

Comparison of the rate of excited-state proton transfer from photoacids to alcohols and water



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ABSTRACT

Steady-state and time-resolved techniques were employed to study the excited-state proton-transfer (ESPT) rate of two newly synthesized photoacids – quinone cyanine diindolium (QCy7) and its dipicolinium analog (QCy9) – in three protic solvents, water, methanol and ethanol. The ESPT rate constant k_{PT} of QCy7, whose $pK_a^* \sim -6.5$ in water, methanol and ethanol is $1.2 \times 10^{13} \text{ s}^{-1}$, $8 \times 10^{11} \text{ s}^{-1}$, $7 \times 10^{11} \text{ s}^{-1}$ respectively. k_{PT} for QCy9 ($pK_a^* \sim -8.5$), is 10^{13} s^{-1} for all three protic solvents used. We qualitatively explain these results and also the previously found solvent dependence of k_{PT} of weaker photoacids by adiabatic and non-adiabatic proton-transfer formalism.

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1. Introduction

Photoacids are aromatic organic molecules that are weak acids in their ground electronic state, but of acidity greater by many orders of magnitude in their first excited electronic state. Thus, photo-excitation to the excited state, by short UV–vis laser pulses, enables one to follow the photoprotolytic processes. Intermolecular excited-state proton transfer (ESPT) from the acidic group of the excited photoacid to a nearby solvent molecule [1–15] is widely researched.

In recent studies we reported on the photoprotolytic properties of a new class of photoacids, the quinone cyanine dyes [16–18]. We found that QCy7 (shown in Scheme 1) has dual emission bands when excited from its ground-state neutral form (the protonated form, ROH). The bands correspond to emission from the protonated ROH* (band maximum at 532 nm) and from the deprotonated RO^{−*} (700 nm) species of QCy7. The decay of the time-resolved emission of ROH* in water is fast, slightly shorter than 1 ps at room temperature. The time-resolved emission of RO^{−*} has a distinctive rise time with about the same time constant as the decay time of ROH*. The decay time of RO^{−*} in water is ~ 130 ps, and its fluorescence quantum yield is roughly 10%.

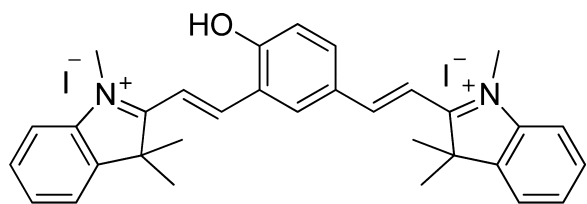
In a recent study we reported on the photoprotolytic properties of QCy9 (shown in Scheme 2)

We found that QCy9 is a super-photoacid with $pK_a^* \approx -8.5$; an even more remarkable finding is that it exhibits a very large ESPT rate constant, $k_{PT} \approx 1 \times 10^{13} \text{ s}^{-1}$. This is the largest k_{PT} value reported in the literature up to now.

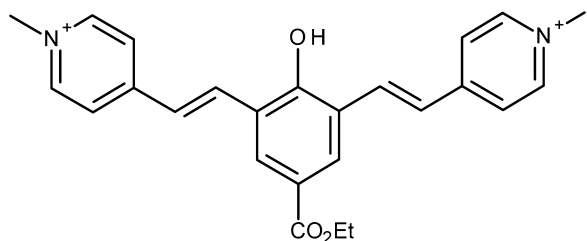
Relatively weak photoacids whose $pK_a^* > 0$ are incapable of transferring a proton to a protic solvent like methanol or ethanol, whereas stronger photoacids ($pK_a^* < 0$) transfer a proton within the ROH excited-state lifetime. For 8-hydroxy-1,3,6-pyrenetrisulfonate (HPTS), a commonly used photoacid with $pK_a^* = 1.3$, we found [19] that the ESPT rate in water/methanol mixtures decreases as the methanol content in the mixture increases. By extrapolation, we estimate that the ESPT rate constant, k_{PT} , in neat methanol is $\sim 5 \times 10^6 \text{ s}^{-1}$, whereas in water it is 10^{10} s^{-1} , three-and-a-half orders of magnitude larger than in methanol. Since the radiative rate is $2 \times 10^8 \text{ s}^{-1}$, the ESPT efficiency is of the order of only 1% or less. In more recent studies, we found that 5,8-dicyano-2-naphthol (DCN2) [20–22], whose $pK_a^* \approx -4$, efficiently transfers a proton to methanol and ethanol with proton-transfer rates of $1.6 \times 10^{10} \text{ s}^{-1}$ and $8.3 \times 10^9 \text{ s}^{-1}$, respectively. N-methyl-6-hydroxy quinolinium, NM6HQ⁺, is an even stronger photoacid with pK_a^* of ~ -6 . The ESPT rate constant of this photoacid in water, methanol and ethanol is $5 \times 10^{11} \text{ s}^{-1}$, $1.25 \times 10^{11} \text{ s}^{-1}$ and $0.5 \times 10^{11} \text{ s}^{-1}$, respectively. These examples indicate that the difference in the values of k_{PT} in water and in alcohols decreases as the strength of the photoacid increases.

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Scheme 1. Molecular structure of QCy7



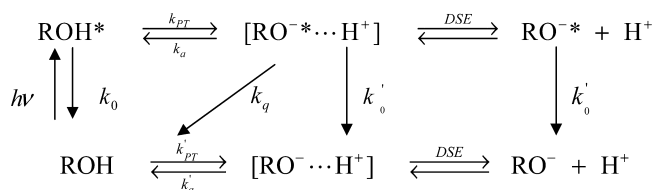
Scheme 2. Molecular structure of QCy9

Ernsting, Kovalenko and Coworkers studied the ESPT process of 6-hydroxyquinolinium (6HQc) and 6-hydroxy-1-methylquinolinium (6MQc) to water and alcohols [15], and also solvation of the zwitterionic conjugate base 1-methylquinolinium-6-olate (6MQz). Transient emission spectra from 6MQz in acetonitrile and protic solvents exhibits a bathochromic dynamic shift of the emission spectra without changing their shape and intensity. The shift dynamics matches the solvation correlation function $C(t)$ measured with known solvatochromic probes. This indicates that 6MQz monitors the solvation dynamics and that no intramolecular electron transfer occurs on a subpicosecond or longer time scale. The PT dynamics from 6HQc and 6MQc closely follows $C(t)$. This allows for their conclusion that PT is controlled by solvation dynamics.

In the current study, we have extended the photoacidity scale over which comparisons of k_{PT} for protic solvents are performed. We measured the ESPT rates in methanol and ethanol of both QCy7 and QCy9 whose pK_a^* values in water are ~ -6.5 and -8.5 , respectively. We also measured it in the corresponding deuterated solvents. The ESPT rate of QCy7 was found to change only slightly in these solvents. For water, methanol and ethanol, the k_{PT} of QCy7 is $1.25 \times 10^{12} \text{ s}^{-1}$, $0.84 \times 10^{12} \text{ s}^{-1}$ and $0.7 \times 10^{12} \text{ s}^{-1}$ respectively. For QCy9, the strongest reported photoacid up to now, we find that the ESPT rate is nearly the same for water, methanol and ethanol, $k_{PT} \approx 10^{13} \text{ s}^{-1}$. We explain these interesting results qualitatively with the use of adiabatic and non-adiabatic proton-transfer theories.

1.1. Reversible and irreversible photoprotonic cycles of photoacids

Excitation of a photoacid solution of pH lower than its ground-state pK_a , generates a vibrationally relaxed, electronically excited ROH molecule (denoted by ROH^*) that initiates a photoprotonic cycle (Scheme 3).



Scheme 3. The photoprotonic cycle.

Proton dissociation, with an intrinsic rate constant k_{PT} , leads to the formation of an ion-pair $RO^{-*} \cdots H_3O^+$ that subsequently forms an unpaired RO^{-*} and a solvated proton, which diffuses into the bulk of the solvent. The proton and the RO^{-*} may recombine via reversible (adiabatic) recombination with a rate constant k_a and reform the excited acid, ROH^* . In general, back-protonation may also proceed by an irreversible (non-adiabatic) pathway, involving fluorescence quenching of the RO^{-*} by a proton with a rate constant k_q , forming the ground-state ROH. 1-Naphthol and its derivatives are known to exhibit considerable fluorescence quenching of the deprotonated form, RO^{-*} , in acidic aqueous solutions.

Removal of an ion-pair from the contact radius, a , to infinity is described by the transient numerical solution of the Debye–Smoluchowski equation (DSE) [23,24]. The motion of the transferred proton in water near the photoacid depends strongly on the electrical potential existing between it and the deprotonated form. The diffusion-assisted geminate recombination of the RO^{-*} with the proton could be quantitatively described with the use of the numerical solution of the DSE under the initial and boundary conditions of the photoprotonic process. In addition, the fluorescence lifetimes of all excited species are considered, with $1/k_0 = \tau_{ROH}$ for the acid, and $1/k'_0 = \tau_{RO^-}$ for the conjugate base. Generally, k'_0 and k_0 are much smaller than both the proton-reaction and the diffusion-controlled rate constants. The amplitude of the long-time fluorescence tail of ROH^* depends on the intrinsic rate constants, k_a and k_{PT} , on the proton-diffusion constant, D_{H^+} , and on the electrical potential between RO^{-*} and the proton.

2. Experimental

The fluorescence up-conversion technique was employed in this study to measure the time-resolved emission of QCy9 and QCy7 in several protic solvents at room temperature. The laser used for the fluorescence up-conversion was a cavity-dumped Ti:sapphire femtosecond laser (Mira, Coherent), which provides short, 150 fs, pulses at about 800 nm. The cavity dumper operated with a relatively low repetition rate of 800 kHz. The up-conversion system (FOG-100, CDP, Russia) operated at 800 kHz. The samples were excited by pulses of ~ 8 mW on average at the SHG frequency. The time response of the up-conversion system is evaluated by measuring the relatively strong Raman–Stokes line of water shifted by 3600 cm^{-1} . It was found that the full width at half-maximum (fwhm) of the signal is 340 fs. Samples were placed in a rotating optical cell to avoid degradation. We found that, during our five-minute time-resolved measurements in a cell rotating at a frequency of 10 Hz, the degradation of the sample was marginal and had no effect on the decay profile of the signal. The QCy7 and QCy9 samples were excited in their protonated ROH form (Scheme 1).

Experiments were carried out on samples at concentrations of about 1 mM or less. Measurements of time-correlated single-photon counting (TCSPC) were performed using the same laser as a light source, and in the same set-up. The TCSPC detection system was based on a Hamamatsu 3809 U photomultiplier and an Edinburgh Instruments TCC 900 computer module for TCSPC. The overall instrument response was approximately 40 ps (fwhm) where the excitation pulse energy was reduced to about 10 pJ by neutral-density filters.

The steady-state emission and absorption spectra were recorded by a Horiba Jobin Yvon FluoroMax-3 spectrofluorimeter.

Both QCy7 and QCy9 were synthesized by the Shabat group of Tel Aviv university, as described in references [16,17]

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