

Photoacids as singlet oxygen photosensitizers: Direct determination of the excited state acidity by time-resolved spectroscopy



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ABSTRACT

Photophysical properties of some 1-naphthol and 2-naphthol sulfonate derivatives and their efficiency as singlet oxygen photosensitizers in aqueous media are reported. The fluorescence emission is mainly from the deprotonated form (conjugate base) and their maxima cover the range of 433–529 nm. The fluorescence decay of these derivatives was found to be fitted with bi-exponential function with χ^2 of about 1.0 ± 0.1 in all cases. Rate constants for oxygen quenching of the excited singlet states of these compounds in H₂O are found to be $(1.2 \pm 0.2) \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ for the neutral form and much lower for the quenching of their conjugate bases. pK_a^* values were found to be in the range 7.4–9.5 while pK_a are close to zero and about 3.3 for 2-naphthol and 2-naphthol-6-sulfonate using Förster equation and in the range of 1.4–3.0 using the fluorescence titration method obtained from the relative integrated fluorescence intensity. Singlet oxygen quantum yields photosensitized by these photoacids were reported in D₂O and found to be in the range 0.13–0.35 for the sulfonated derivatives.

1. Introduction

Hydroxyaromatic molecules show remarkable changes in their acidity upon excitation to their first electronic excited singlet state and become stronger acid than in their ground state. The phenomenon of increased acidity upon electronic excitation, which was attributed to the intramolecular charge transfer (ICT) in the excited singlet state, is called photoacidity and the molecules are termed photoacids [1–10]. Tolbert and Haubrich synthesized a series of 2-naphthol derivatives with cyano group at different positions on the distal ring and reported pK_a^* values for these derivatives lower than that of 2-naphthol itself and therefore called these derivatives “super photoacids” [11]. They have also reported naphthol derivatives with electron-withdrawing groups such as cyano or methanesulfonyl at C-5 and C-8 and found that they exhibit greatly enhanced photoacidity that enables excited state proton transfer (ESPT) to non-aqueous solvents such as alcohols and (CH₃)₂SO [12]. Tolbert and Solntsev showed that the most crucial step in excited state proton transfer is the initial hydrogen-bonding complex in the ground state followed by a rapid Hydrogen bond formation and solvent reorganization, which will accommodate the solvated proton in its product state, followed by the proton transfer itself [10]. Agmon showed that the proton transfer step itself, which occurs in picoseconds,

appears to depend crucially on the solvent due to the dependence of the dissociation rate parameter on water concentration and temperature. The dissociated proton diffuses in aqueous solutions anomalously fast, each proton hop taking place in just 1–2 ps [8]. Carmile et al. studied the ultrafast proton transfer from electronically excited 5,8-dicyano-2-naphthol to the solvent by time-resolved fluorescence and found that unlike most naphthol derivatives, excited 5,8-dicyano-2-naphthol is a very strong acid ($\text{pK}_a^* = -4.5$) and therefore is capable of transferring protons to protic solvents [13]. Finkler et al. have introduced a series of five new derivatives of pyranine (HPTS) as highly photostable “super”photoacids. They reported pK_a values in the range 4.4–5.7 and pK_a^* values in the range -0.8 to -3.9 as determined via Förster cycle and in the range -0.3 to -2.9 as evaluated by fluorescence titration [14].

Photosensitized generation of singlet oxygen has been extensively studied in a variety of solvents and compiled in a number of review articles [15–21], and in supercritical carbon dioxide and the unique heavy atom supercritical xenon [21–24]. The majority of singlet oxygen generation studies have been reported for ruthenium (II) bipyridyl complexes and some other coordination complexes [15,18,25,26]. In addition there have been many studies on of singlet oxygen production by nanoparticle-bound photosensitizers and other systems [21,27]. To the best of our knowledge, studies on photosensitized generation of

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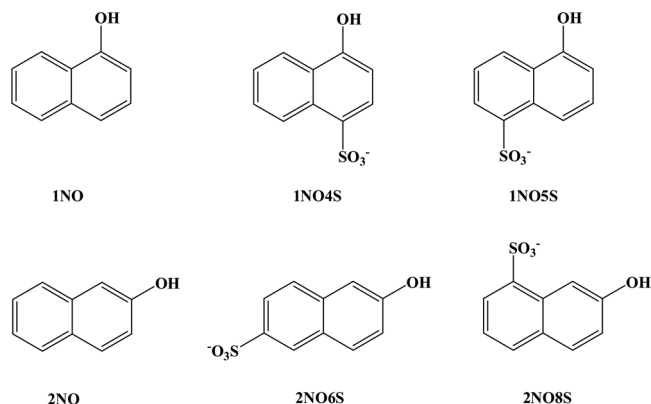
singlet oxygen photosensitized by water soluble aromatic hydrocarbons are very few compared with other classes of compounds and solvents [28–31].

In order to study the interaction between naphthol derivatives with oxygen in aqueous media; it is first necessary to study their photophysical and electrochemical properties. Therefore, the photophysical properties of 1-naphthol (1NO), 1-naphthol-4-sulfonate (1NO4S), 1-naphthol-5-sulfonate (1NO5S), 2-naphthol (2NO), 2-naphthol-6-sulfonate (2NO6S) and 2-naphthol-8-sulfonate (2NO8S) are examined. Förster cycle has been used for the determination of the excited state acidity, pK_a^* , for long time. However, many controversies were always associated with values obtained using its equation [9] partly due to the difficulty in the determination of the fluorescence emission of the photoacid. In this article, we report on using the phenomenon of inclusion in cyclodextrin for better allocation of the fluorescence emission of the photoacids in aqueous solution due to the increased rate of deprotonation in these systems. It has also been reported that the fluorescence titration curves give the best approximation for the determination of the excited state acidity, however; this method was not applicable in many cases [9]. Therefore, in this article we have also introduced the use of the relative integrated fluorescence intensity titration curves for the evaluation of pK_a^* as a more sensitive and reliable sort of the fluorescence titration curves based on simultaneous determination of the decay parameters of the photoacid (PA, neutral form ROH) and its conjugate base (CB, anionic form RO⁻). Proton quenching of the excited photoacids and their conjugate bases is reported. In addition, quenching of the excited singlet state of photoacids and conjugate bases by molecular oxygen is examined; and quantum yield of singlet oxygen thereby produced via photosensitized by these dynamic systems is reported.

2. Experimental part

Photoacids and cyclodextrin derivatives studied in this work were obtained from Aldrich. Photoacids were recrystallized twice from ethanol. Structure and abbreviations of the studied photoacids are given in Scheme 1. Cyclodextrin derivatives and organic solvents were of highest purity grade from Aldrich and were used as received. Phenalenone (Aldrich 97%) was purified by column chromatography. D₂O (Aldrich 99.9%) was used as received and deionized H₂O was used. Absorption spectra were recorded on Shimadzu 1800-UV-vis spectrophotometer. Steady state fluorescence measurements were obtained using Thermo Scientific Lumina spectrofluorophotometer. Excited state lifetimes were measured with EasyLife from OBB using different LEDs with different wavelengths as excitation light source. pH measurements were performed on Adwa (AD 1000 pH /mv).

For singlet oxygen luminescence measurements, the fourth harmonic of Nd:YAG laser (Brilliant) from Quantel was employed for excitation at 266 nm. The emission was observed in right angle



Scheme 1. Structures and abbreviations of naphthol derivatives.

arrangement with Applied Photophysics laser flash photolysis LKS.60 assembly at 1270 nm onto a Hamamatsu H10330-45N IR detector. The emission experiments at 1270 nm (20 averages) were done with air saturated solutions in D₂O at 25 °C with varying the excitation pulse energy by means of attenuation filters. Singlet oxygen luminescence intensity at zero time was measured at different laser intensities and compared with those obtained from the optically matched solution of phenalenone in D₂O as a standard [32] thereby yielding relative singlet oxygen quantum yield (Φ_{Δ}) values. Rate constants for oxygen quenching of the excited singlet states in neutral aqueous solution were obtained by following the changes in the observed rate constants, k_{obs} , of photoacids (PA, $1/\tau_1$) and their conjugate bases (CB, $1/\tau_2$) for Argon purged, air saturated and oxygen saturated solutions. Oxygen concentrations were taken as 0.27 mM and 1.27 mM in air saturated and oxygen saturated water, respectively [33]. The absorbance of sample solutions did not exceed 0.1 at the wavelength of excitation in all measurements. Cyclic voltammetry measurements were carried out in a three-electrode conventional glass cell containing 0.001 M of the photoacids with 0.1 M tetrabutyl-ammoniumperchlorate (TBAP) in deoxygenated acetonitrile using eDAQ Potentiostat (EA161). The potential of the platinum disc working electrode was measured against standard calomel electrode while pure Pt wire was used as a counter electrode. The sweep rate was 100 mVs⁻¹ covering a potential range between 0.0 to +2.0 V.

3. Results and discussion

3.1. Photophysical properties of the photoacids and their conjugate bases

The absorption spectra of naphthol derivatives in neutral aqueous solution are shown in Fig. 1; which clearly shows that sulfonate derivatives of 1-naphthol and 2-naphthol are red shifted relative to 1-naphthol and 2-naphthol; respectively. The electronic absorption peaks of naphthol derivatives are assigned to transitions to the first excited singlet state, ¹L_b, and to the second excited singlet state, ¹L_a. The ¹L_a and ¹L_b bands overlap in the absorption spectra for 1-naphthol and its derivatives and are well separated for 2-naphthol and its derivatives as shown in Fig. 1. Fig. 2 shows the normalized fluorescence spectra of naphthol derivatives in neutral aqueous solution collected with excitation wavelength equals to wavelength of the longest absorption maximum (λ_{abs}^{max}). The fluorescence spectra are dominated by emission from the deprotonated form “the conjugate base, CB”. The fluorescence emission from the neutral species “the photoacid, PA” is only observed for 2-naphthol and its derivatives (Fig. 2). The absorption and emission maxima of photoacids and their conjugate bases are collected in Table 1.

The fluorescence decay of naphthol derivatives in neutral aqueous

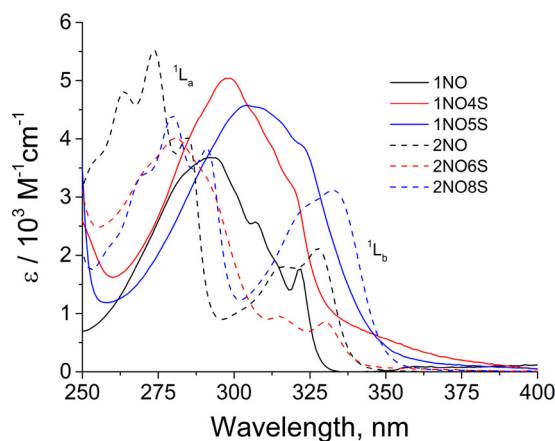


Fig. 1. Absorption spectra of naphthol derivatives in neutral aqueous solution.

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