The degradation of diethyl phthalate (DEP) during ozonation: oxidation by-products study

Yeon Jung Jung, Byung Soo Oh, Kyoung Suk Kim, Minoru Koga,
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ABSTRACT

The degradation of diethyl phthalate (DEP) in an aqueous solution during ozonation was investigated by identifying the oxidation intermediates using GC–MS. The experiments were carried out in semi-batch mode with a $1.5\,\mathrm{mg\,l^{-1}}$-min ozone dose. The proposed degradation pathways were divided into hydrolysis of the aliphatic chain (pathway (A)) and hydroxylation resulting from ·OH attack in the aromatic ring (pathway (B)). With increasing ozone dose, the aromatic ring of DEP was opened and acidic compounds, such as malonic acid, succinic acid and glutaric acid were formed. In addition, the ozonation of DEP for 18 min induced hydrogen peroxide (H_2O_2) generation at levels six times higher than pure water. Of the intermediates indentified, phthalic acid (PA) and phthalic anhydride (PAH) enhanced the degradation of DEP by promoting ozone decomposition.

Key words | degradation, diethyl phthalate (DEP), hydroxyl radical, intermediates, ozone

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INTRODUCTION

Phthalate esters (PEs), which are commonly called phthalates, are widely used as an additive for polyvinyl chloride (PVC) resins, rubber, cellulose and styrene production to improve their flexibility and softness (Page & Lacroix 1995; Staples *et al.* 1997; Kamrin 2009). The worldwide production of phthalate esters has reached more than 5.2 million tons per year (Parkerton & Konkel 2001). Owing to their high levels of production and utilization, PEs leaching out of water have become persistent organic pollutants in aquatic environments. These compounds have been reported to accumulate in animal fat (Jobling *et al.* 1995; Pereira *et al.* 2006; Barse *et al.* 2007), act as endocrine disruptors and have adverse effects on organisms and humans even at low concentrations (Harris *et al.* 1997;

Hashimoto *et al.* 2003). For these reasons, some of these compounds belong to the chemicals list of endocrine disruptors issued by the World Health Organization (WHO), USEPA, WWF and other agencies (WHO 2006; Kamrin 2009).

Short-chained esters, such as diethyl phthalate (DEP), which originate mainly from the discharge of wastewater and leaching from plastic products during their use and after disposal (Staples *et al.* 1997), are one of the most frequently identified PEs in environmental samples, including surface water (Oh *et al.* 2006; Zeng *et al.* 2008), wastewater (Vogelsang *et al.* 2006; Kong *et al.* 2008), and sediments (Tan 1995; Myung *et al.* 2002; Zeng *et al.* 2008), because the water solubility ($1{,}100\,\mathrm{mg\,l^{-1}}$ at $25°C$) of DEP

is much higher than that of other long-chain PEs ($5 \times 10^{-4} \sim 11.2\,\mathrm{mg\,l^{-1}}$ at 25°C) (Staples *et al.* 1997). Pereira *et al.* (2006) reported that exposure to a low concentration of DEP for a long period could lead to an enhanced toxic effect by severe hepatocellular damage. Furthermore, many studies have demonstrated that DEP is difficult to degrade biologically and photochemically (photooxidation half-life time = $7 \sim 12$ years) (Staples *et al.* 1997). Therefore, the release of DEP into water environments is an emerging issue in public health.

Several studies have examined the elimination of DEP using advanced oxidation processes (AOPs) involving the generation of the hydroxyl radical ($\cdot$OH), such as UV/H_2O_2 (Xu *et al.* 2007), TiO_2/UV (Muneer *et al.* 2001), $UV/H_2O_2/Fe^{2+}$ (Yang *et al.* 2005) and Fe(III)/solar light (Mailhot *et al.* 2002). These studies agree that the reaction of DEP with $\cdot$OH is dominant for the removal of DEP, indicating that AOPs are effective processes for removing DEP from water.

The ozone process is used widely in drinking water and wastewater treatment because of its powerful oxidation and disinfection ability. In Korea, there are 14 water treatment plants using ozone facilities, which treat from 28,000 to 1,550,000 $\mathrm{m^3/day}$ of drinking water depending on their treatment capacity of water, and its application is increasing gradually (Mun *et al.* 2005). Considering these trends, there is a strong need to examine the elimination of DEP in water using the ozone process. However, there have been relatively few studies on the elimination of DEP by ozone. Although Legube *et al.* (1984) reported the removal of DEP by ozonation and aeration, the experiment was carried out under limited conditions, such as acidic pH and a mixture solution of water and methanol.

A previous study (Oh *et al.* 2006) investigated the removal efficiency of DEP and its estrogenic efficiency by ozone, UV and combined ozone/UV processes. Of the processes tested, the ozone/UV process showed the highest efficiency for the removal of both DEP and its estrogenic activity. However, the ozone unit process, even in a continuously ozone-injected mode, had difficulty in completely removing the parent compound, DEP. In addition, highly persistent unknown by-product peaks of DEP formed during ozonation were detected by HPLC/UV–Visible detection. Moreover, mineralization was remarkably low even at a high ozone dose ($480\,\mathrm{mg\,l^{-1}}$), indicating that the oxidation by-products of DEP still remained in solution. To our knowledge, there has been no detailed study of the DEP degradation pathway by ozonation, even though there are a few reports on the identification of the DEP oxidation intermediates formed in UV, Fe(III)/solar light and UV/H_2O_2 processes (Balabanovich & Schnabel 1998; Mailhot *et al.* 2002; Xu *et al.* 2007). Therefore, this study examined the degradation pathway of DEP by identifying the oxidation intermediates by GC–MS analysis in the ozone process as well as the effect of the intermediates identified (i.e. phthalic acid and phthalic anhydride) on DEP degradation during ozonation.

EXPERIMENTAL METHODS

Standards and reagents

All reagents used in these experiments were either of the grades recommended by the method or of the purest available quality. DEP (diethyl phthalate, >99.5%) was purchased from Sigma–Aldrich and phenanthrene-d_{10}, as the internal standard, was obtained from Wako Pure Chemical (Osaka, Japan). As a derivatization reagent for trimethylsilyl (TMS) and methylation, *N,O*-bis(trimethylsilyl)-trifluoroacetamide (BSTFA) and *N*-methyl-*N*-nitro-n-nitro-soguanidine (MNNG) were purchased from GL Science (Tokyo, Japan). The commercial standards (phthalic acid, phthalic anhydride, and 4-hydroxy phthalic acid), which are the intermediates identified in this study, were purchased from Kanto Chemical, Tokyo Chemical Industry and Wako Pure Chemical, respectively.

Extraction procedure for DEP and the intermediates and GC/MS analysis

The intermediates and/or by-products were identified by direct extraction and liquid–liquid extraction (LLE). In the direct method, the ozonated samples (50 ml) according to the reaction time were evaporated completely with a rotary evaporator and 1 ml of acetone was added to the residue of the sample. The residues were dried completely under nitrogen gas. In the LLE method, the ozonated samples (50 ml) were extracted twice using a total volume of 20 ml

dichloromethane. The extracts were dehydrated with Na_2SO_4 and SiO_2 wool and evaporated to 2 ml using a Kuderna-Danish (KD) concentrator. The residue solution was dried completely under a gentle nitrogen flow. The dried residues after extraction by direct and LLE were then derivatized with BSTFA. In the case of TMS with BSTFA, 200 μl of BSTFA was added to the dried residues and heated for 1 h at 70°C. The solutions were again concentrated under a gentle nitrogen stream until little remained. The volume was adjusted with 200 μl of benzene containing 10 mg l^{-1} of an internal standard. Three commercial intermediates (phthalic acid, phthalic anhydride and 4-hydroxylphthalic acid) were also derivatized using the TMS method to determine the peaks of the chromatogram.

GC/MS conditions

DEP and its intermediates were analysed by gas chromatography/mass spectroscopy (GC/MS), which consisted of HP6890 GC (Agilent, USA) and JMS-700 (JEOL, Japan). The scanning mode (50–650 msu) was operated in electron impact positive (EI +) ionization mode at a resolution of $R = 1,000$. The fused silica capillary column used was a 30 m × 0.25 mm i.d. with a 0.25 μm thick film of DB-5 (J&W Scientific, USA). The injector temperature was 260°C. The temperature program of the GC started at 70°C and was held at that temperature for 1 min. The column was then heated to 280°C at a rate of 10°C/min and held at that temperature for 3 min. A 2 μl sample volume was injected in splitless mode.

Computational chemistry

The MOPAC (version 2000) program with a CAChe package (Fujitsu Co. Ltd, Japan) was used to calculate the optimum geometry, a frontier electron density (FED) and atom partial charges (PC). The AM1 (Austin Model 1) level Hamiltonian parameter was used to optimize the stable structures. An initial position for possible ·OH attack could be estimated by calculating frontier electron densities and partial electric charge in the DEP structures (Watanabe et al. 2003). This can provide basic information on the degradation mechanisms of DEP.

Ozonation experiments for DEP

The ozonation of DEP was performed with a cylindrical, semi-batch reactor (Pyrex, 0.5 or 4 l) to examine the removal pattern of DEP and acquire the ozonated DEP solution to identify the intermediates. The ozone reactor system and analysis method of DEP are described in detail elsewhere (Oh et al. 2006). Briefly, the net ozone dose was set to 1.5 and 4 mg l^{-1} min with the flow rate fixed at 0.5 l min^{-1} for DEP oxidation study. A 100 μM DEP stock solution was prepared in distilled-deionized water (DDI). All DEP solutions, except for the sample of ozone decay test at pH 3, were adjusted to pH 7 with 0.01 M phosphate buffer solution. The sample for the test of ozone decomposition at pH 3 was adjusted with 0.1 N H_2SO_4 solutions. The residual ozone concentration in solution during ozonation was monitored continuously with a specifically devised

Table 1 | Calculations of the frontier electron density and partial charge of DEP by MOPAC

Structure of DEP
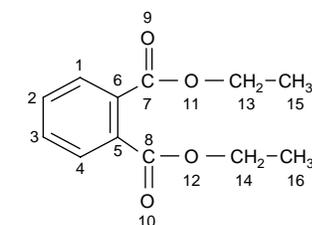
Atom	Frontier electron density (FED)	Partial charge (PC)
C_1	0.193	−0.109
C_2	0.248	−0.140
C_3	0.246	−0.145
C_4	0.211	−0.104
C_5	0.286	−0.082
C_6	0.286	−0.075
C_7	0.090	0.452
C_8	0.106	0.451
O_9	0.064	−0.411
O_{10}	0.097	−0.413
O_{11}	0.050	−0.357
O_{12}	0.059	−0.354
C_{13}	0.026	−0.020
C_{14}	0.021	−0.015
C_{15}	0.005	−0.301
C_{16}	0.009	−0.335

analytical set-up based on the indigo colorimetric method using a flow injection analysis (FIA) technique (Park et al. 2001). The degradation of DEP was tested in the presence and absence of methanol (MeOH), acetate, phthalic acid, and phthalic anhydride to determine the effect of the ·OH scavenger. The concentrations of DEP remaining in the treated water were analysed by high performance liquid chromatography (HPLC) equipped with a column (reverse phase C_{18}, Waters) and UV/Vis wavelength detector (Gilson Co.). The sample was eluted with methanol/10 mM phosphate-buffered water as the mobile phase (4/6 v/v) at a flow rate of 1 ml/min. The volume of the injected sample for HPLC analysis was 300 μl.

RESULTS AND DISCUSSION

Identification of oxidation intermediates

Table 1 shows the results of the MOPAC calculations. There are two possible sites for ·OH attack in the DEP chemical structure, the aliphatic chain and aromatic ring. Bajt et al. (2001) and Mailhot et al. (2002) examined the degradation of

dialkyl phthalates by photocatalysis with Fe(III) and TiO_2, and reported that ·OH attack occurs mainly on the aromatic ring for phthalates with shorter alkyl chains (i.e. dimethyl and diethyl phthalate), while it occurred on the aliphatic chains in the case of longer dialkyl phthalates (e.g. dibutyl phthalate). However, Xu et al. (2007) observed that ·OH formed in the UV/H_2O_2 process occurred mainly on the aliphatic chain rather than on the aromatic ring of DEP. In order to examine the initial positions of ·OH attack toward DEP, the frontier electron density (FED) and partial charge (PC) of the DEP structure (carbon and oxygen) were calculated using the MOPAC program, from which the initial position of ·OH attack toward DEP was estimated. The C_5 and C_6 carbons in the two C–C bonds connecting a carbonyl group (C–C=O) with the aromatic ring showed the largest frontier electron density (0.286), followed by the carbons (C_2 and C_3) in the aromatic ring (0.248 and 0.246). A higher electron density indicates more electrons in the bonds. Consequently, it was expected that ·OH would most likely attack these sites through an electrophilic reaction (Watanabe et al. 2003; Horikoshi et al. 2004; Kaneco et al. 2006). The hydrolysis of the DEP was estimated from the simulation of the molecular partial charge (Table 1).

Table 2 | GC/MS/EI retention times and spectral characteristics of the intermediate products of DEP by ozonation

MWs of DEP and intermediates	Retention time (min)[*]	Characteristic ions[†] (m/z)
(a) 222[‡]	10.33	222:(M+), 177, 149, 105, 76
(b) 194	10.84	266:(M+), 251:(M+-CH₃), 221:(M+-C₂H₅O), 193:(M+- C₂H₅O-CO), 177:(M+-OTMS), 73
(c) 166[‡]	11.46	310:(M+), 295:(M+-CH₃), 221:(M+-OTMS), 147, 73
(d) 148[‡]	6.91	148:(M+), 104:(M+-CO₂), 76: (M+-CO₂-CO)
(e) 238	15.65	310:(M+), 295:(M+-CH₃), 265:(M+-C₂H₅O), 237:(M+-TMS), 221:(M+-OTMS), 73
(f) 254	17.42	398:(M+), 383:(M+-CH₃), 353:(M+-C₂H₅O), 325:(M+-C₂H₅O-CO), 309:(M+-OTMS), 147, 73
(g) 198	16.72	486:(M+), 471:(M+-CH₃), 413:(M+-TMS), 397:(M+-OTMS), 353:(M+-OTMS-CO₂), 147, 73
(h) 142	14.71	430:(M+), 415:(M+-CH₃), 357:(M+-TMS), 341:(M+-OTMS), 313, 329:(M+-TMS-CO), 147, 73
(i) 182	14.12	326:(M+), 311:(M+-CH₃), 281:(M+-C₂H₅O), 237:(M+-OTMS), 147, 73
(j) 182[‡]	15.20	398:(M+), 383:(M+-CH₃), 353, 309:(M+-OTMS), 147, 73
(k) 342	16.59	342:(M+), 327:(M+-CH₃), 269:(M+-TMS), 253:(M+-OTMS), 73
Malonic acid[‡]	5.40	248:(M+), 233:(M+-CH₃), 204, 147, 73
Succinic acid[‡]	6.85	262:(M+), 247:(M+-CH₃), 218, 173:(M+-OTMS), 147, 73
Glutaric acid[‡]	7.51	276:(M+), 261:(M+-CH₃), 233, 147, 73

[*]This is the retention time (RT) of direct/BSTFA, but (e) and (k) are that of LLE/BSTFA.
[†]This is the characteristic ion peak derivatized by BSTFA.
[‡]These compounds were confirmed by commercial standards.

The most negative partial charge atoms were the two carbonyl oxygen atoms (O_9 and O_{10}; -0.411 and -0.413), with the next being the two ether oxygen atoms (O_{11} and O_{12}; -0.357 and -0.354). Therefore, it was deduced that a hydrolysis reaction would occur on the side-chain of the DEP molecule including four oxygen atoms. These calculations provided basic information to elucidate the degradation mechanism of DEP. Referring to these calculations, the definite degradation pathway by the ozonation of DEP was determined from the total ion chromatogram (TIC) of the intermediates of DEP decomposition with BSTFA derivatization detected by GC/MS.

Table 2 lists the mass spectral data of DEP and its main intermediates obtained by GC/MS analysis as well as the characteristic ions of the possible fragments. Of the molecular weight numbers, [M^+-15] was formed by the characteristic loss of a methyl group (CH_3) from the THM-derivatized products. The mass spectrum of the trimethylated compounds detected was presented with fragment patterns at $m/z = 73$ and 147, which correspond to $(CH_3)_3Si^+$ and $[(CH_3)_2Si = O-Si(CH_3)_3]^+$, respectively. The fragment of $m/z = 73$ shows the base peak frequently detected in a TMS derivative, and that of $m/z = 147$ indicates two or more TMS groups in the molecule.

Of the intermediates detected, DEP and its intermediates lettered (c), (d) and (j) were confirmed using the reference compounds, phthalic acid, phthalic anhydride and 4-hydroxy phthalate, respectively. The others were
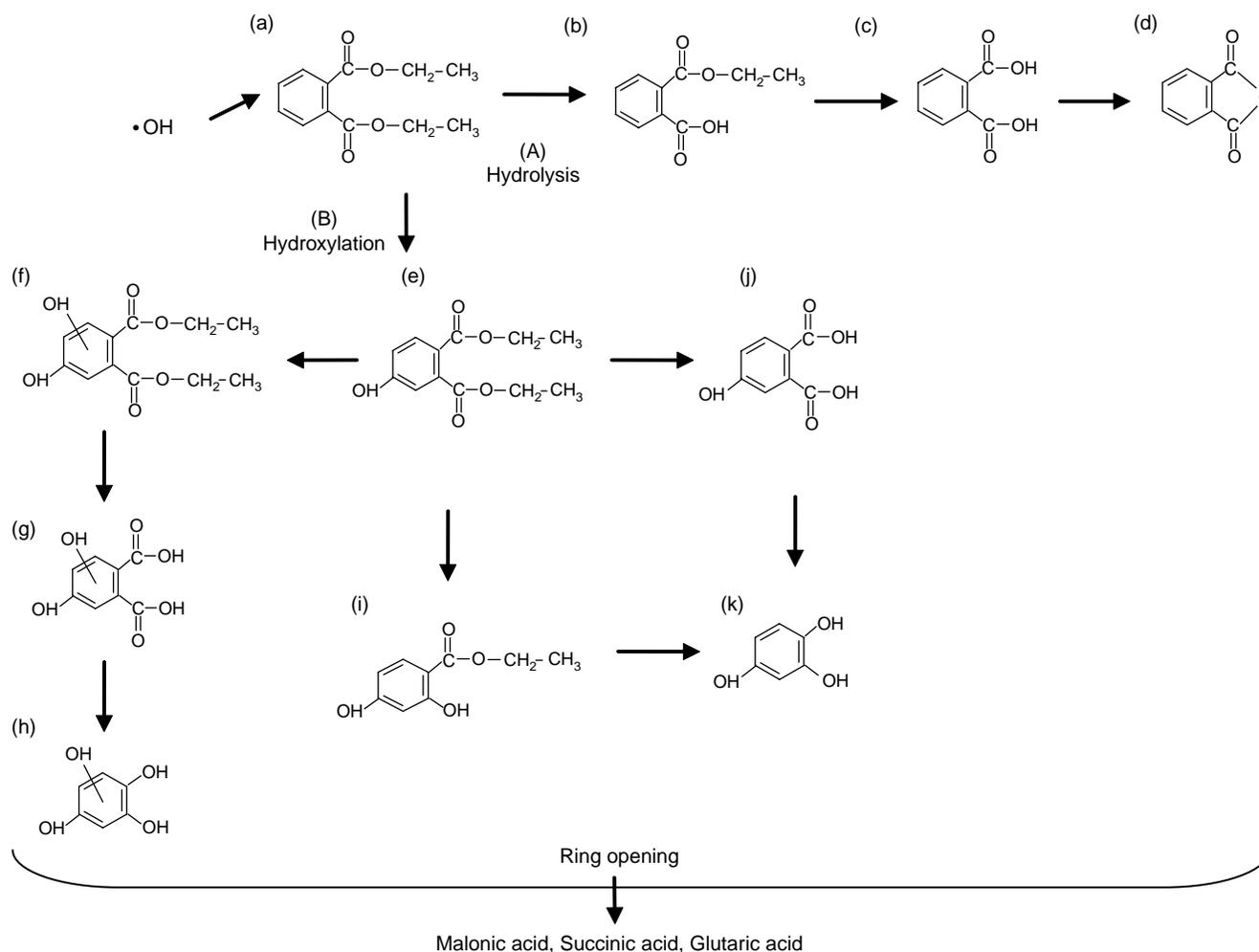

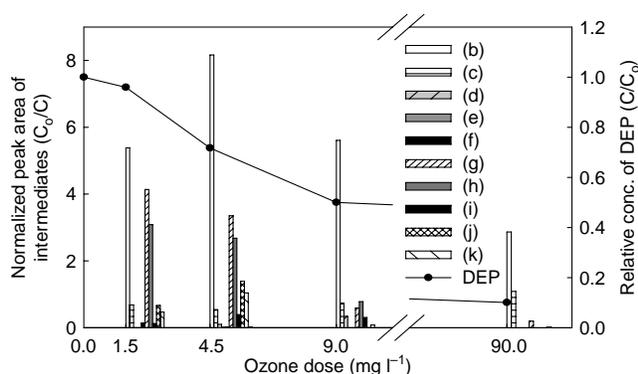**Figure 1** | Proposed degradation pathways for DEP during ozonation.

Figure 2 | Normalized peak areas of the DEP intermediates and the depletion of DEP with respect to the ozone dose. DEP intermediates detected by GC/MS; $[DEP]_0 = 100\,\mu M$, initial pH = 7, temp. = 20°C. The legends (b–k) indicate the intermediates of DEP labelled in Figure 1, respectively. C_0 = the peak area of the internal standard, $1\,mg\,l^{-1}$ of phenanthrene-d_{10}, C = peak area of each compound detected by GC/MS. Each peak area was normalized to that of the internal standard peak area.

identified by interpretation of the TMS-derivatized fragment intermediate products, which correspond to the characteristic loss of a methyl group (M^+-CH_3). In addition, the acidic compounds (malonic acids, succinic acid and glutaric acid) after cleavage of the aromatic ring were also confirmed by a comparison with commercial standards.

Figure 1 shows the proposed degradation pathway of DEP during ozonation. Based on the information of intermediates identified and estimations from the FED and PC calculations, two probable categories of products were suggested: a hydrolysis reaction in the aliphatic chain (A) and hydroxylation in the aromatic ring resulting from the attack of ·OH (B). Pathway (A) is a hydrolysis reaction in the aliphatic chain leading to three products (b)–(d), whereas pathway (B) includes products (e)–(k), which is the hydroxylation of the aromatic ring. From pathway (A), it could be suggested that product (b), also identified by Muneer *et al.* (2001), produces phthalic anhydride (PAH) (d) via phthalic acid (PA) (c). This observation is consistent with Paxéus (1996) in that the hydrolysis of phthalates is responsible for the formation of phthalic acid (PA).

In pathway (B), the attack of ·OH to the aromatic ring showed a relatively large frontier electron density (FED) leading to the formation of hydroxylated and dihydroxylated products for DEP, products (e) and (f). The further attack of ·OH could be given to the aliphatic chains of the hydroxylated and dihydroxylated products. When ·OH

attacks the positions C_5 and C_6 with the largest frontier electron density, OH-adducted products, such as (h) and (k), are formed. Finally, the aromatic ring is opened, producing intermediates with some acids, such as malonic acid, succinic acid and glutaric acid.

Figure 2 compares the normalized peak areas of the DEP intermediate products with the relative depletion of DEP with respect to the ozone dose (1.5, 4.5, 9.0 and $90\,mg\,l^{-1}$). Each peak area was normalized by that of the internal standard (phenanthrene-d_{10} in this study). All compounds identified (b–k and acidic compounds) were detected, even at a low ozone dose of $1.5\,mg\,l^{-1}$, and new peaks with the exception of 13 compounds were not observed at higher ozone doses. Of the intermediates identified, compound (b), mono ethyl phthalate (MEP), showed the highest peak area, which increased with increasing ozone dose to $4.5\,mg\,l^{-1}$ and still remained in solution at an ozone dose of $90\,mg\,l^{-1}$. Compounds (c) and (d) (phthalic acid (PA) and phthalic anhydride (PAH), respectively) were also formed with increasing ozone dose, showing similar peak areas regardless of the ozone dose, and PA was still detected at $90\,mg\,l^{-1}$ ozone.

Figure 3 shows the formation trends of hydrogen peroxide (H_2O_2) during ozonation in the presence and absence of DEP. In pure water (i.e. without DEP addition), the residual H_2O_2 concentration increased to $0.02\,mg\,l^{-1}$ at an ozonation time of 2 min, which was maintained until the end of
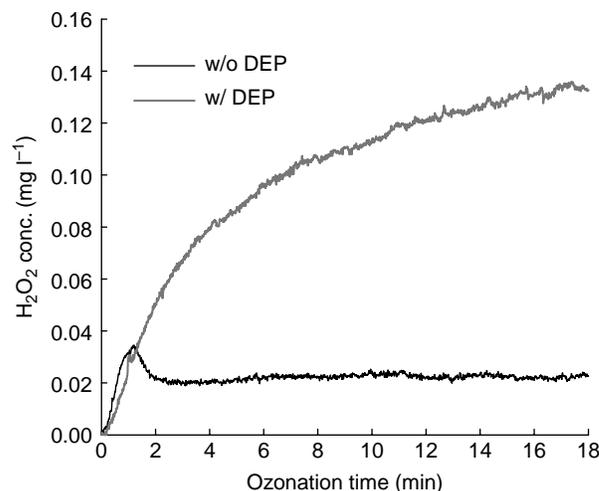

Figure 3 | Hydrogen peroxide formation during ozonation in the presence and absence of DEP; $[DEP]_0 = 100\,\mu M$, ozone dose = $1.5\,mg\,l^{-1}\,min^{-1}$.

ozonation reaction, yielding 3.8 wt% (mg H_2O_2/mg O_3, w/w). However, in the case of DEP addition, the H_2O_2 concentration increased parabolically to $0.13\,mg\,l^{-1}$ at 18 min (9.5 wt% mg H_2O_2/mg O_3), showing an approximately six times higher level than pure water. This suggests that the ozonation of DEP contributes to the generation of H_2O_2.

Effect of intermediates (PA, PAH) on DEP degradation

The ozone decay patterns in DEP solution were observed in a batch reactor with a $1\,mg\,l^{-1}$ (corresponding to $20.8\,\mu M$) ozone dose at pH 3 and 7, and compared with pure water (Figure 4a and b). The ozone degradation in DEP solution at pH 3 showed an almost equal rate to pure water, indicating a significantly low ozone decay rate (only 3.6–6.3% of depletion, $k_o = 0.01\,min^{-1}$). However, at pH 7, the ozone injected in the DEP solution ($k_o = 0.23\,min^{-1}$) degraded rapidly compared with pure water ($k_o = 0.02\,min^{-1}$). Previous work showed that DEP barely reacts with the ozone molecule ($k_{O3,DEP} = 0.14\,M^{-1}\,s^{-1}$) (Oh et al. 2006). Consequently, ozone decay by DEP addition at pH 7 is believed to be responsible for the formation of intermediates via DEP oxidation. To confirm this, the rate of ozone decomposition at pH 7 with $10\,\mu M$ phthalic acid (PA) and phthalic anhydride (PAH), which are the intermediates of DEP and can be obtained commercially, were compared with pure water. As shown in Figure 4(c), both PA and PAH lead to rapid ozone degradation ($k_{o,PA} = 0.46\,min^{-1}$, $k_{o,PAH} = 0.35\,min^{-1}$) including a $0.5\,mg\,l^{-1}$ instantaneous ozone demand (IOD). This suggests that the PAH and PA have high reactivity to ozone and cause rapid ozone decay during the ozonation of DEP.

Regarding the ozone decomposition mechanism, a wide variety of compounds can initiate, promote or inhibit the radical-chain reaction in the ozone process and affect the ozone decomposition rate, and are defined as initiators, promoters and inhibitors, respectively (Bruno et al. 1991). The DEP removal patterns were investigated in the presence of methanol, acetate, PA and PAH to examine the effects of PA and PAH formation on DEP removal during ozonation. Of the model chemicals used in this study, methanol was selected as a clean promoter, because

it can regenerate the superoxide radical, $O_2^-\cdot$, from the hydroxyl radical and promote ozone decomposition (Bruno et al. 1991). Acetate was used as an inhibitor because it can consume $\cdot OH$ without regenerating $O_2^-\cdot$, making the radical chain cycle unsustainable (Bruno et al. 1991).
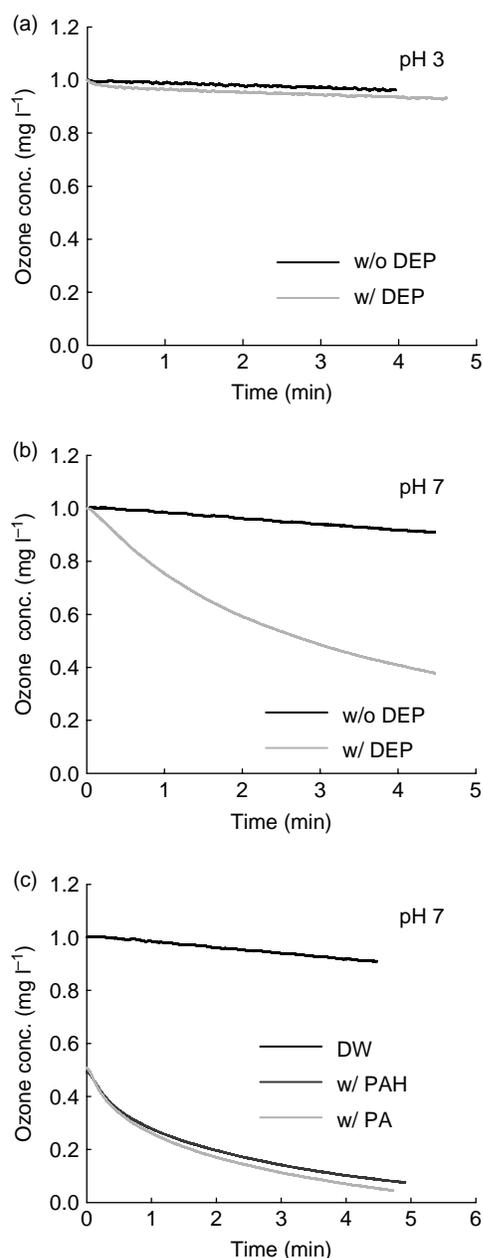

Figure 4 | Ozone decay patterns of DEP and its oxidation by-products; batch test, ozone dose = $1\,mg\,l^{-1}$ ($= 20.8\,\mu M$), $[DEP]_0 = 10\,\mu M$, $[PAH]_0 = 10\,\mu M$, $[PA]_0 = 10\,\mu M$, pH = 7, temp. = 20°C.
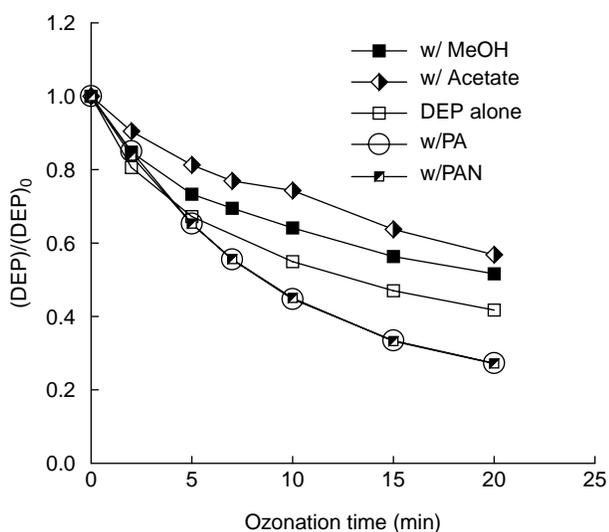
Figure 5 | Effect of DEP by-products and ·OH scavengers on the degradation of DEP; ozone dose = $1.5\,mg\,l^{-1}\,min^{-1}$, $[DEP]_0 = 100\,\mu M$, $[PA]_0 = 50\,\mu M$, $[PAH]_0 = 50\,\mu M$, $[MeOH]_0 = 50\,\mu M$, $[Acetate]_0 = 50\,\mu M$.

$$CH_3OH + \cdot OH \rightarrow \rightarrow O_2^- \cdot \qquad (1)$$

$$CH_3COOH + \cdot OH \rightarrow \rightarrow O_2^- \cdot \qquad (2)$$

$$O_3 + O_2^- \cdot \rightarrow O_3^- \cdot + O_2 \qquad (3)$$

Figure 5 shows the effect of methanol, acetate, PAH and PA on the removal of DEP during ozonation in semi-batch mode, in which the ozone was injected continuously into the reactor at an ozone dose of $1.5\,mg\,l^{-1}\,min^{-1}$. Both methanol and acetate clearly suppressed the removal of DEP compared with the DEP unit run. This suggests that both the model promoter and inhibitor acted as ·OH scavengers in the semi-batch mode. However, in the case of PAH and PA addition, both intermediates enhanced the rate of DEP removal under the same conditions. This indicates that PA and PAH are initiators, which are compounds capable of inducing the decomposition of ozone and subsequently ·OH. Therefore, the PA and PAH formed during DEP ozonation partially promote the degradation of DEP.

CONCLUSIONS

This study examined the degradation pathways of DEP during ozonation. The initial positions of ·OH attack and the hydrolysis reaction on the DEP molecule were estimated from the frontier electron density (FED) and partial charge (PC) calculations. The 13 intermediates during DEP ozonation were detected by GC/MS analysis, of which phthalic acid (PA), phthalic anhydride (PAH), 4-hydroxy phthalate and acidic compounds were confirmed using commercially available reference compounds. Referring to the estimation and the intermediates identified, two probable categories of intermediates were proposed as a result of a hydrolysis reaction in the aliphatic chain or hydroxylation of the aromatic ring resulting from the attack of ·OH. After the initial hydroxylation and hydrolysis reactions, with increasing ozone dose, the aromatic ring of DEP was opened and some acidic compounds, such as malonic acid, succinic acid and glutaric acid, were formed. In addition, the ozonation of DEP induced the generation of hydrogen peroxide (H_2O_2), at a level six times higher than pure water during ozonation for 18 min.

Of the intermediates of DEP, PAH and PA have high reactivity with ozone and consequently cause rapid ozone decay during the ozonation of DEP, and partially contribute to promoting the degradation of DEP as an initiator. PA and PAH are the representative intermediates formed from the degradation of most phthalate esters including DEP. Therefore, these results may be a useful source of information on the degradation of other phthalate esters (PEs) by ozonation.

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