Ozonation of parabens in aqueous solution: Kinetics and mechanism of degradation

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A B S T R A C T

This study investigated the reaction kinetics and degradation mechanism of parabens (methylparaben, ethylparaben, propylparaben and butylparaben) during ozonation. Experiments were performed at pH 2, 6 and 12 to determine the rate constants for the reaction of protonated, undissociated and dissociated paraben with ozone. The rate constants for the reaction of ozone with dissociated parabens (3.3 × 10^5–4.2 × 10^6 M⁻¹ s⁻¹) were found to be 10^4 times higher than the undissociated parabens (2.5 × 10^2–4.4 × 10^4 M⁻¹ s⁻¹) and 10^7 times higher than with the protonated parabens (1.02 × 10^2–1.38 × 10^5 M⁻¹ s⁻¹). The second-order rate constants for the reaction between parabens with hydroxyl radicals were found to vary from 6.8 × 10^5 to 9.2 × 10^7 M⁻¹ s⁻¹.

Characterization of degradation by-products (DBPs) formed during the ozonation of each selected paraben has been carried out using GCMS after silylation. Twenty DBPs formed during ozonation of selected parabens have been identified. Hydroxylation has been found to be the major reaction for the formation of the identified DBPs. Through the hydroxylation reaction, a variety of hydroxylated parabens was formed.

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1. Introduction

The presence of pharmaceuticals and personal care products (PPCPs) in the environment has drawn much attention among the scientific community recently due to their ubiquity and health effects (Fatta et al., 2007). Consequently, it has been a challenge for water treatment facilities to remove these compounds during wastewater treatment and drinking water production. Ozone, chlorine and chlorite dioxide are the commonly used oxidizing agents for the removal of organic compounds in water treatment. Among these oxidation processes, ozone with higher standard oxidation potential is expected to oxidize organic pollutants more efficiently than chlorine and chlorite dioxide (Weinberg et al., 2008). During ozone oxidation, organic pollutants undergo a series of oxidation processes, and in some cases, toxic degradation by-products (DBPs) might be formed (Ikehata et al., 2006). Following the discharge of incompletely treated effluents, these DBPs may emerge in the aquatic environment. Because ozonation is a common disinfection method used in water treatment, evaluation and determination of by-products produced from ozonation are important consideration for environmental protection purposes.

Parabens are commonly used as antimicrobial preservatives in cosmetics, food, pharmaceutical products and personal care products. These compounds have been reported to have estrogenic (Terasaka et al., 2006) and antiandrogenic-like properties (Chen et al., 2007). A potential relationship between breast cancer and application of paraben-containing products on skin is speculated since these compounds have been reported to be found in breast tumors (Darbre et al., 2004). Even though parabens are expected to be removed using conventional water and sewage treatments (Canosa et al., 2006), their presence in river water (Benjits et al., 2004) and effluent of waste treatment plants (Andersen et al., 2007; Trenholm et al., 2008) has expelled this perception. Based on our literature review, formation of DBPs of parabens via chlorination has been evaluated by Canosa et al. (2006) but the DBPs of parabens formed during ozonation of have not been characterized.

The objectives of this work are: (i) to determine the second-order rate constants for the direct reaction between individual paraben with ozone and hydroxyl radicals, (ii) to identify the degradation by-products (DBPs) of parabens generated during ozonation, and (iii) to propose the degradation pathways of parabens during the ozonation. Methylparaben (MeP), ethylparaben (EtP), propylparaben (PrP) and butylparaben (BuP) were selected for this study.

2. Materials and methods

2.1. Chemicals

Parabens (esters of 4-hydroxybenzoic acid, MeP, EtP, PrP, BuP and BzP), phenol and nitrobenzene (NB) were obtained from Fluka. tert-Butanol (t-BuOH) was obtained from Sigma–Aldrich. All...
solvents (Merck) were of the HPLC grade. Individual parabens stock solutions were dissolved in boiled ultrapure deionized water (Elga, USA). A mixture of BSTFA (N-O-bis(trimethylsilyl)trifluoroacetamide) and TMSCl (trimethylchlorosilane) in a ratio of 99:1 was obtained from Supelco (USA). Sodium phosphate monobasic and Sodium phosphate dibasic were purchased from Sigma and Riedel-de-Haën, respectively.

2.2. Determination of second-order rate constants for the reaction of parabens with ozone

The aqueous ozone stock solution was prepared by sparging ozone at the rate of 0.70 g h⁻¹ into water placed inside a water-jacketed beaker at the temperature of 2 °C. The concentration of ozone was measured using indigo method (Bader and Hoigné, 1981). The determination of ozone rate constants was carried out using competitive kinetics method at pH 2, 6 and 12. A detailed description of the kinetic method was given previously by Huber et al. (2003). Briefly, a competitive kinetics method was applied using phenol as a reference compound. Phenol was used as reference compound because it was expected to have similar rate constant and reaction mechanism as parabens. Phenol has been used as a reference compound for the determination of rate constants of the reaction between other phenolic compounds such as n-nonylphenol, bisphenol A, 17α-ethynylestradiol, 17β-estradiol with ozone (e.g. Huber et al., 2003; Deborde et al., 2005). Experiments were performed at room temperature (25–30 °C) in 20 mL vials with solution containing equal concentrations of paraben and phenol (reference compound) (4 μM) as well as 20 mM of t-BuOH. The pH of solution was adjusted using 20 mM of phosphate buffer. Finally, ozone solutions with concentrations ranging from 1.5 to 7.5 μM were added. The final volume of the mixtures was 20 mL, and this would also minimized the headspace. The vial was then shaken vigorously. After ozone was completely consumed, remaining concentrations of paraben and phenol were analyzed by injecting 100 μL of the reaction mixture into HPLC. The time of total ozone consumption was estimated from the half-lives of ozone in the parabens solution under different pH conditions. The half-lives for ozone in water at pH 2, 6 and 12 were found to be 28, 11 and <2 min, respectively. t-BuOH was added as a radical scavenger so as to allow only ozone reaction. t-BuOH reacts favorably with -OH, forming inert intermediates, therefore causing the termination of the radical chain reaction (Ma and Graham, 2000). In this experiment, t-BuOH was in excess ((t-BuOH)/[ozone] >1000) to ensure the suppression of radical reaction. The scavenging activity of t-BuOH especially at high pH condition was confirmed in our previous study (Tay et al., 2009).

2.3. Determination of second-order rate constants for the reaction of selected PPCPs and EDCs with hydroxyl radical (-OH) through Fenton reaction

For this experiment, competitive kinetics method with nitrobenzene (Buxton et al., 1988) as reference compounds was used to determine the second-order rate constants. Reaction was performed at room temperature in a 50 mL flat bottom flask containing 10 μM of paraben, nitrobenzene and iron (II) sulphate at pH 3.0. pH was adjusted using 1.0 M of sulfuric acid. Reaction was started by the addition of hydrogen peroxide (H₂O₂) solution at the final concentration of 200 μM and the final volume of the reaction mixture was 50 mL. One milliliter of the aliquot was withdrawn every minute for 10 min and the reaction was quenched immediately using 100 μL of 0.01 M of sodium thiosulphate (Na₂S₂O₃) solution (Liu et al., 2003). 100 μL of the reaction mixture were then injected into the HPLC for the determination of remaining target compound and reference compound.

2.4. Determination of ozonation by-product of parabens

Ozonation was performed on the selected parabens individually in 1000 mL cylindrical jacketed beaker at 25 °C. The detail of the ozonation and extraction procedure was given in a previous study (Tay et al., 2009). Extracts obtained from extraction were silylated using BSTFA and TMSCl (99:1) mixture for 4 h at 70 °C. Silylated extracts were dried using nitrogen stream and re-dissolve in 100 μL of dichloromethane. A 1.0 μL aliquot of the solution was injected into GCMS.

2.5. Instrumental analysis

All HPLC analyses were performed using Shimadzu HPLC system consisted of a LC-20AT pump, a SPD-M20A diode array detector, a SIL-20AHT auto sampler, a CTO-20AC column oven and a CBM-20A communication bus module (Shimadzu, Japan). A reversed-phase Chromolith RP-18 monolithic column (100 mm × 4.6 mm; Merck, Germany) was used for separation.

Analysis of degradation by-products was carried out using a Hewlett-Packard Model 6890 GC, with a HP-5 (5% phenylmethylpolysiloxane) column. The detail of the setting and the GC temperature program was given in previous study (Tay et al., 2009).

3. Results and discussion

3.1. Determination of rate constants for the reaction of parabens with ozone (kO3-paraben)

kO3-paraben were determined at pH 2, 6 and 12. Angelov et al. (2008) reported that at pH lower than 3, protonation of parabens occurred at the oxygen atom of the ester group, at pH between 3 and 5 parabens occurred as undissociated species and dissociation of hydroxyl group of parabens occurred at the pH higher than 6.5 (Fig. S1 in supporting information). kO3-paraben were estimated using competitive kinetics method derived from the following equation:

\[
\ln \left( \frac{[\text{Paraben}]}{[\text{Paraben}]_0} \right) = k_{\text{O3-Paraben}} \ln \left( \frac{[\text{Phenol}]}{[\text{Phenol}]_0} \right)
\]

where [Paraben]₀ and [Phenol]₀ represent the initial concentration of parabens and phenol; [Paraben] and [Phenol] represent the concentration of parabens and phenol after the ozonation reaction at different ozone dose, n. kO3-Paraben is the second-order rate constants for the reaction of ozone with phenol. Thus, a plot of \( \ln \left( \frac{[\text{Paraben}]}{[\text{Paraben}]_0} \right) \) versus \( \ln \left( \frac{[\text{Phenol}]}{[\text{Phenol}]_0} \right) \) yields a straight line whose slope is \( k_{\text{O3-Paraben}} \).

The detailed of this competitive kinetics method was described by Benitez et al. (2003). The values of \( k_{\text{O3-Phenol}} \) were calculated using Eq. (2) where \( k_{\text{O3-Phenolate}} = 1.3 \times 10^8 \text{ M}^{-1} \text{ s}^{-1} \), \( k_{\text{O3-Phenol}} = 1.4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1} \) and \( k_{\text{pK}} = 9.9 \) (Lee et al., 2003; Deborde et al., 2005).

\[
k_{\text{app-Phenol-O}} = k_{\text{O3-Phenolate}} \left( \frac{10^{-\text{pK}_a}}{10^{-\text{pK}_a} + 10^{-\text{pK}} + 10^{-\text{pK}_a - \text{pK}}} \right) + k_{\text{O3-Phenolate}} \left( \frac{10^{-\text{pK}_a}}{10^{-\text{pK}_a} + 10^{-\text{pK}} + 10^{-\text{pK}_a - \text{pK}}} \right)
\]
Second-order rate constants for the reactions between each paraben with ozone and \( \text{OH} \).

<table>
<thead>
<tr>
<th>Paraben</th>
<th>( k_{\text{OH-paraben}} \left( \text{M}^{-1} \text{s}^{-1} \right) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>MeP</td>
<td>((3.3 \pm 0.3) \times 10^2)</td>
</tr>
<tr>
<td>EtP</td>
<td>((3.6 \pm 0.2) \times 10^2)</td>
</tr>
<tr>
<td>PrP</td>
<td>((3.9 \pm 0.1) \times 10^2)</td>
</tr>
<tr>
<td>BuP</td>
<td>((4.2 \pm 0.6) \times 10^2)</td>
</tr>
</tbody>
</table>

The obtained \( k_{\text{OH-paraben}} \) were within the typical range of the rate constants for the aromatic compound, \(10^9 - 10^{10} \text{ M}^{-1} \text{s}^{-1}\) (Boonrattananik et al., 2009). These \( k_{\text{OH-paraben}} \) were found to increase with the increasing ester chain length of the parabens. The rate of hydrogen abstraction from the ester chain by \( \text{OH} \) which was found to be increased with the ester chain length (Behnke et al., 1988) is suggested to be the main reason for the difference. More ester chain hydroxylation by-products also have been detected in this study (Section 3.3).

3.2. Determination of rate constants for the reaction of parabens with \( \text{OH} \) \( (k_{\text{OH-paraben}}) \)

Decomposition of ozone during water treatment produced \( \text{OH} \). \( \text{OH} \) as highly reactive species also reacts with pollutants during water treatment. The determined \( k_{\text{OH-paraben}} \) were presented in Table 1. In this experiment, Fenton reaction was used to produce \( \text{OH} \). \( k_{\text{OH-paraben}} \) were determined using competitive kinetics method with nitrobenzene (NB) as reference compound.

\[
\ln \left( \frac{[\text{Paraben}]_t}{[\text{Paraben}]_0} \right) = k_{\text{OH-paraben}} \text{OH-} \ln \left( \frac{[\text{NB}]_t}{[\text{NB}]_0} \right) \tag{3}
\]

Fig. 1b shows a plot used for rate constants determination. NB with the rate constant \( k_{\text{OH-NB}} \) of \(3.9 \times 10^9 \text{ M}^{-1} \text{s}^{-1}\) was selected from the list of suggested reference compounds reported by Buxton et al. (1988). Experiments also were carried out to examine the direct oxidation of selected parabens and NB by \( \text{H}_2\text{O}_2 \). The results showed that parabens and NB were not oxidized by \( \text{H}_2\text{O}_2 \) during the experimental period (Fig. 52). The efficiency of the selected experimental condition for the Fenton process was evaluated using atenolol and metoprolol. In a recent study, Benner et al. (2008) reported the rate constants for the reaction between OH, generated from UV photolysis of \( \text{H}_2\text{O}_2 \) and atenolol, and metoprolol were of \((8.0 \pm 0.5) \times 10^8 \) and \((7.3 \pm 0.2) \times 10^8 \text{ M}^{-1} \text{s}^{-1}\), respectively, which were again very close to the values obtained here, i.e., \((7.5 \pm 0.5) \times 10^9 \) and \((6.9 \pm 0.2) \times 10^9 \text{ M}^{-1} \text{s}^{-1}\).

The obtained \( k_{\text{OH-paraben}} \) were within the typical range of the rate constants for the aromatic compound, \(10^9 - 10^{10} \text{ M}^{-1} \text{s}^{-1}\) (Boonrattananik et al., 2009). These \( k_{\text{OH-paraben}} \) were found to increase with the increasing ester chain length of the parabens. The rate of hydrogen abstraction from the ester chain by \( \text{OH} \) which was found to be increased with the ester chain length (Behnke et al., 1988) is suggested to be the main reason for the difference. More ester chain hydroxylation by-products also have been detected in this study (Section 3.3).

3.3. Identification of stable DBPs of parabens

GCMS analyses were performed by comparing the chromatogram of the initial parabens solution as a control sample with the chromatograms of the aliquots taken at consecutive ozonation time. All samples were subjected to similar derivatization procedure as mentioned in experimental section. Chromatograms showing the distribution of DBPs and parabens are presented in Fig. S3.

The results from mass spectrum showed that all derivatized compounds occurred as trimethylsilyl derivative which is characterized by the \( m/z \) 73 peak in the mass spectrum. In some cases, derivatization process was not completed (e.g. MeP-b1 and MeP-b2; PrP-a1 and PrP-a2). However, identification of these compounds could still be carried out from the obtained mass spectrum (Table 2).

<table>
<thead>
<tr>
<th>Compound</th>
<th>( k_{\text{OH-paraben}} \left( \times 10^9 \text{ M}^{-1} \text{s}^{-1} \right) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>MeP</td>
<td>(3.3 \pm 0.3)</td>
</tr>
<tr>
<td>EtP</td>
<td>(3.6 \pm 0.2)</td>
</tr>
<tr>
<td>PrP</td>
<td>(3.9 \pm 0.1)</td>
</tr>
<tr>
<td>BuP</td>
<td>(4.2 \pm 0.6)</td>
</tr>
</tbody>
</table>

Table 2
Stable DBPs of parabens.

<table>
<thead>
<tr>
<th>Compounds identified in GCMS (M⁺)</th>
<th>RT (min) [Label]</th>
<th>Structure of proposed DBPs (Molecular weight)</th>
<th>Name of proposed DBPs</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Methylparaben</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[m/z 224]</td>
<td>17.57 [MeP]</td>
<td><img src="image" alt="Structure of Methyl paraben" /></td>
<td>Methyl paraben</td>
</tr>
<tr>
<td>[m/z 254]</td>
<td>15.35 [MeP-a]</td>
<td><img src="image" alt="Structure of Methyl paraben" /></td>
<td>Hydroquinone</td>
</tr>
<tr>
<td>[m/z 240]</td>
<td>18.07 [MeP-b1]</td>
<td><img src="image" alt="Structure of Methyl paraben" /></td>
<td>1-Hydroxy-methylparaben</td>
</tr>
<tr>
<td>[m/z 312]</td>
<td>21.73 [MeP-b2]</td>
<td><img src="image" alt="Structure of Methyl paraben" /></td>
<td></td>
</tr>
<tr>
<td>[m/z 312]</td>
<td>21.39 [MeP-c]</td>
<td><img src="image" alt="Structure of Methyl paraben" /></td>
<td>Monohydroxy-methylparaben</td>
</tr>
<tr>
<td>[m/z 400]</td>
<td>24.97 [MeP-d]</td>
<td><img src="image" alt="Structure of Methyl paraben" /></td>
<td>Dihydroxy-methylparaben</td>
</tr>
<tr>
<td>[m/z 488]</td>
<td>26.49 [MeP-e]</td>
<td><img src="image" alt="Structure of Methyl paraben" /></td>
<td>Trihydroxy-methylparaben</td>
</tr>
<tr>
<td><strong>Ethylparaben</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[m/z 238]</td>
<td>20.75 [EtP]</td>
<td><img src="image" alt="Structure of Ethyl paraben" /></td>
<td>Ethyl paraben</td>
</tr>
<tr>
<td>[m/z 254]</td>
<td>15.25 [EtP-a]</td>
<td><img src="image" alt="Structure of Ethyl paraben" /></td>
<td>Hydroquinone</td>
</tr>
<tr>
<td>[m/z 254]</td>
<td>19.85 [EtP-b1]</td>
<td><img src="image" alt="Structure of Ethyl paraben" /></td>
<td>Monohydroxy-ethylparaben</td>
</tr>
<tr>
<td>[m/z 326]</td>
<td>22.26 [EtP-b2]</td>
<td><img src="image" alt="Structure of Ethyl paraben" /></td>
<td></td>
</tr>
<tr>
<td>[m/z 326]</td>
<td>22.73 [EtP-c]</td>
<td><img src="image" alt="Structure of Ethyl paraben" /></td>
<td>1-Hydroxy-ethylparaben</td>
</tr>
<tr>
<td>[m/z 414]</td>
<td>24.68 [EtP-d]</td>
<td><img src="image" alt="Structure of Ethyl paraben" /></td>
<td>1,2-dihydroxy-ethylparaben</td>
</tr>
<tr>
<td>[m/z 414]</td>
<td>25.34 [EtP-e]</td>
<td><img src="image" alt="Structure of Ethyl paraben" /></td>
<td>Dihydroxy-ethylparaben</td>
</tr>
<tr>
<td><strong>Propylparaben</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[m/z 252]</td>
<td>20.75 [PrP]</td>
<td><img src="image" alt="Structure of Propyl paraben" /></td>
<td>Propyl paraben (Propyl 4-hydroxybenzoate)</td>
</tr>
<tr>
<td>Compounds identified in GCMS (M⁺)</td>
<td>RT (min) [Label]</td>
<td>Structure of proposed DBPs (Molecular weight)</td>
<td>Name of proposed DBPs</td>
</tr>
<tr>
<td>-----------------------------------</td>
<td>-----------------</td>
<td>---------------------------------------------</td>
<td>-----------------------</td>
</tr>
<tr>
<td>4-Hydroxybenzoic acid</td>
<td>19.26 [PrP-a1]</td>
<td><img src="image" alt="Structure" /></td>
<td></td>
</tr>
<tr>
<td>4-Hydroxybenzoic acid</td>
<td>19.85 [PrP-a2]</td>
<td><img src="image" alt="Structure" /></td>
<td></td>
</tr>
<tr>
<td>Monohydroxy-propyl paraben</td>
<td>21.22 [PrP-b1]</td>
<td><img src="image" alt="Structure" /></td>
<td></td>
</tr>
<tr>
<td>1-Hydroxy-propylparaben</td>
<td>24.36 [PrP-c]</td>
<td><img src="image" alt="Structure" /></td>
<td></td>
</tr>
<tr>
<td>1-Hydroxy-2-oxobutyl 4-hydroxybenzoate</td>
<td>26.85 [BuP-e]</td>
<td><img src="image" alt="Structure" /></td>
<td></td>
</tr>
<tr>
<td>Butylparaben</td>
<td>22.49 [BuP]</td>
<td><img src="image" alt="Structure" /></td>
<td></td>
</tr>
<tr>
<td>4-Hydroxybenzoic acid</td>
<td>21.01 [BuP-a]</td>
<td><img src="image" alt="Structure" /></td>
<td></td>
</tr>
<tr>
<td>Monohydroxy-butyl paraben</td>
<td>23.08 [BuP-b1]</td>
<td><img src="image" alt="Structure" /></td>
<td></td>
</tr>
<tr>
<td>1-Hydroxy-butylparaben</td>
<td>25.15 [BuP-b2]</td>
<td><img src="image" alt="Structure" /></td>
<td></td>
</tr>
<tr>
<td>4-(4-hydroxybenzoyloxy)butanoic acid</td>
<td>26.33 [BuP-d]</td>
<td><img src="image" alt="Structure" /></td>
<td></td>
</tr>
<tr>
<td>1-Hydroxy-2-oxobutyl 4-hydroxybenzoate</td>
<td>27.87 [BuP-e]</td>
<td><img src="image" alt="Structure" /></td>
<td></td>
</tr>
</tbody>
</table>

(continued on next page)
Most of the DBPs of parabens can be divided according to their structures as follows:

### 3.3.1. Aromatic ring hydroxylated parabens

Mono- (MeP-c, EtP-b, PrP-b and BuP-b), di- (MeP-d, EtP-e, PrP-d, BuP-f) and tri- (MeP-e, PrP-e, BuP-g) hydroxylated parabens were detected in almost all extracts from the ozonated parabens solutions. Addition of 88 amu for monohydroxylated parabens, 176 amu for dihydroxylated parabens and 264 amu for trihydroxylated parabens indicate the addition of one, two and three \[(\text{CH}_3\text{OSi})\] groups to the parabens, respectively (Fig. S5–S7). Beside the molecular ion peak (M⁺), other significant peaks showing similar characteristic are \(m/z\) 281 for monohydroxylated parabens, \(m/z\) 369 for dihydroxylated parabens and \(m/z\) 457 for trihydroxylated parabens. These three peaks represent the loss of alkoxy group from mono-, di- and tri- hydroxylated parabens in mass spectrum. The presence of these fragment ions indicated that hydroxylation occurred at the aromatic ring of parabens.

### 3.3.2. Ester chain hydroxylated parabens

1-Hydroxyparabens (MeP-b, EtP-c, PrP-c and BuP-c) were also observed as one of the DBP formed during ozonation process. The major peaks observed for 1-hydroxyparabens are at \(m/z\) 73, \(m/z\) 193 and the molecular ion peak (M⁺) (Fig. S8). For the silylated parabens, \(m/z\) 193 fragment refers to the free radical of 4-(trimethylsilyloxy)benzaldehyde with only one \[(\text{CH}_3\text{OSi})\] substituent attached to the aromatic ring. Addition of 88 amu confirmed the presence of one hydroxyl group at the ester chain of parabens.

### Table 2 (continued)

<table>
<thead>
<tr>
<th>Compounds identified in GCMS (M⁺)</th>
<th>RT (min) [Label]</th>
<th>Structure of proposed DBPs (Molecular weight)</th>
<th>Name of proposed DBPs</th>
</tr>
</thead>
<tbody>
<tr>
<td>(TMSO)₃OAr₃ (m/z 442)</td>
<td>28.24 [BuP-f]</td>
<td>[BuP-f]</td>
<td>Dihydroxy-butyl paraben</td>
</tr>
<tr>
<td>(TMSO₂OAr₂) (m/z 530)</td>
<td>29.05 [BuP-g]</td>
<td>[BuP-g]</td>
<td>Trihydroxy-butyl paraben</td>
</tr>
</tbody>
</table>

**Fig. 2.** Proposed reaction pathway for the hydroxylation of the aromatic ring of parabens via: (a) ozone and (b) hydroxyl radical. [MeP, \(R = \text{H}\); EtP, \(R = \text{CH}_3\); PrP, \(R = \text{CH}_3\text{CH}_2\); and BuP, \(R = \text{CH}_3\text{CH}_2\text{CH}_2\)].
1,2-dihydroxy-ethylparaben (EtP-d) was the only detected dihydroxylated parabens at the ester chain of parabens. For dihydroxylated ethylparaben, the molecular ion peak at $m/z$ 414 indicates the addition of two silylated hydroxyl groups to EtP. This compound shows a base peak at $m/z$ 193 similar to the monohydroxylated compounds. In addition, this compound also shows stronger peaks at $m/z$ 210, $m/z$ 281 and $m/z$ 399 in the mass spectrum (Fig. S9). For butylparaben, additional two DPBs, namely 4-(4-hydroxybenzoyloxy)butanoic acid (BuP-d) and 1-hydroxy-2-oxobutylparaben (BuP-e) were detected which were presumably formed through further oxidation of the ester chain of the hydroxylated butylparaben. Since the molecular ion peak did not appear in their mass spectra the structure of these compounds were proposed based on their fragmentation patterns (Fig. S9).

3.3.3. Breakdown products of parabens

Hydroquinone and 4-hydroxybenzoic acid were two major breakdown products generated during ozonation of parabens. These compounds were identified through their mass spectrum and comparing with those in the database.

3.4. Proposed degradation mechanism of parabens in ozonation

Hydroxylation was found to be a significant reaction in the ozonation of parabens, mostly at the aromatic ring and the ester chain of parabens. Hydroxylation at the aromatic ring produced a series of aromatic ring hydroxylated products ($P$, $Q$ and $R$) which can occur via a direct reaction with ozone (Fig. 2a) or -OH which was generated from the decomposition of ozone in water (Fig. 2b). Due to its electrophilic nature of ozone, ozone can only react with the aromatic ring of parabens. Thus, -OH is the only species available for reaction with the ester chain of parabens in the ozonation. Pathway I shows the hydroxylation at the ester chain of parabens and pathway II shows the formation of parabens breakdown products (Fig. 3). Presumably, formation of ester chain hydroxylation products began with the hydrogen abstraction to produce the radical $S$ which react with dissolved oxygen to form peroxyl radical $T$. $T$ which could further dissociate into carbocation $U$ (von Sonntag, 2006) which could further react with -OH to form ester chain hydroxylation products, $V$. Reaction of $V$ with ozone or -OH formed aromatic ring and ester chain hydroxylation product, $W$. Parabens breakdown products could be formed from breakdown of C–O bond by -OH to form radical $X$ which could directly react with water to give $Y$. $X$ could also rearrange to lose CO$_2$ and further reacts with -OH to form Z. DBPs can also further react with the highly reactive -OH and ozone present in the reaction mixture to form other products which are not identified in this study.

4. Conclusion

Second-order rate constants for the reaction of four parabens (methylparaben, ethylparaben, propylparaben and butylparaben) with ozone were measured at pH 2, 6 and 12. At pH 2, 6 and 12, parabens occurred in the aqueous solution as protonated, undisassociated and dissociated species, respectively. The dissociated parabens were found to be the most reactive species toward the reaction with ozone followed by undisassociated and protonated species. Characterization of DBPs formed during ozonation processes was performed using GCMS. The experiment showed various DBPs of parabens were generated during ozonation process. Hydroxylation of parabens was found to be the major reaction that occurred during the ozonation and a series of hydroxylation compounds were detected. Monohydroxylated parabens formed by hydroxylation of aromatic ring and the hydroxylation of ester chain of parabens were found to be the common DBPs detected in the applied ozonation process. Hydroquinone and 4-hydroxybenzoic acid were two detected major parabens breakdown products in this experiment.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.chemosphere.2010.09.004.
References


