rate constant (k) value to be $1.02 \pm 0.23 \times 10^{10}$ M^{-1} s^{-1} for BPA at pH 7.35, whereas Baeza and Knappe (2011) measured the k value to be $5.80 \pm 0.08 \times 10^{9}$ M^{-1} s^{-1} in the UV/H_2O_2 system. Felis et al. (2011) compared the degradation of BPA under the UV and UV/H_2O_2 processes. Their results support that •OH oxidation was attributed to fast BPA degradation rather than direct photolysis. Meanwhile, density functional theory (DFT) is widely used to study degradation kinetics of BPA by •OH (Rissi et al., 2002). Numerous studies have reported that the DFT method features an excellent performance–to–cost ratio in describing and/or predicting reaction mechanisms, byproduct formation, and reaction kinetics (Galano and Alvarez-Idaboy, 2013; Yang et al., 2015). For example, Xiao et al. (2014) investigated the k value between •OH and ibuprofen at IEFPCM/B3LYP/6–311++G**//B3LYP/6–31G* level of theory. The calculated k value between neutral ibuprofen and •OH was 6.72×10^{9} M^{-1} s^{-1}, which was consistent with the experimental k value, $6.5 \pm 0.2 \times 10^{9}$ M^{-1} s^{-1}. Dai et al. (2016) studied the kinetics and mechanism of •OH oxidation of BPA at M05–2X theory in a Fenton's reaction system. They suggested that •OH attack on hydroxyl groups on BPA molecule is the primary pathway for degradation. However, it is rarely seen in the literature the investigation of •OH oxidation of BPA by the combination of experimental and theoretical approaches. This work aimed to combine these two methods with advantages in addressing limitations on the capabilities of analytical tools for product identification and providing another layer of confidence for experimental measurements (Luo et al., 2017a).

In this study, we employed a combination of experimental and theoretical approaches to study the thermodynamics and kinetics of BPA degradation by •OH. First, we used the relative rate method to determine k value for the reaction. In order to confirm our experimental observation, M05–2X functional was used to study the thermodynamic and kinetic behaviors between BPA and •OH. The enthalpies $\left(\Delta H_{\mathrm{R}}^{0}\right)$, free energies $\left(\Delta G_{\mathrm{R}}^{0}\right)$, height of activation energy barrier ($\Delta^{\ddagger}G^{\circ}$), and second–order rate constants (k) of the reaction were calculated. The theoretical k was then compared with the experimental values. We aimed to provide mechanistic insight into the molecular level of mechanism of •OH oxidation of BPA, and shed light on future application of AOPs for removing EDCs in wastewater treatment plants.

2. Materials and methods

2.1. Materials

BPA (99%), p–chlorobenzoic acid (p–CBA, 99%), H_3PO_4 (85–90%), Na_2HPO_4 (99%), and NaH_2PO_4 (99%) 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 all the solutions was from a Molecular water system (Molresearc 1010A). Solution pH was measured by a S220 pH meter (Mettler Toledo).

2.2. Experimental method

Stock solutions of BPA and p–CBA were prepared in DI water and stored at ambient temperature in the dark. For the kinetic studies, the initial concentrations of the working solutions for BPA and p–CBA were 10 μM. Solution pH was adjusted to 7.55 and buffered in 10 mM phosphate buffer system. There are two reasons for choosing this pH. First, pH 7.55 is of environmental relevance. Second, BPA is a weak organic acid containing two ionizable hydroxyl groups with pKa values of 9.6 and 10.2 (Choi and Lee, 2017). Thus, BPA exists in the neutral form at pH 7.55.

The photochemical reactor used in our experiments is presented in Fig. 1. 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. The average light intensity per volume (I_0) in the UV reactor was determined to be 7.60×10^{-6} Einstein L^{-1} s^{-1} with potassium ferrioxalate as a standard chemical actinometer (Hatchard and Parker, 1956; Parker, 1953). The effective optical path length (b) was 0.93 cm measured by H_2O_2 actinometery method (Beltran et al., 1995; Xiao et al., 2015b). The photochemical reactor was equipped with a Neslab chiller (SC150-A25B, Thermo Fisher Scientific) to maintain solution temperature at 20 ± 0.1 °C. The solution was continuously stirred by a magnetic bar. During UV irradiation, 1 mL sample was taken from the reactor at designated time with a glass syringe (Gastight 1001, Hamilton Corp.) for target compound concentration qualification. The experiments were carried out at least in duplicate.

When the photons are absorbed by the compound molecules, the photochemical reaction takes place. Fig. 2 illustrates the absorption spectra of BPA as a function of wavelength (λ). The ability of the compound to absorb photons at a specific wavelength is defined by the molar absorption coefficient (ε) (Schwarzenbach et al., 1993; Yang et al., 2017). The ε was determined by measuring the absorbance (A) of 10 μM BPA solution at pH 7.55 with a 1 cm path length (z) quartz cuvette in this study:

$$\mathrm{A} = \varepsilon \times \mathrm{z} \times \mathrm{C} \tag{1}$$

The quantum yield (φ) of BPA represent the ability to utilize photons that were absorbed by the compound (Bolton and Stefan,

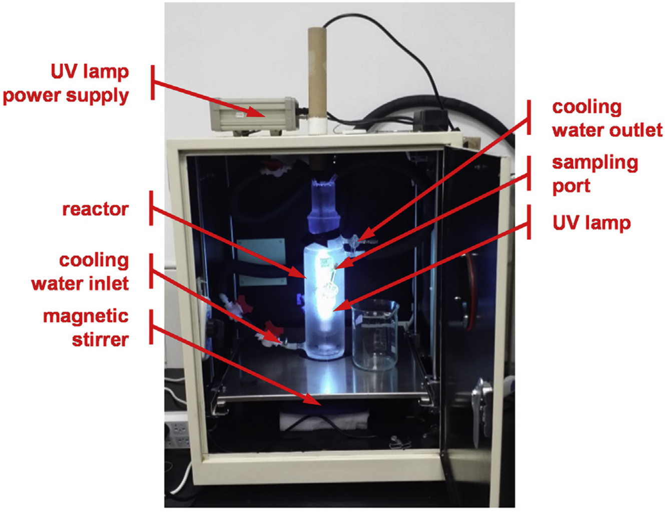

Fig. 1. The experimental setup for the photochemical reactor in this study.

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