



Theoretical investigation on the kinetics and mechanisms of hydroxyl radical-induced transformation of parabens and its consequences for toxicity: Influence of alkyl-chain length



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ABSTRACT

As emerging organic contaminants (EOCs), the ubiquitous presence of preservative parabens in water causes a serious environmental concern. Hydroxyl radical ($\cdot\text{OH}$) is a strong oxidant that can degrade EOCs through photochemistry in surface water environments as well as in advanced oxidation processes (AOPs). To better understand the degradation mechanisms, kinetics, and products toxicity of the preservative parabens in aquatic environments and AOPs, the $\cdot\text{OH}$ -initiated degradation reactions of the four parabens were investigated systematically using a computational approach. The four studied parabens with increase of alkyl-chain length were methylparaben (MPB), ethylparaben (EPB), propylparaben (PPB), and dibutylparaben (BPB). Results showed that the four parabens can be initially attacked by $\cdot\text{OH}$ through $\cdot\text{OH}$ -addition and H-abstraction routes. The $\cdot\text{OH}$ -addition route was more important for the degradation of shorter alkyl-chain parabens like MPB and EPB, while the H-abstraction route was predominant for the degradation of parabens with longer alkyl-chain for example PPB and BPB. In assessing the aquatic toxicity of parabens and their degradation products using the model calculations, the products of the $\cdot\text{OH}$ -addition route were found to be more toxic to green algae than original parabens. Although all degradation products were less toxic to daphnia and fish than corresponding parental parabens, they could be still harmful to these aquatic organisms. Furthermore, as alkyl-chain length increased, the ecotoxicity of parabens and their degradation products was found to be also increased.

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1. Introduction

In recent years, the presence of emerging organic contaminants (EOCs) in water and wastewater has already become a global public concern in almost all parts of the world (Schwarzenbach et al., 2010, 2006). Parabens, a group of EOCs with antimicrobial and preservative properties, are widely used in toothpastes, cosmetics, textiles, foodstuffs, and beverages (Calafat et al., 2010; Liao et al., 2013b). Approximately 8000 tons of parabens are consumed annually around the world (Ramaswamy et al., 2011), and most are continuously released into the environment during their production, use, and disposal. As such, parabens are now detected in various aquatic environments (Kasprzyk-Hordern et al., 2008; Liao

et al., 2013a; Liu and Wong, 2013), imposing potential risks to aquatic organisms (An et al., 2014a; Terasaki et al., 2009; Yamamoto et al., 2011). Furthermore, parabens have been detected in breast tumor tissue, and may be associated with the formation of these cancers (Darbre and Harvey, 2008; Kuş et al., 2013). Recent studies on a series of parabens, including methyl- (MPB), ethyl- (EPB), propyl- (PPB), and butyl-parabens (BPB) (structures are shown in Fig 1) (Karpuzoglu et al., 2013), have revealed that parabens affect estrogen levels, potentially impacting female reproductive health (Smith et al., 2013). Due to their potential toxicity to aquatic organisms and human beings, it is important to study the transformation and removal of these pollutants from water environments.

Conventional wastewater treatment technologies are still inadequate for removing parabens (Leal et al., 2010). However, advanced oxidation processes (AOPs) have proven to be successful in destroying and mineralizing recalcitrant organic pollutants in

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water (An et al., 2015,2010). Recently, different AOPs including UV irradiation (Błędzka et al., 2012; Sánchez-Martín et al., 2013), photocatalytic (Lin et al., 2009; Yang et al., 2010), photo-sonochemical (Daghrir et al., 2014), electrochemical (Steter et al., 2014), and ozone oxidation (Tay et al., 2010a,2010b), which generate highly reactive hydroxyl radicals ($\cdot\text{OH}$), have been frequently used in experiments to detoxify parabens (Fang et al., 2013). In fact, $\cdot\text{OH}$ is also one of the main photo-generated species involved in the indirect phototransformation of a wide spectrum of EOCs in surface waters (Dong and Rosario-Ortiz, 2012; Wenk et al., 2011). Therefore, the $\cdot\text{OH}$ -initiated reactions of parabens could likely occur, either in surface water environments or in AOP systems.

Recent studies suggest that some of the degradation products from these AOPs and photochemical transformation are found to be more toxic than these parental EOCs (Boxall et al., 2004; Daghrir et al., 2014; Prasse et al., 2012). For parabens, only a fraction of them can be completely oxidized into water and carbon dioxide due to the TOC removal of 43%–80%, and some can be transformed into by-products (Daghrir et al., 2014; Lin et al., 2009). However, there is still very limited attention paid to the transformation products of parabens, as well as their potential toxicity during $\cdot\text{OH}$ -induced transformation of parabens. In our previous experimental study, the acute toxicity was found to be increased during PPB degradation (Fang et al., 2013), suggesting that the transformation products formed in the treatment process maybe more toxic than the parental PPB. However, the study has not identified how PPB's degradation products are formed during $\cdot\text{OH}$ -based oxidation processes, why the transformation products are more toxic than the parental PPB, and what about the cases in the transformation of other parabens. In particular, the alkyl chain length of parabens may significantly affect the transformation products and their consequences for the toxicity toward aquatic organisms. To the best of our knowledge, the systematic research on the relationship among the transformation mechanisms, environmental fate, aquatic toxicity and the alkyl chain length of a series of parabens have not been yet fully explored.

Given the large and ever-increasing number of EOCs, theoretical calculations are found very crucial to evaluate their environmental photodegradation behavior, ecological risk assessment as well as pollution prevention, as experimental methods are costly and time-consuming, and cannot evaluate all emerging chemicals (Zhang et al., 2010; Zhou et al., 2011). It have been demonstrated that computational approaches have provided important information on the reaction intermediates or active species involved in chemical reactions, which are necessary for the mechanism clarification but are difficult to be detected experimentally (An et al., 2015,2014b,2011; Fang et al., 2013). Also, theoretical calculations have successfully used to predict the toxicity assessments of EOCs in water (Gao et al., 2014a,2014b; Madden et al., 2009).

Given this background, in this work, theoretical calculations on the structure-dependency degradation mechanisms and the toxicity of degradation products of different parabens during $\cdot\text{OH}$ -mediated transformation processes were performed based on the density functional theory (DFT), and the mechanisms, kinetics and toxicity evolution of the $\cdot\text{OH}$ -initiated oxidation of four different parabens (MPB, EPB, PPB, and BPB) were systematically compared. The ecological risks posed by parabens as well as their transformation products were evaluated using the most extensively validated and used tool, named the US EPA "ecological structure–activity relationships" (ECOSAR) program. These theoretical results will help explain paraben degradation mechanisms and assess the potential risks associated with their $\cdot\text{OH}$ -mediated degradation processes.

2. Computational methods

2.1. Mechanism and kinetics computations

All quantum chemical calculations were carried out using the Gaussian 03 program (Frisch et al., 2003). The geometrical parameters of reactants (RC), transition states (TS), and products (PC) were optimized at the B3LYP level with a standard 6-31G(d,p) basis set. At the same level, the vibrational frequencies were calculated to

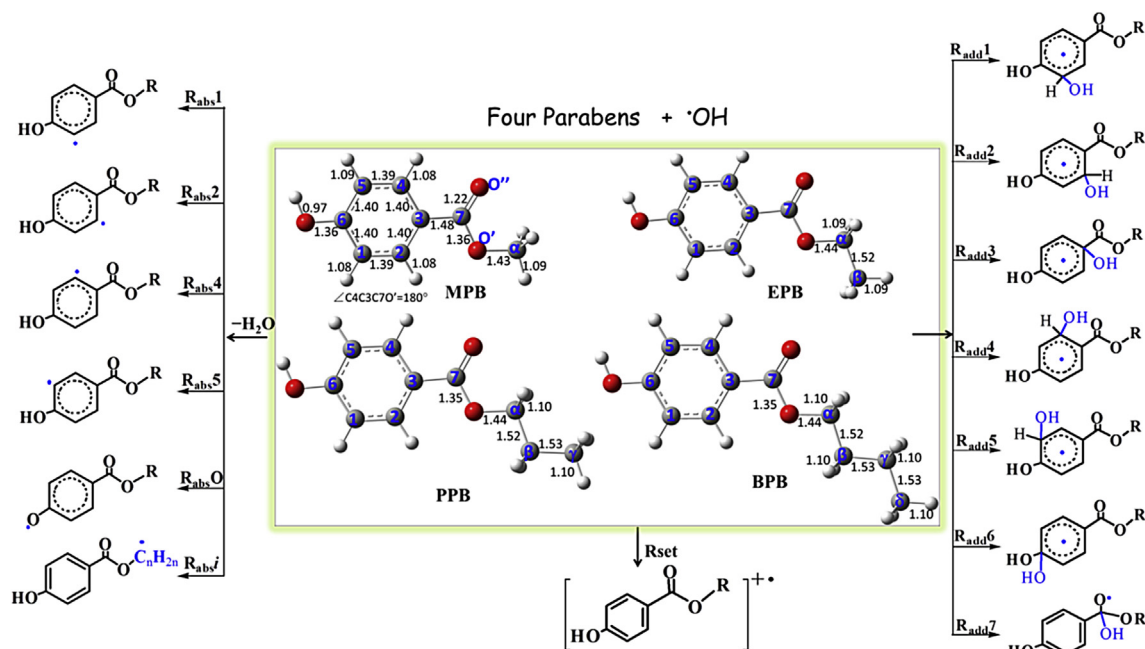


Fig. 1. Four parabens conformation optimized at B3LYP/6-31G (d,p) level, as well as all possible routes for their degradation reactions with $\cdot\text{OH}$. Herein, the same geometrical parameters for the four parabens are listed only in MPB. Bond lengths are in angstroms. \bullet = C, \circ = H, \bullet = O.

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