



Initial photocatalytic degradation intermediates/pathways of 17 α -ethynylestradiol: Effect of pH and methanol

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ABSTRACT

This study investigated the photocatalytic degradation of the synthetic oral contraceptive 17 α -ethynylestradiol (EE2). Particular attention was paid on the effects of pH and the co-solvent methanol on the degradation intermediates of EE2. Twelve intermediates were identified, and several intermediates reported herein have not been found in previous studies. The degradation efficiency of EE2 and the number of identified intermediates decreased evidently at pH 3 and in the presence of methanol at pH 7. Three photocatalytic degradation pathways were proposed: The transformation of the phenolic moiety (pathway I) is the primary initial reaction pathway; the initial photocatalytic degradation in the aliphatic carbon linked to the aromatic ring (pathway II) only took place at pH 7; the isomerization of EE2 (pathway III) could occur only in the presence of methanol at pH 7. Results from this study underscore the importance of photocatalytic degradation on the removal of estrogenic activity mainly expressed by the phenol moiety of EE2.

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1. Introduction

Endocrine disrupting chemicals (EDCs) can interfere with the hormonal activities of aquatic lives, animals, and probably also humans and are a cause of concern (Sumpter and Jobling, 1995; Routledge et al., 1998). All humans and animals excrete steroid hormones (Cargouët et al., 2004), which are released into the aquatic system through sewage discharge and animal waste disposal and have been frequently detected in the effluents of sewage treatment plants and surface water (Hohenblum et al., 2004; Pothitou and Voutsas, 2008). 17 α -ethynylestradiol (EE2), a principal synthetic estrogen, is widely used in oral contraceptives and hormone replacement therapy. It is one of the most potent estrogens, which is ~11–27 times more estrogenic potent than 17 β -estradiol, based on *in vivo* tests (Thorpe et al., 2003) with a predicted no effect concentration of 0.35 ng L⁻¹ in surface water (Caldwell et al., 2008). Moreover, EE2 is a biologically persistent analogue of estrogen with a dissipation time for about 20–40 d in river systems (Jürgens et al., 2002). Therefore, Johnson and Sumpter (2001) claimed that the elimination of EE2 could have the largest single impact on the estrogenicity of the effluent.

The frequent detection of EE2 in the environment and its adverse effects on human beings and animals make it necessary to find advanced treatment processes with high removal efficiency

for this compound. Several studies (Ohko et al., 2002; Coleman et al., 2004; Zhang and Zhou, 2008) have shown that photocatalytic oxidation is a promising technology for the elimination of hormone steroids during water treatment without the further formation of estrogenic intermediates. Hence, the photocatalytic degradation of EE2 has been studied extensively (Coleman et al., 2004, 2005; Karpova et al., 2007a,b). However, most of the previous work focused on the reaction kinetics and factors affecting the photocatalytic degradation, and little research has investigated the intermediates arising from the photocatalytic degradation of EE2. One study (Lee et al., 2008) has identified the oxidation products of EE2 by ·OH radicals, and it was found that besides the two main initial products 2-OH-EE2 and 4-OH-EE2, 6-oxo-EE2 was also formed when ·OH reacts with the aliphatic rings of EE2. Although the dominant photocatalytic degradation mechanism of EE2 is ·OH radical mediated advanced oxidation, the data were not sufficient to construct a detailed reaction pathway for the photocatalytic degradation of EE2.

As for many investigations, a water-miscible organic solvent was often used to enhance the water solubility of hydrophobic organic compounds. However, photocatalytic degradation could be influenced by the co-solvent, and contradictory results were obtained (Chen and Cao, 2005; Woo et al., 2009). Methanol or toluene inhibited the photocatalytic oxidation of dichlorvos (Chen and Cao, 2005). The presence of acetone improved the degradation degree of polycyclic aromatic hydrocarbon (PAHs) by enhancing water solubility of hydrophobic PAHs (Woo et al., 2009), but acetone also affected the pathways of photocatalytic degradation of the PAHs

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(Woo et al., 2009). Mai et al. (2008) also demonstrated the appearance of new intermediates resulting from the photocatalytic degradation of 17 β -estradiol at neutral pH in the presence of methanol. Several studies have shown that the degradation rate of EE2 was pH dependent (Liu et al., 2003; Malygina et al., 2005; Karpova et al., 2007a). Moreover, pH may affect the formation of the organic photocatalytic byproducts (Mai et al., 2008). However, for EE2, the effects of the co-solvent and pH on the photocatalytic degradation pathways and intermediates have not been thoroughly studied.

In this study, the photocatalytic degradation of EE2 was investigated in aqueous solution with or without addition of methanol. Specific attention was paid on the identification of photocatalytic degradation intermediates, especially the initial reaction intermediates of EE2, using liquid chromatography with ion-trap mass spectrometry (LC–MSⁿ, $n = 1–4$). Based on the identified intermediates, three degradation pathways were proposed. Moreover, the role of methanol and pH in photocatalytic degradation pathways of EE2 was also elucidated in detail.

2. Experimental

2.1. Materials and reagents

EE2 (purity >98%), used as the target compound, was purchased from Sigma–Aldrich (USA). The aqueous solubility of EE2 is as low as $\sim 9.20 \text{ mg L}^{-1}$ due to its hydrophobicity (Shareef et al., 2006). To investigate the effect of methanol as a co-solvent, stock solutions of EE2 were prepared either in methanol followed by gradual dilution with Milli-Q water (Millipore, Billerica, MA) to about 5 mg L^{-1} with the final methanol concentration in the aqueous solution being $\sim 0.17\%$ (v/v), or directly in Milli-Q water (about 5 mg L^{-1}). During the reaction, the solution was constantly stirred to avoid re-crystallization of EE2. TiO₂ (P-25, Degussa German) was used as received.

2.2. Photocatalytic degradation of EE2

The photocatalytic degradation experiments were conducted as described in our previous study (Mai et al., 2008). An 8 W, low-pressure mercury UV lamp (Beijing Lighting Research Institute, ZW8S15 W) with irradiating wavelength 365–370 nm was placed 4 cm above the reactor horizontally. The lamp was warmed up for 10 min before each reaction, and the total useful radiation arriving to the reactor was $7.38 \times 10^{-8} \text{ Einstein s}^{-1}$. The reaction temperature was maintained at $25 \pm 1 \text{ }^\circ\text{C}$ and the pH of the EE2 solution was adjusted by sodium hydroxide or nitric acid over the pH range of 3–10. The optimum concentration of 0.5 mg mL^{-1} TiO₂ was used (Mai et al., 2008). The suspension was magnetically stirred for 30 min in darkness to ensure that the adsorption equilibrium was achieved. Then, the suspension was added into the reactor under the lamp that has been warmed up. During the irradiation, samples were withdrawn at timed intervals and were centrifuged at 9730g to separate TiO₂ from water before further analysis. An initial EE2 concentration up to about 5.0 mg L^{-1} permitted the identification of the intermediates by LC–MSⁿ directly, without the need for multi-step processing to concentrate the trace levels of EE2.

2.3. Intermediates analysis

The intermediates of photocatalytic degradation in aqueous solutions of irradiated samples were separated by a HPLC system equipped with a Zorbax Eclipse XDB-C18 LC column (Agilent $2.1 \times 150 \text{ mm}$, particle size $5 \mu\text{m}$, pore size 80 \AA , monomeric, double-ended), with injection volume of $5 \mu\text{L}$. Starting from initial

conditions of methanol/water 25/75 (v/v), the mobile-phase gradient increased linearly to 75/25 (v/v) over 15 min, was held constant for 17 min, and finally decreased to 25/75 (v/v) and was held for another 8 min. The flow rate was set to 0.18 mL min^{-1} . To identify EE2 and the reaction intermediates, an LC–MS equipped with electrospray interface (HP 1100 LC–MSⁿ Trap SL System, Agilent, USA) operated in the negative ionization mode was used. The instrument was tuned with the parent compound (EE2 in this case) to achieve the maximum sensitivity. Thereafter, multiple reaction monitoring mode was used to acquire MS and MSⁿ spectra of EE2 and the intermediates with a scan range of m/z 50–500. The amplitude was set to 1.3 V to fragment the product ions obtained.

2.4. Molecular orbital calculations

The semi-empirical molecular orbital calculations were operated at the single determinant (Restricted Hartree–Fock) level for optimizing the minimum energy obtained at the PM3 level. All semi-empirical calculations were performed using the software of MOPAC (version 7.0, Fujitsu). The frontier electron densities (FEDs) of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) in the EE2 molecule were calculated. $2\text{FED}_{\text{HOMO}^2}$ and $\text{FED}_{\text{HOMO}^2} + \text{FED}_{\text{LUMO}^2}$ were obtained to predict the initial reaction sites for direct hole-oxidation and $\cdot\text{OH}$ radical attack (Fukui et al., 1952, 1954).

3. Results and discussion

3.1. Identification of intermediates by LC–MS

The total ion chromatogram of a sample of EE2 irradiated for 60 min at pH 7 produced six distinctive peaks (referred to as peaks 1–6, Fig. 1a). The product ions in the average mass spectra of peaks 1–6 (Fig. 1b) were inferred according to the identification of the extracted ion chromatogram (EIC) for the mass spectra. Seven product ions at m/z 359, m/z 343, m/z 311 and m/z 327, m/z 309, m/z 299, and m/z 295 were identified in the average mass spectra of peaks 1–6. The peak areas of EIC were used to quantify the product ions during the photocatalytic degradation processes. As shown in Fig. 2, the peak area of the ion at m/z 295 decreased with the irradiation time. In contrast, the peak areas of the other product ions increased with irradiation time up to a maximum area at about 40 min, beyond which the product started to decrease. Herein, the product ion at m/z 295 was identified as the deprotonated molecular ion ($[\text{M}-\text{H}]^-$) of EE2, using an authentic standard, and all the other product ions corresponded to the deprotonated molecule of the intermediates formed in the photocatalytic degradation of EE2.

Using the aforementioned LC–MS method, the intermediate products from the photocatalytic degradation of EE2 at pH of 3, 7, and 10 in the presence and absence of co-solvent (methanol) were identified. The irradiation time of 60 min, at which the number and intensities of peaks on EIC of the mass spectra can be easily identified, was employed in this study. The co-solvent methanol and pH of the solution have significant effects on the formation of intermediates from the photocatalytic degradation of EE2 (Table 1). The numbers of the detected intermediates are ordered such that $\text{pH } 10 > \text{pH } 7 > \text{pH } 3$ in both the presence and absence of methanol. The product ions at m/z 311 and m/z 359 were observed under all conditions, while the product ions at m/z 377, m/z 391, m/z 393, and m/z 313 were present only at pH 10. The co-solvent methanol hardly influenced the formation of intermediates at either pH 3 or 10. At pH 7, the intermediates at m/z 309, m/z 299, and m/z 343 were not observed in the presence of methanol,

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