

Fenton degradation of dialkylphthalates: products and mechanism

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Received: 17 January 2011 / Accepted: 10 May 2011 / Published online: 21 June 2011
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Abstract Contamination of wastewater by organic pollutants is a major worldwide issue. For instance plastic additives such as phthalates are found in wastewater. Efficient techniques are thus needed to clean wastewaters. The Fenton reaction involving H_2O_2 and Fe(II) salts can be used to treat polluted water. During the Fenton reaction pollutants are decomposed directly by hydroxyl radicals. In some cases toxic by-products are produced. Here dimethyl phthalate, diethyl phthalate, and dipropyl phthalate by-products formed during the Fenton reaction were studied. Fenton degradation of selected phthalates yielded numerous transformation products such as hydroxylated phthalates. The hydroxylation reaction occurred at the aromatic ring of phthalates and yielded mono- and dihydroxylated phthalates. For monohydroxylated phthalate, 3-hydroxy- and 4-hydroxydialkylphthalates are the main transformation products. In addition to hydroxylated derivatives, aliphatic chain degraded mono- and dihydroxylated phthalates were also detected.

Keywords Dimethyl phthalate · Diethyl phthalate · Dipropyl phthalate · Hydroxylation · Hydroxyl radical · Fenton

Electronic supplementary material The online version of this article (doi:10.1007/s10311-011-0317-3) contains supplementary material, which is available to authorized users.

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Introduction

Phthalates are dialkyl or alkyl/aryl esters of 1,2-benzenedicarboxylic acid and are used extensively as additives to improve the workability of plastics (Oehlmann et al. 2008). Because of their extensive use, many different phthalates have been found in various aquatic environments (Tay et al. 2010). Bioaccumulation of phthalates in living organisms has also been reported (e.g., Huang et al. 2008; Pant et al. 2008). The estrogenic properties of phthalates are a major concern because of the potential adverse health effects (Nakai et al. 1999; Parveen et al. 2008).

The Fenton reaction is an advanced oxidation process that has been used in water and wastewater treatment (Trujillo et al. 2006). The Fenton reaction involves the application of hydrogen peroxide (H_2O_2), along with iron(II) salts as a catalyst, to produce the hydroxyl radical ($\cdot\text{OH}$), which is a powerful oxidant with a high oxidation potential of 2.8 V (Ikehata and El-Din 2006). During the Fenton reaction, organic pollutants are removed through a series of radical reactions. However, incomplete treatment of some organic pollutants might produce toxic transformation products (Ikehata et al. 2006). The kinetics of the degradation of dialkylphthalates using various oxidation processes, such as UV/ H_2O_2 (e.g., Xu et al. 2009a), $\text{TiO}_2/\text{H}_2\text{O}_2$ (Xu et al. 2009b), photochemically enhanced Fenton reaction (Yang et al. 2005), photocatalytic degradation (Huang and Chen 2010), and ozonation (Jung et al. 2010; Tay et al. 2010) have been widely reported. However, the transformation products of dialkylphthalates generated from treatment processes that involve $\cdot\text{OH}$ have not been reported. Therefore, the main objectives for this study were to identify the major transformation products of phthalates and to determine the mechanism of the transformation of dialkylphthalates in the Fenton reaction. To our

Table 1 Transformation products of phthalates. *GCMS* gas chromatography–mass spectrometry, *TIC* total ion current

Compound identified by GCMS [Label]	M^+ in TIC	Retention time (min)	Name of identified transformation products
Dimethyl phthalate			
[DMP]	m/z 194	19.22	Dimethyl phthalate
[DMP-1]	m/z 210	20.08	Dimethyl 3-hydroxyphthalate
[DMP-2]	m/z 210	22.82	Dimethyl 4-hydroxyphthalate
Diethyl phthalate			
[DEP]	m/z 222	20.72	Diethyl phthalate
[DEP-1]	m/z 238	21.50	Diethyl 3-hydroxyphthalate
[DEP-2]	m/z 238	23.39	Diethyl 4-hydroxyphthalate
[DEP-3]	m/z 254	22.51	Diethyl dihydroxyphthalate
[DEP-4]	m/z 224	20.85	2-Ethyl 1-methyl 3-hydroxyphthalate
[DEP-5]	m/z 240	21.59	1-ethyl 2-methyl dihydroxyphthalate

Table 1 continued

Dipropyl phthalate			
	<i>m/z</i> 250	22.40	Dipropyl phthalate
[DPP]			
	<i>m/z</i> 266	23.05	Dipropyl 3-hydroxyphthalate
[DPP-1]			
	<i>m/z</i> 266	23.88	Dipropyl 4-hydroxyphthalate
[DPP-2]			
	<i>m/z</i> 238	21.17	1-Methyl 2-propyl 3-hydroxyphthalate
[DPP-3]			
	<i>m/z</i> 282	25.30	Dipropyl dihydroxyphthalate
[DPP-4]			
	<i>m/z</i> 222	23.64	2-((2-Oxopropoxy)carbonyl) benzoic acid
[DPP-5]			
	<i>m/z</i> 236	23.69	methyl 2-oxopropyl phthalate
[DPP-6]			

knowledge, the mechanism of the transformation of dialkylphthalates in the Fenton reaction has not been elaborated elsewhere. These results may provide useful information for the evaluation of transformation products generated from dialkylphthalates during treatment processes that involve $\cdot\text{OH}$. Dimethyl phthalate (DMP), diethyl phthalate (DEP), and dipropyl phthalate (DPP) were selected for this study.

Materials and methods

Materials

Dimethyl phthalate (purity 99%), DEP (purity 99.5%), and DPP (purity, 99%) were obtained from Sigma–Aldrich

(USA) and used without further purification. Iron(II) sulfate was obtained from Ajax Chemicals (Australia). Sulfuric acid and all solvents used were purchased from Merck (Germany). Phthalate solutions were prepared by dissolving all the phthalates (100 $\mu\text{mol/L}$ each) in ultrapure deionized water (Elga).

Fenton reaction

The Fenton reaction was carried out on the phthalate solution individually at room temperature (27°C) in a 500-mL flat-bottomed flask containing 50 $\mu\text{mol/L}$ phthalate and 50 $\mu\text{mol/L}$ iron(II) sulfate. $\text{Fe}^{2+}:\text{H}_2\text{O}_2$ molar ratio was 1:20 (Sato et al. 2007; Nakrst et al. 2010). The pH was adjusted to 3 using 1.0 mol/L sulfuric acid. The reaction was started by the addition of H_2O_2 solution at a

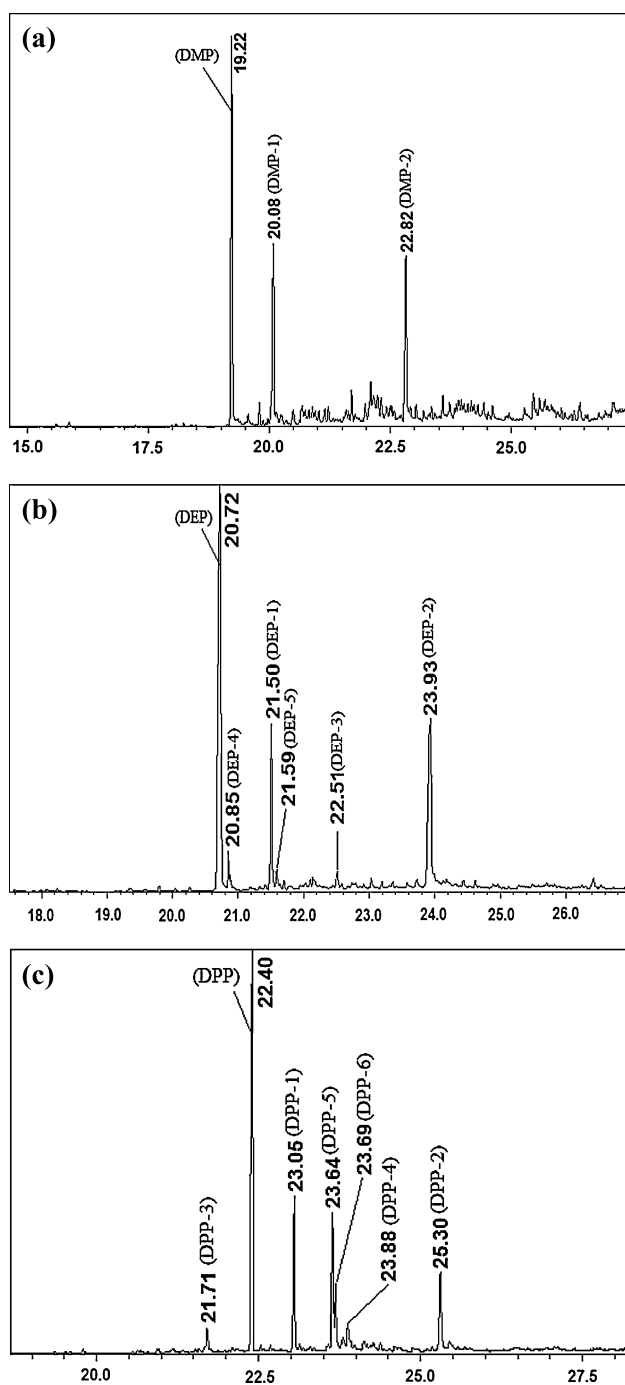


Fig. 1 Total-ion chromatograms (TIC) from GCMS analysis showing the peak and the retention time of identified transformation products of **a** dimethyl phthalate (DMP), **b** diethyl phthalate (DEP), and **c** dipropyl phthalate (DPP) after Fenton reaction. In this work, transformation products identification was performed based on its fragmentation in mass spectrum and also by comparing the obtained mass spectrum data with those previously reported in the literature. Dimethyl 3-hydroxyphthalate (DMP-1), dimethyl 4-hydroxyphthalate (DMP-2), diethyl 3-hydroxyphthalate (DEP-1), diethyl 4-hydroxyphthalate (DEP-2), diethyl dihydroxyphthalate (DEP-3), 2-Ethyl 1-methyl 3-hydroxyphthalate (DEP-4), 1-ethyl 2-methyl dihydroxyphthalate (DEP-5), dipropyl 3-hydroxyphthalate (DPP-1), dipropyl 4-hydroxyphthalate (DPP-2), 1-methyl 2-propyl 3-hydroxyphthalate (DPP-3), dipropyl dihydroxyphthalate (DPP-4), 2-((2-oxopropoxy)carbonyl) benzoic acid (DPP-5), methyl 2-oxopropyl phthalate (DPP-6) were identified as the transformation products of selected phthalates

GCMS analysis

The transformation products were analyzed on a Shimadzu GCMS system (GCMS-QP2010-Plus, Kyoto, Japan) equipped with an Rtx-5MS column (Crossbond 5% diphenyl/95% dimethyl polysiloxane, 30 m × 0.25 mm I.D., 0.25 μm, Restek, Bellefonte, PA). Helium (purity 99.999%) was used as the carrier gas, with an average velocity of 40.2 cm/s. The GC oven temperature was initially held at 60°C for 2 min and then increased to 280°C at 6°C/min and held at this temperature for 2 min. The injection port and transfer line were maintained at 300 and 310°C, respectively. The data for quantitative analysis were acquired in the electron ionization mode (70 eV), with a mass range of 50–700 atomic mass units (amu).

Results and discussion

Identification of transformation products

Gas chromatograph–mass spectrometer analyses were performed by comparing the chromatogram of the initial phthalate solutions as a control sample with the chromatograms of the aliquots taken during the reaction. The details of all the identified transformation products of selected phthalates are presented in Table 1.

Dimethyl phthalate

Figure 1a shows the GC total ion chromatogram (TIC) of the degraded DMP mixture. The peak for DMP appeared at a retention time of 19.22 min. Two transformation products were detected for DMP. The peaks for the two transformation products of DMP appeared at 20.08 and 22.82 min and were identified as dimethyl 3-hydroxyphthalate (DMP-1) and dimethyl 4-hydroxyphthalate (DMP-2), respectively. DMP-1 and DMP-2 were also

final concentration of 1 mmol/L. The final volume for the reaction was 500 mL. A 20 mL aliquot of the sample was withdrawn every 2 min for 10 min, and then the reaction was quenched using 0.01 mol/L sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$) solution. Each aliquot was liquid–liquid extracted using hexane (3 × 15 mL) then ethyl acetate (3 × 15 mL). The extracts were then concentrated to 50 μL, and 1 μL of the concentrated extract was injected into a gas chromatograph–mass spectrometer (GCMS) for analysis.

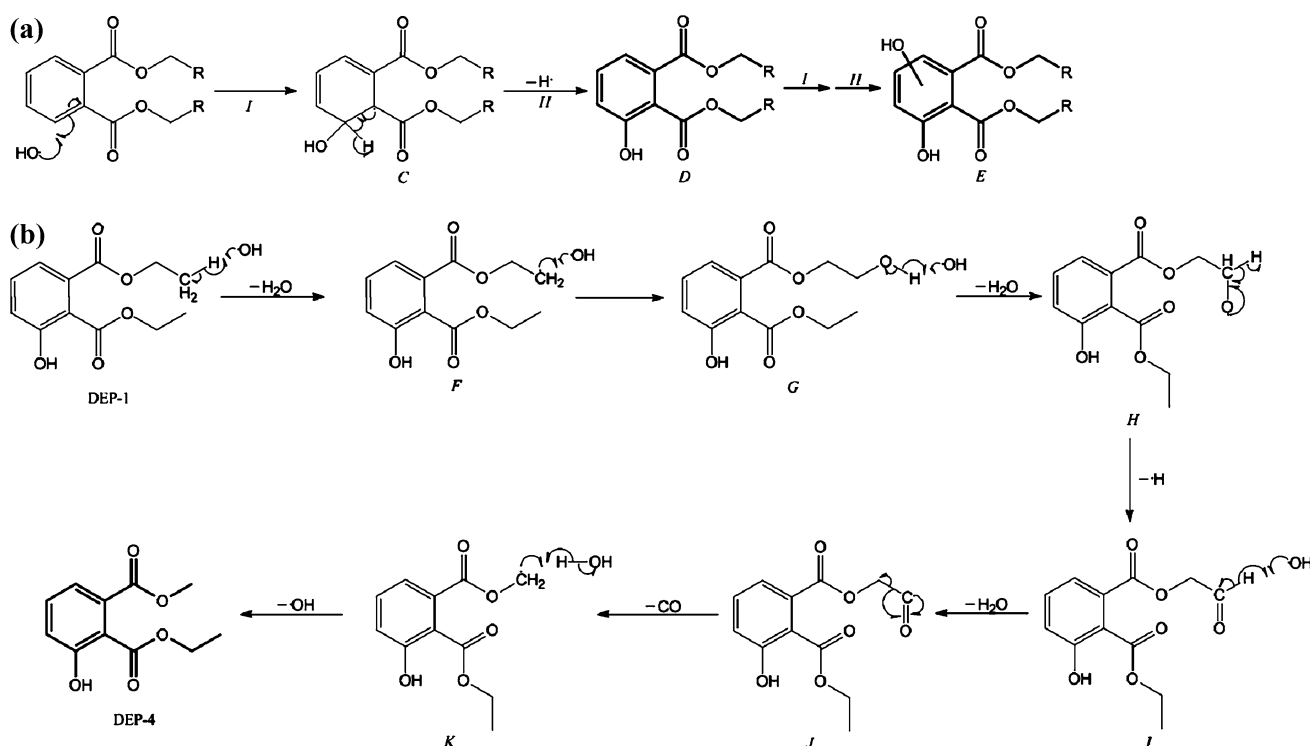


Fig. 2 Proposed mechanism for **a** the hydroxylation of phthalates for the formation of aromatic ring monohydroxylated phthalates (DMP-1, DMP-2, DEP-1, DEP-2, DPP-1, and DPP-2) and dihydroxylated phthalates (DEP-3 and DPP-4), and **b** the formation of DEP-4 from DEP-1, an example of the alkyl chain breakdown reaction for phthalates. The reactions were proposed based on hydrogen

abstraction and hydroxyl addition at the aliphatic chain and aromatic ring of phthalates, respectively. These mechanisms show the main reactions that occurred at the aromatic ring and aliphatic chain of phthalates during Fenton reaction. [dimethyl phthalate (DMP), R = H; diethyl phthalate (DEP), R = CH₃; dipropyl phthalate (DPP), R = CH₂CH₃]

detected by Xu et al. (2009a) in the degradation of DMP by the UV/H₂O₂ process. These two transformation products were identified based on data reported by Galyashin et al. (1983). The mass spectra of DMP-1 and DMP-2 are presented in Figs. S1a and b (supplementary material).

Diethyl phthalate

Five transformation products were detected for DEP. The peak with a retention time of 20.72 min represents DEP (Fig. 1b). Based on the elution patterns of DMP-1 and DMP-2, the peaks at retention times of 21.50 and 23.93 min were identified as diethyl 3-hydroxyphthalate (DEP-1) (Fig. S1c) and diethyl 4-hydroxyphthalate (DEP-2) (Fig. S1d), respectively. An additional three transformation products were detected. The peaks for these three transformation products appeared at 20.85, 21.59, and 22.51 min and were labeled as DEP-4, DEP-5, and DEP-3, respectively. Based on the molecular ion peak, DEP-3 was identified as diethyl dihydroxyphthalate with a molecular mass of 254 amu (Fig. S1e). For DEP-3, the peak at *m/z* 180 in the mass spectrum was identified as the neutral fragment of dihydroxyisobenzofuran-1,3-dione. Dihydroxyisobenzofuran-1,3-dione was formed through the loss of ethoxy and

ethyl groups from DEP, followed by the formation of a furan ring. Therefore, the presence of a peak at *m/z* 180 indicated the presence of two OH groups on the aromatic ring of DEP. These mono- and dihydroxylated derivatives were also detected as ozonation transformation products of DEP (Jung et al. 2010). 2-Ethyl 1-methyl 3-hydroxyphthalate (DEP-4) and 1-ethyl 2-methyl dihydroxyphthalate (DEP-5) are the suggested transformation products of DEP-1 and DEP-3, respectively. Peaks for DEP-4 and DEP-5 appeared at 20.85 and 21.59 min, respectively. DEP-4 and DEP-5 were formed through the loss of one methylene (14 amu) group from DEP-1 and DEP-3, respectively. Like DEP-1, DEP-4 also showed a base peak at *m/z* 120 (Fig. S1f). As for DEP-3, the presence of a peak at *m/z* 180 in the mass spectrum of DEP-5 indicated the presence of two OH groups at the aromatic ring (Fig. S1g). The DEP transformation products identified in this work were different to the transformation products generated by photocatalytic degradation (Huang and Chen, 2010).

Dipropyl phthalate

For DPP, six transformation products were identified (Fig. 1c). The peak for DPP appears at a retention time of

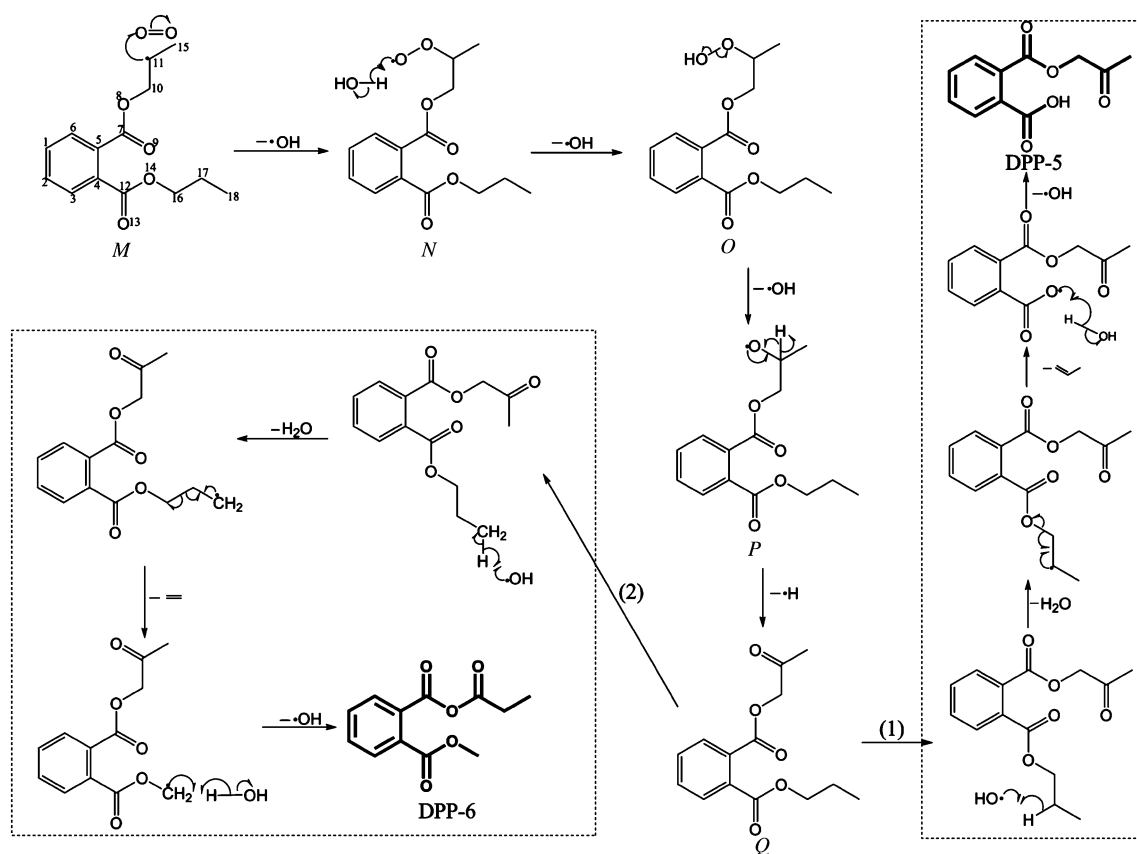


Fig. 3 Mechanism for the formation of DPP-5 [2-((2-Oxopropoxy)carbonyl) benzoic acid] and DPP-6 (methyl 2-oxopropyl phthalate). The reaction was proposed to start from the formation of 2-oxopropyl formate moiety and followed by the breakdown of propyl

chain (pathway 1 and 2) of the dipropyl phthalate (DPP). This mechanism shows the oxidation and breakdown of the aliphatic chain of DPP

22.40 min. Peaks at 23.05 and 23.88 min were identified as dipropyl 3-hydroxyphthalate (DPP-1) and dipropyl 4-hydroxyphthalate (DPP-2), respectively, based on their retention times in comparison with the 3-hydroxy- and 4-hydroxy derivatives of DMP and DEP. The mass spectra of DPP-1 and DPP-2 are presented in Figs. S1h and i.

The peak at 21.71 min was identified as 1-methyl 2-propyl 3-hydroxyphthalate (DPP-3), which is a transformation by-product of DPP-1. Apart from the molecular ion peak, the major difference between DPP-3 and DPP-1 is the presence of a peak at m/z 179 (Fig. S1k). This peak was formed through the loss of a propoxy group followed by the formation of a furan ring. Therefore, the presence of the m/z 179 peak indicates a methyl ester group is present in DPP-3. The peak at 23.88 min in the TIC can be attributed to dipropyl dihydroxyphthalate (DPP-4). Like DEP-3, DPP-4 also shows a base peak at m/z 180 (Fig. S1j).

Other transformation products detected for DPP were 2-((2-oxopropoxy) carbonyl) benzoic acid (DPP-5) and methyl 2-oxopropyl phthalate (DPP-6). These two compounds were formed through the degradation and oxidation

of the aliphatic chain of DPP. The peaks for DPP-5 and DPP-6 appeared at 23.64 and 23.69 min, respectively. The mass spectra of DPP-5 (Fig. S1l) and DPP-6 (Fig. S1m) and their fragmentation pathway (Fig. S2) are presented in supplementary Material.

Mechanism for degradation of the phthalates

Mechanisms for the degradation of phthalates are proposed based on the reaction of organic compounds with $\cdot\text{OH}$ such as hydrogen abstraction and hydroxyl addition (da Silva et al. 2009). Based on the identified transformation products, hydroxylation of the aromatic ring of the phthalates was found to be the main reaction that occurred during the Fenton reaction. Figure 2a shows an example for the mechanism of the formation of mono- and dihydroxylated phthalates. For the hydroxylation reaction at the aromatic ring of the phthalates, the reaction was thought to be initiated by the addition of $\cdot\text{OH}$ at the aromatic ring to form radical C. This radical was then rearranged through elimination of the hydrogen radical to form aromatic ring-monohydroxylated phthalates, D. Further hydroxylation of

the monohydroxylated phthalates formed dihydroxylated phthalates, *E*.

Degradation of the aliphatic chain of the hydroxylated phthalates was also found to occur during the Fenton reaction. The formation of DEP-4 is used as an example to elaborate the mechanism (Fig. 2b). The reaction was proposed to start with the formation of radical *F* through hydrogen abstraction of DEP-1 by $\cdot\text{OH}$. Radical *F* could react with $\cdot\text{OH}$ to form the aliphatic hydroxylated intermediate, *G*. Further hydrogen abstraction of *G* led to the formation of radical *H*. Intermolecular rearrangement of *H* through the loss of one hydrogen radical formed intermediate *I* with an aldehyde group, and *I* then reacted with $\cdot\text{OH}$ to form radical *J*. Intramolecular rearrangement of intermediate *J* through the loss of carbon monoxide formed radical *K*, which then reacted with water to give DEP-4.

For DPP, two additional transformation products, 2-((2-oxopropoxy)carbonyl) benzoic acid (DPP-5) and methyl 2-oxopropyl phthalate (DPP-6), were detected. The mechanisms for the formation of these two transformation products are presented in Fig. 3. For the formation of the 2-oxopropyl formate moiety in these two transformation products, the reaction was proposed to start with formation of radical *M*. Radical *M* could be formed through hydrogen abstraction by $\cdot\text{OH}$ at C₁₁ or C₁₇. Radical *M* could react with dissolved oxygen to form the peroxy radical *N*, which then reacted with water to form *O*. Instability of the hydroperoxide, *O*, leads to formation of the radical *P* through the elimination of $\cdot\text{OH}$. *P* then rearranges through the elimination of the hydrogen radical to form intermediate *Q*, which contains a 2-oxopropyl formate moiety. The formation mechanisms for the carboxylic acid (Pathway 1) and carboxylic acid methyl ester moieties (Pathway 2) lead to the formation of DPP-5 and DPP-6, respectively.

Conclusion

Fenton degradation of dimethyl phthalate (DMP), diethyl phthalate (DEP), and dipropyl phthalate (DPP) proceeds through the formation of numerous transformation products, which are mainly hydroxylated derivatives. Hydroxylation of phthalates yielded mono- and dihydroxylated dialkylphthalate. Hydroxylated DEP and DPP with degraded aliphatic chains were also detected. For DPP, two additional transformation products were formed through the degradation and oxidation of the aliphatic chain of DPP. For phthalates with longer alkyl chains, more transformation products were detected, which might be because of the increased rate of hydrogen abstraction on the alkyl chain by $\cdot\text{OH}$ with the longer alkyl chain lengths (Behnke et al. 1988).

Acknowledgments This research was supported financially by the Malaysia Toray Science Foundation (MTSF), Ministry of Higher Education Malaysia (FRGS-FP018-2008C) and University of Malaya (PS354-2010A).

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