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# Ultrafast Excited-State Proton Transfer from Cyano-Substituted 2-Naphthols

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The rate of excited-state proton transfer from four cyano-substituted 2-naphthols was measured in $H_2O$ and $D_2O$ by picosecond time-resolved fluorescence. The excited-state acidity constant, $pK_a^*$, was calculated and compared with previous results and was found to be substitution-dependent, as predicted by the charge-transfer theory. The isotope effect was evaluated for all the compounds of the series. As reported for many other hydroxyaromatic compounds, this effect was more important for the dissociation rate constant than for the recombination rate constant.

## Introduction

Proton-transfer reactions are among the most common and important chemical processes in aqueous solutions.[1−4] In recent years, intermolecular proton transfer in the excited state has been the subject of intensive theoretical and experimental investigations, since photophysical techniques provide valuable information about the mechanism and the nature of acid−base reactions in aqueous solutions.[5−7]

Hydroxyarenes undergo an enhancement of acidity, a Förster shift, upon photoexcitation. The fluorescence spectra of such compounds consist of two emission bands. The band at shorter wavelength corresponds to emission from the neutral form (ROH*), while the other, at longer wavelength, is that of the conjugate base ($RO^{-*}$). Thus, hydroxyarenes are ideal substrates for examining fundamental aspects of proton transfer using steady-state and time-resolved fluorescence measurements.

Most studies in photoexcited proton transfer have concentrated on the commercially available 1- and 2-naphthols, on their sulfonated derivatives, and on 8-hydroxy-1,3,6-pyrenetrisulfonate. Unfortunately, a limitation of these studies is the relatively modest change in acidity, ca. 6−8 $pK_a$ units, which occurs upon photoexcitation with conventional hydroxyarenes. This limitation confines most photophysical investigations to solvents in which proton transfer competes with the ca. 10 ns decay lifetime.

To expand the range of photoacids available for fundamental studies in proton-transfer kinetics, 2-naphthols substituted in the distal ring by the cyano group, i.e., 5-cyano-2-naphthol **(**5CN2**)**, 6-cyano-2-naphthol **(**6CN2**)**, 7-cyano-2-naphthol (7CN2), 8-cyano-2-naphthol (8CN2), were synthesized[8] and their photophysical behavior was studied by means of steady-state and nanosecond time-resolved fluorescence emission. Most of the data analysis has been based on rate equations for which the proton-transfer process exhibits an exponential time-dependence. A different approach is to look at the proton-transfer process as a transient, nonequilibrium dissociation of an excited-state molecule, using a two-step reaction model, as in Scheme 1. The first chemical step is described by the back-reaction boundary condition with intrinsic rate constants $k_{diss}$ and $k_{rec}$ and is followed by a diffusional step in which the hydrated proton is separated from the contact radius, $a$, to infinity. The second step is described by the exact transient (numerical) solution of the Debye−Smoluchowski equation (DSE)[9,10] with the above-mentioned boundary condition.

**SCHEME 1**

$$\mathrm{RHO}^* \underset{k_{rec}}{\overset{k_{diss}}{\rightleftharpoons}} [\mathrm{RO}^{-}{}^*\cdots\mathrm{H}^+]_{(r=a)} \overset{\mathrm{DSE}}{\longleftrightarrow} [\mathrm{RO}^{-}{}^* + \mathrm{H}^+]_{(r\to\infty)}$$

Extensive studies of the 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 decay tail that decays as a power law at $t^{-3/2}$.

All cyano-substituted 2-naphthols exhibited strong emission in aqueous solution, characterized by anionic emission at neutral pH. The apparent $pK_a^*$ values were determined from fluorescence titration of anion emission as well as from use of the Förster cycle with both fluorescence and absorption data. Nevertheless, excited-state $pK_a$ measurements were complicated by competing decay processes, including fluorescence and nonradiative decay.

We have used the geminate proton recombination scheme to analyze quantitatively the picosecond time-resolved luminescence of cyanonaphthols. Scheme 1 provides the basic concept of the reversible excited-state proton transfer followed by a geminate recombination process. In addition, we have measured the proton-transfer rate to deuterated water to analyze the isotope effect. The experimental setup enables us to monitor the transient behavior on a picosecond time scale and the theoretical model to determine the different rate constants that are involved in the overall process.

## Experimental Section

**Materials.** Deionized water had a resistance greater than 10 MΩ. $D_2O$, 99.8% isotopically pure, was purchased from

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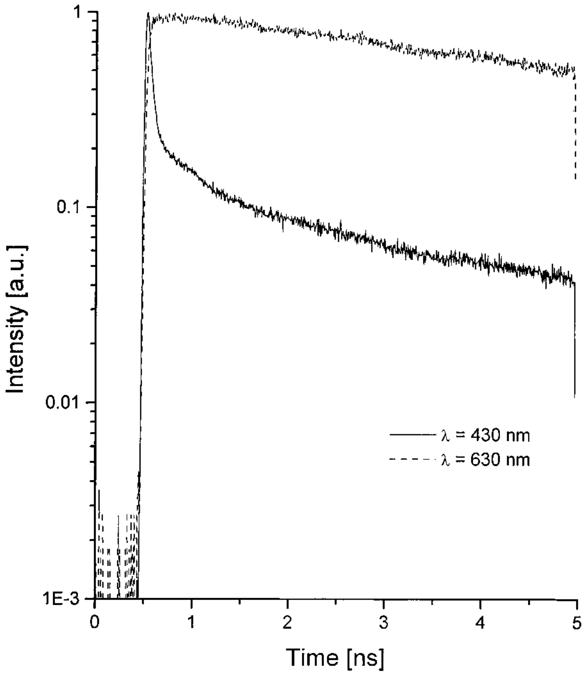
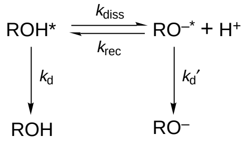


**Figure 1.** 5CN2 in $H_2O$.

**SCHEME 2**



Aldrich. MeOH, spectroscopic grade, was purchased from Merck. The solvents were used without further purification. The cyano-substituted 2-naphthols were readily prepared by sodium cyanide/$Me_2SO$ demethylation of the corresponding methyl ethers, as described elsewhere.[8a]

**Samples.** Solutions were prepared immediately prior to fluorescence measurements. The experiments were carried out at pH = 5.5−6.0, where only the acid form exists.

**Time-Resolved Fluorescence Measurements.** Transient fluorescence was detected using time-correlated single-photon counting as described earlier.[16] The overall instrumental response at full width at half-maximum (fwhm) was approximately 35 ps. Emission was collected at a 10 nm spectral width. Measurements were taken at 5 and 20 ns full scale.

## Results

The steady-state emission spectra of these compounds consisted of two bands with maxima located at ca. 420 and 520 nm, which are assigned to the emission of the ROH* and $RO^{-*}$, respectively. The $pK_a^*$ was estimated by the Förster cycle to be −1.2, 0.2, −1.,3 and −0.4 for 5CN2, 6CN2, 7CN2, and 8CN2 respectively.[8] In the ROH* fluorescence, an additional long-lived component was observed. The source of this luminescence could arise from (a) impurities, (b) decomposition of the original compounds, or (c) dimers or other oligomers. This additional fluorescence was treated as background signal; it was typically less than 3% in all cases.

Time-resolved emission spectra measured at the corresponding wavelengths of the neutral and anionic species of 5CN2 and 6CN2 in water are shown in Figures 1 and 2.

The analysis of the time-resolved data has been based on Scheme 2.

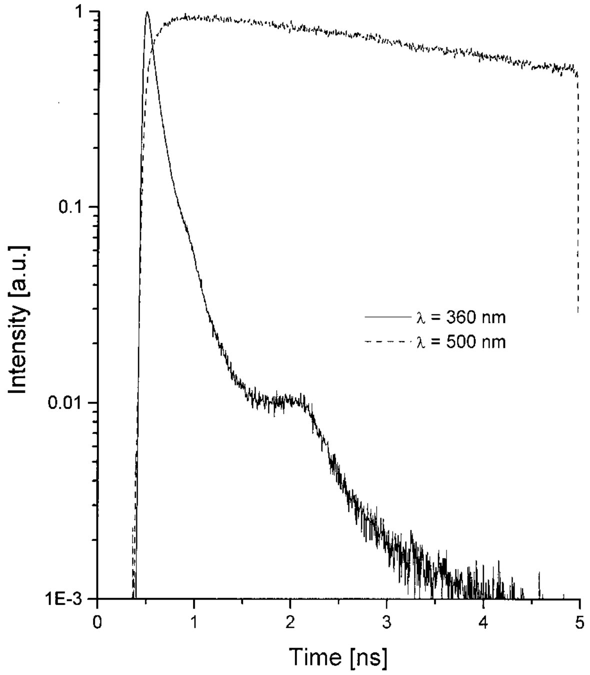


**Figure 2.** 6CN2 in $H_2O$.

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) was used to quantitatively describe the excited-state ROH* and $RO^{-*}$ time-dependent concentrations:

$$\frac{\partial p(r,t)}{\partial t} = \frac{D}{r^2}\frac{\partial}{\partial r} r^2 \mathrm{e}^{-V(r)} \frac{\partial}{\partial r} \mathrm{e}^{V(r)} p(r,t) - \frac{p(r,t)}{\tau_\mathrm{f}} \qquad (1)$$

Here, $p(r,t)$ is the probability density function of finding the geminate proton at a distance $r$ at time $t$. The mutual attraction of the proton and the $RO^{-*}$ anion is described by a distance-dependent potential $V(r)$:

$$V(r) = -\frac{R_\mathrm{D}}{r}, \quad R_\mathrm{D} = \frac{|z_1 z_2| e^2}{\epsilon k_\mathrm{B} T}$$

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

$$4\pi a^2 D\, \mathrm{e}^{-V(r)} \frac{\partial}{\partial r} \mathrm{e}^{V(r)} p(r,t)|_{r=a} = k_\mathrm{rec} p(a,t) - k_\mathrm{diss} p(\mathrm{ROH}^*,t)$$

Here $a$ is the contact distance and $k_\mathrm{diss}$ and $k_\mathrm{rec}$ are the intrinsic dissociation and recombination rate constants while $D$ is the diffusion coefficient. The initial condition is that of 100% ROH*. Therefore, $p(r,0) = 0$ and $p(\mathrm{ROH}^*,0) = 1$. The contact distance $a$, diffusion coefficient $D$, and Debye radius $R_\mathrm{d}$ were taken from the literature.[11,12] The adjustable parameters are the dissociation and recombination rate constants.

The proton-transfer rates to water and $D_2O$ are summarized in Table 1. The $pK_a^*$ was calculated according to eq 2, and the values obtained are shown in Table 2.

$$K^* = \frac{k_\mathrm{diss} \exp(R_\mathrm{D}/a)}{4\pi a^2 k_\mathrm{rec}} \frac{1000}{N_\mathrm{A}} \qquad (2)$$

Here, $a$ was taken as 7 Å, which corresponds to bare naphtholate plus one or two solvation layers. $R_\mathrm{D}$ was calculated to be 7.1

**TABLE 1: Proton Dissociation Rate Coefficients for Excited Cyano-2-naphthols**[a]

| compound | solvent | $\lambda$ (nm)[b] | species | $k_{diss}$ (ps$^{-1}$)[c] | $k_{rec}$ (Å/ps)[c] | $\tau$ (ROH) (ns) | $\tau$ (RO$^-$) (ns) |
|---|---|---|---|---|---|---|---|
| 5CN2 | $H_2O$ | 430 | ROH | 0.07[d] | 0.08 | 3.0 | 5.5 |
| 5CN2 | $H_2O$ | 630 | RO$^-$ | 0.07[d] | 0.08 | 3.0 | 5.5 |
| 5CN2 | $D_2O$ | 430 | ROH | 0.03 | 0.07 | 6.0 | 11.0 |
| 5CN2 | $D_2O$ | 630 | RO$^-$ | 0.03 | 0.07 | 6.0 | 11.0 |
| 5CN2 | MeOH | 370 | ROH | 0.0002 | 0.0006 | 7.0 | 15.0 |
| 5CN2 | MeOH | 650 | RO$^-$ | 0.0006 | 0.0006 | 7.0 | 15.0 |
| 6CN2 | $H_2O$ | 360 | ROH | 0.011 | 0.04 | 5.0 | 7.0 |
| 6CN2 | $H_2O$ | 500 | RO$^-$ | 0.011 | 0.04 | 4.2 | 6.0 |
| 6CN2 | $D_2O$ | 360 | ROH | 0.0033 | 0.022 | 4.2 | 6.0 |
| 6CN2 | $D_2O$ | 500 | RO$^-$ | 0.0033 | 0.022 | 4.2 | 6.0 |
| 7CN2 | $H_2O$ | 380 | ROH | 0.0055 | 0.03 | 5.2 | 6.5 |
| 7CN2 | $H_2O$ | 530 | RO$^-$ | 0.0055 | 0.03 | 5.2 | 6.5 |
| 7CN2 | $D_2O$ | 380 | ROH | 0.0018 | 0.02 | 5.2 | 11 |
| 7CN2 | $D_2O$ | 530 | RO$^-$ | 0.0018 | 0.02 | 5.2 | 11 |
| 8CN2 | $H_2O$ | 410 | ROH | 0.027 | 0.04 | 5 | 7 |
| 8CN2 | $H_2O$ | 510 | RO$^-$ | 0.0027 | 0.04 | 5 | 6 |
| 8CN2 | $D_2O$ | 400 | ROH | 0.013 | 0.03 | 5.2 | 10 |
| 8CN2 | $D_2O$ | 510 | RO$^-$ | 0.013 | 0.03 | 5.2 | 10 |

[a] Physical parameters used for the data in the table: $\epsilon = 78$ ($H_2O$ and $D_2O$) and 32 (MeOH); charge = 0; $T = 298$ K; $D = 0.96$ Å$^2$/ps ($H_2O$), 0.66 Å$^2$/ps ($D_2O$), and 0.27 Å/ps (MeOH). [b] Fluorescence wavelength measurement. [c] $k_{diss}$ and $k_{rec}$ are the proton dissociation and recombination rate constants. [d] Owing to the limited time resolution of the experimental system, the error in the determination of $k_{diss}$ for 5CN2 is ~20%.

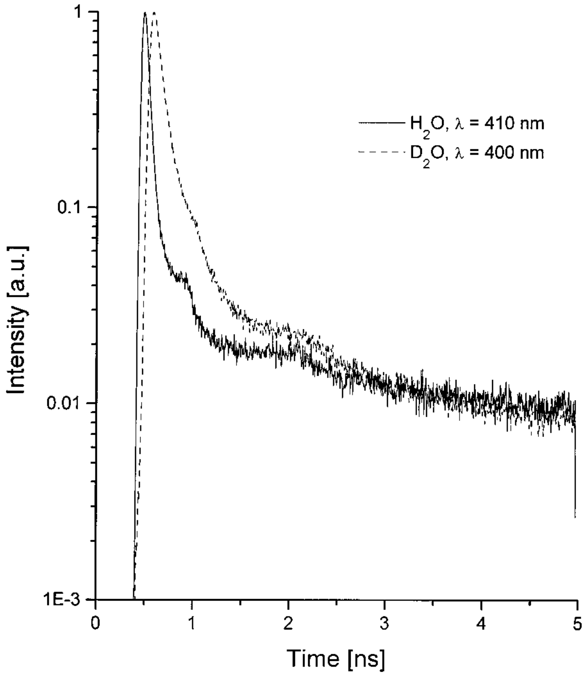


**Figure 3.** 8CN2 in $H_2O$ and $D_2O$.

**TABLE 2: Equilibrium Constants for Cyano-Substituted 2-Naphthols**

| compound | p$K_a$* (direct) | p$K_a$* (Förster)[8] | p$K_a$* (fluorescence)[8] |
|---|---|---|---|
| 5CN2 | −0.75 | −1.2 | 1.7 |
| 6CN2 | −0.37 | 0.2 | 0.5 |
| 7CN2 | −0.21 | −1.3 | 2.0 |
| 8CN2 | −0.76 | −0.4 | 0.7 |

Å.[13] Figure 3 shows the time-resolved ROH* and ROD* (measured in $H_2O$ and $D_2O$, respectively) fluorescence data of 8CN2. Table 3 summarizes the computer-fitting parameters.

## Discussion

The fastest proton-transfer rates are observed on the 5- and 8-substituted compounds. This is in accord with the model that suggests that the enhanced photoacidity of 1-naphthol over 2-naphthol is associated with the population of the $L_a$ state in the former. Substitution at the 5 or 8 position by electron-withdrawing groups would be expected to lower the $L_a$ state and to lead to enhanced acidity.[14] The discrepancy with the p$K_a$* values obtained by the Förster cycle can be explained by the fact that proton transfer is one of several competing decay pathways for photoexcited naphthols. Given the processes competing with proton transfer, the p$K_a$* values determined by the Förster equation are approximate, since they include ground-state acidities involving molecular geometries and solvation changes considerably different from those in the excited state. The p$K_a$* obtained using the solution to the DSE equation are, therefore, considered more accurate than those obtained previously. This belief is reinforced by the fact that the p$K_a$* values show the behavior expected, namely, that 5- and 8-substitution affects the excited-state acidity more markedly than 6- and 7-substitution. This prediction could not be verified previously using the Förster values.

**TABLE 3: Isotope Effect for Cyano-Substituted 2-Naphthols**

| rate constant | $H_2O$ | $D_2O$ | $k_{H^+}/k_{D^+}$ |
|---|---|---|---|
| | 5CN2 | | |
| $k_{diss}$[a] | 0.07 | 0.03 | 2.33 |
| $k_{rec}$[b] | 0.08 | 0.07 | 1.14 |
| | 6CN2 | | |
| $k_{diss}$[a] | 0.011 | 0.0033 | 3.33 |
| $k_{rec}$[b] | 0.04 | 0.022 | 1.81 |
| | 7CN2 | | |
| $k_{diss}$[a] | 0.0055 | 0.0018 | 3.06 |
| $k_{rec}$[b] | 0.03 | 0.02 | 1.50 |
| | 8CN2 | | |
| $k_{diss}$[a] | 0.027 | 0.013 | 2.08 |
| $k_{rec}$[b] | 0.04 | 0.03 | 1.33 |

[a] $k_{diss}$ in ps$^{-1}$. [b] $k_{rec}$ in Å/ps.

The isotope effect appears to be more important for the dissociation rate constant, $k_{diss}$, than for the recombination rate constant, $k_{rec}$, in agreement with previously findings for HPTS and sulfonated-2-naphthols.[15] The value of $k_{H^+}/k_{D^+}$ is close to 3 for 6CN2 and 7CN2, in accordance with the value reported for other hydroxyaromatic compounds,[16,17] probably reflecting the molecular properties of the donor and those of water.

5CN2 and 8CN2, on the other hand, show a smaller isotope effect, probably indicating that, as the reaction becomes more "diffusion controlled" and reorganization of the solvent instead of proton transfer becomes the rate-determining step, the isotope effect becomes less important. This observation needs more study before a total understanding can be reached, since a straightforward explanation is complicated by the many factors playing a role in proton-transfer reactions.

Finally, we would like to briefly compare the behavior of 5CN2 in MeOH to that of 5,8-dicyano-2-naphthol (5,8CN2) in the same solvent.[18] For 5,8CN2 in MeOH, $k_{\mathrm{diss}} = 0.012$ ps$^{-1}$ (cf. 0.0002 ps$^{-1}$) while $k_{\mathrm{rec}} = 0.033$ Å ps$^{-1}$ (cf. 0.0006 Å ps$^{-1}$), showing a forward and reverse rate 60 times greater than those of the monosubstituted compound and suggesting a synergistic effect of the two substituents on the excited-state acidity.

## Conclusions

The rate of excited-state proton transfer can be correlated with the position of the substituent on the distal ring on cyano-substituted 2-naphthols. The isotope effect shows a diminished influence as the reaction becomes faster and the proton transfer ceases to be the rate-determining step.

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