Excited-state proton transfer from pyranine to acetate in methanol

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Abstract. Excited-state proton transfer (ESPT) of pyranine (8-hydroxypyrene-1,3,6-trisulphonate, HPTS) to acetate in methanol has been studied by steady-state and time-resolved fluorescence spectroscopy. The rate constant of direct proton transfer from pyranine to acetate (k_1) is calculated to be $\sim 1 \times 10^9$ M^{-1} s^{-1}. This is slower by about two orders of magnitude than that in bulk water (8×10^{10} M^{-1} s^{-1}) at 4 M acetate.

Keywords. Excited-state proton transfer; pyranine; fluorescence spectroscopy; direct proton transfer.

1. Introduction

Proton transfer is fundamental in many natural processes e.g. in abnormally high mobility of proton in water ('Grotthuss mechanism')[1] and transport of a proton through a membrane.[2] Dissociation of an acid (HA) in an aqueous solution involves transfer of a proton to a water molecule to form a geminate ion pair consisting of the deprotonated species (A^-) and the hydronium ion (H_3O^+). Subsequently, the geminate ion pair dissociates to give a solvent-separated ion pair. Excited-state proton transfer (ESPT) of pyranine (8-hydroxypyrene-1,3,6-trisulphonate, HPTS) has been widely studied to explore the mechanism of proton transfer in different media.[3–13] In the ground state, pyranine is a weak acid ($pK_a = 7\cdot4$).[3] In the excited state, pK_a value of pyranine decreases to $0\cdot4$.[3] According to a femtosecond fluorescence up-conversion study, ESPT of HPTS in water involves three time constant $0\cdot3$, $2\cdot5$ and 87 ps. The $0\cdot3$ and $2\cdot5$ ps components are ascribed to solvation dynamics and LE-CT transition, respectively while the 87 ps component to the proton dissociation and diffusion in water.[4,5] More recently, femtosecond mid-IR study suggests that the inter-conversion between the two electronic states of HPTS occurs on a time scale <150 fs.[6] The transient response of the O–H stretch of HPTS displays two ultrafast components ($0\cdot3 \pm 0\cdot2$ ps and $3 \pm 1\cdot5$ ps) which are assigned to solvent relaxation affecting the hydrogen bonds between HPTS and water. This is followed by two additional components arising from proton transfer to water (90 ± 30 ps) and rotational diffusion (200 ± 50 ps).[6]

Proton transfer rate from HPTS to a proton scavenger (i.e. acetate) is very fast.[7–9,11] Rini *et al*[9] studied ESPT from HPTS to acetate by monitoring the rise of the carbonyl IR band at 1720 cm^{-1} arising from acetic acid. Rise of this band clearly indicates arrival of the proton at the acetate. They detected very fast ESPT (<0·15 ps) for those HPTS which are already hydrogen-bonded to the acetate in the ground state[9]. For the uncomplexed HPTS, diffusion is needed before formation of a H-bond in the excited state and, hence, proton-transfer rate is slower.[9,10] When a base (e.g. acetate) is introduced into a solution, direct proton transfer to acetate competes with proton-transfer rate to the solvent. Genosar *et al*.[7] studied direct excited-state proton transfer from pyranine to acetate in water in the concentration range of 0·5–4 M acetate. They reported that in the presence of 4 M acetate, the pseudo first-order rate of proton abstraction is $\approx (3 \text{ ps})^{-1}$ This corresponds to a rate constant $\approx 8 \times 10^{10}$ M^{-1} s^{-1} and represents one of the fastest intermolecular reactions observed in bulk water. In the present work, we have studied excited-state proton transfer from HPTS (pyranine) to acetate in methanol. We show that in the case of methanol there is no proton transfer from HPTS to methanol (solvent) and we exclusively observe direct proton transfer to acetate.

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Table 1. Picosecond decay parameters of HA emission (at 420 nm) and A^- emission (at 515 nm) of pyranine (HPTS) in methanol at different acetate concentrations.

[Acetate] (M)	HA emission[1] decay time τ_1 ps (a_1)	A^- emission[1] Rise time τ_1 ps (a_1)*	Decay time τ_2 ps (a_2)	Acetic acid added (M)
0·00	4000 (1·0)	–	–	0
0·25	2000 (1·0)	1950	5000 (0·10)	0·02
0·50	1250 (1·0)	1200	5000 (0·10)	0·23
0·75	950 (1·0)	900	5000 (0·09)	0·40
1·00	750 (1·0)	700	5000 (0·07)	0·58
1·50	600 (1·0)	500	5000 (0·07)	0·93
2·00	450 (1·0)	400	5000 (0·06)	1·28

[1] $\pm 10\%$

*$a_1 = -a_2$, (4)
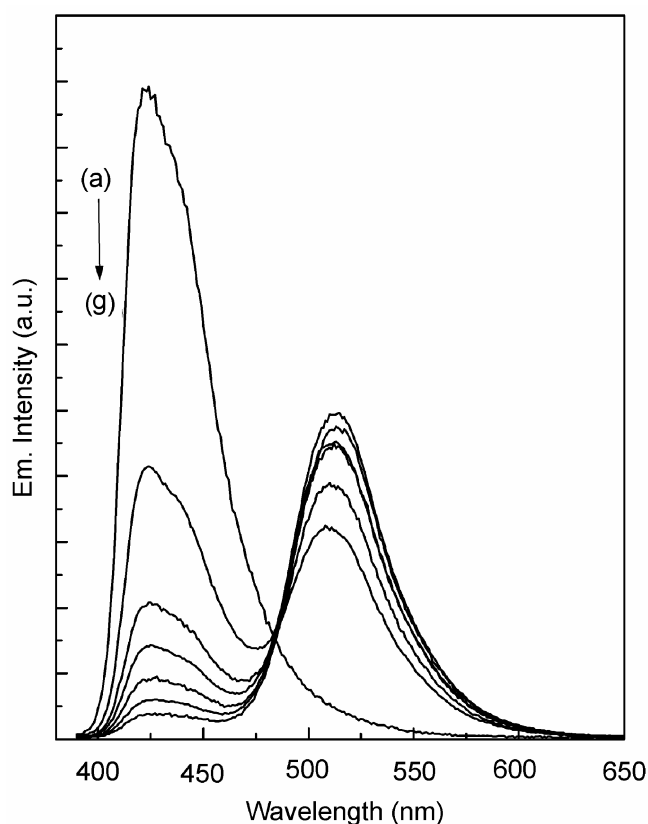
Figure 1. Steady state emission spectra (λ_{ex} = 375 nm) of 20 μM HPTS (a–g) in methanol containing 0, 0·25, 0·5, 0·75, 1, 1·5 and 2 M. acetate.

2. Experimental

HPTS (Fluka) and methanol (99·7%, Uvasol, Merck) were used as received. The steady-state absorption and emission spectra were recorded on a Shimadzu UV-2401 spectrophotometer and a Spex FluoroMax-3 spectrofluorimeter respectively.

For picosecond lifetime measurements, the samples were excited at 375 nm using a picosecond diode laser (IBH Nanoled-11) in an IBH Fluorocube apparatus. The emission was collected at magic angle polarization using a Hamamatsu MCP photomultiplier (5000U-09). The time-correlated single-photon counting (TCSPC) setup consists of an Ortec 9327 CFD and a Tennelec TC 863 TAC. The data were collected with a PCA3 card (Oxford) as a multi-channel analyser. The typical FWHM of the system response using a liquid scatterer is about 90 ps. The fluorescence decays were deconvoluted using IBH DAS6 software.

3. Results

3.1 *Steady state spectra*

In methanol, HPTS exhibits an absorption maximum at 403 nm due to the protonated form (HA) and no absorption band for the deprotonated form (A^-) is observed. In neat methanol, HPTS shows only one prominent emission peak at 420 nm due to the protonated form (HA). This indicates that only the HA form exists in the excited state, in methanol.
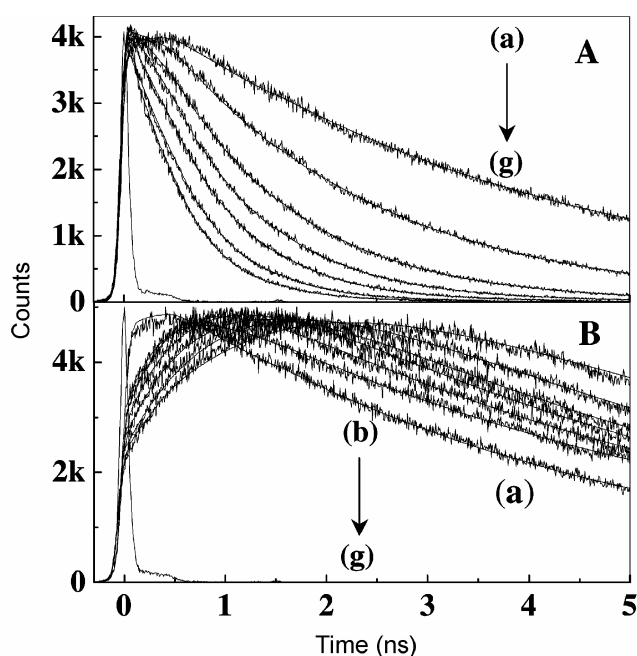
On addition of sodium acetate, a new absorption band at ≈ 450 nm arises due to formation of A^-. To suppress formation of the anion (A^-) in the ground state (i.e. ground-state proton transfer from HPTS to acetate), requisite amount of acetic acid was added (table 1). In the presence of added acetic acid, there is no noticeable change in the absorption band at about 403 nm with variation in concentration of sodium acetate.

On addition of sodium acetate, emission intensity of the protonated form of HPTS (at 420 nm) decreases with a concomitant increase in the emission

intensity at 515 nm due to the formation of deprotonated form (figure 1).

3.2 *Time-resolved studies*

Time-resolved fluorescence decays of the protonated form were monitored at λ_{em} = 420 nm, and for the deprotonated form the decays were recorded at λ_{em} = 515 nm. In pure methanol, the decays at both 420 nm and 515 nm are similar and found to be single exponential with a time constant of ~4·0 ns. The absence of a rise at 515 nm (where the anion A⁻ emits) clearly indicates that there is no ESPT from HPTS to methanol in the absence of acetate.

Figure 2. Picosecond transients of HPTS in methanol containing (a–g) 0, 0·25, 0·5, 0·75, 1, 1·5 and 2 M sodium acetate at λ_{em} (**A**) 420 nm and (**B**) 515 nm (λ_{ex} = 375 nm).
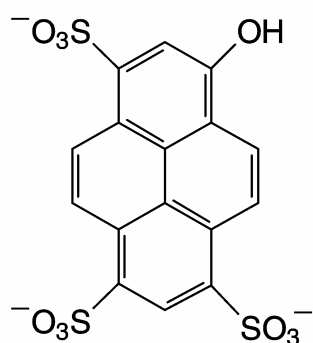

Scheme 1. Structure of HPTS (pyranine).

On addition of sodium acetate to a solution of HPTS in methanol, at 515 nm a distinct rise component precedes the decay. The rise component is a clear indication that the excited-state proton transfer process occurs from HPTS to acetate. The decays at 420 nm are found to be single exponential for all acetate concentrations (0·25–2 M) (figure 2A, table 1).

The decay component at 420 nm is almost similar to the rise time observed at 515 nm (figure 2A and 2B, table 1). The rise time at 515 nm (or decay at 420 nm) gradually decreases with the increase of acetate concentration from 1·95 ns at 0·25 M acetate to 400 ps at 2 M acetate.

4. Discussion

Evidently, in methanol, there is no proton transfer to solvent and direct ESPT from HPTS to the acetate ion takes place. It may be recalled that the rate of proton transfer in bulk water is $\approx 9\cdot4 \times 10^9$ s⁻¹ which is in marked contrast to that in bulk methanol where no ESPT occurs at all.[11] This is due to the fact that methanol is a very poor proton acceptor compared to water, and hence no methanol-mediated proton transfer takes place. For the solvent to take part in the proton-transfer process, it must stabilise the discharged proton by screening it from the negative charge of the conjugate base, and provide an efficient mode for the diffusion of the proton to the bulk.

To analyse the observed decay characteristics of HPTS in the presence of acetate, we now use a simple kinetic model[14,15] as follows
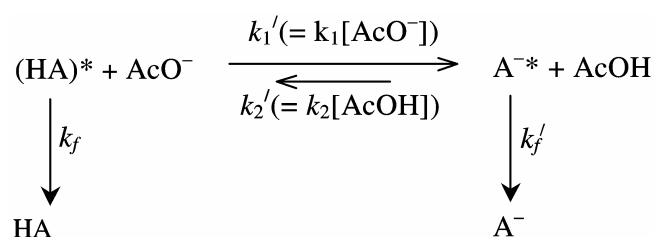
In this case, the excited photoacid HA* donates its proton directly to the acetate ion to produce A⁻*. k_1' and k_2' are the pseudo-first order rate constants respectively for the forward and backward processes in the excited state. The differential equations corresponding to the above scheme are

$$-\mathrm{d}\left[HA\,*\right]/\mathrm{d}t = (k_1' + k_f)[HA^*] - k_2'[A^-\,*], \qquad (1)$$

$$\mathrm{d}[A^-\,*]/\mathrm{d}t = k_1'[HA^*] - (k_2' + k_f')[A^-\,*], \qquad (2)$$

where, $k_1' = k_1[\text{AcO}^-]$ and $k_2' = k_2[\text{AcOH}]$

Using the conditions, at $t = 0$, $[\text{HA*}] = [\text{HA*}]_0$ and $[\text{A}^-*] = 0$ we obtain,

$$[\text{HA*}](t) = \frac{[\text{HA*}]_0}{m_1 - m_2}$$
$$\times [(X - m_2)\exp(-m_1 t) + (m_1 - X)\exp(-m_2 t)], \quad (3)$$

$$[\text{A}-*](t) = \frac{k_1[\text{AcO}^-][\text{HA*}]_0}{m_1 - m_2}$$
$$\times [\exp(-m_2 t) - \exp(-m_1 t)], \quad (4)$$
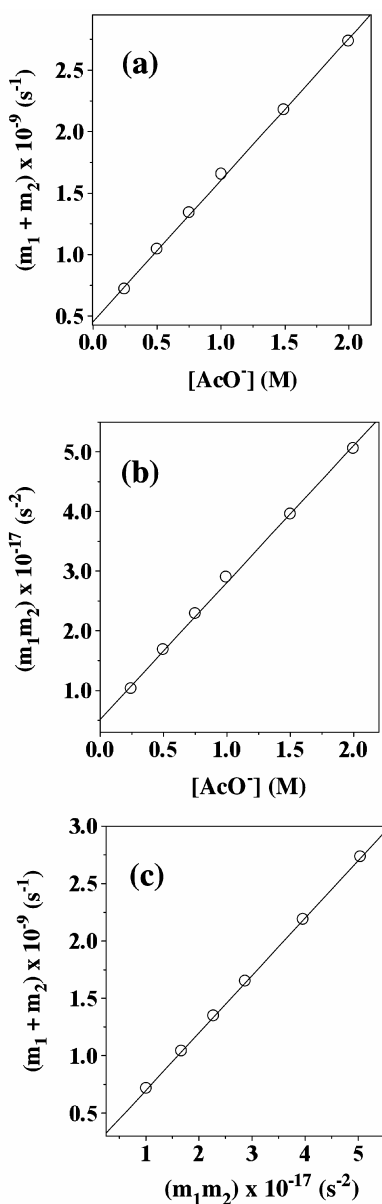
where $X = k_1' + k_f$ and $Y = k_2' + k_f'$ $m_1 = \tau_1^{-1}$, $m_2 = \tau_2^{-1}$

$$m_1, m_2 = \frac{1}{2}[(X + Y) \pm \{(Y - X)^2 + 4k_1'k_2'\}^{1/2}]. \quad (5)$$

According to the scheme discussed above, the decay of the deprotonated form at 515 nm should be a sum of two exponentials, whose amplitudes are equal in magnitude but opposite in sign. Moreover, the exponents of the transients at 420 nm and 515 nm should be identical, as is actually observed. However, the observed decay at 420 nm is found to be single exponential. This may be due to the negligible contribution of the component τ_2 and the very small value of the recombination rate constant (k_2), compared to that of proton transfer (k_1').

The rate constants k_1, k_f and k_f' may be evaluated using the following equations which can be derived from the scheme discussed above.

$$(m_1 + m_2) = k_1[\text{AcO}^-] + (k_f + k_2' + k_f'), \quad (6)$$

$$(m_1 + m_2) = k_f + Y\left(1 - \frac{k_f}{k_f'}\right) + \frac{m_1 m_2}{k_f'}, \quad (7)$$

$$m_1 m_2 = k_f' k_1[\text{AcO}^-] + k_f Y. \quad (8)$$

As indicated in table 1, with increase in $[\text{AcO}^-]$, a larger amount of acetic acid is needed to suppress the absorption due to A^-. Thus, $k_2'(= k_2[\text{AcOH}])$ and hence, Y $(= k_2' + k_f')$ varies with $[\text{AcO}^-]$. Thus, the plot of $m_1 m_2$ against $[\text{AcO}^-]$ should not be a straight line. However, the excellent linearity of this plot (figure 3b) suggests that the term k_2' is negligible. In other words, back proton transfer is much slower than radiative decay of A^-, i.e. $k_f' \gg k_2'$. Neglecting k_2', from (6)–(8) we obtain excellent linear plots of $m_1 + m_2$ against $[\text{AcO}^-]$ (figure 3a), of $m_1 m_2$ against $[\text{AcO}^-]$ (figure 3b) and of $m_1 + m_2$ against $m_1 m_2$ (figure 3c). The values of rate constants k_1, k_f and k_f' are calculated from the slopes and intercepts of the plots in figure 3. The values of k_1, k_f and k_f' are found to be $1 \cdot 0 \times 10^9$ M^{-1} s^{-1}, $2 \cdot 6 \times 10^8$ s^{-1} and $2 \cdot 3 \times 10^8$ s^{-1}.

The rate constant for quenching of HA emission by acetate is determined from a simple bimolecular quenching equation. According to this, the lifetime decay (τ) of HA in methanol decreases with quencher (acetate) concentration $[Q]$ as,

Figure 3. Plot of (**a**) $(m_1 + m_2)$ versus $[\text{AcO}^-]$, (**b**) $m_1 m_2$ versus $[\text{AcO}^-]$ and (**c**) $(m_1 + m_2)$ versus $m_1 m_2$ for HPTS in methanol at different acetate concentrations (0·25 M–2 M).

$$1/\tau = 1/\tau_0 + k_q [Q], \qquad (9)$$

where τ_0 is the lifetime in the absence of the acetate. A typical plot of the reciprocal of lifetime of the
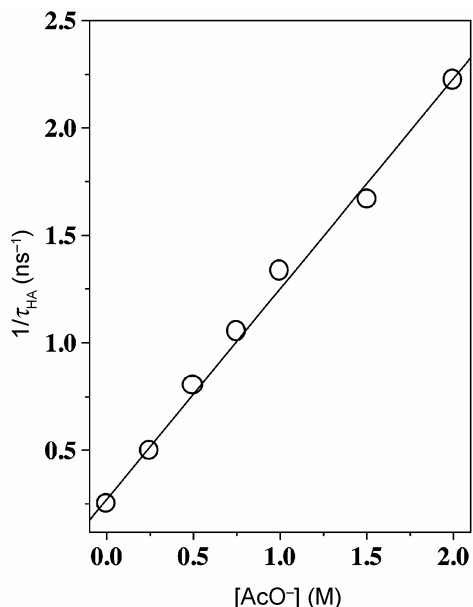
Figure 4. A plot of inverse of decay time ($1/\tau_{HA}$) of the protonated (HA) form of HPTS against concentration of AcO$^-$ in methanol.
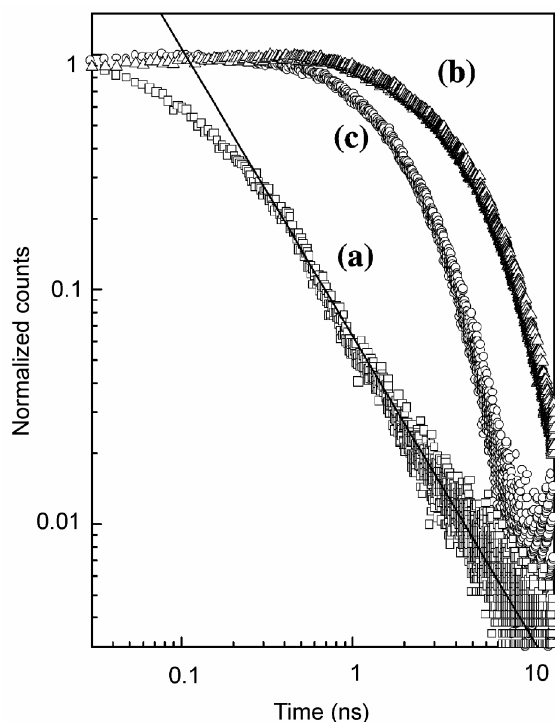
Figure 5. Log–log plot of fluorescence decay of HPTS in (a) water ($\lambda_{ex} = 405$ nm, $\lambda_{em} = 440$ nm), (b) methanol ($\lambda_{ex} = 375$ nm, $\lambda_{em} = 420$ nm) and (c) methanol containing 2 M acetate ($\lambda_{ex} = 375$ nm, $\lambda_{em} = 420$ nm).

protonated form of pyranine (HA) against acetate concentration is given in figure 4. The bimolecular quenching constant k_q is found to be 0.96×10^9 M^{-1} s^{-1}.

It may be noted that the observed value of k_q (0.96×10^9 M^{-1} s^{-1}) is close to the calculated value of the rate constant for proton transfer, k_1 (1.0×10^9 M^{-1} s^{-1}). This indicates relatively simple kinetic behaviour of HPTS in methanol.

As noted earlier, the proton transfer rate of pyranine to acetate (4 M) in water is one of the fastest reactions investigated so far with a rate constant of 8×10^{10} M^{-1} s^{-1} [7]. The rate constant of ESPT from HPTS to acetate in a 2 M solution of acetate in methanol is slower by ≈ 2 orders of magnitude compared to that (ESPT to acetate) in water. The slowing down of the proton-transfer process in methanol is due to inefficient stabilization of the ejected proton and lack of solvent participation in proton transfer by the Grotthuss mechanism.[1] Absence of solvent mediation hardly allows the reactants (HPTS and acetate) to come in close proximity with the proper geometry suitable for reverse proton transfer. This results in a much slower recombination rate.

According to several recent works on ESPT of HPTS, the long time-decay part of the photoacid should display power-law kinetics. The power-law $t^{-3/2}$ decay of the fluorescence intensity is the fingerprint of spherical symmetrical diffusion assisted reversible geminate recombination.[16,17] In bulk water, the decay of HA emission clearly shows power-law behaviour at long time range for two decades of time (figure 5). This indicates the existence of geminate ion pairs in the proton-transfer process. In methanol, HPTS does not exhibit ESPT to methanol and shows a clear single-exponential decay kinetics of HA emission with no power-law decay behaviour (figure 5). On addition of acetate, when ESPT occurs, the decay of the photoacid exhibits exponential decay behaviour with no power-law decay kinetics (figure 5).

In summary, in methanol, ESPT from HPTS to acetate occurs directly without involving a geminate ion pair. The non-existence of the geminate ion-pair in the excited-state proton-transfer of HPTS to acetate in methanol may be due to the low stabilization energy of the geminate ion-pair.

5. Conclusion

The present work demonstrates that ESPT from HPTS to methanol does not occur because of poor stabili-

zation of the ejected proton and the deprotonated species. In methanol, ESPT from HPTS to acetate is explained in terms of the direct proton transfer model without involving a geminate ion-pair. This is in sharp contrast to the situation in water, where both solvent-mediated and direct proton transfer between HPTS and acetate are observed, depending on the concentration of acetate ion.[9,10] The rate of proton transfer from HPTS to acetate in methanol is slower by about two orders of magnitude with respect to that in water.

Acknowledgements

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