

Photodegradation of 4,4-Bis(4-hydroxyphenyl)valeric acid and its inclusion complex with β -cyclodextrin in aqueous solution

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ABSTRACT

Nanosecond laser flash photolysis and time-resolved fluorescence were used to study photochemistry of 4,4-Bis(4-hydroxyphenyl)valeric acid (diphenolic acid, DPA) and complex of DPA with β -cyclodextrin (DPA- β CD) in aqueous solutions. For both systems the primary photochemical process was found to be photoionization with the formation of a hydrated electron–phenoxy radical pair. Inclusion of DPA in cyclodextrin cavity leads to the great increase of photoionization and fluorescence quantum yield (from 0.01 to 0.14) as well as fluorescence lifetime (from 0.17 to 2.9 ns) due to decreasing of the quenching rate of the singlet excited state of complexed DPA by solvent molecules.

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1. Introduction

4,4-Bis(4-hydroxyphenyl)valeric acid (DPA) is industrially important chemical, which is widely used in production of alkyl resin, phenol-formaldehyde resins, printing-inks, adhesives and coatings [1]. DPA is a close structural analog of widely known endocrine disruptor-bisphenol A and so DPA potentially can exhibit estrogenic activity and toxicity in environment [2,3]. During their production and consumption bisphenols spread and accumulate in environment causing damage to the living organisms [4,5]. Ordinary water treatment processes are not enough effective to removal of majority of synthetic estrogens and in some cases leads to formation of byproducts of unknown nature and toxicity [6]. These facts lead to prohibition of production of bisphenol A and several of their analogs in some countries.

Cyclodextrins (CD) are cyclic oligosaccharides composed of 6(α -CD), 7(β -CD) or 8(γ -CD) residuals of α -D-glucopyranose molecules joined in macrocycles by α -D-1,4 glycosidic linkages. Such structure ensures the presence of an inner hydrophobic

cavity and an external hydrophilic periphery which allows them to form “host-guest” inclusion complexes with various hydrophobic molecules [7]. Such complexation often leads to significant changes in the “guest” molecule photochemistry and photophysics and to an increase of the “guest” photodegradation in particular. As bisphenols exhibit rather intensive absorption bands in UV region both direct and CD-assisted photolysis of bisphenols could be one of possible technique of water purification among other (bio)chemical and catalytic approaches [8].

It was found recently that DPA forms stable 1:1 inclusion complex with β -CD ($K_{st} = 6 \times 10^4 \text{ M}^{-1}$) and such complexation leads to great increase of UV degradation of the bisphenol [9]. This work is devoted to investigation of photophysics and photochemistry of DPA and DPA- β CD complex by means of nanosecond laser flash photolysis and picosecond fluorescence methods. Main attention is paid to determination of nature, spectral and kinetic properties of excited states and primary intermediates as well as clarification of mechanism of DPA photodegradation enhancement upon complexation with β -CD.

2. Materials and methods

A set-up for laser flash photolysis which utilizes forth harmonic (266 nm) of a Nd:YAG laser (LS-2137U, Solar, Belarus) as an

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excitation source (pulse duration 6 ns, pulse energy 0.5–12 mJ/pulse) [10] was used in the experiments. Time resolution of the set up was 50 ns. For calculation of quantum yields (mean errors $\pm 20\%$), laser intensity were measured by means of SOLO 2 laser power meter (Gentec EO). For monitoring the transient absorption changes in millisecond time domain the stationary diode ($\lambda = 400$ nm, 1 mW) was used as a probing light source.

UV absorption spectra were recorded using an Agilent 8453 spectrophotometer (Agilent Technologies). The fluorescence spectra and kinetics were measured on a FLSP920 spectrofluorimeter (Edinburg Instrument). As excitation sources ozone free xenon lamp Xe900 ($\lambda_{\text{ex}} = 270$ nm) and laser diode EPLED-280 ($\lambda_{\text{ex}} = 280$ nm, pulse duration of 800 ps) were used, correspondingly. The fluorescence quantum yields of DPA and DPA- β -CD complex were determined as described in [11] using solutions of tryptophan in water ($\phi = 0.14$) as a standard. Kinetic curves were fitted by iterative reconvolution of one or two exponential functions with the instrument response function, which allows to determine fluorescence life-times as short as 50 ps.

LCMS experiments were performed using ESI ion trap mass-spectrometer Esquire 6000 (Bruker Daltonics) with the HPLC-separation system Agilent 1200 Series. Separation was performed on an analytical column Zorbax SB300-C8, 1.0 mm \times 150 mm, 3.5 μm in the gradient ACN/0.1% formic acid: 2% (0–5 min), 2–40% (5–10 min), 40–95% (10–37 min), 95% (37–43 min), 95–2% (43–44 min), 2% (44–55 min); flow rate 50 $\mu\text{l}/\text{min}$, sample volume 8 μl . Experimental parameters: registration of ions in negative mode, range 50–1000 m/z , HV capillary 4000 V, end plate offset –500 V, ESI nebulizer pressure 20 psi, dry gas flow (N_2) 10 l/min, temperature 300 $^\circ\text{C}$.

HPLC experiments were performed using the Agilent LC 1200 chromatograph with diode array detector. Separation was performed on an analytical column Zorbax Eclipse XBD-C18 4.6 mm \times 150 mm in the gradient ACN/0.05% trifluoroacetic acid: 0% (0–5 min), 0–50% (5–45 min), 50–100% (45–50 min), 100% (50–55 min) 100–0% (55–55.1 min), 0% (55.1–65 min); flow rate was 0.5 ml/min. Registration of chromatogram (260, 280, 320 and 400 nm) and peak area integration was done by software package Agilent ChemStation.

DPA (“Aldrich”, 98%) and β -CD (“Wako Pure Chemical Inc.”, >97%) (Fig. 1), acetonitrile (ACN, “Cryochrom”, quality “O”) and butylacetate (BuOAc, LC grade) were used without further purification. Typical concentrations of reagents in photochemical experiments were 3.6×10^{-4} and 1.5×10^{-3} M for DPA and β -CD, accordingly. In these conditions main part of DPA is bound in 1:1 complex with β -CD ($K_{\text{st}} = 6 \times 10^4 \text{ M}^{-1}$ [9]).

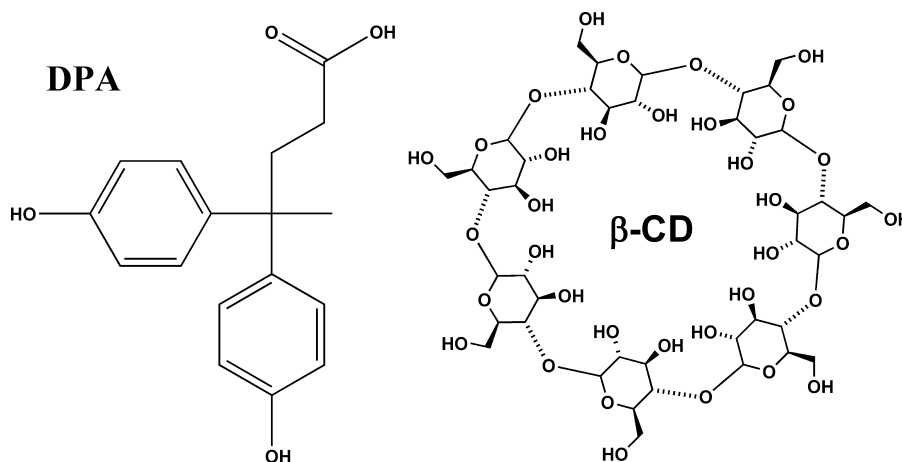


Fig. 1. Structural formulae of 4,4-Bis(4-hydroxyphenyl)valeric acid and β -cyclodextrin.

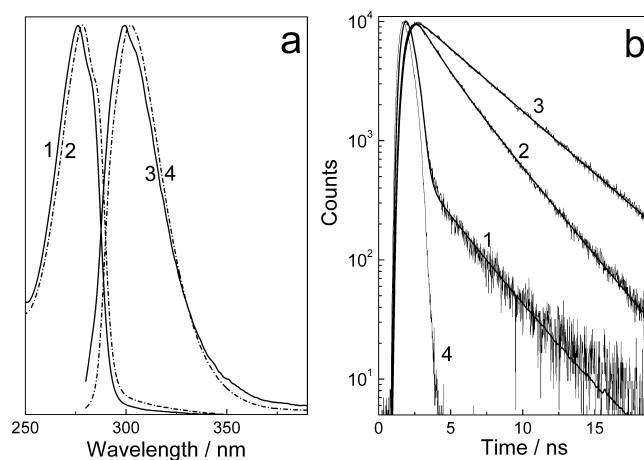


Fig. 2. (a) Normalized absorption (1, 2) and fluorescence (3, 4) spectra of DPA (1, 3) and DPA- β -CD (2, 4) complex. (b) Kinetic curves of fluorescence at 310 nm for DPA in water (1), DPA- β -CD in water (2), DPA in ACN (3) and the instrument response function (4). Smooth lines are the best mono and biexponential fit after reconvolution with the instrument response function. The second very weak component (1.5% of amplitude) at curve (1) corresponds to fluorescence of an impurity in DPA.

Unless otherwise stated, all experiments were run in a fused-silica cell with an optical path length of 1 cm at room temperature and atmospheric pressure in argon- or oxygen-saturated ($[\text{O}_2] = 1.4 \times 10^{-3} \text{ mol/l}$ [12]) aqueous solutions. Double distilled or deionized water was used in all experiments.

3. Results and discussion

3.1. Spectroscopy of DPA and DPA- β -CD complex

Optical and fluorescence spectra of the DPA- β -CD complex and DPA are shown in Fig. 2a and the fluorescence decay curves in Fig. 2b. Complexation of DPA with β -CD leads only to a small red shift of the long-wavelength absorption band (π - π transition) (Table 1) and practically does not change the shape of the fluorescence band. However, drastic increase of fluorescence quantum yield and lifetime was observed upon complexation of DPA with β -CD (Table 1). This fact could be explained by restricted mobility of DPA in β -CD cavity leading to sharp decrease of the rate of internal conversion in the excited state, by shielding of this state from water molecules or by changing of the local polarity of media [13–15].

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