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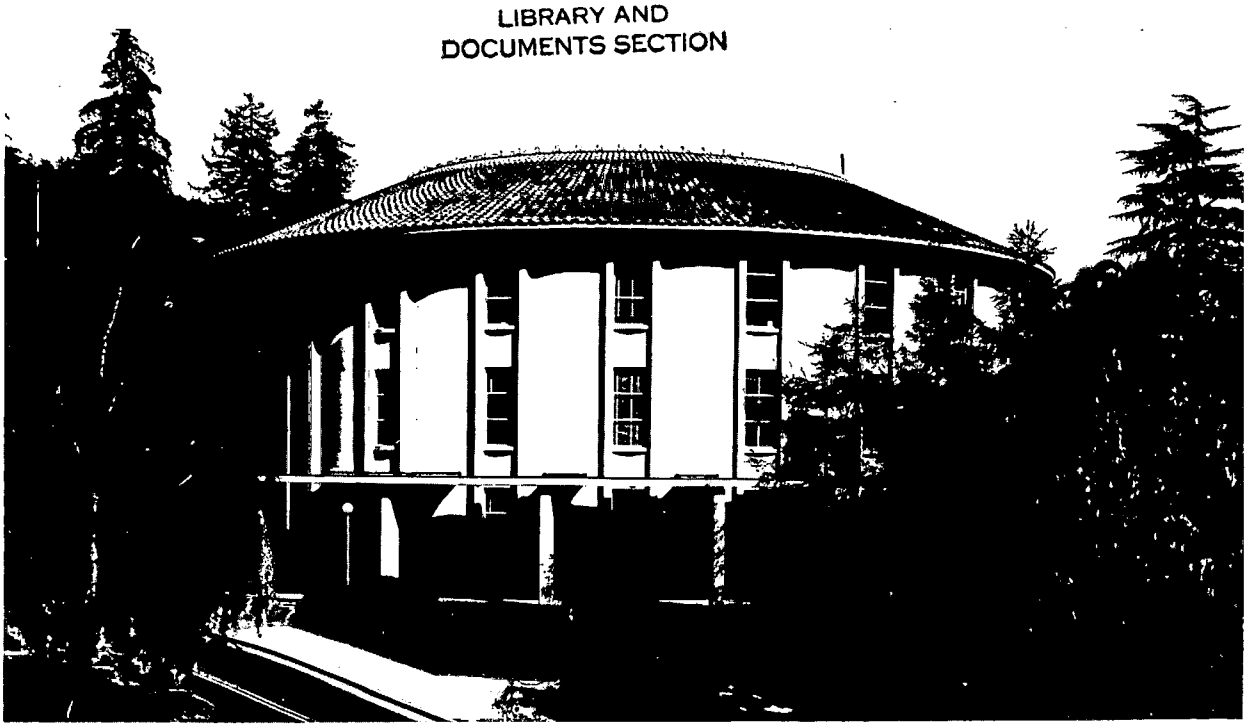

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Excited-State Proton-Transfer Reactions in 1-Naphthol*

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1. Introduction

Proton-transfer reactions provide the fundamental basis for acid-base chemistry in protic solvents. Literally hundreds of examples of excited-state proton-transfer reactions are known[1]. Picosecond, time-resolved measurements on spectrally distinct acid-base pairs yield direct kinetic information and provide insight into the effect of molecular structure on excited-state proton-transfer dynamics[2,3]. One particularly interesting and seemingly paradoxical system is 1-naphthol. From a Förster cycle calculation, 1-naphthol is predicted to have an excited state pK similar to 2-naphthol[4], for which steady-state emission from both the neutral (acidic) and anionic (basic) excited-state species is clearly observed. In contrast, the neutral form of excited 1-naphthol shows "very weak" fluorescence which is "extremely difficult" to measure[5]. Detailed studies of the mechanism and kinetics of excited-state proton transfer in 1-naphthol are needed to elucidate how the differences in molecular structure between these molecules affect excited-state proton-transfer processes.

2. Experimental

Samples of preparative-HPLC-purified 1-naphthol in degassed aqueous (H_2O or D_2O) solution were excited with 266 nm, ~20 ps pulses obtained by quadrupling the output of a passively modelocked Nd:YAG oscillator/amplifier system (Quantel, YG400). Temporal profiles of emission were monitored using an ultrafast streak camera (Hadland Photonics, IMACON 500) system described elsewhere in this volume[6]. The $\sim 10^{-3}$ M solutions were prepared by dissolving 1-naphthol in a pH 12 solution of NaOH and adjusting to the desired pH with concentrated HCl. All solutions were maintained and studied under oxygen-free conditions. A similar procedure was used to prepare samples in D_2O using NaOD and DCl.

3. Results and Discussion

The ultimate goal of this work is to develop predictive models for excited-state proton-transfer reactions. This can be accomplished by isolating and quantitatively determining those rates that are significantly altered as the experimental conditions (e.g., molecular structure, solvent, temperature, and pressure) are changed. Kinetic schemes for coupled, two-state systems, Fig. 1, have been previously developed[1]. They provide an accurate description of

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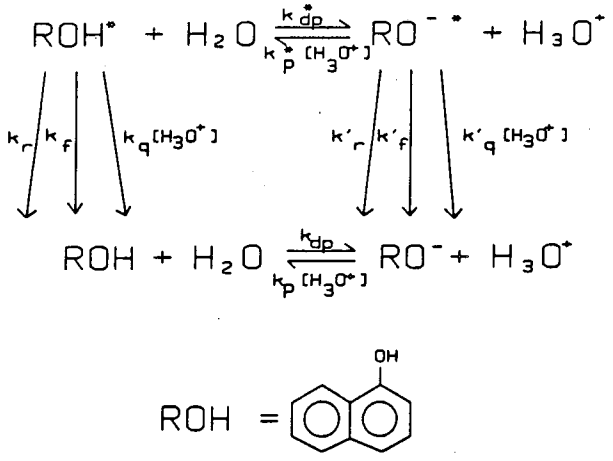

Fig. 1 Kinetic scheme for excited-state proton-transfer in 1-naphthol: k_{dp}, k^*_{dp}, k_p, and k^*_p represent the ground and excited state deprotonation and protonation rate constants, respectively; and k_r, k'_r, k_f, k'_f, k_q, and k'_q are the rate constants for radiationless processes, fluorescence, and proton-induced quenching for the neutral and anionic species, respectively

excited-state proton-transfer reactions in 1-naphthol[4]. The clear isosbestic point at ~450 nm in the picosecond, time-resolved emission spectra, Fig. 2, demonstrates the validity of a two-state model. Kinetic expressions for the time dependence of the emission intensity from the neutral, $I_{(ROH^*)}$, and anionic, $I_{(RO^{-*})}$, species, as derived from such a model, have the general form:

$$I_{(ROH^*)} = A_1 e^{-\gamma_1 t} + A_2 e^{-\gamma_2 t} \qquad (1)$$

$$I_{(RO^{-*})} = B(e^{-\gamma_2 t} - e^{-\gamma_1 t}). \qquad (2)$$

The good agreement between the fall time of the emission from the neutral form and the risetime of the emission from the anion, Fig. 3, confirms the validity of the kinetic model. Previous steady-state results have not provided accurate rate constants for this system[5]. However, the complex relationship between the observed double exponential behavior of the emission and the various kinetic parameters also makes analysis based solely on time-dependent methods difficult. While all the needed rates can, in principle, be extracted from a measure of γ_1, γ_2, and the ratio A_1/A_2 as a function of hydrogen ion concentration, scatter in the experimental results have thus far made it impossible to obtain both the slopes and intercepts with high accuracy.

Combination of the results of steady-state measurements with direct, time-resolved measurements yields the most accurate determination of the desired rates. For example, the rate constants τ_0 ($1/\tau_0 = k_f + k_r$) and k^*_{dp} (see Fig. 1) can be readily determined from

$$\Phi'/\Phi'_0 = k^*_{dp}/\gamma_1 = k^*_{dp}/(k^*_{dp} + 1/\tau_0), \qquad (3)$$

where Φ'/Φ'_0 is the quantum yield of fluorescence of the anion at neutral pH relative to that at high pH, and γ_1 is obtained from the neutral fall time and/or the anion risetime at pH 7. A short summary of representative results from such an analysis are given in Table 1 for both H_2O and D_2O. 1-Naphthol fluorescence in D_2O shows similar overall behavior but considerably slower kinetics, by a factor of ~3.5, compared to the H_2O results. At neutral pD, where quenching by D_3O^+ is negligible, there is still a substantial isotope effect. Both k^*_{dp} and τ_0 become markedly slower. This result strongly suggests that there is significant solvent quenching of the neutral fluorescence, and points up the importance of hydrogen bonding in these systems.

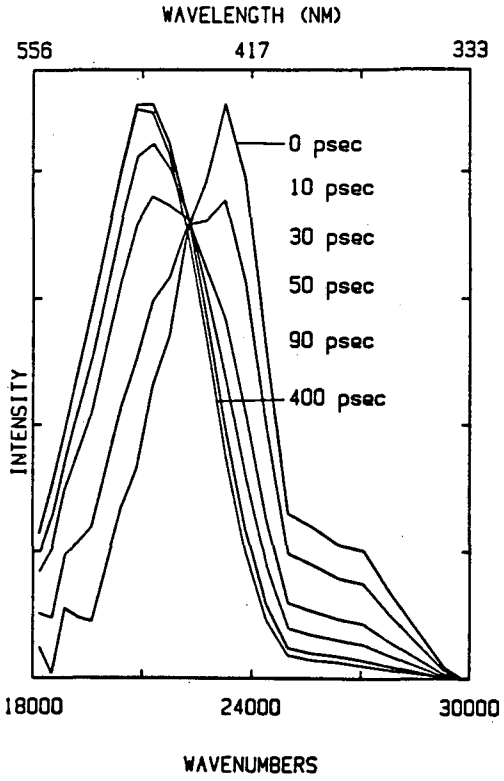

Fig. 2 Time-resolved emission spectra of 1-naphthol in pH 7 aqueous solution

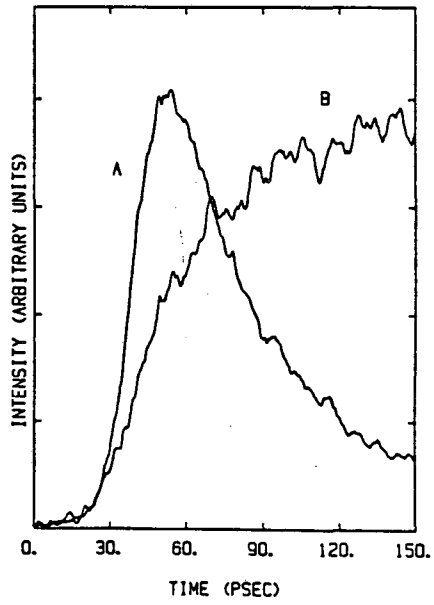

Fig. 3 Time-resolved emission from the neutral (A, 350 ± 5 nm) and anionic (B, 500 ± 5 nm) forms of 1-naphthol in pH 7 aqueous solution. Best fit fall time for curve A is 35 ± 4 ps. Best fit risetime for curve B is 30 ± 3 ps

Table 1. Measured rates, lifetimes, and relative fluorescence quantum yields for 1-naphthol in H_2O and D_2O solutions. $1/\tau_0' = k_f' + k_r'$

Solvent	Φ'/Φ_0'	γ_1^{-1} [ps]	k^*_{dp} [s^{-1}]	τ_0 [ps]	τ_0' [ns]
H_2O	0.66	33	2.1×10^{10}	100	8.0
D_2O	0.69	105	6.6×10^{9}	340	20.0

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