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Excited-State Proton Transfer in Nonaqueous Solvent

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Excited-state proton transfer from pyranine to urea in methanol solution was studied by using both steady-state quenching and fluorescence lifetime measurements at room temperature. Proton transfer initially requires a urea monomer to form a protonated urea monomer, which is then solvated by methanol. The experimental data demonstrates the emission that would be attributed to an encounter pair. A set of rate constants is obtained on the basis of a simple kinetic model.

KEY WORDS: Excited-state proton transfer; fluorescence quenching; urea; pyranine; fluorescence decay.

INTRODUCTION

A great deal of work has been done on the excited-state proton transfer (ESPT) reactions to understand better on the role of proton acceptor and the nature of proton transfer process. Because the dynamics of the proton transfer depends largely on the nature and number of proton acceptor molecules, the measurements of proton transfer rates from some photoacids to the solvent water have revealed the importance of water structure in the proton transfer reactions in aqueous solutions. For weak photoacids, a cluster of 4 ± 1 molecules of water has been proposed as the proton acceptor [1], whereas a water dimer seems to be an effective proton acceptor in the case of strong photoacids [2,3].

Pyranine is one of the hydroxyarenes that has a pK^* value in the range of 0.5–1.4 [4] and thus is able to transfer its proton to suitable acceptor in the excited state. Its nonexponential decay has been attributed to a reversible one-stage time-dependent geminate recombination [5,6]. The fluorescence decay of pyranine in methanol-water mixtures has revealed that solvent-induced variations in the deprotonation rate coefficients are in fact quite close to the variations in the corresponding equilibrium constants because of localized counterion stability in water-rich solutions and to proton stability in methanol-rich solutions [7]. The studies of proton transfer from some cyanonaphthols to nonaqueous solvents have shown the reversible nature of proton transfer and its rate being influenced by the solvent [8–10]. The proton transfer from protonated cation of 2-(2′-hyroxyphenyl) benzimidazole to water, methyl urea, and dimethyl sulfoxide in acetonotrile solution has occurred via a 1:1 hydrogen-bonded adduct between the photoacid and the base, which is then followed by the reaction of the adduct with a second molecule of base [11]. The proton transfer from biphenyldiols to urea and methyl urea has indicated the formation of intermolecular hydrogen-bonded exciplex as the intermediates, while the proton transfer from the same to triethylamine has revealed a single step without forming an exciplex [12].

It is therefore constructive to extend the study on the excited-state proton transfer in nonaqueous medium with suitable bases to gain more insights into the deprotonation mechanism and interaction with the solvent molecules. In this paper, the ESPT from pyranine to urea in methanol solution at room temperature has been presented. The proton transfer proceeded through an encounter pair in the solvent cage and was found to be an activation-controlled.

EXPERIMENTAL

Pyranine was procured from the Institute of Physical Chemistry, Stuttgart and used as received. Urea was

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purchased from Fluka. Samples were prepared in spectroscopic grade methanol from Merck and the concentration of pyranine in all samples was kept at 10^{-5} *M*. All measurements were carried out at 25°C.

Absorption spectra of pyranine in methanol solution at different concentrations of urea were recorded by a UV/VIS lambda-5 spectrophotometer. Steady-state fluorescence spectra were taken by using a SPF-500 spectrofluorometer after a correction for the response characteristics from the spectrofluorometer components.

A mode-locked Nd:YAG laser (Spectra-Physics Model 3800) with a mode-locker (Spectra-Physics Model 451) operating at 82 MHz repetition rate was used to pump the rhodamine 6G-dye laser. The output of the dye laser was cavity-dumped at 4 MHz. The output pulses with 4 MHz repetition rate were then frequency doubled to 300 nm by using a frequency doubler (Spectra-Physics Model 390). All samples were excited at 300 nm and a time-correlated, single-photon counting was used to collect the fluorescence decays of pyranine at 420 nm and 540 nm. A curve-fitting deconvolution program supplied by Applied Photophysics was used for the analysis to extract the fluorescence lifetimes of pyranine in methanol solution.

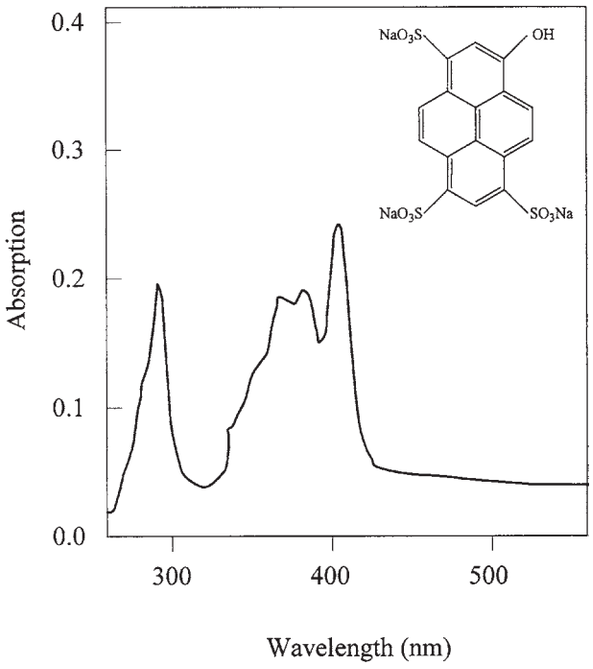


Fig. 1. Absorption spectrum of pyranine in neat methanol.

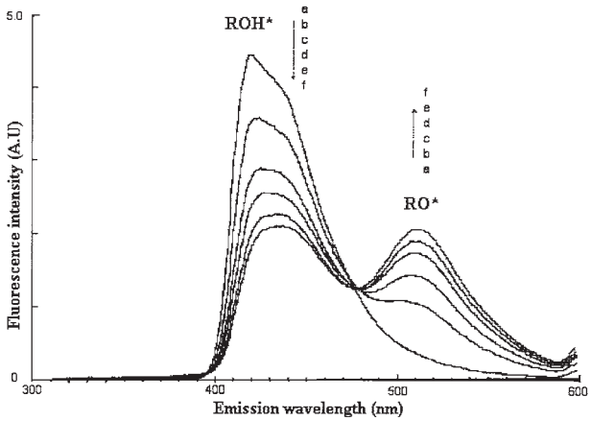


Fig. 2. Fluorescence emission spectra of pyranine (a) in neat methanol and at (b) 0.50 *M* urea, (c) 1.0 *M* urea, (d) 1.5 *M* urea, (e) 2.0 *M* urea, and (f) 2.5 *M* urea in methanol.

RESULTS

Absorption

As shown in Fig. 1, the absorption spectrum of pyranine in methanol showed an acidic form alone and agrees very well with that previously reported [13]. When urea was added to a solution of pyranine in methanol, even up to the maximum concentration of urea, that is, 2.80 *M*, no change in absorption spectrum was observed.

Steady-State Fluorescence

Unlike absorption spectra, the fluorescence spectra of pyranine were quite sensitive to the concentration of urea (Fig. 2). In neat methanol, pyranine displayed a single emission band at 420 nm because of its acidic form (ROH*); upon addition of urea, the fluorescence intensity of the acidic band decreased with an emergence of a new fluorescence band at 515 nm due to its anionic form (RO^*) [13]. An isoemissive point appeared at 480 nm.

Fluorescence Decays

By keeping the excitation wavelength at 300 nm, fluorescence decays were measured at 420 nm to see the effect of added urea on the fluorescence lifetime of pyranine in methanol solution. The fluorescence decay of pyranine was a single exponential in neat methanol with a lifetime of 3.43 ns. However, in the presence of urea, the decay became a biexponential. Figures 3 and 4 show the

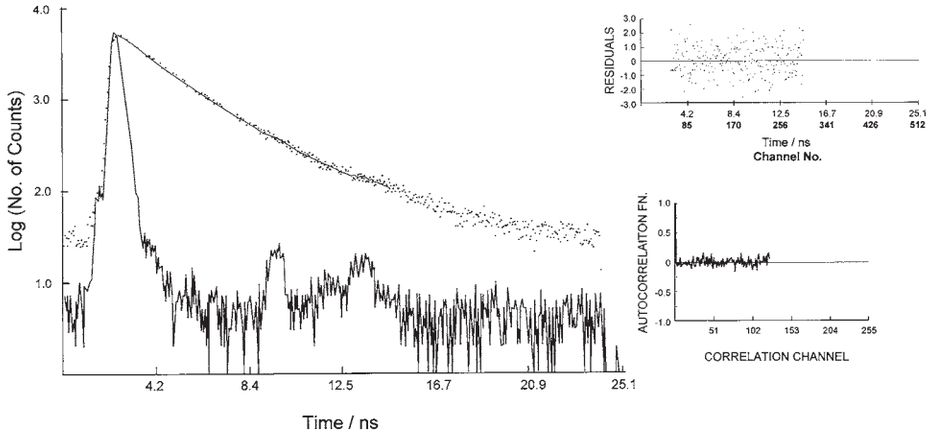


Fig. 3. The fluorescence decay of ROH* at 420 nm in methanol solution at 1.0 *M* urea at 25°C. The solid line is the fit of the fluorescence decay. Plots of weighted residuals and autocorrelation function for the fitted curve are shown.

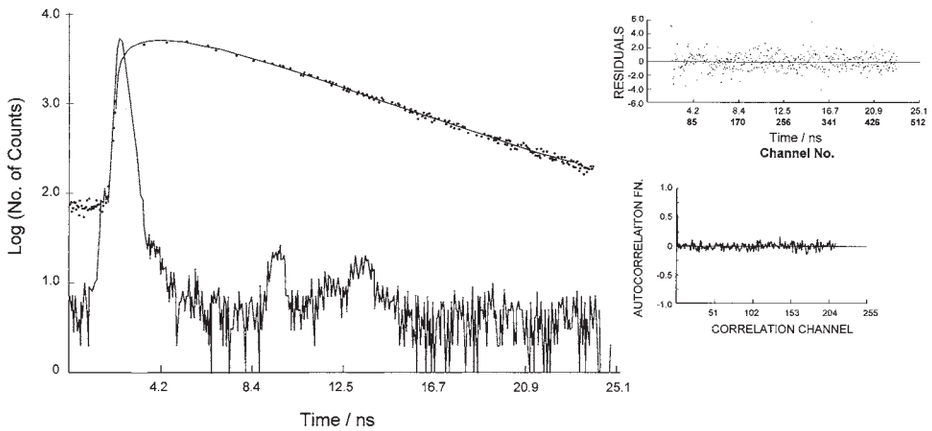


Fig. 4. The fluorescence decay of ROH* at 540 nm in methanol solution at 1.0 *M* urea at 25°C. The solid line is the fit of the fluorescence decay. Plots of weighted residuals and autocorrelation function for the fitted curve are shown.

fluorescence decays of ROH* at 1.0 *M* urea at 420 nm and 540 nm in methanol solution. As reported in Table I, with increasing urea concentration, one of the time components (τ_1) decreased from 3.4 ns in neat methanol to 1.2 ns in methanol solution with 2.5 *M* urea while the other time component (τ_2) remained around 3 ns without varying significantly with the added urea concentration.

The fluorescence decays of ROH* at 540 nm could be described by a triexponential function, one of the components showing negative amplitude (Table II). One decay component (τ_4) showed decreasing decay time and increased contribution to the decay upon increasing the concentration of urea. The other decay component (τ_5) had a decay time of around 4 ns that did not change significantly by varying the urea concentration, while its contribution to the decay decreased with increasing concentration of urea in methanol solution. The time component τ_3 was a rise time of the base RO* in the excited state.

DISCUSSION

Pyranine does not form a complex with urea in the ground state. The appearance of the isoemissive point in the fluorescence spectra of ROH* suggests that the proton transfer takes place from pyranine to urea in the excited state. As depicted in Fig. 5, steady-state quenching

Table I. Steady-state Quenching and Fluorescence Decay Data of ROH* in Methanol Solution at 25°C (λ_{exc} = 300 nm; λ_{em} = 420 nm)

[Urea] (mol dm^{-3})	%A_1	τ_1 (ns)	%A_2	τ_2 (ns)	χ^2	I_o/I (420 nm)	λ_1 ($\times 10^8$ s^{-1})	λ_2 ($\times 10^8$ s^{-1})
0	100	3.4 ± 0.0	–	–	1.1	1.00	2.90	–
0.20	5	3.1 ± 0.6	95	3.1 ± 0.0	1.1	1.11	3.23	3.19
1.0	43	1.6 ± 0.5	57	3.0 ± 0.4	1.0	1.64	6.17	3.34
1.2	48	1.6 ± 0.4	52	2.9 ± 0.3	1.1	1.68	6.40	3.47
1.5	50	1.5 ± 0.3	50	2.8 ± 0.2	1.1	1.90	6.85	3.53
2.0	62	1.4 ± 0.1	38	2.7 ± 0.1	1.1	2.24	7.09	3.62
2.2	60	1.3 ± 0.0	40	2.7 ± 0.0	1.1	2.39	7.85	3.72
2.5	58	1.2 ± 0.2	42	2.6 ± 0.2	1.0	2.55	8.54	3.85

Table II. Fluorescence Decay Data of RO* in Methanol Solution at 25°C (λ_{exc} = 300 nm; λ_{em} = 540 nm)

Urea (mol dm^{-3})	Rise		Decays				
	A_3	τ_3 (ns)	A_4	τ_4 (ns)	A_5	τ_5 (ns)	χ^2
0.20	−4.3 ± 0.0	2.8 ± 0.0	0.40 ± 0.0	3.1 ± 0.2	5.4 ± 0.0	4.2 ± 0.0	1.2
1.0	−4.2 ± 0.1	2.3 ± 0.1	0.35 ± 0.04	2.3 ± 0.5	5.2 ± 0.1	4.3 ± 0.0	1.2
1.2	−4.3 ± 0.0	2.2 ± 0.0	0.24 ± 0.01	2.7 ± 0.2	5.2 ± 0.0	4.3 ± 0.0	1.1
1.5	−3.7 ± 0.3	1.9 ± 0.2	0.82 ± 0.03	1.9 ± 0.5	4.2 ± 0.4	4.5 ± 0.2	1.2
2.0	−3.6 ± 0.0	2.0 ± 0.0	0.86 ± 0.0	2.0 ± 0.0	4.2 ± 0.0	4.4 ± 0.0	1.2
2.2	−3.8 ± 0.0	1.9 ± 0.0	0.75 ± 0.03	2.2 ± 0.1	4.2 ± 0.0	4.4 ± 0.0	1.1
2.5	−3.6 ± 0.1	1.8 ± 0.1	0.86 ± 0.03	1.9 ± 0.3	4.0 ± 0.1	4.5 ± 0.0	1.0

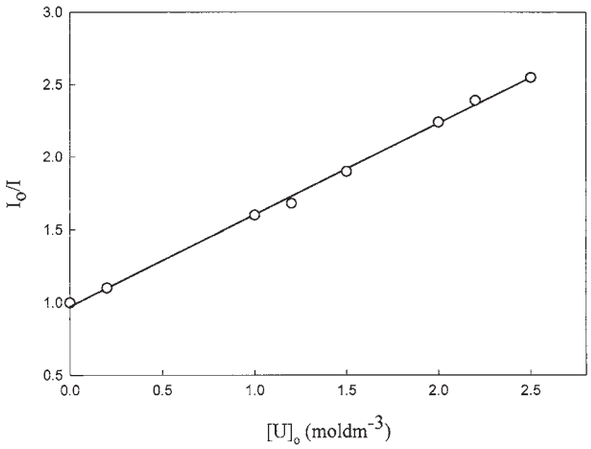


Fig. 5. A steady-state Stern-Volmer plot of pyranine-urea system in methanol solution at 25°C.

of pyranine by urea follows a linear Stern-Volmer relationship [14] with a regression coefficient of 0.99 and a slope of 0.627 dm^{3}mol^{-1}.

$$I_o/I = 1 + k_q \tau_o [U]_o \quad (1)$$

Where I_o and I are fluorescence intensities of ROH* in the absence and presence of urea in methanol solution, $[U]_o$ is the molar concentration of added urea, τ_o is the fluorescence lifetime of ROH* in the absence of urea that is 3.43 ns, and k_q is the bimolecular quenching constant of ROH* by urea. The estimate of k_q from the slope of Eq. (1) is 1.83×10^8 dm^{3}mol^{-1}s^{-1}. The linear Stern-Volmer plot is indicative of an involvement of the urea monomer in the proton transfer process and of the absence of ground-state complex formation between pyranine and urea in methanol solution, which is, in agreement with the observation that there was no change in the absorption spectra of pyranine in the presence of urea. However, the k_q value implies that the quenching of ROH* by urea is considerably below that for diffusion-controlled quenching.

The molar concentration of urea monomer in methanol solution at each concentration of added urea may be calculated by using Eq. (2), because the equilibrium constant (K) for the formation of urea dimer in methanol is known [15,16].

$$[U] = [U]_o - 2K[U]_o^2 \quad (2)$$

where $[U]$ is the ground-state concentration of urea monomer and K = 0.0238 M^{-1}. As depicted in Fig. 6, the molar concentration of urea monomer is a linear function over the concentration of added urea in methanol

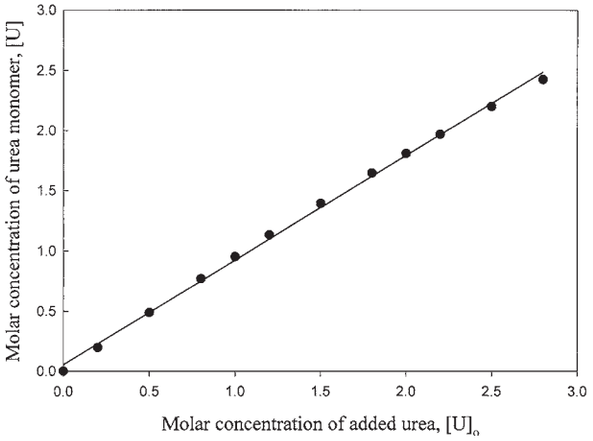


Fig. 6. A plot of the molar concentration of urea monomer versus the concentration of added urea.

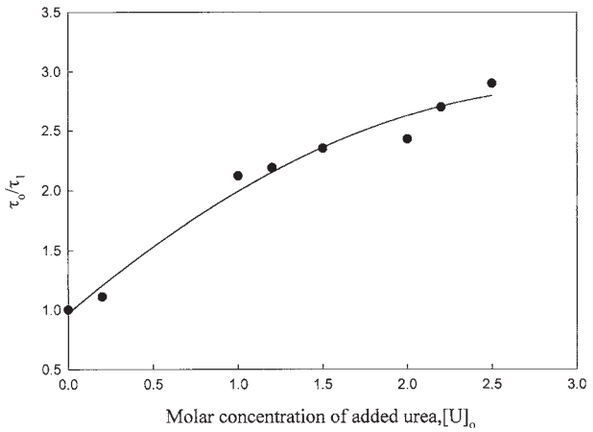


Fig. 7. A Stern-Volmer plot of τ_0/τ_1 against the molar concentration of added urea for pyranine-urea system in methanol solution at 25°C.

solution, showing the substantial involvement of urea monomer alone in the proton transfer. This would be true in view of a small increase in the molar volume of urea in methanol solution and the concentration of urea monomer being about 37 times higher than that of urea dimer within the used concentration of added urea. Therefore the contribution of urea dimer in the proton transfer is less likely and assumed to be negligible. Apparently, the proton transfer takes place effectively with the urea monomers.

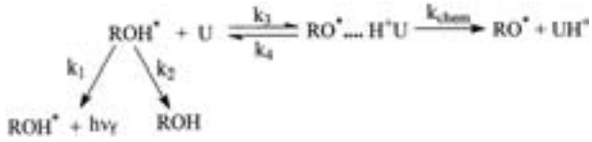
The fluorescence decay of ROH* at 420 nm was biexponential with the time components τ_1 and τ_2. When τ_0/τ_1 is plotted against the molar concentration of added urea (Fig. 7), the plot displays a negative deviation from linearity at higher concentrations of added urea, suggesting that τ_1 at higher concentrations of urea had a slightly higher value than its actual lifetime. This, in fact, suggests the presence of a reverse reaction in the fluorescence decay of ROH* [17]. Hence, τ_2 would be the time component for the reverse reaction to form ROH*. Figures 5 and 7 demonstrate that as the concentration of added urea is increased, the fluorescence yield of the ROH* (I) is found to decrease less rapidly than the lifetime (τ_1). Moreover, I_0/I and τ_0/τ have the same values at 0.20 *M* urea, and the difference between these values starts above 0.20 *M* of added urea. This again supports the absence of ground-state complex formation between pyranine and urea, and the quenching of ROH* by urea may therefore be a dynamic.

The fluorescence decay of ROH* at 540 nm was triexponential. The pre-exponential factor (A_3) had negative amplitude, whereas two other pre-exponential factors (A_4 and A_5) had positive amplitudes. The rise time (τ_3) coincided with the decay time of τ_4. The pre-exponential factor A_5 had a major contribution to the decay at 540 nm, and its time component τ_5 was around 4.3 ns, independent of urea concentration in methanol solution. Thus τ_5 may be the time component for the decay of free RO* that is formed as a result of effective proton transfer.

The presence of the reverse reaction in the decay of ROH* at 420 nm and of short-lived time component (τ_4) in the fluorescence decay of ROH* at 540 nm strongly suggest the presence of intermediate species in the proton transfer process, which may possibly be an encounter pair. Because of the lower concentration of detached proton in methanol solution, its recombination to the free RO* is least expected. Therefore the reverse reaction may be caused mainly by the recombination of the detached proton and RO* within the encounter pair while in the solvent cage. Hence, τ_4 is believed to be the lifetime of the encounter pair.

In agreement with the interpretations above, the ESPT from ROH* to urea occurs in two steps. In the first step, ROH* and urea monomer diffuse together to form the encounter pair, and in the second step, the encounter pair dissociates finally into free ions (i.e., UH^+ and RO*). As presented in scheme 1, a simple kinetic model [18] is adopted to rationalize the observed fluorescence decay data.

Scheme I



Plots of time constants λ_1 ($= 1/\tau_1$) and λ_2($= 1/\tau_2$) associated with the decays of pyranine are shown in Fig. 8. Since ($\lambda_1 + \lambda_2$) may be related to the rate constants by [19],

$$\lambda_1 + \lambda_2 = k_1 + k_2 + k_3\,[U] + k_4 + k_{chem}. \qquad (3)$$

Thus a plot of ($\lambda_1 + \lambda_2$) should be linear approximately with the scatter shown in Fig. 8 and yield a slope of k_3 with an intercept of $k_1 + k_2 + k_4 + k_{chem}$. However, to get the better estimate for k_3, the intercept of $\lambda_1 + \lambda_2$ is obtained by using the intercept of the plot of λ_2 versus urea concentration and the unquenched lifetime of pyranine as λ_1 approaches τ_o in the absence of urea. This yields a value of k_3 of about 2.46×10^8 $dm^3mol^{-1}s^{-1}$. Substituting the known values of k_q and k_3 into Eq. (4),

$$k_4/k_{chem} = (k_3/k_q) - 1 \qquad (4)$$

gives the rate constants $k_4 = 9.42 \times 10^7\ s^{-1}$ and $k_{chem} = 2.74 \times 10^8\ s^{-1}$, respectively. Thus an estimate of equilibrium constant ($K = k_3/k_4$) for the formation of encounter pair (RO*. . . . H^+U) is about 2.60 dm^3mol^{-1}. Though this value is small, it supports the early assumption of encounter pair formation in the proton transfer. The calculated rate constants are summarized in Table III. Because $k_{chem}/k_4 = 2.9$ and $k_{chem} = 2.74 \times 10^8\ s^{-1}$, the quenching efficiency must be low and the kinetics approach that of an activation-controlled process. The value of k_q is about 26% less than that of k_3.

The extent of the diffusion-controlled process in the decay of ROH* can be estimated by the quenching efficiency. Therefore the diffusion-controlled bimolecular rate constant (k_d) for pyranine-urea system is calculated by using Smoluchowski's equation [20],

$$k_d = (4\ \pi\ N\ D_{AB}\ R_{AB})\ 10^3\ dm^3mol^{-1}\ s^{-1} \qquad (5)$$

taking R_{AB} (the collision distance between ROH* and urea) = 8.45 Å and D_{AB} (the sum of diffusion coefficients of ROH* and urea) = $1.8 \times 10^{-9}\ m^2s^{-1}$, respectively. For a methanol solution with 1.0 *M* urea, k_d is around 1.15×10^{10} $dm^3mol^{-1}s^{-1}$. The comparison of k_3 to k_d results in a quenching efficiency of approximately 0.02, indicating that only 2% of the quenching between ROH* and urea is effective. Thus the ESPT from ROH* to urea is an activation-controlled reaction. It is possible that although the rate of reaction is, to a smaller extent, governed by the rate at which the ROH* and urea monomer diffuse through the medium, considerable activation energy must be involved in the reaction of RO*. . . . H^+U as a result of its interaction with methanol. Methanol (Kamlet-Taft parameters of the acidity = 0.93 and of the basicity = 0.62) [20] is capable of solvating the encounter pair and may limit the hydrogen bond formation between the proton and urea monomer within the encounter pair.

The constant lifetime (τ_5) of RO* aftermath of the proton transfer also points to the stability of both RO* and UH^+ through the solvation of methanol. Taking this into account, the final entity of the proton acceptor in methanol solution may be envisaged as a mixed UH^+. . . $(CH_3OH)_n$ cluster, where $n \geqslant 1$. The nature of methanol solvation on the protonated urea monomer is not yet known comprehensively; thus further work in this direction is needed to know the value of "n." However, in the case of a protonated urea monomer in aqueous solution, UH^+. . . (H_2O) has been reported to be the most stable cluster [21]. Evidently, the efficiency of proton transfer depends not only on the size and geometry of the proton acceptor but also on the acidity and basicity of the solvent.

Table III. Calculated Rate Constants for a Pyranine-Urea System in Methanol Solution at 25°C

	Pyranine-Urea System
k_q	1.83×10^8 $dm^3mol^{-1}s^{-1}$
$k_1 + k_2$	$2.92 \times 10^8\ s^{-1}$
k_3	2.46×10^8 $dm^3mol^{-1}s^{-1}$
k_4	$9.42 \times 10^7\ s^{-1}$
k_{chem}	$2.74 \times 10^8\ s^{-1}$
K ($= k_3/k_4$)	2.60 dm^3mol^{-1}

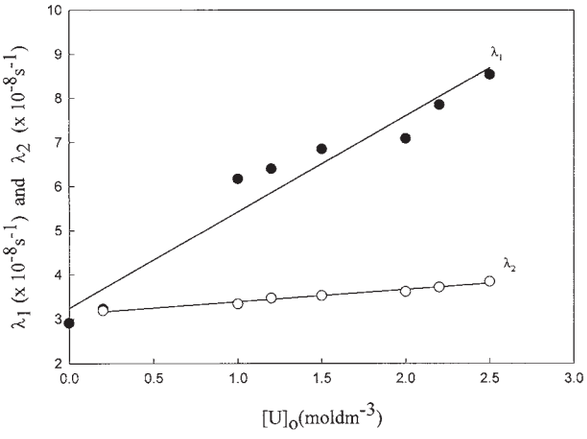


Fig. 8. Plots of the decay constants associated with the decay of pyranine against the concentration of urea.

CONCLUSIONS

The proton transfer rate from pyranine to urea in methanol solution is found to be an activation-controlled. As a result of methanol solvation, a substantial amount of energy barrier exists in the encounter pair for an effective proton transfer. The urea monomer is found to be an effective proton acceptor and further methanol solvation of it is expected for its stability. The experimental data suggests the proton acceptor as a mixed cluster in its final entity.

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