E-beam radiolysis of aqueous dimethyl phthalate solution

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Abstract   To investigate the influence of radiolysis on kinetics and factors of dimethyl phthalate(DMP), the aqueous DMP solution is degraded by 1.8 MeV E-beam, following pseudo-first-order kinetics. The rate constant of DMP degradation decreased exponentially with increasing initial DMP concentration. The DMP is favorably degraded by radical scavengers under its low concentration and alkaline condition. At high doses, the DMP is attacked by e_{aq}^- and ·OH, producing monomethyl phthalate, phthalate acid, and a series of aliphatic carboxylic acids, which are completely mineralized into H_2O and CO_2.

Key words   Dimethyl phthalate, E-beam, Degradation, Kinetics, Mechanism

1   Introduction

Dimethyl phthalate (DMP) has been widely used as a softener in plastic industry[1–5], but it is an endocrine-disrupting chemical that may cause the nervous system and liver to functionally disturbance[6–8]. The US Environmental Protection Agency has listed it as a priority pollutant.

Usually DMP is degraded by photochemical method, which costs much and causes secondary pollution due to the added catalysts or oxidants; or by biological method, which takes a longer reaction time. Ionizing radiations is a promising technique to destroy contaminants or elucidate reaction kinetics[9]. As shown in Eq.(1), water is degraded into hydroxyl and hydrogen radicals, and hydrated electron[10], with different *G*-values ($\mu mol \cdot J^{-1}$). And the radicals can react with the pollutants[11], of dyes[12], tetracycline antibiotics[13], poly(methylmethacrylate)[14], N-succin-yl chitosan[15], etc.

$$H_2O \rightarrow (0.28)^{\cdot}OH + (0.27)e_{aq}^- + (0.06)^{\cdot}H + (0.05)H_2 + (0.07)H_2O_2 + (0.27)H^+ \tag{1}$$
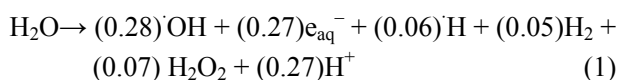
In this study, aqueous DMP solution was irradiated by E-beam, and effects of initial DMP concentration, pH and H_2O_2 on the DMP radiolysis, radical scavenger on its degradation rate, and the kinetics, were investigated.

2   Materials and methods

2.1   Materials

DMP (>99%), acetonitrile, and *t*-butyl alcohol (HPLC grade) were obtained from Sigma. Na_2CO_3, $NaHCO_3$ and H_2O_2 were purchased from Shanghai Chemical Reagent Corp. $HClO_4$ and NaOH were used to adjust the pH of DMP solution. N_2O and N_2 (99.999%) were blown into the DMP solution before radiolysis. All chemicals were of analytical grade unless otherwise stated. All solutions were prepared by ultra-pure water (>18 M$\Omega \cdot$cm).

2.2   Irradiation

The solutions were irradiated at ambient temperatures by 1.8 MeV E-beam from an electron accelerator with the beam current of up to 10 mA.

2.3 Analytical methods

The HPLC (Aglient 1200), consisted of C_{18} column (150 mm×4.6 mm) and an auto-sampler with 10-μL volume injection, was used to detect DMP concentration at 224 nm by a VW detector. The mobile phase was a mixture of acetonitrile and water (40:60, v:v) at rate of 1.0 mL·min^{-1}.

Organic acids produced by DMP radiolysis were detected by IC (Metrohm) incorporating a hydrophilic anion exchange column and a METRO-SEP A SUPP 5-250 (5 μm particle size, 250 mm×4 mm) column. The 3.2-mmol·L^{-1} Na_2CO_3 and 1.0-mmol·L^{-1} $NaHCO_3$ solution was used as eluent at rate of 0.70 mL·min^{-1}.

The intermediates were extracted with dichloromethane, and analyzed by GC/MS instrument (QP2010, Shimadzu) with a DB-5 MS column (30 m × 0.25 mm) in total ion mode through an EI interface. After the sample was injected at 250℃, the GC oven temperature was programmed as keeping at 40℃ for 2 min, increasing to 280℃ at a rate of 15℃·min^{-1}, and keeping it for 10 min. Helium gas was used as the carrier at a flow rate of 1 mL·min^{-1}.

$$\text{Degradation rate}(\%)=[C_{\text{Degraded DMP}}/C_{\text{Initial DMP}}]\times100 \quad (2)$$

3 Results and discussion

3.1 Effect of initial DMP concentration on degradation

The aqueous DMP solutions of 10–300 mg·L^{-1} were irradiated to 1–20 kGy. In Fig.1, the degradation rate of DMP at various concentrations increased with dose, but the DMP degradation rate at the same dose decreased with increasing initial concentrations, The 1 kGy degradation rates for 10, 50, 100, 200 and 300 mg·L^{-1} DMP were 89%, 73%, 63%, 49% and 43%, respectively, indicating that the dilute DMP can be effectively degraded by low dose irradiation.

The DMP concentration (*C*) exponentially decreased with the initial concentration. By a regressive analysis, the ln*C*-initial concentration relationship is linear with regression coefficients of >0.98, demonstrating that the DMP degradation followed pseudo-first-order kinetics. Fig.2 gives the rate constants (k_1) estimated by the slopes of the fitted

lines. Considering the dependence of the active species on the dose and effective reactants, the active species decreased with increasing initial DMP concentration at the same dose. When the radicals react with reactants, the k_1 is the absolute second-order rate constant for radical concentrations.
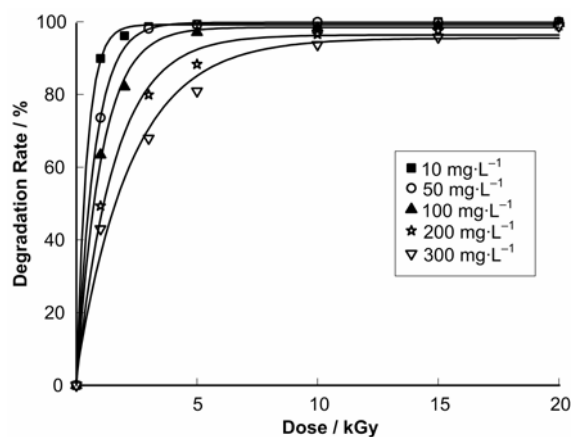

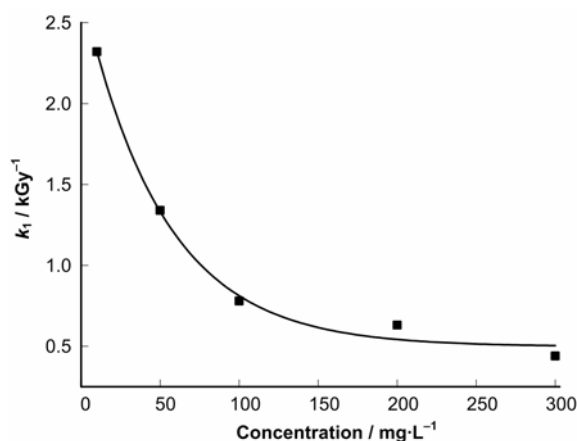**Fig.1**   Effect of DMP concentration on radiolytic degradation.

Fig.2 k_1 as a function of initial DMP concentration at 1–20 kGy.

3.2 Effect of pH on DMP degradation

The DMP radiolytic degradation at pH=4.0, 6.8 and 9.1 showed that alkaline solution was slightly effective to form high e_{aq}^- concentration (Fig.3). The e_{aq}^-, generated via the reaction of H· with OH$^-$ in alkaline solution, as shown in Eqs.(3) and (4), decreased with increasing amount of H$^+$.
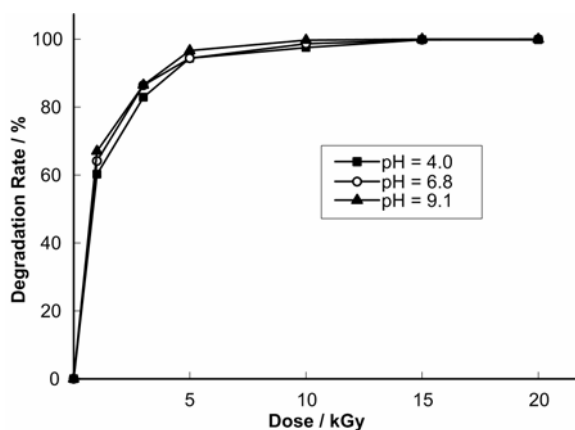
$$H· + OH^- \rightarrow e_{aq}^- + H_2O \quad (3)$$

$$e_{aq}^- + H^+ \rightarrow H· \quad (4)$$
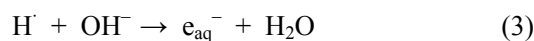
Fig.3   Effect of pH on 100 mg·L^{-1} DMP radiolysis.

3.3 Effect of H$_2$O$_2$ on DMP degradation

As shown in Fig.4, at 0−0.5 mM H$_2$O$_2$, over 98% DMP could be degraded by 10-kGy irradiation, indicating that H$_2$O$_2$ is not favorable for DMP degradation. On decomposing organic pollutants, H$_2$O$_2$ neither absorb high energy E-beam nor generate sufficiently active species[16,17], but H$_2$O$_2$ can consume the active species of ·OH and e$_{aq}^{-}$ [18], as shown in Eqs.(5) and (6).
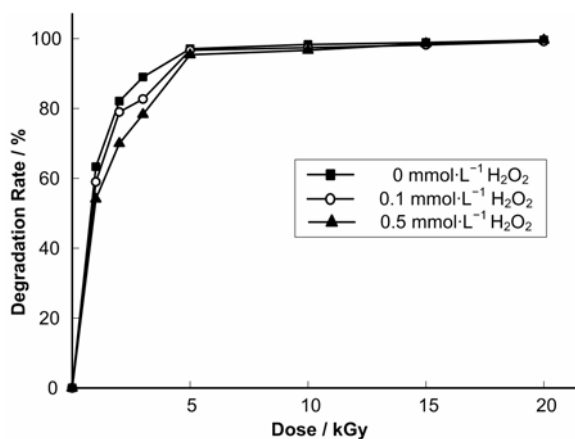
$$H_2O_2 + e_{aq}^{-} \rightarrow ·OH + OH^{-} \tag{5}$$

$$H_2O_2 + ·OH \rightarrow H_2O + HO_2· \tag{6}$$

Fig.4   Effect of H$_2$O$_2$ on 100 mg·L^{-1} DMP degradation.

3.4 Effect of radical scavengers on DMP degradation

After saturated by N$_2$O or 0.1 M *t*-BuOH, which is deoxygenated by N$_2$, the e$_{aq}^{-}$ or ·OH scavenger can degrade the aqueous DMP solution. As shown in

Eqs.(7) and (8), the reaction of e$_{aq}^{-}$ and ·H with N$_2$O forms ·OH active species, and e$_{aq}^{-}$ active species occur in the *t*-BuOH solution because the ·OH and ·H are converted into H$_2$O and H$_2$ to form inert *t*-BuO·, as shown in Eqs.(9) and (10). In Fig.5, over 98% DMP in the two solutions was degraded by 10-kGy irradiation.
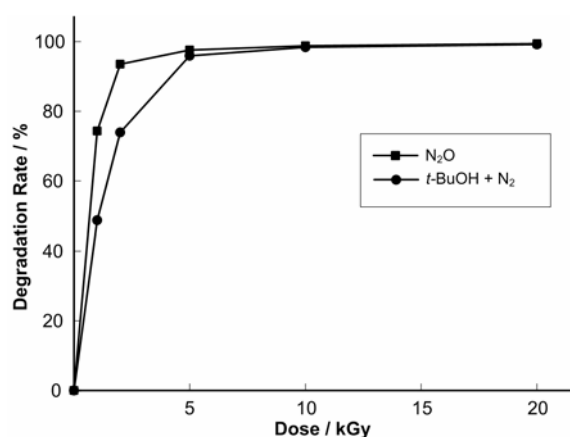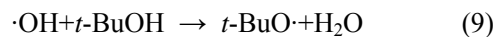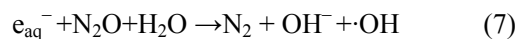
$$e_{aq}^{-} + N_2O + H_2O \rightarrow N_2 + OH^{-} + ·OH \tag{7}$$

$$·H + N_2O \rightarrow N_2 + ·OH \tag{8}$$

$$·OH + t\text{-BuOH} \rightarrow t\text{-BuO·} + H_2O \tag{9}$$

$$·H + t\text{-BuOH} \rightarrow t\text{-BuO·} + H_2 \tag{10}$$

Fig.5   Effect of e$_{aq}^{-}$ and ·OH on 100 mg·L^{-1} DMP degradation.

3.5 Degradation mechanism

The IC and GC/MS detection for the DMP degradation showed that the resultant intermediates were formic acid, acetic acid, and oxalic acid, while monomethyl phthalate and phthalate acid could be observed by comparing the GC/MS profiles of DMP radiolysis with NIST library records. Fig.6 shows that the ·OH and e$_{aq}^{-}$ had significant influence on radiolytic degradation of aqueous DMP. On transferring the e$_{aq}^{-}$ to ester groups of DMP, the radical anions (DMP·$^{-}$) were easily formed[19]. Next, the ·OH was added with DMP·$^{-}$ to produce OH-DMP^{-} and monomethyl phthalate *via* loss of a methoxy anion. Similarly, after the e$_{aq}^{-}$ transferring, the reaction of ·OH with DMP·$^{-}$ produced an unstable phthalate acid, thus forming a benzoic acid *via* decarboxylation[20]. Finally, aliphatic carboxylic acid was mineralized into CO$_2$ and H$_2$O.
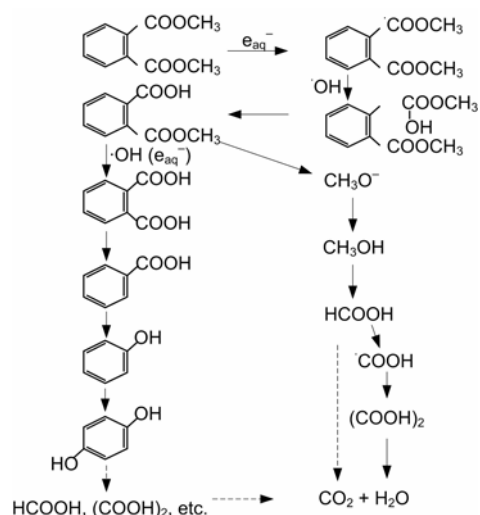
Fig.6 A probable mechanism of aqueous DMP degradation.

4   Conclusion

In summary, the DMP can be effectively degraded by E-beam irradiation under alkaline condition, and decreasing exponentially with increasing initial concentration, followed pseudo-first-order kinetics. The H_2O_2 adding cannot increase its degradation efficiency. The DMP degradation is performed by the ·OH and e_{aq}^- scavenger to form monoethyl phthalate, phthalate acid, and aliphatic carboxylic acids, and mineralized completely into CO_2 and H_2O.

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