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EXCITED-STATE PROTON-TRANSFER KINETICS IN 1-NAPHTHOL, 1-NAPHTHOL-SULFONATES, AND ORGANOMETALLIC COMPLEXES

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Introduction

Upon photoexcitation many aromatic compounds are known to undergo ultrafast proton-transfer reactions in aqueous solution [1]. Picosecond spectroscopy offers the opportunity for modeling and understanding proton-transfer processes in solution by allowing direct measurements of proton-transfer kinetics to be carried out for broad classes of compounds. Given the important role of proton transfer in vast numbers of important chemical and biological processes, such studies can be expected to provide new, fundamental insight into the chemistry of the proton.

Aromatic molecules can become considerably more acidic upon absorption of light quanta due to the alteration of electronic structure, often changing dissociation constants for proton ejection by many orders of magnitude [1]. For naphthols and substituted naphthols in aqueous solution, the proton transfer to neighboring water molecules may be represented schematically as follows:

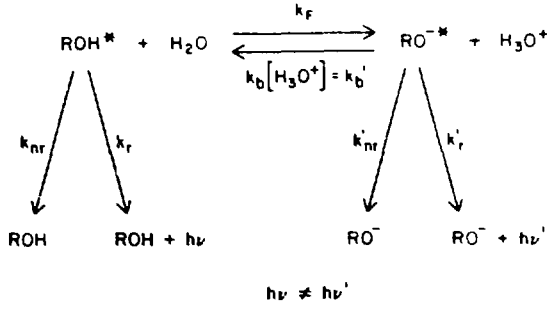

Fig.1 Simplified schematic of excited-state proton transfer in naphthol compounds. Also possible are nonradiative deactivations induced by interactions with protons (vide infra).

where k_r and k_{nr} represent the radiative and nonradiative decay rates for the excited naphthol molecule (ROH*), k_f is the excited-state

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deprotonation rate, k_b represents the protonation rate from the excited naphtholate to the excited naphthol, and ν and ν' are the emission frequencies from the excited protonated and deprotonated species, respectively. The classic work of FORSTER [2] and WELLER [3] established the theoretical framework for understanding proton-transfer phenomena in the naphthols. Because the ground-state pK_a values for the naphthols are in the range 9-11, the only ground-state species present in solutions with pH < 7 is ROH. Following excitation of ROH with a picosecond pulse of the appropriate frequency, the protonation kinetics can be directly determined by observing the decay of emission from ROH* at frequency ν, or the risetime of the emission from RO^{-}* at the red-shifted frequency ν'.

The dissociation of 1-naphthol in aqueous solution occurs so rapidly that the fluorescence from the neutral form, ROH*, has been previously described as "completely extinguished" [3] and as "hardly noticeable" [4]. Apparently nearly all of the fluorescence orginates from the naphtholate ion. Here we report on the proton-transfer characteristics of a series of 1-naphthol compounds. We also report preliminary data on excited-state proton transfer in an organometallic complex of ruthenium.

Experimental Arrangement and Sample Preparation

Crucial to the success of these experiments and to their interpretation are sample preparation and purification. All samples were obtained from LC Laboratories (Newton, Massachusetts) and were determined to be greater than 99.5% pure by analytical liquid chromatography using a fluorescence detector. Samples were prepared in a nitrogen filled glove-box, and all solvents were thoroughly degassed by undergoing successive freeze-pump-thaw cycles.

The experimental arrangement is shown in Fig.2. A single 30-ps pulse is selected from the pulse train of a Nd:YAG modelocked laser, is

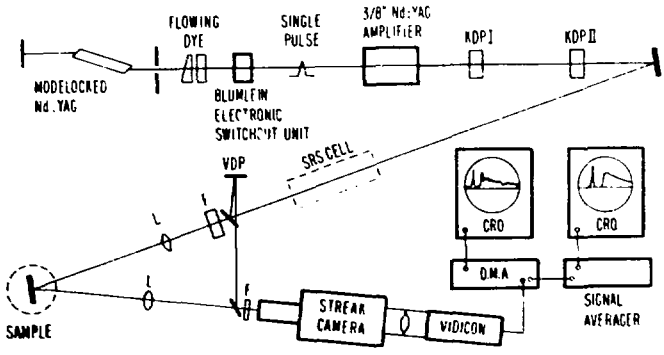


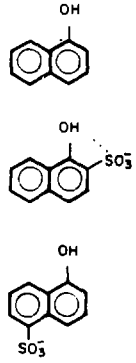
Fig.2 Experimental Arrangement for Measuring Rapid Proton Transfer.

amplified to a level of 10 mJ, and can be frequency doubled, tripled or quadrupled with the appropriate KDP crystals. The naphthols are excited with 266-nm radiation, and the organometallic complexes are excited with 355-nm radiation. Light emitted by the samples is collected onto the

slit of a Hadland Photonics Photochron II streak camera. Streaks are imaged onto an OMA, and the individual shots can be accumulated on a Nicolet 1074 signal averager. A relative time reference provided by means of a precursor marker pulse ensures accurate signal averaging. Fall times of the protonated species are obtained by observing the emission through a Corning 7-54 filter, and risetimes of the deprotonated species with a Corning 2-62 filter.

1-Naphthol and 1-Naphthol Sulfonates: Results and Discussion

The experimental results for the relaxation of the excited protonated species in 1-naphthol and two of its sulfonated derivatives are summarized in Fig.3. Note that 1-naphthol and the two 1-naphthol



	τ_D
1-naphthol	25 ± 10 ps
1-naphthol-2-sulfonate	55 ± 15 ps
1-naphthol-5-sulfonate	≤ 20 ps

Fig.3 Relaxation time for emission from the protonated form of 1-naphthol, 1-naphthol-2-sulfonate, and 1-naphthol-5-sulfonate.

derivatives dissociate extremely rapidly. Kinetics of the rapid proton transfer indicate that the excited-state pK value (pK*) for all three derivatives is in the vicinity of zero. This estimate is confirmed by a FORSTER-cycle calculation [2] based on the absorption and emission spectra of the pure compounds. Notice also that the dissociation rate for 1-naphthol-2-sulfonate is slower than for the other two derivatives. Evidently, the intramolecular hydrogen bond formed between the adjacent hydroxy and sulfonate groups leads to a slowdown in the proton ejection rate in this derivative. Such an effect has previously been postulated [5].

Our result in 1-naphthol-2-sulfonate differs strikingly from that of ZAITZEV et al. [6] who, using nanosecond techniques, reported that the dissociation rate for this compound is 5.4×10^8 sec^{-1} (1.85 ns). Our experiments indicate that this long decay time may be due to impurities. For example, a sample of 1-naphthol-2-sulfonate that was obtained from Eastman Kodak, for which no attempt was made at further purification or to prevent exposure to air during sample preparation, yields only a long-lived component, also a few ns in duration.

Further confirmation for the 55 ps lifetime reported here is obtained from the emission spectrum of purified, oxygen-free 1-naphthol-2-sulfonate excited at 313 nm, which is completely dominated by the emission from the deprotonated species. This is in contrast to

the spectrum obtained by ZAITZEV, et al. [6], in which the ratio of the emission intensities of the deprotonated species to that of the protonated form is only 2 to 1.

On the other hand, we have found that the proton-transfer kinetics of 2-naphthol-6-sulfonate samples reported upon previously [7], do not appear to change when carefully purified samples are used. This may be due to a fortuitous coincidence between the proton-transfer rates of 2-naphthol-6-sulfonate and the fall time of the impurity fluorescence. Sample analysis by high-pressure liquid chromatography is currently being carried out to establish in more detail the role of impurities both in the measurements reported here and in our previous measurements on 2-naphthol-6-sulfonate [7].

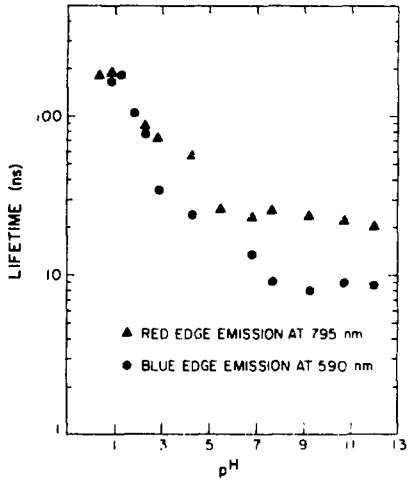
For the case of 1-naphthol, MARTYNOV, et al. [8] estimated a dissociation rate of $> 3 \times 10^9$ sec^{-1}. Our measurement of 25 ± 10 ps is in accord with this estimate. We have also observed a deactivation of the excited 1-naphtholate due to interaction with hydronium ions. The fluorescence lifetime of the deprotonated species varies from nanoseconds to picoseconds with decreasing solution pH. The values obtained from these direct measurements are in accord with the quantum efficiencies reported by WELLER [3].

Previously, we suggested that by using intense laser pulses, the pH of a solution could be changed in a manner analogous to the temperature change in a T-jump experiment [7]. This laser pH jump technique [7,9] might allow the study of rapid acid-base reactions. The rapid deprotonation of the 1-naphthol compounds demonstrates that the pH of a solution may be manipulated on a time scale of less than 20 ps. This rapid rate, the fastest intermolecular proton transfer process observed to date, offers the possibility of producing very large and rapid pH jumps for studying rapid chemical reactions.

Proton Transfer in an Organometallic Complex of Ruthenium

Organometallic complexes are known to display a rich and varied photochemistry [10]. There is an increasing awareness that it may be possible to exploit this chemistry for the efficient conversion of solar energy to easily transportable fuels. Recently, excited-state proton transfer was observed in an organometallic complex [11]. We report here preliminary measurements on the kinetics of this process. Figure 4 shows the schematic for the excited-state proton-transfer reaction of the organometallic complex (2,2'-bipyridine)$_2$Ru(4,7-dihydroxy-1,10 phenanthroline). Also shown in Fig.4 are the decay times for the fluorescence from the protonated and deprotonated forms of this complex in nondegassed solutions, plotted as a function of pH. The emission from the protonated form decays in about 200 ns at pH 1. Previous studies by GIORDANO, et al. [11] indicate that between pH 5 and pH 2.5, the protonated form will be the main species present in the ground state. Upon excitation between these pH values, we could then expect to observe a risetime for the 795-nm band corresponding to the formation of the deprotonated species. Because of the insensitivity of the streak camera S-20 photocathode at a wavelength of 800 nm, we have estimated this risetime using a photomultiplier and a fast oscilloscope to temporally resolve the emission. The risetime thus obtained is limited by the 5-ns response time of the photomultipler tube. We are presently studying

organometallic proton-transfer processes from complexes that emit in a region of the visible spectrum more amenable to streak camera detection.



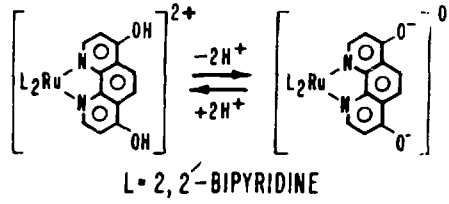


Fig.4 Lifetime of deprotonated (triangles) and protonated (circles) forms of the organometallic ruthenium complex.

Acknowledgments

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