In the case of HCNO such a study was carried out thoroughly,[20] and a slight dependence of the barrier height on vibrational state was observed. The equilibrium structure of HCNO is linear, but even in the ground state the zero-point vibrational contributions from the stretching vibrations ν_1 and ν_2 to the effective HCN bending potential give a barrier of 11.5 cm^{-1} to linearity. Because of the large number of vibrations and difficulties arising from additional pyrolysis products such a project is not feasible for butatrienone. However, we have shown that in cyclopropylidenemethanone which also has a low-lying in-plane and out-of-plane bending motion the barrier height does not change significantly on excitation of the in-plane mode.[18]

Unfortunately we have not been able to carry out a similar analysis including the in-plane mode for butatrienone although a sufficient number of vibrational statellites are still available. However, in analogy to cyclopropylidenemethanone we do not expect a large dependence of the potential on excitation of other modes and hence no reduction of symmetry when going to the vibrationless state. We therefore conclude that butatrienone is *not* kinked.

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Registry No. H_2C_4O, 63766-91-6; D_2C_4O, 71546-36-6.

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Hydration Dynamics of Protons from Photon Initiated Acids

J. Lee,[†] G. W. Robinson,*[†] S. P. Webb,[‡§] L. A. Philips,[‡§] and J. H. Clark[‡⊥]

Contribution from the Picosecond and Quantum Radiation Laboratory, Texas Tech University, Lubbock, Texas 79409, and Lawrence Berkeley Laboratory, University of California, Berkeley, California 94720. *Received April 11, 1986*

Abstract: Proton transfer from the excited states of 1-naphthol and 2-naphthol to the water solvent is studied in water/alcohol mixtures. In pure water, the deprotonation rate of 1-naphthol is insensitive to temperature ($\Delta H^{\ddagger} \approx 0$), while that of 2-naphthol exhibits an activation energy of about 2600 cal mol^{-1}. The deprotonation rates in both molecules decrease nonlinearly as the alcohol concentration increases, becoming effectively zero in pure alcohol. Variation of solvent concentrations in the mixed solvent thus serves as a probe for studying the local reaction environment. Using a Markov random walk theory, a water cluster, $(H_2O)_{4\pm1}$, is identified as the effective acceptor for both molecules, indicating that the structure $H_9O_4^+$ plays a direct role in the proton hydration dynamics. At high water concentrations the proton hydration rate is "reaction controlled", while at high alcohol concentrations it can become "diffusion controlled". Proton transfer dynamics in the naphthol systems are similar to the dynamics measured for electron photoionization into water, with the rates having low or zero activation barrier but being entropically inhibited to various degrees. The ~1:3 deuterium effect on the rates is in fact derived almost entirely from entropic considerations. A correspondence between the thermodynamic quantities ΔH°_i and ΔS°_i and the rate parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for acid dissociation processes is suggested.

1. Introduction

Reactions of acids and bases constitute some of the most fundamental processes in chemistry.[1,2] Though the concept of spontaneous ionic dissociation in aqueous solutions is about 100 years old,[3] the exact nature of the process and the role played by the surrounding solvent remain subjects of considerable speculation. Central questions concern the state of H^+ and OH^- ions in water and the rates of hydration of these ions. Applications of picosecond spectroscopy to the study of fast chemical reactions[4] has made it possible to observe such ion hydration processes directly. For example, measurement of the rates of electron[5-7] and proton[8-12] charge transfer to the water solvent has already revealed the importance of solvent structure on very short timescales.

Early seminal studies[13,14] have shown that moderately strong acids ($pK_a^* < 3$) can be prepared "instantaneously" by light-pulse excitation of certain molecules to their excited electronic states. Thus the sudden introduction of an acid into an otherwise unchanged solution[11] is possible. The molecules 2-naphthol and 1-naphthol in their excited states are good examples of such "photon initiated acids", and they constitute relatively simple systems on which to base modern investigations of proton transfer and hydration dynamics on ultrafast timescales.

[†] Picosecond and Quantum Radiation Laboratory.

[‡] Lawrence Berkeley Laboratory.

[§] Present address: Department of Chemistry, University of Chicago, 5735 South Ellis Avenue, Chicago, IL 60637.

[⊥] Alfred P. Sloan Research Fellow and Henry and Camille Dreyfus Teacher/Scholar. Present address: Amoco Research Center, P.O. Box 400, Naperville, IL 60566.

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(12) Lee, J.; Griffin, R. D.; Robinson, G. W. *J. Chem. Phys.* **1985**, *82*, 4920–4925. Because of error compensation, evaluation of good prefactors and activation energies requires very accurate rate determinations. The 2-naphthol data in this reference were obtained without a cavity dumper. Values originally reported for the rate parameters (H_2O) were $k_{dis}^{\circ} = 3.99 \times 10^{10}$ s^{-1} and $\Delta H_{dis}^{\ddagger} = 3.45$ kcal mol^{-1} with χ^2 for the data fit about 3.5. The new determinations, using data obtained with a cavity dumper, are $k_{dis}^{\circ} = 8.5 \times 10^9$ s^{-1} (H_2O), 2.2×10^9 s^{-1} (D_2O); and $\Delta H_{dis}^{\ddagger} = 2.6$ kcal mol^{-1} (H_2O), 2.4 kcal mol^{-1} (D_2O), with $\chi^2 \simeq 1.5$.

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Though they are extremely weak acids in their ground electronic states (pK_a = 9.23 and 9.49),[15] when excited, both 1- and 2-naphthol at neutral pH readily lose a proton to water (p$K_a^* \simeq$ 0.4[11,16] and 2.78,[17] respectively). However, deprotonation does not occur from the excited state of either molecule in pure alcohol solvents.[18] In spite of these similarities, there are spectroscopic differences between 1- and 2-naphthol. The absorption spectrum of 1-naphthol is congested by overlapping of the ^1L_b and ^1L_a states.[19,20] Dissimilar frequency shifts in the fluorescence have been interpreted as a difference of emitting states: ^1L_a for 1-naphthol, ^1L_b for 2-naphthol.[19] In addition, the Stokes shift of the emitting state in 1-naphthol is much larger than that in 2-naphthol.[19] The excited state of deprotonated 1-naphthol lies about 2500 cm^{-1} lower in energy than that of deprotonated 2-naphthol, with respect to their excited neutral analogues. Finally, the emission intensity from protonated (neutral) 1-naphthol in water is extremely weak.[13,14] This is in contrast to the strong emission from neutral 2-naphthol. Many explanations have been proposed for the lack of emission intensity in 1-naphthol.[16,19-30] However, none of these earlier papers has presented a detailed description of the excited-state dynamics involved in these processes.

Time-resolved experiments in water/alcohol mixtures have already shown that the dynamical proton transfer from 2-naphthol to the solvent can be quantitatively analyzed.[12] This analysis is based on the description of the local environment in the mixed solvent system in terms of the probability for the existence of clusters of water molecules. Proton transfer in 2-naphthol was found to require cluster formation of at least 4 ± 1 water molecules. A strikingly similar result has been found for electron transfer.[5-7] To test this model further and to attempt a correlation of the behaviors of these photon initiated acids with other acids, additional quantum yield and lifetime experiments have been performed on both 1- and 2-naphthol in water/alcohol mixed solvent systems.

2. Experimental Section

The (fast) lifetime measurements on 1-naphthol at high water concentrations were carried out at Berkeley, while most of the quantum yields and the slower lifetimes were determined, along with their temperature dependence, at Texas Tech. A variety of sources and purification methods of the naphthols and the solvents were employed. In all cases the water/alcohol mixed solvent was prepared on a volume fraction basis and carefully deoxygenated either by a number of freeze-pump-thaw cycles or by purging with dry nitrogen gas prior to use.

Sample preparation procedures for the fast lifetime studies are presented in more detail elsewhere.[11,31] The source of the water solvent in these experiments was Alhambra (steam distilled), and the ethanol was Gold Shield (95%). The remainder of the measurements utilized 1-naphthol (Aldrich), deionized water, and ethanol (U.S. Industrial Chemical Co., "absolute"). Except for deoxygenation, all solvents were used without further purification. The pH of the solutions was not modified in any of the experiments to be reported here and remained near pH 7. A full discussion of the pH effects in the 1-naphthol system is reported in other work.[11] In all experiments, concentrations of the naphthols were kept below 10^{-4} mol L^{-1}.

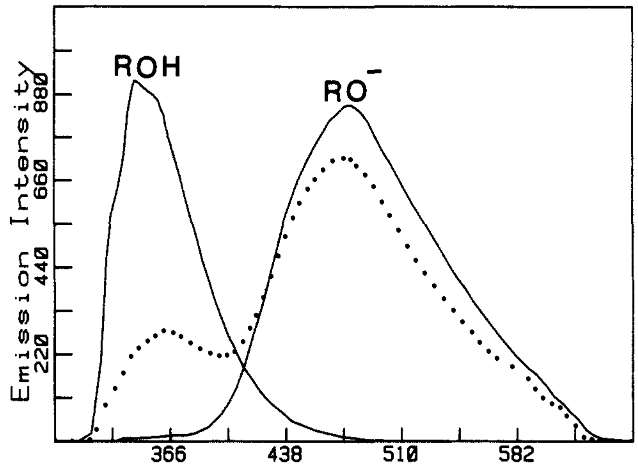

Figure 1. Emission spectra for 1-naphthol in ethanol and water solvents. Dotted line is for [H_2O] = 0.4.

Table I. Overall Fluorescence Quantum Yields (Φ), Intensity Ratios (I_{RO^-}/I_{ROH}) and Lifetimes (τ) for 1-Naphthol in Water/Alcohol Mixtures

[H_2O][a]	Φ[b]	I_{RO^-}/I_{ROH}[c]	τ[d]
1.00	0.114	60.7	32
0.81	0.128	21.3	94
0.62	0.125	3.60	306
0.40	0.120	2.49	627
0.20	0.100	0.73	1260
0.00	0.224	0	5750

[a] Volume fraction. [b] Values at 20 °C; $\Phi = \Phi_{ROH} + \Phi_{RO^-}$. [c] Intensity obtained from the peak heights. [d] Lifetimes in ps; values reported in ref 31 for [H_2O] = 0.43, 0.24, and 0.05 are 570, 1300, and 5700 ps, respectively.

The apparatus for measuring fluorescence lifetimes with streak camera detection has been fully described elsewhere.[31,32] In the present work, time-resolved experiments over the range ~30 ps to ~1 ns were carried out with a Hadland-Photonics Imacon 500 streak camera, "synchroscanned" at 10 Hz. A 20 ps fourth-harmonic pulse (266 nm) derived from an active passive mode-locked Nd:YAG laser system (Quantel, YG400) was used to excite the sample. The fluorescence signal collected at a 90° angle was spectrally filtered with appropriate narrow-band (~10 nm FWHM) interference filters and temporally resolved with the streak camera. Typically, streak records from 500 laser shots were accumulated for each sample. The signals were digitized with an intensified photodiode array (Tracor-Northern, IDARSS) and transferred to a microcomputer (DEC, LSI 11/73) for averaging.

Steady-state absorption and emission spectra were measured on a Lambda 5 UV-vis spectrophotometer and a Perkin-Elmer MPF-44B spectrofluorimeter with DCSU-2 correction unit, respectively. The absolute quantum yield (Φ), corrected[33] by a quinine sulfate standard (Φ = 0.546), was obtained by integrating the emission spectrum by using 305-nm excitation.

Because of expected greater precision, "slow" lifetimes (≳500 ps) were measured by using a cavity dumped argon-ion synchronously pumped Rhodamine-6G dye laser (Coherent CR599) for excitation. Time resolved signals were obtained by using time-correlated single-proton-counting methods.[34] The cavity dumper was operated at 13 MHz to avoid pulse pileup errors that are typically experienced if the full pulse train is used in this lifetime range. Since this piece of equipment was not available in our earlier investigations,[12] the 2-naphthol lifetime experiments in the pure water solvent were repeated for better comparison with the 1-naphthol results. Temperature variations were made over the range 0-80 °C for the quantum yields and the slow lifetime studies.

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Table II. Photophysical Parameters for Neutral 1-Naphthol in Water and Ethanol

solvent	Φ	τ (ps)	k_r (s^{-1})	k_{nr} (s^{-1})
H_2O	0.001[a]	32	4.26×10^7	3.12×10^{10}[b]
EtOH	0.224	5750	3.90×10^7	1.35×10^8

[a] Value from ref 16 and 19. [b] $k_{nr} = k_{nr}^{\circ} + k_{dis}$. See text.

Control of temperature to ±1 °C was afforded by a Borg-Warner LHP-150 heat pump and TC-108 temperature controller.

3. Results

The absorption spectra of both 1- and 2-naphthol are insensitive to the relative concentrations of water and alcohol in the solvent mixture. However, their fluorescence spectra depend sensitively on the fraction of water in the solvent.

In a pure alcohol solvent, the fluorescence spectrum of 1-naphthol shows an intense band at 354 nm (FWHM = 60 nm). On addition of water, the intensity of this band decreases, and a new band grows in at 480 nm (FWHM = 108 nm). The short wavelength emission has been attributed to neutral 1-naphthol (1-ROH), the long wavelength emission to the deprotonated 1-naphtholate anion (1-RO$^-$)[13] (see Figure 1). The type of alcoholic solvent, either ethanol or methanol, does not affect the spectroscopy of 1-naphthol. In both alcohols the fluorescence quantum yield of 1-ROH is 0.224 ± 0.004 at 20 °C.

Table I lists the overall quantum yields ($\Phi_{1\text{-ROH}} + \Phi_{1\text{-RO}^-}$) and the fluorescence intensity ratios between the naphtholate anion and the neutral molecule in different solvent mixtures. The fluorescence intensity ratio is seen to be highly sensitive to the water concentration. Though considerable effort was made to uncover even a small temperature effect, it was found that the fluorescence intensity ratio in 1-naphthol at neutral pH is insensitive to temperature from 0 to 80 °C.

The proton transfer rate from 2-naphthol, in contrast to that from 1-naphthol, does depend on temperature and corresponds to an activation energy, $\Delta H^{\ddagger} \simeq 2.6$ kcal mol^{-1}, for the proton-transfer process.[12] The relative acid properties in the excited states of 1-naphthol and 2-naphthol partly depend on this difference in activation energy (see section 5).

Table II summarizes the photophysical parameters for neutral 1-naphthol in water and ethanol solvents. The radiative rate constants are similar in the two solvents, while the nonradiative rate constant is about 230 times larger in water than in ethanol. The short lifetime corresponds to fast proton transfer to the water solvent upon excitation of 1-naphthol and is consistent with the extremely low quantum yield in pure water ($\Phi \simeq 0.001$).[16,19]

In Figure 2 the experimental decay rates (τ^{-1}) of neutral 1-ROH in different water/ethanol mixtures are plotted as hexagons. The rate is seen to vary nonlinearly with the ethanol concentration. The same kind of nonlinearity has been observed earlier for 2-naphthol[12] and other charge-transfer systems, involving protons[9] as well as electrons.[5-7] The nonlinearity with increasing alcohol concentration has been attributed to the breaking up of water clusters of critical size, $(H_2O)_{4\pm1}$, with the concomitant termination of the charge-transfer process.[12]

The time-resolved emission intensity of the deprotonated product, 1-naphtholate, clearly displays rise- and fall times, with the rise time in pure water equaling the fall time of the neutral species (τ = 32 ps). Preliminary data[31] in mixed water/alcohol solvent systems has indicated that the 1-RO$^-$ rise times become shorter than the corresponding fall times of 1-ROH as the alcohol concentration increases, but further work is required to verify this aspect.

We adopt the terminology used by Eigen and co-workers[35,36] in their studies of acid recombination rates: the forward proton (or electron) transfer to the solvent is designated dissociation (dis) while the reverse reaction of the hydrated proton (or electron) with its parent anion (cation) is termed recombination (rec). The decay time τ' of 1- or 2-RO$^-$ depends on radiative and nonradiative processes, including the proton recombination rate. Determination of the excited state acid constant K_a^* can be made if both the proton dissociation rate k_{dis} and the proton recombination rate k_{rec} are known. A detailed study of this type has been carried out on 1-naphthol and is described more fully elsewhere.[11] In that work, a standard state pK_a^* of 0.4 ± 0.2 was obtained, which is to be compared with p$K_a^* \simeq 0.5$ for 1-naphthol and pK_a^* = 2.78 for 2-naphthol determined previously by Harris and Selinger.[16,17]

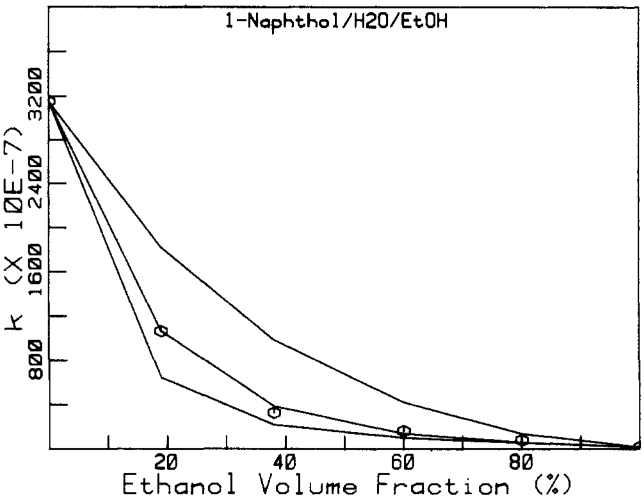

Figure 2. Overall decay rates of neutral 1-naphthol in H_2O/EtOH mixtures: ○, experimental values; top, calculated value for cluster size of 2; middle, calculated value for cluster size of 4; bottom, calculated value for cluster size of 6.

4. Markov Random Walk Model

Addition of alcohol has been seen to slow down the proton-transfer rates. In pure alcohols, the deprotonation of excited 1-naphthol and 2-naphthol is completely inhibited.[18] The charge-transfer process in the mixed solvent system might then be expected to be "reaction controlled" at high water concentrations and "diffusion controlled" at low water concentrations. The "reaction" consists of rotational fluctuations of water molecules into appropriate orientations to accept the charge, while "diffusion" in the mixed solvent system corresponds to the translational motion of water molecules required to build up a local concentration of four water molecules.

A Markov random walk model[37] has been used to simulate the fluorescence quenching in water/alcohol mixed solvents. This model can be briefly summarized as follows. An $N \times 1$ row matrix describes at time t the concentration of each of the $N - 1$ cluster configurations and the ground-state "trap". Initially, a binomial distribution of cluster configurations is assumed. A square matrix of order N describes for each configuration the probabilities during a small time interval Δt for alcohol $\rightleftharpoons$ water solvent exchange and excited-state decay. The overall excited state decay rate is given by $k = \tau^{-1} = k_r + k_{nr}$, where k_r is the radiative rate and $k_{nr} = k^{\circ}_{nr} + k_{dis}$ is the total nonradiative rate, with k°_{nr} conventional and k_{dis} the proton dissociation rate. The solvent exchange probability is scaled to the volume fractions, $[E]$ for alcohol and $[W]$ for water, in the following way[7]

$$J_{p,p+1} = [(N - p - 1)/(N - 2)]P[W] \quad (1)$$

$$J_{p+1,p} = [p/(N - 2)]P'[E] \quad (2)$$

for $p = 1, N - 2$, where $J_{p,p+1}$ is the probability during Δt for a water molecule to replace an alcohol molecule in the inner coordination shell containing $p - 1$ water molecules, while $J_{p+1,p}$ represents the reverse exchange. See the rate diagram in ref 7. The value of $N - 2$ is the "critical cluster size", and P (or P') are

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(37) See ref 5 and 7. The notation in these references is not the same. For clarification, see the rate diagram in ref 7. In this and subsequent papers we shall use the notation of ref 7.

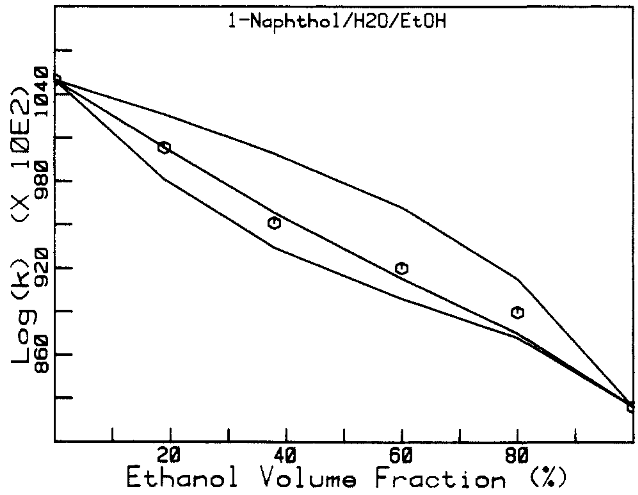

Figure 3. Same data as in Figure 2, except that log k is plotted.

"elementary probability factors" for the hypothetical case of unit volume fraction of W (or E) in the bulk solvent but zero volume fraction of W (or E) in the inner coordination shell. Intrinsic to these calculations is the assumption that the deprotonation rate constant k_{dis} is *zero for a cluster of subcritical size and is equal to the rate in the pure bulk water solvent for clusters of critical size or larger.*

Carrying out m-fold repetitive multiplications of the square matrix by the initial concentration matrix gives the new concentration matrix at time $m\Delta t$. Hence, one can monitor the decay kinetics of the neutral species by determining the concentration matrix for various time lapses. The critical cluster size can then be deduced from the best agreement between experimental and calculated curves, by using different matrix sizes. Except for data at the two endpoints (100% water and 100% alcohol), the only other required input parameter is the cluster size. Past experience[7] has indicated good sensitivity of the theoretical model to cluster size.

The theoretical overall decay rates k of neutral 1-naphthol are plotted as solid curves in Figure 2 for cluster sizes of 2, 4, and 6. Among these three curves, a cluster size of 4 is seen to give good agreement with the experimental data (hexagons). Thus, as in the case of 2-naphthol,[12] the hydrated proton structure $H_9O_4^+$ seems to play a direct role in the dynamics of the proton dissociation/hydration reaction in 1-naphthol.

When the solvent has high alcohol content, the theoretical rate for 1-naphthol decay is somewhat lower than the observed one. This is most easily seen from the logarithmic plot shown in Figure 3. Only for the most rapid electron transfers (ANS[6] and TNS[7]) have such deviations from the theory at high alcohol content been observed. When the charge-transfer process is relatively slow, it is reaction controlled effectively over the entire concentration range of the mixed solvents. In these reaction controlled cases, it has been adequate to assume that the elementary solvent exchange probability per unit time for exchange of any two molecules at the reaction interface is given as $P = P' = \eta(\text{cp})^{-1} \times T(K) \times 10^8\ \text{s}^{-1}$.[7] This is the assumption that was utilized in constructing Figures 2 and 3.

The cases where the results deviate from the predictions of the model are assumed to be "diffusion controlled". In the diffusion controlled limit, the details of the diffusion process itself become important, and the simple expression for P and P' in the preceding paragraph may no longer be adequate for describing solvent exchange. Since the deviations are not large and furthermore occur in the less interesting concentration regime, no further attempt will be made to account for them at this time.

5. Proton Dissociation Rates

Proton dissociation rates can be described in terms of the ordinary Arrhenius equation, $k_{dis} = k^\circ_{dis} \exp[-\Delta H^{\ddagger}_{dis}/RT]$, where the prefactor k°_{dis} contains the entropy factor $\exp[\Delta S^{\ddagger}_{dis}/R]$. One might expect the activation energy $\Delta H^{\ddagger}_{dis}$ to be related in some way to the standard enthalpy of ionization ΔH°_i. The value of ΔH°_i for any acid is obtained by summing up a number of large molecular and hydration contributions.[38] The resulting value of ΔH°_i is always a small difference between these large quantities and is therefore not capable of being theoretically predicted with great accuracy.

Table III. Self-Consistent Parameters for Proton Dissociation in Water: 1- and 2-Naphthol, T = 298 K[a]

	1-naphthol		2-naphthol	
	H	D	H	D
k_{dis} (s^{-1})	2.5×10^{10}	7.9×10^9	1.1×10^8	3.9×10^7
$\Delta H^\circ_i = \Delta H_{dis}^{\ddagger}$	0	0	+2600	+2400
Ω	0.46	0.46	0.46	.46
k_{rec} ($\text{M}^{-1}\ \text{s}^{-1}$)	6.44×10^{10}	5.06×10^{10}	6.44×10^{10}	5.06×10^{10}
pK_a	0.41	0.81	2.77	3.12
ΔG°_i	+560	+1100	+3780	+4260
$T\Delta S^\circ_i = T\Delta S_{dis}^{\ddagger}$	−560	−1100	−1180	−1860

[a] $\Delta H^{\ddagger}_{dis}$ and k_{dis} are experimental values; all other values are calculated from eq 3 and 4 by using estimated $\Omega = 0.46$, $\tau_D^{-1}(H_2O) = 1.4 \times 10^{11}\ \text{s}^{-1}$, and $\tau_D^{-1}(D_2O) = 1.1 \times 10^{11}\ \text{s}^{-1}$. Energy values in cal mol^{-1}.

The pK_a^* values for the excited states of 1-naphthol[11,16] and 2-naphthol[17] have been measured near the standard temperature of 25 °C. These values are $pK_a^* = 0.4 \pm 0.2$ for 1-naphthol and 2.78 ± 0.07 for 2-naphthol. Using these pK_a^* results, the ΔG°_i values ($= -RT^\circ \ln K_a^*$) for the dissociation are $+(545 \pm 270)$ and $+(3790 \pm 100)$ cal mol^{-1}, respectively. In this work we have found that in the case of 2-naphthol, $\Delta H^{\ddagger}_{dis}$ is 2600 cal mol^{-1}, while it is ~0 cal mol^{-1} for 1-naphthol (see Table III). For both 1-naphthol and 2-naphthol, these numbers are consistent with a picture[39] for weak acids ($\Delta G^\circ_i \gtrsim 0$) where $\Delta H^{\ddagger}_{dis} \simeq \Delta H^\circ_i$ (for $\Delta H^\circ_i > 0$), but $\Delta H^{\ddagger}_{dis} = 0$ (otherwise), and $\Delta S^{\ddagger}_{dis} = \Delta S^\circ_i$.

Since ground state pK_a's for 1- and 2-naphthol are about the same, the Förster cycle[12,13] predicts that the ΔH°_i difference between 1- and 2-naphthol is related to the spectroscopic energy differences between ROH and RO^- in the two molecules. While a quantitative determination is not possible because of extreme spectral overlap, the relatively low lying excited state of 1-RO^- compared with 2-RO^- is consistent with a less positive ΔH°_i for 1-naphthol and thus a lower $\Delta H^{\ddagger}_{dis}$.

From the above data, the ΔS°_i values would be −1.8 and −4.0 cal K^{-1} mol^{-1} for 1- and 2-naphthol, respectively. In the deuterated cases, the entropies decrease further to −3.7 and −6.2 cal K^{-1} mol^{-1}. The negative entropy for acid dissociation is usual,[38,40] and in the case of 1-naphthol, as for a number of other weak acids (acetic acid, for example) where ΔH°_i is negative or zero, there is a *purely entropic activation barrier for the dissociation process.*

The prefactors k°_{dis} for the proton dissociation rates have temperature independent values[11,12] of 2.5×10^{10} and 0.85×10^{10} s^{-1}, respectively, for 1- and 2-naphthol. Using the above $\Delta S^\circ_i = \Delta S^{\ddagger}_{dis}$ values and dividing the two prefactors by $\exp[+\Delta S^{\ddagger}_{dis}/R]$ gives "basic rates": 6.2×10^{10} and 6.4×10^{10} s^{-1}, respectively, for protonated 1- and 2-naphthol. In the deuterated systems, the prefactors are 7.9×10^9 and 2.2×10^9 s^{-1}, giving basic rates of 5.1×10^{10} and 5.0×10^{10} s^{-1}. The basic rate is the rate that the dissociation process would have if it were unencumbered by an entropy or enthalpy of activation. The equivalence of the basic rates in 1- and 2-naphthol (H or D) is to be noted.

The reciprocals of these basic rates are about twice as long as rotational correlation times (Debye rotational times) for pure H_2O and D_2O, $\tau_D = f\tau_d$, where τ_d is the dielectric relaxation time, and f is a factor with a value between 1.0 and ~0.68.[41] At 25 °C, $\tau_d(H_2O) = 0.82 \times 10^{-11}$ s, so that τ_D^{-1} lies between 1.2×10^{11} s^{-1} and 1.8×10^{11} s^{-1}. A value $\tau_D^{-1} = 1.4 \times 10^{11}$ s^{-1} is consistent with the $H^+ + OH^-$ recombination rate in H_2O [1.4 (±0.2) ×

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[38] Reference 1, p 91, Table 9.

[39] Robinson, G. W.; Thistlethwaite, P. J.; Lee J. *J. Phys. Chem.*, in press.

[40] Harned, H. S.; Owen, B. B. *The Physical Chemistry of Electrolytic Solutions*, 3rd ed.; Reinhold: New York, 1958; p 667, Table 15-6-2.

[41] Hasted, J. B. *Aqueous Dielectrics*; Chapman and Hall: London, 1973; pp 21–22, p 47, Table 2.2.

10^{11} M^{-1} s^{-1}] suggested by Eigen and co-workers.[35,36,42] The analogous value for D_2O would be 1.1 × 10^{11} s^{-1}.[43] The similarity between the basic rates of proton dissociation and the Debye rotational correlation times in pure water supports the model where a solvent rotational "bottleneck" stands in the way of the overall ion hydration reaction.

The somewhat lower value for the basic rate of proton dissociation in acids compared with τ_D^{-1} can be rationalized in the same manner that Eigen and Kustin[36] have explained this difference for the reverse recombination reaction. There is not only a mobility factor, which can be as small as 0.5 in proton dissociation from a very large molecule, but in addition the full 4π solid angle is not available for proton release. A combined factor $\Omega = 0.46 \pm 0.03$ fits proton dissociation in the naphthols when the above values of τ_D^{-1} are used.[44] Note particularly that the basic rate is much slower than that given by the classical factor kT/h. The main reason for this is that the "basic rate" contains its own activation energy, to which the temperature dependence[45] of the rotational correlation time and the viscosity of water are ordinarily attributed. A fuller description of these aspects will appear in separate publications.[39,46]

The above discussion suggests quantitative expressions for weak acid ($\Delta G^\circ_i \gtrsim 0$) dissociation and recombination rates

$$k_{\rm dis} = \Omega \tau_D^{-1} e^{+\Delta S^\circ_i/R} e^{-\Delta H^{\ddagger}_{\rm dis}/RT} \tag{3}$$

$$k_{\rm rec} = \Omega \tau_D^{-1} e^{-(\Delta H^{\ddagger}_{\rm dis} - \Delta H^\circ_i)/RT} \tag{4}$$

where ΔS°_i is assumed negative and Ω lies between 0.25 and 1.0. Use of standard 1 M concentrations is implied in the two equations. The basic rates $\Omega \tau_D^{-1}$ for the forward and reverse reactions are governed by *detailed balancing* and must of course be the same.[47] Another important point to realize when utilizing these equations is that both τ_D^{-1} and ΔG°_i give rise to non-Arrhenius behavior. However, as the temperature increases, a decreasing activation energy for τ_D^{-1} tends to be cancelled by an increase of ΔG°_i, so that a relatively constant experimental $\Delta G^{\ddagger}_{\rm dis}$ is the result. More will be said about this aspect in another paper.[39]

In the case of the naphthols, where $\Delta H^\circ_i \simeq \Delta H^{\ddagger}_{\rm dis}$, measurement of $k_{\rm dis}$ as a function of temperature, an estimation of Ω and the use of eq 3 and 4 then provides sufficient data for the determination of all the required rate and equilibrium parameters. This is illustrated in Table III for Ω taken as 0.46. The calculated values in this table should be compared with the experimental quantities described in this section. The agreement is excellent. However, for a complete confirmation of these ideas, the temperature dependence of $k_{\rm rec}$ must be known. These experiments have been carried out in our laboratory and do support the validity of the proposed rate equations.[48]

6. Discussion

Because of the 4-cluster nature of the hydration process near threshold energies, one would expect the dissociation dynamics of all weak acids and electron precursors to be the same if specific molecular contributions can be cleared away. This unifying feature should conceptually simplify discussions of electron and proton dissociations in aqueous media.

In this work, we have determined a "basic rate" for proton dissociation from 1- and 2-naphthol. Within a steric/mobility factor Ω, this basic rate approaches the rotational correlation rate τ_D^{-1} in pure liquid water. Rotational reorientation of water molecules is therefore rate limiting, and weak acid dissociations in water cannot take place on time scales shorter than τ_D.

The deuterium effect on τ_D is insufficient to account for the ~1:3 ratio of deuteron vs. proton dissociation rates uncovered in this work. Since the 1-naphthol reaction in particular is accompanied by zero activation energy, the remaining isotope factor (~2.3) must arise from entropies of hydration and molecular entropy changes. This rate factor corresponds to an entropy difference $\Delta S_H^{\ddagger} - \Delta S_D^{\ddagger} \approx +1.66$ cal K^{-1} mol^{-1}. The total gas phase contribution to $\Delta S_H^{\ddagger} - \Delta S_D^{\ddagger}$ can be estimated[49] to be only about +0.4 cal K^{-1} mol^{-1}. This gives ~+2 cal K^{-1} mol^{-1} to be attributed to hydration entropy differences, the entropy change in D_2O being more negative than that in H_2O. The direction of this change is expected considering the lower vibrational frequencies in liquid D_2O compared with H_2O and the severe stiffening of these vibrations in the $H_9O_4^+$ and $D_9O_4^+$ complexes. Thus, the deuterium effect on the rates of weak acid and electron dissociations can very likely be understood within a thermodynamic framework based on conventional entropy calculations for a small group of interacting water molecules.

Franck–Condon effects enter into the rate considerations only if an *intramolecular* rearrangement necessary for proton dissociation is so slow that it becomes rate limiting.[50] In the "hydration controlled" limit, within which 1- and 2-naphthol fall, any intramolecular processes must be relatively so fast that variation of their Franck–Condon factors and rates through deuteration make no impact on the measured dynamics.

In spite of the quantitative differences, proton transfer has been found to be the dominant decay path for both 1-naphthol and 2-naphthol in water. Furthermore, a water cluster of 4 ± 1 molecules is the proton acceptor in each case, indicating that the hydrated proton structure[39,51,52] $H_9O_4^+$ plays a direct role in the dynamics. The facts presented provide evidence that the most important feature controlling proton transfer into an aqueous medium for the moderately weak acids studied here is the presence of this specific water structure and the time required to form it. The findings are in general agreement with the results of earlier work on proton transfer[8-12] and electron transfer[5-7] in water.

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Registry No. 1-Naphthol, 90-15-3; 2-naphthol, 135-19-3; D_2, 7782-39-0.

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(42) Eisenberg, D.; and Kauzmann, W. *The Structure and Properties of Water*; Oxford University Press: New York and Oxford, 1969; pp 224–227.

(43) Reference 42, Table 4.5, p 207.

(44) The value of Ω may be scaled slightly to accommodate somewhat different values of τ_D^{-1}. Using $\tau_D^{-1} = 1.8 \times 10^{11}$ s^{-1} (H_2O), for example, gives $\Omega = 0.36$.

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