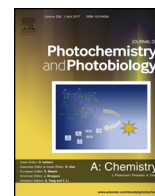




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The photoacidity of phenol chloro benzoate cyanine picolinium salt photoacid in alkanols



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ABSTRACT

Steady-state and time-resolved fluorescence techniques were employed to study the excited-state proton transfer (ESPT) rate to methanol, ethanol and propanol of a new photoacid, the chloro benzoate phenol cyanine picolinium salt (CBCyP). We found that the ESPT rate constants for methanol, ethanol and propanol are about $3 \times 10^{12} \text{ s}^{-1}$, $2 \times 10^{12} \text{ s}^{-1}$ and $1.2 \times 10^{12} \text{ s}^{-1}$ respectively, whereas for water it is $6 \times 10^{12} \text{ s}^{-1}$. The photoacid pK_a^* in water is about $\text{pK}_a \sim -7$. The kinetic isotope effect as measured from the fluorescence decay rate of the protonated form is 1.5 and 1.25 for methanol and ethanol respectively, whereas in water it is 1.7. We suggest that a nonradiative process takes place and reduces the measured kinetic isotope effect in both methanol and ethanol.

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1. Introduction

Photoacids are a class of organic compounds that are weak acids in their ground electronic state, with pK_a in the range of 5–10, whereas in their excited-state they are stronger acids with a change in their pK_a , $\Delta\text{pK}_a = 6\text{--}13$, lower than in their ground electronic state. These compounds have been extensively studied by optical spectroscopy over the last fifty years. For the last thirty years, time-resolved spectroscopy has enabled us to monitor directly the excited-state proton-transfer (ESPT) process to the solvent and deduce the ESPT rate constant of many photoacids [1–17]. Recently, new photoacids have been synthesized for which the photoacidity is high and the values of pK_a^* are lower than -5 [18–21]. For these photoacids the ESPT rate constant, k_{PT} , in water is equal to or greater than 10^{12} s^{-1} .

In a previous publication, we classified the photoacids into four regimes according to the strength of the photoacids [20]. In group I are the weak photoacids with $\text{pK}_a^* > 0.4$. For $\text{pK}_a^* = 0.4$ the ESPT rate constant, $k_{\text{PT}} \approx 5 \times 10^{10} \text{ s}^{-1}$ and for pK_a^* of 2.7 (2-naphthol) $k_{\text{PT}} \approx 10^8 \text{ s}^{-1}$. k_{PT} for an ESPT to methanol and ethanol for photoacids with $\text{pK}_a^* \geq 1$ is about three orders of magnitude lower than for water.

In group II of photoacids, $-4 < \text{pK}_a^* < 0.4$. The ESPT rate is higher the more negative the pK_a^* . This class can transfer protons to

protic solvents like alkanols and DMSO. For $\text{pK}_a^* = 0$ The ESPT rates to methanol and ethanol are lower than to water by about two orders of magnitude and for $\text{pK}_a^* \approx -2$ by about one order of magnitude.

For group III of photoacids with $\text{pK}_a^* \approx -4$, solvent orientational motion controls the ESPT rate, and for water, k_{PT} is about 10^{12} s^{-1} or somewhat lower. In a recent study [21], we found that phenol benzoate cyanine picolinium salt, shown in Scheme 1b belongs to the “solvent-control” ESPT group [20]. We found that in water the average ESPT rate constant is about $0.5 \times 10^{12} \text{ s}^{-1}$, similar to that of NM6HQ⁺ that was studied by several groups [15,22].

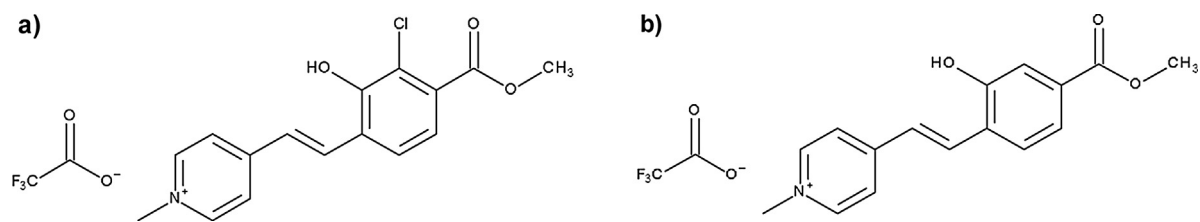
For group IV, the ESPT rate constant is larger than 10^{12} s^{-1} and $\text{pK}_a^* < -5$. For the photoacidity of chloro benzoate phenol cyanine picolinium salt (CBCyP), shown in Scheme 1a, we found pK_a^* about -7 and the k_{PT} to water $\sim 6 \times 10^{12} \text{ s}^{-1}$.

Thus in water, the ESPT rate is ultrafast and the CBCyP photoacid belongs to the strongest photoacid class in which the k_{PT} is about an order of magnitude higher than the water-reorientation rate. The intermolecular-vibration time-constant in water is of the order of 100 fs (10^{-13} s).

In the current work we measured the ESPT rates of the newly synthesized CBCyP in methanol, ethanol and propanol. We found that the ESPT rate constant in these solvents is lower than in water. We also measured the kinetic isotope effect (KIE) of the ESPT rate constant in methanol-D and ethanol-D. The KIE in water was found to be ~ 1.7 , whereas in methanol it is 1.5 and in ethanol the KIE is only ~ 1.25 . We therefore suggest that nonradiative processes occur in methanol and ethanol and compete with the ESPT rate. If we

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Scheme 1. Molecular structure of a. chloro benzoate cyanine picolinium (CBCyP), b. benzoate cyanine picolinium (BCyP).

assume that the true KIE values for methanol and ethanol are that of water (KIE=1.7), we can calculate the nonradiative rate constant, k_{nr} . We calculate that k_{nr} is about 10^{12} s^{-1} for both methanol and ethanol.

2. Experimental methods

The time-resolved fluorescence at short times ($t < 100 \text{ ps}$) was measured by the up-conversion technique. The fluorescence of chloro benzoate cyanine picolinium (CBCyP), was studied in methanol, ethanol and propanol at room temperature. The laser used for the fluorescence up-conversion was a cavity-dumped Ti: sapphire femtosecond laser (Mira, Coherent), which provides short, 120 fs, pulses at about 800 nm. The cavity dumper was operated at a low repetition rate of 800 kHz. The up-conversion system is a commercial system (FOG-100, CDP, Russia). The samples were excited by SHG pulses of about 8 mW at wavelengths of 390–420 nm on average. The time response of the up-conversion

system is determined by the Raman-Stokes line of water, red-shifted by 3600 cm^{-1} . We found that the fwhm of the signal is 330 fs. To avoid photodegradation, samples were placed in a rotating optical cell, rotated at a frequency of 10 Hz. Sample degradation was minimal and did not affect the profile of the signal decay.

For the time-correlated single-photon counting (TCSPC) measurements for long-time decay of $t > 100 \text{ ps}$, we used, for sample excitation, the same laser as was used for the fluorescence up-conversion system. The TCSPC detection system was based on a Hamamatsu 3809U multichannel plate photomultiplier and an Edinburgh Instruments TCC 900 integrated TCSPC system. The time response of the instrument was approximately 40 ps, fwhm. The excitation pulse energy was reduced by neutral-density filters to about 10 pJ.

Time-resolved experiments for fluorescence up-conversion were carried out on solutions at concentrations of about 0.5 mM. The steady-state fluorescence and excitation spectra were

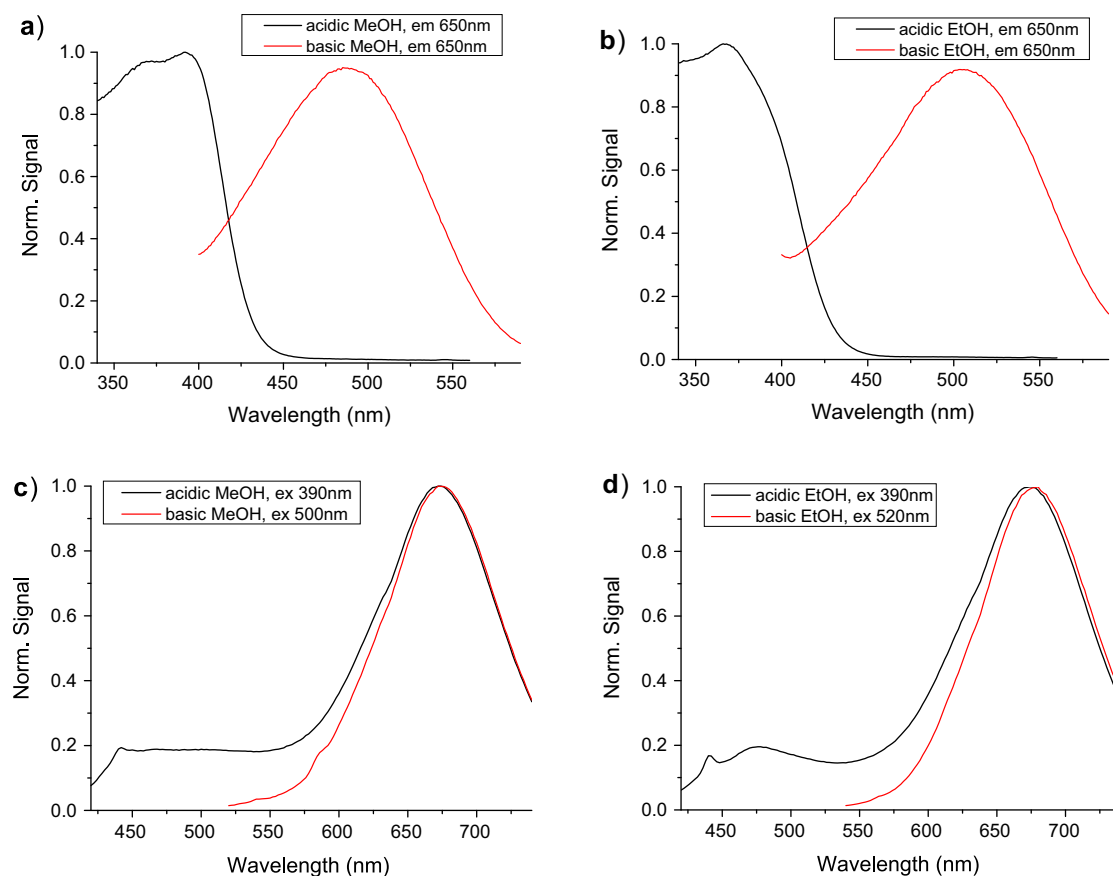


Fig. 1. Steady-state fluorescence and excitation spectra of CBCyP. a. excitation spectrum of CBCyP in slightly basic and in slightly acidic methanol, collected at 650 nm. b. excitation spectrum of CBCyP in slightly basic and in slightly acidic ethanol, collected at 650 nm. c. fluorescence spectrum of CBCyP in slightly basic and in slightly acidic methanol. d. fluorescence spectrum of CBCyP in slightly basic and in slightly acidic ethanol.

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