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Kinetics and mechanisms studies on dimethyl phthalate degradation in aqueous solutions by pulse radiolysis and electron beam radiolysis

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ABSTRACT

The kinetics and mechanisms of hydroxyl radical/hydrated electron reactions with dimethyl phthalate (DMP) were investigated using pulse radiolysis and electron beam radiolysis techniques. The bimolecular rate constants for the reaction of hydroxyl radical and hydrated electron with DMP were measured to be $3.4\times10^{9}\ M^{-1}\ s^{-1}$ and $1.6\times10^{10}\ M^{-1}\ s^{-1}$ under pulse radiolysis experiments, respectively. The major products after radiation were elucidated by LC/MS/MS and ion chromatography analysis. It was found that DMP degradation had different mechanisms in oxidative and reductive conditions: hydroxyl radical attacked aromatic ring of DMP leading to the fracture of benzene ring, formed a series of byproducts which were completely mineralized while hydrated electron attacked the ester group of DMP, formed the product of phthalic acid in reductive conditions.

1. Introduction

As one of the phthalate esters (PAEs), dimethyl phthalate (DMP) is typically applied in cellulose ester-based plastics, such as cellulose acetate and butyrate (Staples et al., 1997). DMP is a component of coating, food packing, cosmetics, lubricants, decorative cloths and other products (Baikova et al., 1999). As a result of its wide and large quantities use in industry, DMP has been recognized as a significant environmental pollutant, which has been detected in various environmental samples, such as surface waters, freshwaters, mineral waters, seawaters, urban lakes, sediments and landfill leachate (Gledhill et al., 1980; Mersiowsky, 2002; Montuori et al., 2008; Ogunfowokan et al., 2006; Penalver et al., 2000; Zeng et al., 2009). The concerns on the environmental healthy, particularly the physiological and biochemical effect on organisms of DMP have been recognized for many years (Wang et al., 2004). It has been reported that DMP and its intermediates are suspected to be the reason of functional disturbances in the liver and nervous systems of animals (Wang et al., 2008; Yuan et al., 2008a). Known as the endocrine-disrupting chemical, it may have the possibility of promoting chromosome injuries in human leucocytes and interfering with the reproductive systems and normal development of animals and humans (Jobling et al., 1995; Lottrup et al., 2006). Therefore, the US Environmental Protection Agency has listed DMP as a priority pollutant (US EPA, 1992).

Advanced oxidation and reduction processes (AO/RPs) are alternatives to traditional treatments and have been developed for the removal of many compounds (Ikehata et al., 2006; Zhang et al., 2007). AO/RPs typically involve the formation of hydroxyl radicals as oxidizing species and hydrated electrons as reducing species. Both of these species can be utilized in the degradation of organic contaminants present in drinking water or wastewater (Song et al., 2008a). The processes based on the generation of hydroxyl radicals have been applied to the degradation of DMP, such as Fenton's reaction (Zhao et al., 2004), UV/H_2O_2 process (Xu et al., 2009), TiO_2-UV and Fe(VI)-TiO_2-UV photocatalyst (Ding et al., 2008; Yuan et al., 2008b), ozone-based oxidation (Chang et al., 2009; Chen et al., 2008), denitrifying degradation (Liang et al., 2007) and many combinations of them (Wang et al., 2009; Zhou et al., 2007). However, ionizing radiation can produce both oxidizing and reducing species. Radiolysis of water produces three highly reactive species, viz. hydroxyl radicals ($^{\bullet}OH$), hydrated electrons (e^{-}_{aq}), hydrogen radicals ($^{\bullet}H$), in addition to the less reactive H_2 and H_2O_2 (see Eq. (1), where the numbers in parentheses are the *G*-values (μmol J^{-1}); Buxton et al., 1988).

$$H_2O \rightarrow (0.28)^{\bullet}OH + (0.27)e^{-}_{aq} + (0.06)^{\bullet}H + (0.05)H_2 + (0.07)H_2O_2 + (0.27)H^{+} \quad (1)$$

Creating oxidative or reductive conditions using radiolysis makes it an excellent approach for clarifying reaction mechanisms. The oxidative and reductive behavior of DMP in aqueous solutions has been investigated by steady-state and pulse radiolysis. The main objective of this study is to determine the rate constant and the possible reaction pathways for the reaction of hydroxyl radical/hydrated electron with

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DMP. In this study, transient spectra observed by pulse radiolysis give a better understanding of the characteristic of the intermediate species. Product studies of DMP degradation using electron beam irradiation in aerated solutions were made to provide further insight into the mechanisms occurring under oxidative and reductive conditions.

2. Methods and materials

2.1. Materials

DMP standard was obtained from Sigma (> 99% purity). Tert-butyl alcohol (t-BuOH) was of HPLC grade and also purchased from Sigma. All solutions were prepared using triply distilled water and all experiments were carried out at room temperature and natural pH levels. The experiment solutions were purged with high purity N_2O (99.999%) for hydroxyl radical experiments, or with high purity N_2 (99.999%) to remove dissolved oxygen for hydrated electron experiments.

2.2. Pulse radiolysis and electron beam radiolysis

Pulse radiolysis experiments were carried out with 10 ns pulses of 10 MeV electrons from a linear electron accelerator in the Institute of Applied Physics and the pulse dose used was ~20 Gy. Pulse dosimetry was performed with a 0.1 mol dm^{-3} KSCN solution using $\varepsilon = 7600\ M^{-1}\ cm^{-1}$ for $(SCN)_2^{\bullet -}$ at 480 nm. Analysis was performed with a 300 W xenon lamp, shining perpendicularly through a quartz cuvette having an optical path length of 10 mm.

To study only the reactions of hydroxyl radical, solutions were pre-saturated with N_2O, which quantitatively converts hydrated electrons and hydrogen atoms to hydroxyl radicals via reactions (2) and (3) (Buxton et al., 1988). To achieve hydrated electrons reactions, solutions are pre-saturated with N_2 in the presence of 0.10 M t-BuOH, which can be converted into relatively inert t-BuOH radicals by scavenging hydroxyl radicals and hydrogen atoms (see Eq. (4) and Eq. (5); Buxton et al., 1988).

$$e_{aq}^- + N_2O + H_2O \rightarrow N_2 + OH^- + {}^\bullet OH,\ k_2 = 9.1 \times 10^9\ M^{-1}\ s^{-1} \quad (2)$$

$${}^\bullet H + N_2O \rightarrow N_2 + {}^\bullet OH,\ k_3 = 2.1 \times 10^6\ M^{-1}\ s^{-1} \quad (3)$$

$${}^\bullet OH + (CH_3)_3COH \rightarrow {}^\bullet CH_2(CH_3)_2COH + H_2O,\ k_4 = 6.0 \times 10^8\ M^{-1}\ s^{-1} \quad (4)$$

$${}^\bullet H + (CH_3)_3COH \rightarrow {}^\bullet CH_2(CH_3)_2COH + H_2,\ k_5 = 5.0 \times 10^5\ M^{-1}\ s^{-1} \quad (5)$$

Steady-state experiments were performed using a GJ-2-II electron accelerator with beam energy of 1.8 MeV at Applied Radiation Institute of Shanghai University. Samples were placed in radiation field about 30 cm distance from the source. The experiments were carried out mainly at absorbed doses of 1–20 kGy and the dose rate was kept 0.045 kGy s^{-1}.

2.3. Analytical procedures

The loss of DMP was followed using a HPLC system (Aglient 1200) equipped with a C_{18} column (150 mm × 4.6 mm) and an auto-sampler with the volume injection set to 10 μL. A VW detector monitored at 224 nm. The mobile phase was a mixture of acetonitrile and water (40:60, v/v) at a flow rate of 1.0 mL min^{-1}.

The organic acids produced from DMP electron beam radiolysis were determined by Ion Chromatography (IC-Metrohm MIC advanced) equipped with a METROSEP A SUPP 5–250 (5 μm particle size, 250 mm × 4 mm) column. The determination of these organic acids was achieved on hydrophilic anion exchange column, and the eluent was a mixture of Na_2CO_3 (3.2 mM) and $NaHCO_3$ (1.0 mM) in gradient conditions at a flow rate of 0.70 mL min^{-1}. The injection volume was 10 μL.

A Hybrid Quadrupole-TOF LC/MS/MS analysis was also performed to identify the degradation products, which were consisted of an HPLC (Agilent 1100) Pump and a Q-STAR XL (AB Sciex) Mass Spectrometer with a turbo-spray ionization source. A C_{18} column (150 mm × 4.6 mm) was employed with a mobile phase of acetonitrile/water (30:70, v/v) at a flow rate of 0.8 mL min^{-1}. Mass spectra were operated in both positive and negative mode. The injection volume was 50 μL.

3. Results and discussion

3.1. Hydroxyl radical reactions

Fig. 1 presents the typical transient absorption spectra of DMP reacting with hydroxyl radical in N_2O-saturated 0.5 mM DMP aqueous solutions. This spectrum shows a characteristic absorption from 300 to 350 nm with a maximum absorption at 320 nm. According to the previous report, the transient life-time and maximum absorption in the range 300–350 nm were characteristic of hydroxyclohexadienyl radicals resulting from the attack of hydroxyl radical to the aromatic ring (Merga et al., 1994; Merga et al., 1996), this absorption range 300–350 nm of the intermediates was attributed to the corresponding DMP hydroxyclohexadienyl adducts.

The rate constant for the reaction of hydroxyl radical with a specific functional group could be determined by monitoring the growth kinetics as a function of substrate concentration (Mezyk et al., 2007; Song et al., 2009). The growth kinetics for DMP hydroxyclohexadienyl adduct were monitored at 320 nm by pulse radiolysis with initial DMP concentrations (C_0) ranging from 0.12 mM to 1.23 mM, as inset in Fig. 2. The bimolecular radical rate constant for hydroxyl radical reaction with DMP was determined by plotting exponential curves to the pseudo-first-order growth kinetics (inset in Fig. 2) and fitting the pseudo-first-order rate constants (k_{obs}) as a function of the initial concentrations of DMP (Fig. 2). A fit linear equation (Eq. (6)) was obtained. From the slope of the line, the bimolecular reaction rate constants of $3.4 \times 10^9\ M^{-1}\ s^{-1}$ for reaction of hydroxyl radical with DMP was determined. The obtained rate constants for hydroxyl radical reaction with DMP is comparable to that with benzene

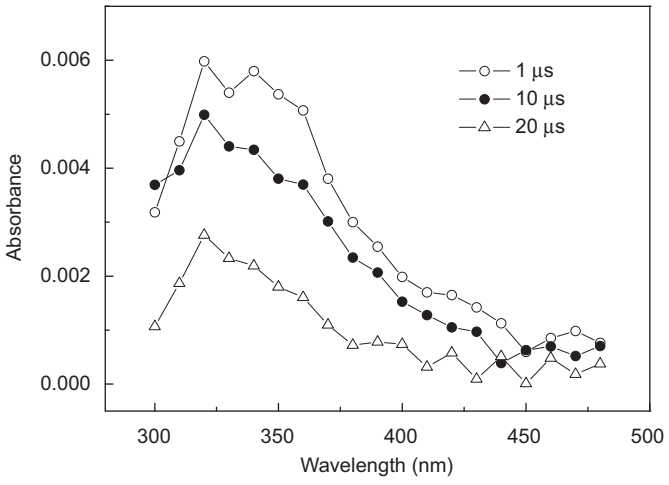

Fig. 1. Transient absorption spectra obtained upon hydroxyl radical oxidation of DMP in N_2O-saturated aqueous solutions.