Excited-State Proton Transfer: From Constrained Systems to "Super" Photoacids to Superfast Proton Transfer†

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ABSTRACT
We have used knowledge of the electronic structure of excited states of acids to design molecules that exhibit enhanced excited-state acidity. Such "super" photoacids are the strongest reversible photoacids known and allow the time evolution of proton transfer to be examined in a wide array of organic solvents. This includes breaking/formation of the hydrogen bonds in hundreds of femtoseconds, solvent reorientation and relaxation in picoseconds, proton dissociation, and, finally, diffusion and geminate recombination of the dissociated proton, observed in nanoseconds.

General Principles

Simple thermodynamics for the ground and excited states of any proton-containing molecule (AH) and its conjugate base predict that its excited state (*AH) is a stronger acid than the ground state if the absorption or emission spectrum of the conjugate base is characterized by a bathochromic shift relative to that of the conjugate acid ($h\nu_1 > h\nu_2$, see Figure 1).[1] This thermodynamic cycle is described by the Förster equation, eq 1,[2] where $pK_a^* =$

$$pK_a^* = pK_a - (h\nu_1 - h\nu_2)/2.3RT \qquad (1)$$

$\Delta G_a^*/2.3RT$ is the ground (excited)-state acidity constant and $h\nu_{1(2)}$ is the energy of the 0−0 electronic transition for the conjugate acid (base). In this scheme, k^*_{pt} and k^*_{-pt} are the rates for forward and back excited-state proton transfer, respectively, $k_f(')$ and $k_{nr}(')$ are rates of acid (base) fluorescence and nonradiative decay, and $k_q(')$ is the rate of acid (base) quenching by protons. A more general and useful treatment is to take ν_1 and ν_2 as the averages of the absorption and fluorescence transitions of each acid and base species.

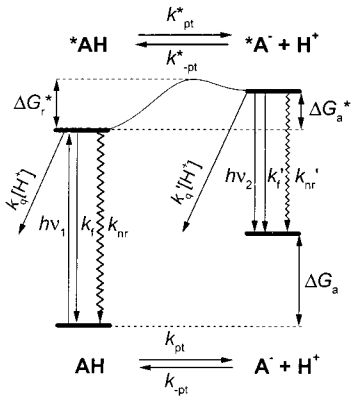

FIGURE 1. Proton transfer and decay processes in photoacids.

Since $pK_a^* = -\log_{10}(k^*_{pt}/k^*_{-pt})$, the pK_a^* obtained from the Förster calculation, referred to here as the Förster acidity, must be considered an approximation. Another approach uses fluorescence titration, in which the emissions from the conjugate acid and base are examined as a function of pH.[3]

Molecules that undergo significant colorization upon deprotonation, e.g., triarylmethane dyes, should thus be powerful proton donors. For instance, 9-phenylfluorene[4] has a predicted pK_a^* of −13! The conjugate bases of such systems are often resonance-stabilized carbanions, and their bathochromic shifts result from the generation of an n→π^* absorption.[4] Regrettably, such thermodynamic acidity has not been evinced in spontaneous deprotonation of photoexcited hydrocarbons to yield excited-state carbanions, although Wan has developed several compelling suggestions of their intermediacy.[5] Despite the predicted acidity, the protolytic photodissociation of 9-phenylfluorene is not observed, because the C−H bond breaks too slowly to establish equilibrium within the lifetime of the excited state. The relevant parameters are inevitably rates, not driving force. Nevertheless, thermodynamics can still be a powerful guide to the choice of appropriate systems.

In contrast to hydrocarbon photoacids, many hydroxyarenes (AH ≡ ArOH) exhibit proton transfer competitive with excited-state decay. The hydroxyarenes have fluorescent conjugate bases with nonbonding oxygen-centered molecular orbitals and excited states with charge distribution at sites distal from oxygen. This reduces the basicity of the excited-state anion and, by analogy, increases the acidity of the conjugate acid. This is equivalent to Weller's "intramolecular charge transfer" rationalization of the acidity in photoexcited hydroxyarenes.[2]

Hydroxyarenes undergo a number of processes in addition to fluorescence and excited-state proton transfer (ESPT), shown in Figure 1. These include various nonradiative processes characteristic of hydroxyarenes such as proton-induced quenching and homolytic OH bond cleavage to produce radicals, studied most extensively for

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† Dedicated to the memory of G. Wilse Robinson, Georgia Tech Outstanding Alumnus, and lifelong contributor to the field of proton transfer.

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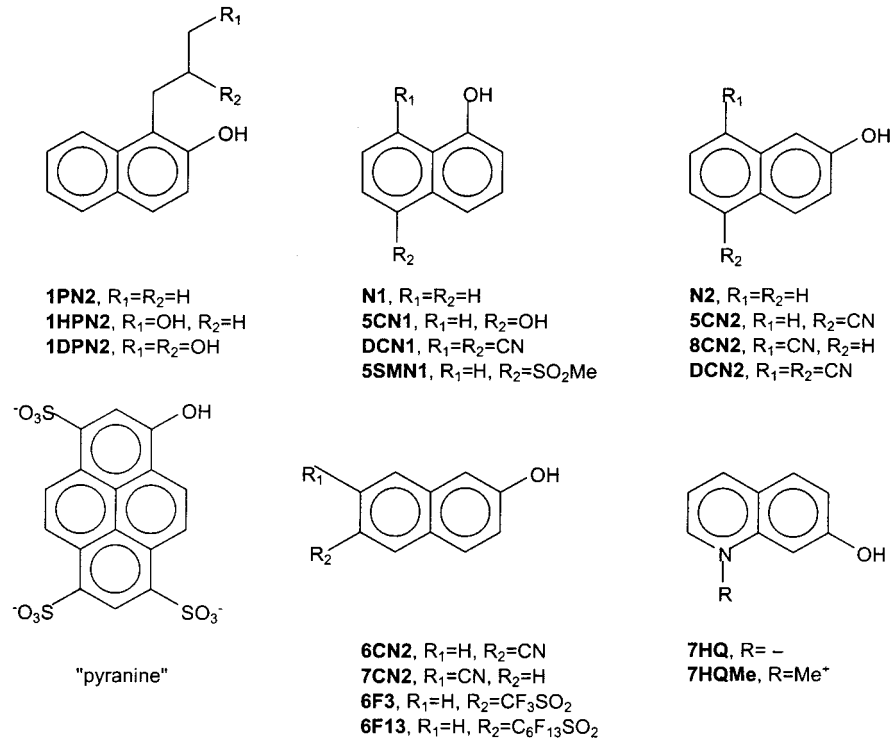
Chart 1. List of Hydroxyarenes Discussed



1-naphthol[1b] and phenol[6] derivatives. Again, the presence of competing processes and incomplete excited-state equilibrium may lead to erroneous results in determination of pK_a* by fluorescence titration. In contrast to phenols and 1-naphthol derivatives, hydroxypyrenetrisulfonate ("pyranine") and various naphtholsulfonates have been popular substrates because of their ready availability, high photochemical stability, paucity of nonradiative processes, and high photoacidity.[1,3,7,8] For our purposes, naphthols combine efficient fluorescence, suitable for investigation of excited-state dynamics by time-resolved luminescence spectroscopy, with a rich synthetic literature that allows access to a number of modified systems. A list of naphthols and other hydroxyaromatics employed is presented in Chart 1.

1-Naphthol vs 2-Naphthol

Naphthalene possesses nearly degenerate singlet excited states, L_a and L_b, which are polarized either along the long axis ("through-bond", or L_b) or along the short axis ("through-atom", or L_a). Substitution by hydroxyl at C-1 or C-2 reduces the symmetry, which means that the two states are heavily mixed. This is more pronounced for 1-naphthol, in which both L_a and L_b bands overlap in both absorption and emission spectra, while for 2-naphthol they are well separated in the absorption spectrum, and only L_b emission is observed in the emission spectrum. The larger polarity of the L_a state is believed to explain the higher reactivity of 1-naphthol (**N1**). Knochenmuss et al.[9] have studied the possible reason for the enhanced photoacidity of **N1** in naphthol−water clusters by experiment and by molecular dynamic/quantum calculations. They have determined that certain vibrations induce

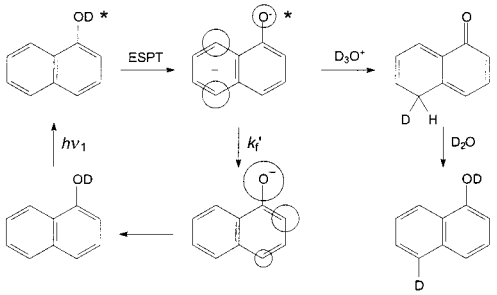


FIGURE 2. Charge densities and proton quenching in 1-naphthol.

mixing between L_b and L_a states. In about 4.5 ps after electronic excitation to the L_b ($S_0 \rightarrow S_1$) state, vibronic coupling between naphthol and solvent causes the inversion from L_b to the much more polar L_a state. This effect is not observed in 2-naphthol (**N2**). Additionally, photoexcited 1-naphthol undergoes facile proton quenching, manifested by the near absence of neutral fluorescence at all pH values.[10] In contrast, 2-naphthol exhibits little or no proton quenching and a "normal" pK_a* of 2.8, which has been attributed to the diffuse nature of the less polar L_b emitting state of the latter and a more localized L_a for the former. Accordingly, we have observed that 1-naphthol undergoes excited-state protonation of the 1-naphtholate anion at the sites of enhanced charge density, namely C-5 and C-8 (see Figure 2).[10] Adiabatic C-protonation yields a highly delocalized tetraenone, which undergoes rapid internal conversion and retautomerization to the ground state. For nonpolar solvents in which an added base (triethylamine) is introduced, no anion emission is observed, but H/D exchange is observed between oxygen and C-5 for for **N1**−**OD**,[11] presumably through the intervention of a photogenerated ion pair. In addition, Kuz'min

et al.[12] proposed *recombination-induced deactivation* as the mechanism of nonadiabatic protonation. This radiationless process, which competes with proton transfer in a reactive H-bonded complex, is caused by the appearance of new modes promoting an efficient internal conversion in the vicinity of the reaction transition state.

The C-5 and C-8 H/D exchange behavior of 1-naphthol, as well as the electronic structural rationale, suggests the use of electron-withdrawing groups at those positions to enhance the photoacidity. Indeed, this is an effective approach, which we will discuss in detail. However, we first consider the role of solvent, particularly water, on the rate of proton transfer and how it relates to molecular structure.

Solvent Effects

One of the earliest and most persistent questions concerning ESPT has been the "anomalous" solvent effect. Simple naphthols exhibit efficient proton transfer in water, but not in alcohols or other nonaqueous basic solvents. This observation is surprising, given the fact that the gas-phase proton affinity of some solvents is higher than that of water.[13] A key ingredient in the efficiency of proton transfer may be the degree of prior formation of the hydrogen-bonded complex. To examine this hypothesis, among others, we have studied solvatochromism on **N2**,[14] while Pines et al. have conducted analogous investigations of **N1** and pyranine.[15] By correlating spectral shifts by the Kamlet−Taft parameters (π^*, β, and α) of the solvents,[16] we have distinguished *three* types of H-bonding between solvents and naphthol. In the case of weakly polar naphthols these specific solvent effects are more energetic than general effects of dipole solvation. In the ground state the hydroxyl group of naphthol can form two types of hydrogen bonds with solvent HS: ArOH···SH, where solvents act as proton acceptors, and ArHO···HS, where solvents donate a proton to naphthol. Solvents more basic than water, such as amides or DMSO, induce the largest solvatochromic shifts, but without deprotonation. A third type of H-bond, $ArO^-\cdots HS$, may also play a crucial role in the thermodynamics by stabilizing the anion. Thus, as a moderate proton acceptor (Taft parameter β), water is one of the strongest proton donors (parameter α) and is, therefore, the best for solvating *both* proton and anion.

These assumptions, made by analysis of steady-state data, have been verified by time-resolved measurements. These include time evolution of the UV−visible spectra in the liquid phase[17] or the ion/electron yield by time-of flight spectrometry in the gas phase.[18] Possibly the most promising and detailed tool is femtosecond vibrational spectroscopy, which is capable of monitoring the dynamics and spectral evolution of selected H-bonds.[19]

The role of water clusters as proton acceptors has long been debated. At intermediate water concentrations, the relationship between the rate of proton transfer and water concentration in ethanol or ethanol solution is roughly fourth-order. Robinson[20] and others have postulated that proton transfer in aqueous solvent systems is the result

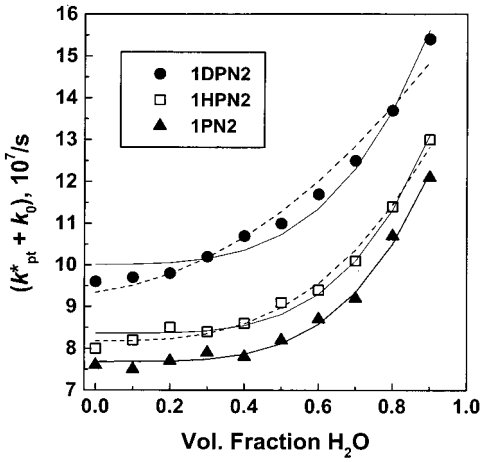


FIGURE 3. Kinetic behavior of 1-hydroxyalkyl-2-naphthols.[24]

of formation of a water cluster of order 4 ± 1, that is, the generation of a tetrahedral coordination sphere for the proton. Thus, the underlying kinetics reflect the rate-limiting kinetics of water cluster formation at the rate-determining step. Pines and Fleming have challenged this model, demonstrating that photoacid dissociation rates correlate very well with the excited-state equilibrium constant determined by both entropy and solvation energy terms.[21] Agmon et al. have also challenged Robinson's model.[22] They postulate that the kinetics simply reflects the number of hydrogen bonds, both made and broken, required to facilitate the proton transfer as well as dielectric stabilization of the anion. The fact that water donates two hydrogen bonds and methanol only one is critical, in that methanol must break its lone hydrogen bond in order to form a new one. This distinction is subtle but has an important impact on the kinetics. Recently, Hynes has used high-level calculations to predict the trajectory of proton transfer and the role of solvent reorganization in the reaction coordinate.[23] From these calculations emerges a picture that is consistent with the Huppert−Agmon model.

To get a structural handle on the role of solvent, we have synthesized a number of 2-naphthols containing hydroxyalkyl groups at the 1 position. These include 1-(3-hydroxypropyl)- (**1HPN2**), 1-(2,3-hydroxypropyl)- (**1-DPN2**), and the parent 1-propyl-2-naphthol (**1PN2**).[24] Our reasoning is that, if a water cluster is strictly required, the presence of an *intra*molecular as opposed to *inter*-molecular alcohol solvating group would not affect the stoichiometry, although the kinetics might be perturbed. In fact, the rate of proton transfer exhibits a remarkable dependence on the structure of the side chain. The kinetics of 1-propyl-2-naphthol are nearly identical, i.e., fourth order (solid lines in Figure 3, $k_0(') = k_f(') + k_{nr}(') \equiv$ *ArOH (*ArO^-) decay rate in pure MeOH), to those of 2-naphthol itself, while the monofunctional hydroxypropyl group and the difunctional dihydroxypropyl group produces third-order and second-order kinetics, respectively, in aqueous methanol (dashed lines in Figure 3). Thus, the rate of proton transfer is dependent not on water molarity,

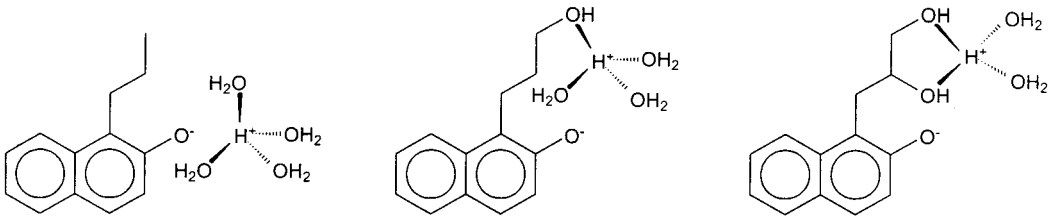


FIGURE 4. Effect of side chain on ESPT in 1-hydroxyalkyl-2-naphthols (solvation of anion not indicated).

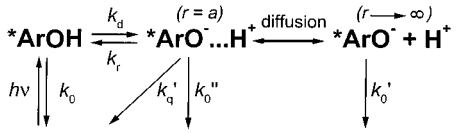


FIGURE 5. Two-step protolytic photodissociation of hydroxyaromatic compounds. Only the excited state is shown.

but on solvent intramolecularity, i.e., an entropic, not enthalpic effect. One of the possible configurations of theESPT transition state (or contact ion pair) is illustrated in Figure 4. The hydroxyalkyl side chain apparently facilitates proton transfer with a smaller water cluster and reduces the entropic requirements for the proton transfer, without changing the molecularity with respect to water. A more complex geometry for the ESPT transition state has been proposed by Agmon.[25]

A simple kinetic scheme from Figure 1 predicts mono- or polyexponential decays of *ArOH and *ArO^-, depending upon the ratio of the rate constants of elementary processes. Eigen has proposed[26] a two-step reaction scheme for the photodissociation (Figure 5). The first step includes reversible formation of a contact naphtholate−proton ion pair with radius a, and the second describes diffusional separation. Historically, diffusional separation and approach of ions have been considered as single, elementary steps. In this case, the theoretical kinetics of *ArOH and *ArO^- decays are again described by mono- and polyexponential functions and match experimental data. However, Huppert and Pines have found that the photodissociation of pyranine in water at neutral pH's can be better described in terms of a surprising long-time $t^{-3/2}$ power law asymptotic decay for *ArOH fluorescence.[27] In collaboration with Agmon,[7a] this problem was solved numerically. In this model the diffusion of a dissociated geminate proton is considered as a random motion in the field of the charged pyranine anion, and the diffusion equation is therefore generalized to the Debye−Smoluchowski equation (DSE). Using this approach, the pK_a* of photoacids can be estimated from a *single* kinetic measurement at neutral pH. For this equation, a is the contact

$$pK_a^* = -\log \frac{k_d \exp(-R_D/a)}{k_r} \qquad (2)$$

distance and k_d and k_r are the intrinsic dissociation and recombination rate constants (Figure 5), while R_D is the Debye radius. The absolute value of the latter reaches 28 Å for pyranine anion in water. To obtain k_d and k_r, the nonexponential decay of *ArOH is usually fit to a numerical solution of a system of differential diffusion equations.[28] For "weak" acids such as 2-naphthol, dissociation is too slow for electrostatic effects to enter into the kinetics. For more acidic species such as pyranine or **N1**, electrostatic effects must be considered explicitly. Recently, the theory and experimental observations of geminate diffusion-influenced reactions have been extended to the case of different lifetimes and quenching rates for the neutral and anion. Pines et al. have observed not only $t^{-3/2}$ power law asymptotic behavior for **N1** *ArOH fluorescence, but also $t^{-1/2}$ decay for *ArO^-,[29] and Agmon et al. derived precise long-time and asymptotic solutions for the observed kinetics.[30]

A deeper understanding of the role of solvent in the photodissociation of naphthols can be attained in gas-phase measurements. Knochenmuss has monitored the changing proton-transfer reactivity of **N1** and **N2** in clusters of water and ammonia with variable number of solvent molecules.[9,31] One of the most striking results is the establishment of the threshold of ionization. **N1** is shown to transfer proton only in water clusters having at least 25 molecules, while **N2** does not show ESPT at all. For endergonic proton transfer to water, the size of solvent cluster correlates with photoacid acidity. Conversely, the cluster size threshold for ESPT is found to be four ammonia molecules for both **N1** and **N2**.

"Super" Photoacids

The influence of substituents on the acidity of hydroxyaromatic compounds[32] in the ground state is well described but less extensively for the excited state. The high acidity of **N1**, coupled with the enhanced basicity at C-5 and C-8, suggests that the introduction of electron-withdrawing groups at these positions should produce even higher acidities by lowering the energy of the conjugate base.

Our first studies involved 5-cyano-1-naphthol (**5CN1**) and 5,8-dicyano-1-naphthol (**DCN1**).[33] These compounds show a remarkably increased photoacidity, and ESPT is observed in nonaqueous solvents such as alcohols and DMSO. The excited-state dissociation rate of **5CN1** in water[34] and in 8 M aqueous sodium acetate solutions[35] is about 8 ps, while ESPT for pyranine in 4 M aqueous sodium acetate solutions occurs at 3 ps.[36] These rates are among the fastest observed to date. Moreover, these values are on the same time scale as the Debye relaxation of water, which is believed to be the rate-limiting step for highly exergonic bi- or pseudounimolecular reactions. Unfortunately, cyano-1-naphthols exhibit very weak fluo-

Table 1. Equilibrium Constants for Cyano-Substituted 2-Naphthols[a]

	pK_a*		
compound	DSE	Förster	fluor
DCN2		−4.5	
5CN2	−0.75[b]	−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
N2		2.8	

[a] DSE and Förster values were calculated using eqs 2 and 1, accordingly; fluor, estimated from fluorescence titration. [b] Data for **5CN2** were later slightly corrected by us in ref 39.

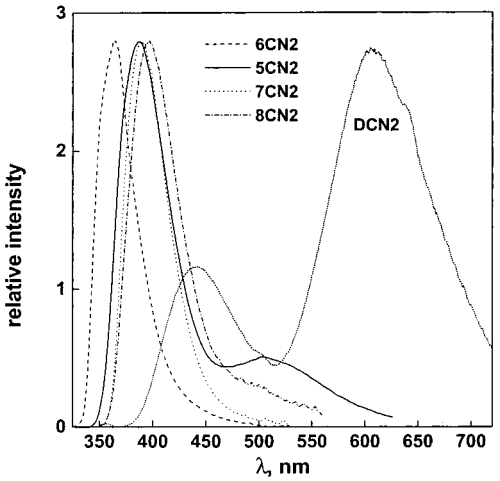


FIGURE 6. Fluorescence spectra of cyanoderivatives of 2-naphthol in methanol.

rescence and strong quenching in protic solvents.[33,34] Thus, we have turned our attention to the 5-, 6-, 7-, and 8-cyano-2-naphthols (**5CN2**, **6CN2**, **7CN2**, and **8CN2**), as well as 5,8-dicyano-2-naphthol (**DCN2**).[33,37] Each of these cyano-2-naphthols is more acidic than **N2** itself. The highest acidity is exhibited by substitution at C-5 and C-8. **DCN2** is the most acidic, with a calculated Förster pK_a* of −4.5 and the highest *ArO$^-$ fluorescence quantum yield (see Table 1 and Figure 6). Application of a simple linear free energy relationship to the monocyano naphthols **5CN2** and **8CN2** predicts a Förster acidity of −4.4 for **DCN2**, thus validating this approach.

In addition to simple but powerful structure−reactivity correlations, there is yet another explanation for the increased photoacidity of cyanonaphthols. In the gas-phase spectra of **5CN2**,[38] in collaboration with Knochenmuss, we observe several close-lying bands, excitation of which clearly indicates vibronic coupling, similar to **N1**. It is quite possible that cyano substitution in **N2**, resulting a richer vibronic structure for cyanonaphthols, produces active modes responsible for the L_b−L_a inversion.

Cyano substitution activates ESPT to solvents less polar than water (Figure 7).[33,39] The large excited-state dipole moment and higher acidity produce a substantial solvatochromic shift as compared to that of the parent **N2**. Direct comparison of the proton-transfer efficiency in various solvents with solvatochromic data for both neutral and dissociated **5CN2** in ground and excited states[39,40] confirms our assumptions made for simple naphthols

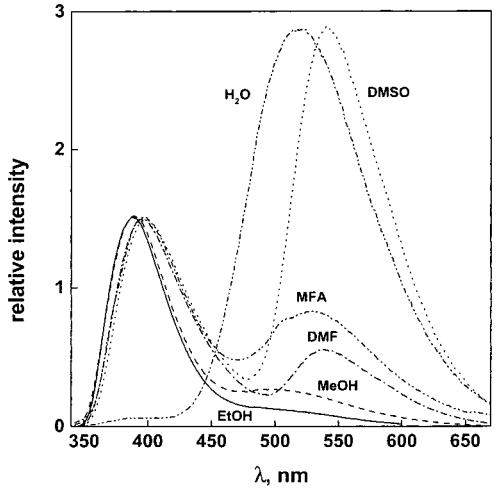


FIGURE 7. Fluorescence spectra of **5CN2** in solvents to which ESPT takes place: DMSO, dimethyl sulfoxide; MFA, *N*-methylformamide; DMF, *N*,*N*-dimethylformamide; MeOH, methanol; EtOH, ethanol.[39]

based on indirect data.[41] That is, the efficiency of excited-state proton transfer from hydroxyarenes depends on (1) solvent polarity, (2) the solvent basicity, which is responsible for proton solvation, and (3) the solvent acidity, which stabilizes the excited anion.

Huppert et al. have been able to determine the pK_a*'s by time-resolved laser spectroscopy.[42] These values are presented in Table 1, together with the excited-state acidity constants estimated from steady-state measurements. Two conclusions emerge from this treatment: the measured pK_a*'s are higher than the calculated ones, and substituents at C-5 and C-8 are more effective at lowering pK_a* for both 1- and 2-naphthol.

The C-5/C-8 effect on naphthol acidity is conceptually identical to the effect that Bardez refers to as "intramolecular electron transfer" [43] in the case of 7-hydroxyquinoline (**7HQ**). The increased basicity at the N-1 position in **7HQ**, which is equivalent to C-8 in **8CN2**, leads to rapid protonation on nitrogen (see Figure 8).[44] Alternatively, nitrogen can be protonated at low pH in the ground state, and the directly excited quinolinium ion has a pK_a* approaching −13. The *N*-methyl quinolinium species has similar properties. For our purposes, the use of a cationic photoacid presents mechanistic complications arising from cation solvation in the ground state. Nevertheless, the Bardez approach may be useful in other applications requiring a reversible super photoacid.

Notwithstanding the remarkable acidity of cyano naphthols, which allows proton transfer at rates competitive with excited-state decay to a number of organic acceptors, including sulfoxides and alcohols, the rates are still too low to initiate bimolecular reactions. Therefore, we have now begun studying the yet more acidic perfluoroalkanesulfonylnaphthols, 6-perfluorohexanesulfonyl-2-naphthol (**6F13**)[45] and 6-trifluoromethanesulfonyl-2-naphthol (**6F3**, see Chart 1). However, a problem which has daunted us with **DCN2** and monocyanonaphthols describes the major solution phase behavior of **6F13**, specifically, aggregation. In polar solvents, efficient Förster quenching due, pre-

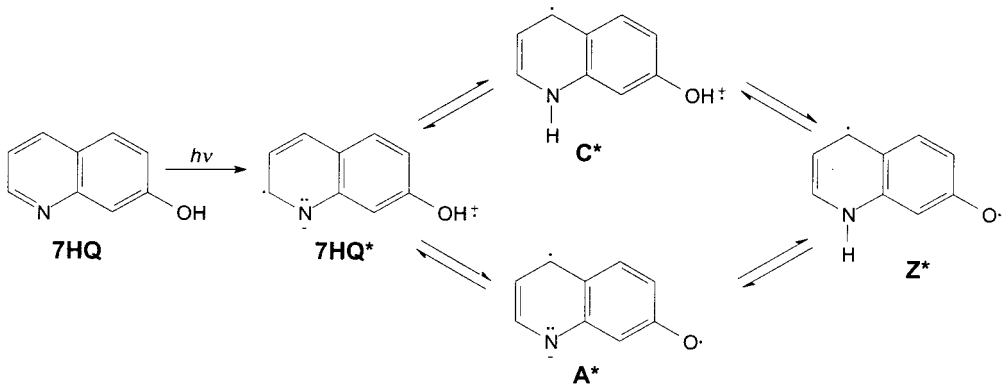


FIGURE 8. Prototropic behavior of 7-hydroxyquinoline.

sumably, to fluoroalkane phase segregation makes conclusions about fully solvated proton transfer elusive. The unusually small spectral separation of *ArOH and *ArO$^-$ bands in both **6F13** and the much more soluble **6F3** complicates the estimation of acidity constants and time-resolved measurements. We have found that, despite the high reactivity of **6F3**, the *ArO$^-$ fluorescence quantum yield is small because of the surprisingly small *ArO$^-$ lifetime.[46] However, this feature of some super photoacids can be turned to an advantage, as will be shown in the next section.

Dynamics

At room temperature, super photoacids have negative pK_a*'s in water, and dicyanonaphthols have negative pK_a*'s even in alcohols. In contrast to ESPT from "normal" naphthols with pK_a* > 0, exergonic protolytic photodissociation of these photoacids in such solvents may be considered activationless ($\Delta G_r^* \approx 0$, Figure 1), depending primarily upon solvent properties. One may expect a very weak temperature dependence of photodissociation,[7b,21] similar to what is observed for **N1**[20] in water from 0 to 80 °C. Indeed, ESPT rates from pyranine to water and from **DCN2** to various alcohols increase insignificantly at room temperature and above. However, the ability of super photoacids to transfer a proton to alcohols widely expands the possible temperature range relative to water. Huppert and co-workers have found an unusual temperature dependence for dissociation in such solvents. The Arrhenius plot is *nonlinear*, demonstrating a high-temperature, nearly barrierless, solvent-dependent process near and above room temperature (nonadiabatic limit), and a ca. 3 kcal/mol barrier at low temperatures which is solvent independent (adiabatic limit, see Figure 9).[7b,47] At low temperatures, the rate of ESPT is close to the dielectric relaxation rate, suggesting that solvent reorganization is rate-limiting. At the high-temperature limit, activationless proton transfer is limited by tunneling.[47] Thus, for the first time, we have observed proton transfer that is rate-limited by solvent relaxation, supporting the Hynes model[23] in methanol. Most curiously, nearly identical kinetic deuterium isotope effects were observed for both steps, consistent with the hydrogen-bonded network being involved in both solvent reorganization and proton transfer.

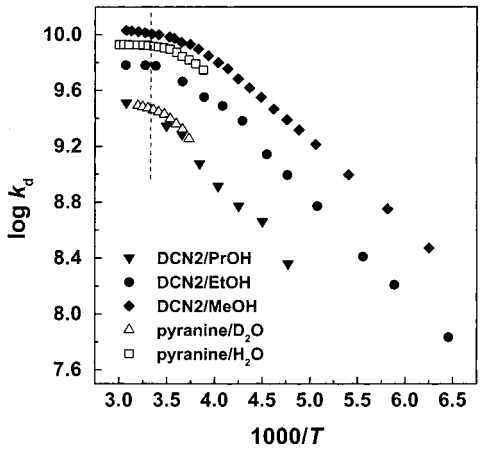


FIGURE 9. Temperature dependence of excited-state proton-transfer rate. Vertical dashed line corresponds to room temperature.[47]

For 1- and 2-naphthol, proton transfer is not observed in nonaqueous solvents. In contrast, **5CN2** and **DCN2** exhibit anion fluorescence even in pure alcohols, requiring the use of the aprotic solvent, tetrahydrofuran, to resolve the water effect. With **5CN2**, the order with respect to water is lowered to 3, while that for **DCN2** is lowered to 2, as can be derived from the analysis of steady-state emission data using the Stern−Volmer equation (see Figure 10). However, if we assume that proton transfer to water and methanol can be considered as two parallel processes, then the water-dependent component can be extracted. From the analysis of kinetic data on ESPT from various photoacids to water-poor methanol, we have found that there is a clear relationship between molecularity and driving force.[48] That is, it appears that for weaker photoacids, the primary proton acceptor is water dimer, while for super photoacids the molecularity with respect to water reduces to 1 or below! We have also observed nonlinear behavior with respect to methanol in methanol/tetrahydrofuran mixtures.[49]

The kinetics of ESPT in cyanonaphthols has been studied in a wide array of solvents. We have found that time-resolved fluorescence data fit the solution of the Debye−Smoluchowski equation for the reversible geminate recombination of ions.[28,39,48,50] As an example, we demonstrate the time-resolved fluorescence of **5CN2** in water/methanol (Figure 11).[48] Under these conditions ESPT is very efficient, and, therefore, the power-law

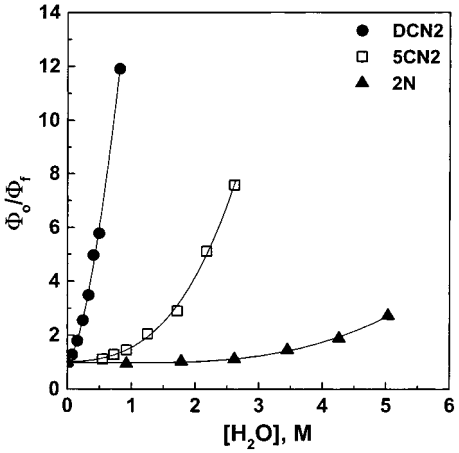


FIGURE 10. Stern−Volmer quenching of naphthol fluorescence by water in aqueous tetrahydrofuran. Φ_f and Φ_0 are *ArOH fluorescence quantum yields in solutions with and without water, accordingly.

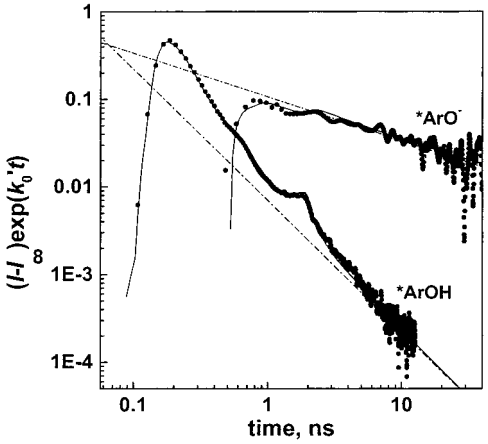


FIGURE 11. Time-resolved kinetics of **5CN2** in 47.5 mol % methanol/water mixture. Experimental fluorescence data for both acid and anion (points, normalized to theoretical amplitudes) are compared with the numerical solution of the DSE (solid lines) after convolution with the instrument response function, which causes the wiggle around 2 ns. All lines are corrected for the lifetime of the anion. Dash−dotted lines are $t^{-3/2}$ and $t^{-1/2}$ asymptotic behaviors for *ArOH and *ArO⁻, accordingly.[48]

asymptotic behavior caused by proton geminate recombination is clear. Interestingly, theory[30] predicts that power-law ($t^{-3/2}$) decay is not the only one possible for *ArOH. However, this decay represents the most frequently observed asymptotic behavior. Depending on the sign of expression $\Delta k \equiv k_0' - (k_0 + k^*_{pt})$, one may confront *three* different behaviors for the "corrected" *ArOH signal, $F(t) \equiv$ [*ArOH] $\exp(k'_0 t)$.[30] When the anion is relatively long-lived ($\Delta k < 0$, the usual case for most hydroxyaromatics), $F(t)$ shows fast conversion from initial exponential into $t^{-3/2}$ decay (Figure 11). In the transition $\Delta k = 0$ regime, $F(t)$ decays mildly and switches into a $t^{-1/2}$ decay. For short-lived anions $\Delta k > 0$, and $F(t)$ *rises* exponentially! **5SMN1** has a surprisingly short anion lifetime and, therefore, is a candidate for such unusual kinetic behavior. In accordance with theory, we have found three kinetic regimes experimentally[51] (Figure 12). Solvent-induced shortening of *ArO⁻ lifetime relative to proton-transfer rate

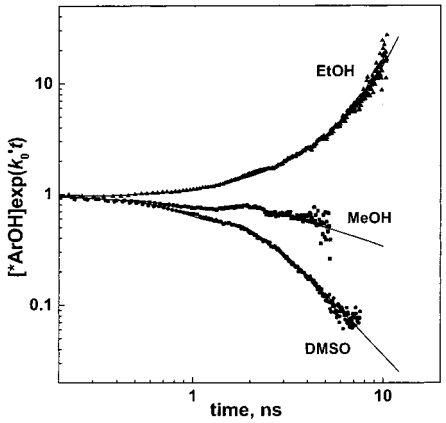


FIGURE 12. Time-resolved kinetics of **5SMN1** in alcohols and DMSO. "Corrected" experimental (dots) and theoretical (lines) *ArOH decay.[51]

induces a transition in the kinetics, from power-law in DMSO to exponential in EtOH.

With Knochenmuss we have also observed enhanced photoacidity of super photoacids in the gas phase,[38] in agreement with their liquid-phase behavior. The threshold size is $n = 3-4$ for **5CN2**/$(NH_3)_n$ clusters and $n = 10$ for **5CN2**/$(H_2O)_n$ clusters. These are much smaller than for nonsubstituted **N2** and the more acidic **N1**. Thus, the structure of the primary proton acceptor correlates with the pK_a* of the photoacids, in both liquid and gas phase. No ESPT was observed in large methanol or small DMSO clusters, in contrast to the liquid-phase behavior.

Concluding Remarks and Future Goals

Excited-state proton transfer from hydroxyarenes has been studied for more than 50 years. However, as we have tried to demonstrate in this Account, new horizons are still opening for this fundamental process. As a result of new substrates, new instrumentation for ultrafast processes, and new calculational tools, a fairly consistent picture of proton transfer has emerged. This consists of a number of key steps: the most crucial of these is an initial hydrogen-bonding complex in the *ground* state. What follows upon photoexcitation is a rapid H-bond and solvent reorganization, which will accommodate the solvated proton in its product state, followed by the proton transfer itself. Time-resolved IR measurements capable of observing the dynamics of breaking/forming of H-bonds in the femtosecond time scale could provide interesting aspects of the early events of H-bond evolution in naphthols. We believe that a coherent model for the early events in the excited-state proton transfer, as well as the rate-limiting steps, can be achieved by a combination of liquid- and gas-phase time-resolved measurements.

Whether tunneling plays a significant role in the last step has not yet been established, although it is an important component of theory. The synthesis of even stronger photoacids that promote ultrafast proton transfer at low temperatures continues to be the subject of active interest for examining such tunneling.

The use of super photoacids provides a unique opportunity to investigate the previously unexamined nonexponential behavior of the simplest unimolecular dissociation in nonaqueous solvents. The close connection between ultrafast spectroscopy and advanced kinetic theory has allowed a gratifying demonstration of the importance of diffusion in treating fast liquid-phase reactions.

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