

Ultrafast excited-state proton transfer from dicyano-naphthol

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Abstract

The rate of proton transfer from electronically excited 5,8-dicyano-2-naphthol (DCN2) to the solvent is studied by time-resolved fluorescence. Unlike most naphthol derivatives, excited DCN2 is a strong acid ($pK^* \approx -4.5$) and therefore is capable of transferring protons to alcohols and other moderate proton acceptor solvents. The rate constant of proton transfer, κ_d , at low temperatures (< 250 K) is slightly larger than the inverse dielectric relaxation time, $1/\tau_D$ and has the same activation energy of the dielectric relaxation. On the other hand, at temperatures above 250 K the temperature dependence of the proton transfer rate decreases monotonically with increasing temperature, while the dielectric relaxation activation energy maintains the low temperature value.

1. Introduction

Proton transfer is a common and fundamental process in chemistry and biology [1]. A certain class of proton chemistry is proton transfer to solvent (PTTS). The study of PTTS is connected to basic aspects of solution rate and equilibrium processes. These include the factors governing proton association [2,3], solvation [4] and mobility [5]. Hydroxyarenes undergo an enhancement of acidity upon photoexcitation [6–8]. The hydroxyarenes are ideal substrates for examining fundamental aspects of proton transfer to solvent using time-resolved fluorescence measurements. Unfortunately, the change in their acidity is relatively modest (≈ 8 pK units), which occurs upon photoexcitation with conventional hydroxyarenes. This limitation confines photophysical investigations to water in which proton transfer rate competes with the excited state lifetime (≈ 10 ns).

The most studied excited state proton transfer to solvent hydroxyarene is 8-hydroxy-1,3,6-pyrene trisulfonate (HPTS) [9–12]. For this compound, at room temperature the proton transfer rate constant in aqueous solution is 120 ps^{-1} . HPTS is incapable of transferring a proton to methanol within its excited state lifetime of ≈ 6 ns. From the free energy relations, it is estimated that the proton transfer rate of HPTS to methanol is lower by about four orders of magnitude than in aqueous solution, i.e. the rate is in the microsecond region.

Tolbert et al. [13] were able to synthesize new photoacids which expand the range of photoacids available for fundamental studies in proton transfer to the solvents. Using the well-studied 1- and 2-naphthols as their starting material, they have substituted electron withdrawing groups on the distal ring, taking advantage of the special activating effects at the 5 and 8 positions. Their choice of electron with-

drawing groups was dictated both by availability and by photostability. In this study we have measured the proton transfer rate to solvent from excited 5,8-dicyano-2-naphthol (DCN2) [14]. From steady state fluorescence measurements it was found that proton transfer to solvent occurs within the excited state lifetime in alcohols. We have measured the PTTS of DCN2 in neat methanol, methanol-*d*, ethanol and ethanol-*d* over a broad temperature range.

2. Experimental

Time-resolved emission data were collected using the time-correlated single-photon counting (TCSPC) technique. The overall instrumental response at full width at half maximum (fwhm) was about 35 ps.

Emission was collected at a 10 nm spectral width. The laser source is a cw mode-locked Nd:YAG-pumped dye laser (Coherent Nd:YAG Antares and a 702 dye laser), providing high repetition rate (< 1 MHz) of short pulses (1 ps, fwhm). The TCSPC detection system is based on a Hamamatsu 3809U photomultiplier, Tennelec 864 TAC, Tennelec 454-discriminator and a personal computer-based multi-channel analyzer (Nucleus PCA-II).

The sample was cooled by a liquid nitrogen cryostat and controlled by a temperature controller. The sample temperature was measured with a PT-100 sensor and the temperature was stable in the range ± 1 K. Samples were allowed to equilibrate five minutes at each temperature prior to a measurement that lasted another five minutes. Subsequent measurements for a sample were done from low to high temperature.

Methanol solvent was BDH HPLC grade with $< 0.05\%$ water without further treatment. Methanol-*d* $> 99.5\%$ was purchased from Aldrich.

3. Results

Steady state fluorescence measurements of DCN2 in the neat alkanols, methanol through pentanol, reveal that proton transfer to solvent occurs within the excited state lifetime of the protonated form, ROH⁺. The steady state emission spectrum consists

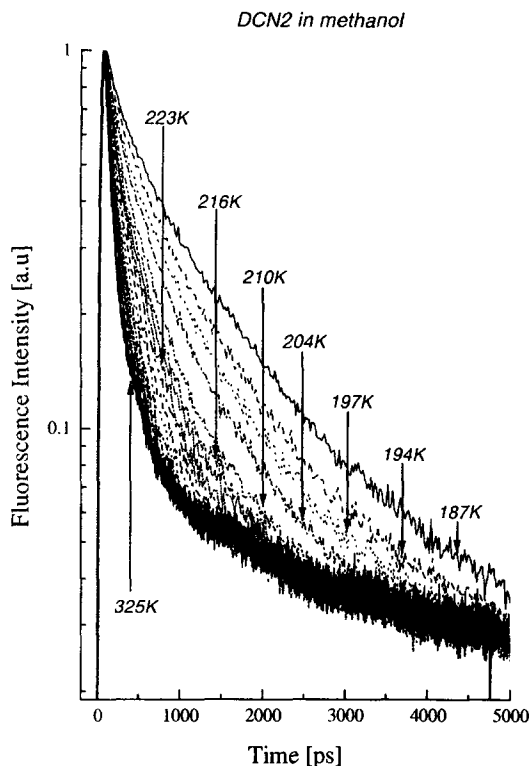
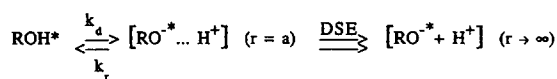


Fig. 1. Time-resolved emission of DCN2 in a methanol solution of the protonated form (ROH⁺) measured at several temperatures in the range 187–325 K.

of two bands with maxima located at 440 and 600 nm which are assigned to the emission of ROH⁺ and RO⁻, respectively [14].

Time-resolved emission of DCN2 in a methanol solution of the ROH⁺ band measured at 470 nm at several temperatures is shown in Fig. 1. Note that the fluorescence intensity is given on a logarithmic scale. The curved signal decay of the luminescence intensity on a logarithmic scale indicates that the decay is nonexponential.

Extensive studies of time-resolved fluorescence of molecules that are capable of transferring a proton to the solvent have shown that the nonexponential decay of the ROH⁺ form arises from an effective reversible proton geminate recombination process. This process increases the time-dependent population of the ROH⁺ and hence the overall effect on the luminescence is a tail that decays as a power law at $t^{-3/2}$ [10–12].



Scheme 1.

We have used the geminate proton recombination scheme to analyze quantitatively the time-resolved luminescence of DCN2. Scheme 1 provides the basic concept of the reversible excited state proton transfer followed by a geminate recombination process.

In Scheme 1 ROH^* and RO^{*-} are the excited state protonated and unprotonated forms of the proton emitting molecules. The excited state proton transfer is followed by proton geminate recombination. The transient Debye–Smoluchowski equation (DSE) has been used by us in the past [10–12] to

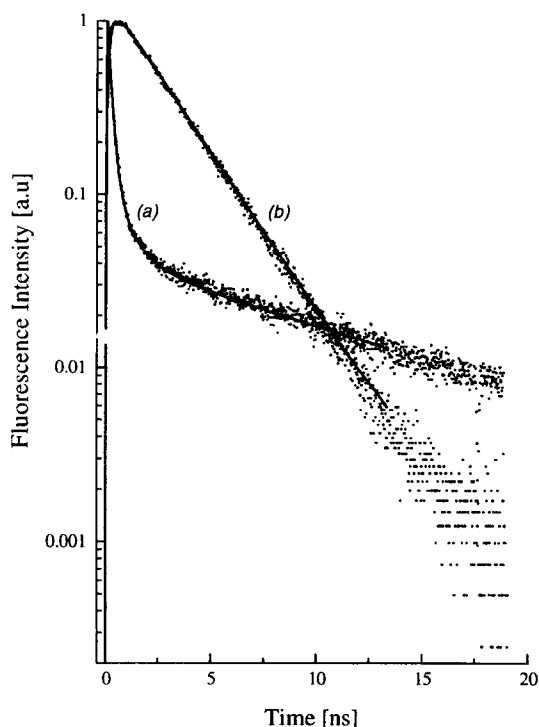


Fig. 2. Fluorescence experimental results of DCN2 in methanol and computer fits using the reversible proton geminate recombination mechanism; (a) the ROH^* band (470 nm); (b) the RO^{*-} band (660 nm).

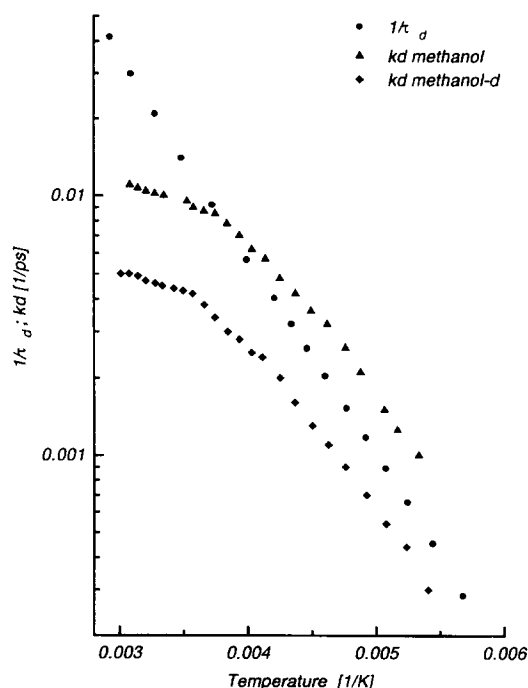


Fig. 3. Arrhenius plots of the proton transfer rate constant of DCN2 in methanol and deuterated methanol; \blacktriangle methanol, \blacklozenge deuterated methanol, \bullet dielectric relaxation data [15].

quantitatively describe the excited state ROH^* and RO^{*-} time-dependent concentration

$$\frac{\partial p(r, t)}{\partial t} = D r^{-2} \frac{\partial}{\partial r} r^2 e^{-V(r)} \frac{\partial}{\partial r} e^{V(r)} p(r, t) - p(r, t) / \tau_f.$$

The mutual attraction of the proton and the RO^{*-} anion is described by a distance-dependent potential, $V(r)$, in units of thermal energy $k_B T$

$$V(r) = -R_D / r,$$

$R_D \equiv |z_1 z_2| e^2 / \epsilon k_B T$. For the DCN2 $z_1 = 1$, $z_2 = -1$ are the charges of the proton and RO^{*-} respectively.

The reversibility of the reaction is described by the “back-reaction” boundary condition

$$4\pi a^2 D e^{-V(a)} \frac{\partial}{\partial r} e^{V(r)} p(r, t) \big|_{r=a} = \kappa_a p(a, t) - \kappa_d p^*(t),$$

where a is the distance of closest approach and $p^*(t)$ is the probability of the protonated form.

The fluorescence begins upon excitation by a short laser pulse which prepares a thermally and vibrationally equilibrated ROH^* in the lowest electronic state S_1 . The initial condition is $p^*(, 0) = 1$, $p(r, 0) = 0$. We solve these equations numerically, convolute $p^*(, t)$ (ROH^*) or the RO^{-*} $[1 - p^*(, t)]$ signal (long wavelength emission band) with the instrument function and compare it with the fluorescence signal.

We have used the abovementioned procedure to analyze the time-resolved emission of DCN2 in methanol, methanol-*d* (deuterated methanol, CH_3OD) ethanol and ethanol-*d* at the broad temperature range of -95 to 60°C .

The comparison of the numerical solution with the experimental results involves several parameters. The contact distance, a , the diffusion coefficient D and R_D have acceptable literature values. The adjustable parameters are the proton dissociation and recombination rate at the contact radius a . The quantitative fits to the transient Smoluchowski equation with the experimental fluorescence data of DCN2 in methanol at room temperature measured at 470 nm (ROH^*) and at 660 nm (RO^{-*}) are shown in Fig. 2.

From the data analysis, we extract the intrinsic proton transfer to the solvent rate constant as a function of temperature. The proton transfer rate constant as a function of $1/T$ for DCN2 in methanol and methanol-*d* is shown in Fig. 3. The figure also shows the temperature dependence of the dielectric relaxation rate constant in methanol [15].

4. Discussion

Water rotational and translational motions, involving hydrogen bond formation or breaking, play an important role in proton transfer reactions. The water solvation dynamics of excited dipolar solute molecule are bimodal [16]. The short-time component (< 100 fs), is followed by a relatively long (≈ 1 ps) component.

The acidity of the electronically excited naphthols, naphthol sulfonates and HPTS is not very large. The $\text{p}K^*$ values are in the range $0.5 < \text{p}K^* < 2.7$. The proton transfer time of 1-naphthol is 35 ps ($\text{p}K^* = 0.5$) and for 2-naphthol it is 10 ns ($\text{p}K^* = 2.7$). These proton transfer times are much longer

than the solvation dynamics of excited large dipolar solute molecules in water. The proton transfer rate is expected to increase when the acid strength increases.

In order to study the role of solvent dynamics in the molecular mechanism of excited state proton transfer to solvent one needs to find stronger acids than the compounds we have studied so far.

The $\text{p}K^*$ of 5,8-dicyano-2-naphthol (DCN2) in water is estimated by the Förster cycle to be -4.5 [19]. For $\text{p}K^* = -4.5$ in water, the proton transfer rate is expected to be ultrafast and might be limited by solvent motion [14].

Three interesting points that emerge from the experimental information on the temperature dependence of DCN2 PTTS rate in methanol and ethanol solutions can be summarized as follows.

(1) The activation energy of proton transfer rate to the solvent in the methanol solution is not constant and is temperature dependent. At high temperatures (above 283 K), the activation energy is small (of the order of 0.6 kcal/mol) while at temperatures below 250 K down to the freezing point, it is 3.3 kcal/mol.

(2) The proton transfer rate in the methanol solution has a distinctive isotope effect. The isotope effect is almost temperature independent, $\kappa(\text{H})/\kappa(\text{D}) \approx 2.5$. Thus, the activation energy and its temperature dependence is similar for both proton and deuteron transfer.

(3) At low temperature (< 250 K) the proton transfer rate constant has the same temperature dependence as the dielectric relaxation rate of methanol. For H^+ transfer the rate constant, is larger by a factor of 1.6 than the dielectric relaxation rate. The rate of deuteron transfer to methanol-*d* is lower by a factor of 1.6 than the dielectric relaxation rate of methanol.

The molecular mechanism of proton transfer to the solvent was recently studied by Ando and Hynes [17]. They studied the HCl acid ionization in water. The overall experimental reaction free energy of HCl ionization in water is -8 kcal/mol. The mechanism is found to involve: first, a nearly activationless motion in a solvent coordinate, which is adiabatically followed by the quantum proton rather than tunneling, to produce a contact ion pair $\text{Cl}^- - \text{H}_3\text{O}^+$, which is stabilized by ≈ 7 kcal/mol; second, motion in the solvent with a small activation barrier, as a second

adiabatic proton transfer produces a solvent-separated ion pair from the contact ion pair in a nearly thermoneutral process. Motion of a neighboring water molecule, to accommodate the change of the primary coordination number from 4 for H_2O to 3 for H_3O^+ of a proton-accepting water molecule, is indicated as a key feature in the necessary solvent reorganizations. It is estimated, via a separate argument, that the remainder of the process to produce the completely separated ions involves a free energy change of less than 1 kcal/mol. It is argued that the reorganization of the heavy atoms between which the proton transfers plays an essential role in assisting the adiabatic (non-tunneling) and stepwise transfer mechanisms, and the concerted pathway of the multiple proton transfers in water is unfavorable.

The detailed two-step mechanism described above involves several distinctive molecular motions. In general, in each step there is a solvent motion and adiabatic proton transfer. Thus, the proton transfer to the solvent can be described by a two-dimensional picture involving the generalized solvent coordinate and the proton transfer coordinate. When the solvent motion is slower than the actual proton transfer, then the rate limiting step will be the solvent motion and vice versa.

Important information on solvent response times comes from dielectric measurements [18]. Many dynamical processes, such as proton mobility, charge recombination and transient solvation, are interpreted in terms of the Debye relaxation time, τ_D . Recent years have seen improvements in dielectric techniques, pushing the maximal frequency to the vicinity of 100 GHz [19]. Taken together with far-infrared spectra, it became possible to resolve picosecond processes.

For simple non-associate liquids, τ_D of polar liquids is thought to reflect a single molecule orientation process [20]. It was recognized [21] that for complex associative hydrogen-bonded solvents, this oversimplified description might not be true.

The temperature dependence of PTTS from DCN2 to methanol clearly shows that the rate limiting step of the proton transfer process at low and high temperatures is not the same. At temperatures below 250 K the PTTS rate is slightly faster than the solvent dielectric relaxation rate. Both processes have the same activation energy from the freezing point 180

K up to 250 K. The similarity of the two processes indicates that at low temperature, solvent motion controls the actual proton transfer rate. At temperatures above 250 K, the temperature dependence of the PTTS rate gradually decreases. The activation energy at low temperature is ≈ 3.3 kcal/mol while at temperatures > 290 K it reduces to ≈ 0.6 kcal/mol. The dielectric relaxation temperature dependence is almost constant from 330 to 180 K and the activation energy is kept constant at ≈ 3.3 kcal/mol. Thus, at around 250 K and higher temperature the PTTS does not follow the dielectric relaxation. This indicates that the rate limiting step of the PTTS process at high temperature switches from solvent control to the proton transfer reaction coordinate.

5. Summary

The DCN2 PTTS experimental data in methanol, methanol-*d*, ethanol and ethanol-*d* provide pertinent information on the molecular mechanism of excited state proton transfer. At low temperatures solvent motion controls the proton transfer rate. The value of the PTTS rate constant is similar to the dielectric relaxation time measured by a macroscopic electrical measurement. Although we have only shown in this Letter the data for DCN2 PTTS in methanol, we have also examined the PTTS rate in ethanol and ethanol-*d*. The PTTS data in these liquids indicate that at low temperatures the value of the proton transfer rate constant is similar to the dielectric relaxation time and the activation energy of PTTS is that of the dielectric relaxation.

At high temperatures (> 250 K), the activation energy of the PTTS process gradually decreases. The proton transfer rate is slower than the dielectric relaxation time. At > 290 K the proton transfer rate is almost temperature independent. This unusual temperature dependence indicates that at a high temperature the rate limiting step of PTTS is not the solvent motion, but the proton transfer reaction coordinate.

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