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Photodegradation kinetics, products and mechanism of timolol under simulated sunlight

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HIGHLIGHTS

- ► The indirect degradation of timolol is first investigated in fulvic acid solution.
- ► $^3FA^*$ and $^1O_2$ accounted for the degradation of timolol in the aerated FA solutions.
- ► The presence of halides inhibited the degradation in the order of $Cl^- < Br^- < I^-$.
- ► The role of I^- in the degradation was first found to be concentration-dependent.
- ► The photoproducts of timolol were identified by LC-DAD/ESI-MS/MS analysis.

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ABSTRACT

The photodegradation of β-blocker timolol in fulvic acid (FA) solution was investigated under simulated sunlight. The triplet excited state of FA ($^3FA^*$) and singlet oxygen ($^1O_2$) were the main reactive species responsible for the degradation of timolol in the aerated FA solutions. Both dissolved oxygen and iodide ions (I^-) are the efficient quenchers of $^3FA^*$. The photodegradation was drastically accelerated after removing the dissolved oxygen. The presence of I^- inhibited the photosensitized degradation of timolol in the deoxygenated FA solutions, whereas the role of I^- in the reaction was concentration-dependent in the aerated solutions. The other halide ions such as chloride (Cl^-) and bromide (Br^-) exhibited less effect on the photodegradation of timolol in both aerated and deoxygenated solutions. By LC-DAD/ESI-MS/MS analysis, the photoproducts of timolol in both aerated and deoxygenated FA solutions were identified. Electron transfer interaction occurred between $^3FA^*$ and amine moiety of timolol, leading to the cleavage of C–O bond in the side chain and oxidation of the hexatomic ring. These findings suggest the photosensitized degradation was a significant pathway for the elimination of timolol in natural waters.

1. Introduction

β-blockers are among the most prescribed pharmaceuticals extensively used for the treatment of heart failure, hypertension and certain types of cardiac arrhythmias [1]. As wastewater treatment plants (WWTPs) are not designed to decompose β-blockers or other micropollutants, β-blockers are not completely removed and then they are released from the effluents. There are many reports on the occurrence of β-blockers in the environment worldwide [2–8]. Although they were generally detected in the ng – μg/L range, the continual infusion into the aquatic environment leads to potential toxicity to the nontarget organisms (e.g. green algae *desmodesmus subspicatus*) in the waters [9–11].

Photodegradation is an important process for the elimination of organic pollutants in the aquatic environment. There are ongoing studies on the direct and indirect photodegradation of β-blockers in aqueous solutions [12–19]. The naturally occurring humic substances (HS) are ubiquitous in the surface waters. It is well established that sunlight-excited HS can lead to the production of reactive species, including $^\bullet OH$, $^1O_2$, $O_2^{\bullet-}/HO_2^\bullet$, H_2O_2, e_{aq}^-, and the HS triplet states ($^3HS^*$), of which $O_2^{\bullet-}/HO_2^\bullet$, H_2O_2 and e_{aq}^- may play a minor role in the photodegradation of pollutants [20–25]. The previous studies have showed that the β-blockers undergo photosensitized degradation via electron transfer reaction with $^3FA^*$ [16,17]. As one of the β-blockers, timolol has two amine-containing groups similar to the others. It is thus expected that electron transfer interaction occur in the FA solution under irradiation. The previous studies mainly focus on the singlet oxygen

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oxidation of timolol and its photofate in sewage treatment plant effluents [14,26–28]. Until recently, the photodegradation of timolol in the HS solution and the underlying mechanism are poorly understood.

It is well known that both halide ions and dissolved oxygen are the quenchers of excited states of sensitizers [29–31]. The common halide ions such as Cl^-, Br^-, and I^- usually coexist with other pollutants in natural waters. There are many studies on the effect of halides on the photodegradation of pollutants [32–37]. Nevertheless, most of them are focused on either Cl^- or their mixtures (e.g. freshwater, sea water). The role of the different halides in the photosensitized degradation of pollutants was still not fully elucidated. Specifically, I^- influence the triplet of aromatic compounds via electron transfer or heavy atom effect [30,31]. To our best knowledge, however, few studies are available for its effect on the photosensitization of humic substances.

This purpose of this study is to investigate the photodegradation of timolol in the FA solutions. The degradation kinetics and the underlying mechanism were discussed via the reactions of timolol with $^{\bullet}OH$, $^1O_2$, and $^3FA^*$. The role of halide ions in the photosensitization was elucidated in the aerated and deoxygenated FA solutions in detail. The photoproducts of timolol were determined by LC-DAD/ESI-MS/MS. The photosensitized degradation pathway of timolol in aqueous FA solutions was proposed.

2. Materials and methods

2.1. Chemicals

Timolol tartrate salt (99%), acetophenone (99.9%), 1,4-diazabicyclo[2.2.2]octane (DABCO, 99%), and isopropanol (99.9%) were purchased from Sigma. Fulvic acid (C, 51.04%; H, 5.22%; O, 39.13%; N, 4.62%) was obtained from Henan ChangSheng Corporation. Furfural alcohol (FFA), Ferrous sulfate ($FeSO_4{\cdot}7H_2O$), hydrogen peroxide (30%), Rose Bengal, NaN_3, NaCl, KBr, and KI were supplied by Wuhan Chemicals Corporation. All chemicals used were of at least analytical-reagent grade.

2.2. Photolysis experiments

The photolysis experiments were conducted in a capped cylindrical Pyrex vessel (40 mm i.d., containing 50 mL of solution) with tubing in the cap to allow for bubbling solutions. The light source used was a 150-W Xenon Short Arc Lamp (Zolix Corporation, Beijing). The light of wavelengths less than 300 nm was filtered with Pyrex glass to simulate sunlight. Deoxygenation was achieved by bubbling nitrogen into the solutions. All photodegradation experiments were conducted in phosphate (10 mM) buffered solutions. Inhibition experiments were performed with the addition of 10 mM isopropanol, NaN_3 and DABCO to the reaction solutions. Aliquots of samples (~300 μL) were withdrawn at various intervals and substrate decay was measured by HPLC. Three replicates were included in all photodegradation experiments.

2.3. Analytical procedures

Carbon, hydrogen, nitrogen, and oxygen contents of FA were determined using a Vario Micro cube Elemental Analyzer (Germany). UV-vis spectra were recorded on a Hitachi U3100 spectrophotometer. The concentration of timolol was analyzed by Shimadzu Essentia LC-15 C HPLC system with Agilent HC-C18 column (5 μm, 250 mm × 4.6 mm). The mobile phase was a mixture of acetonitrile, methanol and pH 2.5 phosphate buffer solutions with a ratio of 15:20:65. The flow rate was 1.0 mL/min and the detection wavelength was 295 nm.

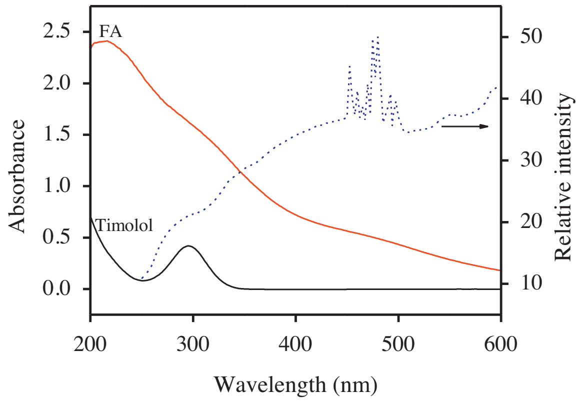

Fig. 1. UV-vis spectra of timolol (50 μM), FA (16.0 mg/L), and the relative intensity of the 150-W Xenon Short Arc Lamp (the light of wavelengths less than 300 nm was filtered with the Pyrex glass).

2.4. Photoproduct analyses

The photoproducts of atenolol and metoprolol were analyzed using an Agilent Technologies 1100 series LC/MSD Trap XCT (Palo Alto, CA, USA) with electrospray ionization in positive ion mode. The MS or MS^2 conditions were set as follows: HV capillary 3500 V; Drying gas (N_2) temperature 325 °C; Drying gas (N_2) flow of 8 L/min; Nebulizer pressure at 30 psi; Trap drive 34.3; Skimmer 40.0 V; Octopole RF amplitude 156.1 V; Capillary exit 114.8; Max. Accumulation time 55.1 ms; ion charge control (ICC) 200,000.

2.5. Determination of rate constants

$^{\bullet}OH$ and $^1O_2$ reactions rate constants for timolol were determined using Fenton's reagent and Rose Bengal, respectively [38,39].

3. Results and discussion

3.1. Photodegradation kinetics

Timolol was hardly degraded in this experiment under simulated sunlight (Fig. A1). Piram et al. found the slow direct photodegradation of timolol with a long half-life of 33 h in pure water [14]. The relative photostability of timolol was likely attributed to the low photodegradation quantum efficiency and sunlight absorption (Fig. 1). Similar phenomena were also found for the direct photodegradation of the other β-blocker [12–17]. In view of the negligible direct photodegradation in this experiment, the indirect photodegradation was the exclusive way for the loss of timolol.

Fig. 2 shows the indirect photodegradation of timolol in the aerated and deoxygenated FA solutions as a function of pH. Timolol underwent photosensitized degradation in both conditions, and the deoxygenation of reaction solutions markedly accelerated the loss of timolol. In addition, the photodegradation of timolol increased markedly with increasing pH. The degradation trend at various pH corresponded well to that of the deprotonated form of timolol (Fig. 2). Accordingly, the deprotonated process facilitated the photosensitized degradation.

3.2. Reactions with $^{\bullet}OH$ and $^1O_2$

The bimolecular rate constant for the reaction between timolol and $^{\bullet}OH$ was determined by competition kinetics according to Eq. (1):

$$k^{S}_{\bullet OH} = \frac{\ln([S]_t/[S]_0)}{\ln([R]_t/[R]_0)} k^{R}_{\bullet OH} \qquad (1)$$