case of the t-C_4H_9·HI complex) compared to the collision frequency.

There is ample evidence from molecular beam studies by Lee and co-workers[44,45] as well as Grice and co-workers[44,47] of such bound complexes being formed during reactions between atoms (or radicals) with diatomic molecules containing iodine. The reactions include the following: CH_3 + IF,[44] CH_3 + ICl,[46] O + ICl,[47] O + IBr,[47] O + I_2,[47] and H + I_2.[45] Mei and Moore[48] have observed unusual temperature dependencies in rate constants of the Cl + HI and Br + HI reactions and have interpreted the results using an analogous mechanism.

The temperature dependence of the CH_3 + HI rate constant that we observed is atypical. There is an indication of a reversal in temperature dependence of the reaction rate constant at the highest temperatures used to study this reaction (see Figure 2). This apparent change, from a negative to a positive activation energy, could indicate the emerging importance of a direct H-atom abstraction route that proceeds over a small potential energy barrier. This more direct process should become the dominant mechanism for reaction 4 (as well as reactions 5–8) at a suitably high temperature. The onset of this changing behavior would be observable first in the CH_3 + HI reaction because the low-temperature route has the lowest rate constant of all the R + HI reactions studied.

Summary

Rate constants of five R + HI reactions have been determined as a function of temperature. The results have been used to recalculate alkyl radical heats of formation and to begin to obtain an understanding of the reaction mechanisms. Use of measured rate constants of these reactions in thermochemical calculations to obtain the radical heats of formation has yielded heats of formation that are in complete accord with values obtained from other kinds of studies, particularly from investigations of dissociation–recombination equilibria. The negative activation energies found for these reactions are interpreted as an indication that these apparently simple H-atom transfer reactions are in fact complex processes proceeding via the formation of a complex intermediate.

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Registry No. CH_3, 2229-07-4; C_2H_5, 2025-56-1; i-C_3H_7, 2025-55-0; s-C_4H_9, 2348-55-2; t-C_4H_9, 1605-73-8; HI, 10034-85-2.

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Solvent Structural Effects on Proton Dissociation

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Abstract: Lifetime and quantum yield measurements are performed on the excited states of 1-naphthol-2-sulfonic acid potassium salt and its associated anion in aqueous solutions. In comparison to 1-naphthol, the intramolecular hydrogen bonding in the sulfonate derivative sterically reduces the extramolecular proton dissociation k_{dis} and recombination k_{rec} rates. Despite the large differences between excited state rates in 1-naphthol-2-sulfonic acid and those in 1- and 2-naphthol, proton dissociation in all these molecules is controlled by reorientational motions of the adjacent water and requires a common $(H_2O)_{4\pm1}$ cluster as the proton acceptor. It is indeed found that k_{dis}^{-1} and k_{rec}^{-1} at different temperatures are scaled to the Debye orientation time τ_D. These findings further support the Robinson–Lee–Moore hydration model for endothermically produced protons in aqueous environments.

The increase in acidity of naphthol derivatives upon photoexcitation was first demonstrated by Förster in 1949.[1] A rate scheme incorporating proton dissociation and recombination was later formulated by Weller.[2] Since that time a considerable research effort has been focused on understanding the variation of k_{dis} and k_{rec} effected by the local solvent environment.[3-8]

Proton dissociation from 1- and 2-naphthol (1- and 2-ROH) was found to depend on a specific water structure.[4,5,8] Lee et al. correlated such a specific structure to a cluster composed of a minimum of four water molecules.[7-10] Robinson et al. further suggested that formation of such a water cluster in these weak acid systems is determined by reorientational motions of the neighboring solvent. These in turn are related to the Debye relaxation time (τ_D) of water.[7,8] Since then, molecular aspects of weak acid dissociation in aqueous solutions have been experimentally and theoretically developed. It is not clear, however, whether the model is applicable to more complicated weak acids, where intramolecular hydrogen bonding, which interferes with proton dissociation,[11,12] occurs. For example, contradictory k_{dis} and an unexpectedly large proton induced quenching rate k_q are still debatable for 1-naphthol-2-sulfonic acid (1-ROH-2-S).[11,12] In this paper it will be of interest to reevaluate systematically k_{dis},

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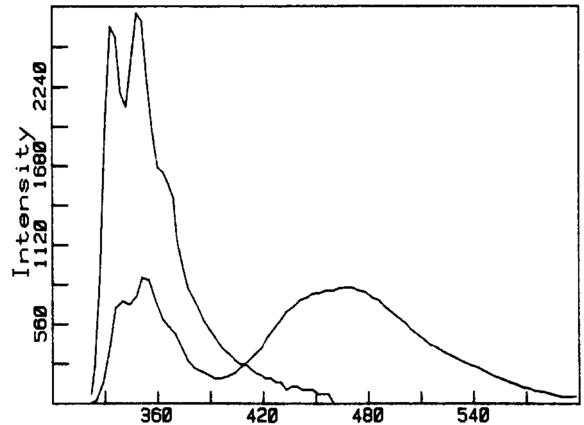

Figure 1. The emission spectra at 20 °C of 1-ROH-2-S excited at 305 nm in EtOH and H_2O. The spectrum in EtOH has no peak at 460 nm. For easy comparison, both spectra are normalized to a constant area.

k_{rec}, and k_q for 1-ROH-2-S and to compare these rates with those of 1- and 2-ROH by using picosecond laser spectroscopy.

Experimental Section

The potassium salt of 1-ROH-2-S was purchased from Kodak. It was purified by passing it through activated charcoal and recrystallizing it three times in ethanol. NMR, TLC, and melting point studies show no differences between the recrystallized and nonrecrystallized samples. This is contrary to Shapiro's findings.[11] Furthermore, the excitation spectra of the emission from the excited states of both 1-ROH*-2-S and its anion 1,2-RO$^-$*-2-S are in agreement with the absorption spectrum of 1-ROH-2-S in neutral aqueous solution. There was no discernable difference in the emission spectra or lifetimes of degassed and nondegassed samples.

Water was distilled, deionized, and passed through a NANOpure three-cartridge system. The measured resistivity of the filtered water is above 15 MΩ/cm. Acid solutions were prepared by dilution of concentrated HCl solutions (du Pont, reagent grade). The pH values between 0 and 7 were corrected by the Brönsted kinetic activity coefficient.[6,13] USP absolute ethanol (U.S. Industrial Chemical Co.) was used to prepare the aqueous alcohol mixtures. Concentrations of 1-ROH-2-S were kept below 10^{-5} M. System temperatures between 0 and 80 °C were controlled by a Borg-Warner LHP-150 heat pump and a TC-108 temperature monitor.

Absorption and fluorescence spectra were measured on a Shimadzu UV-265 spectrophotometer and a Perkin-Elmer MPF-44 fluorescence spectrophotometer. System lifetimes were determined by a time correlated single photon counting apparatus with a picosecond laser light source. The instrumental response of about 150 ps is limited by the present detection system, this time resolution being adequate however for the studies reported here. A more detailed account of the experimental apparatus and data analysis techniques have been discussed elsewhere.[7,10]

Results

Emission spectra in neutral water and alcohol solvents are shown in Figure 1. The emission bands at 360 and 460 nm are attributed to neutral 1-ROH*-2-S and the anion 1-RO$^-$*-2-S, respectively. Deprotonation from 1-ROH-2-S occurs only in water from the excited state. In pure ethanol, only emission from 1-ROH*-2-S is observed.

It was found that the 1-RO$^-$*-2-S emission decreases, while the 1-ROH*-2-S emission increases as the water temperature or water concentration in ethanol decreases. This suggests a temperature and water concentration dependent deprotonation rate. Figure 2 shows the total decay rate $k = k_{dis} + k_r + k_{nr}$ of 1-ROH*-2-S as a function of ethanol concentration at five different temperatures 0–80 °C. The activation energy ΔE determined from these data is 2.08 Kcal/mol in pure water. As the ethanol concentration increases, the temperature dependence of k_{dis} as well as its magnitude decreases. In pure ethanol, $k_{dis} = 0$, $k = k_r + k_{nr}$, and the temperature dependence on k disappears. The nonlinear decrease of k_{dis} upon addition of alcohol shown in Figure 2 has also been observed for 1- and 2-ROH[7,9] and for threshold electron ejection systems.[14] It has been suggested that the need for $(H_2O)_{4\pm1}$ as a proton (or electron) acceptor is responsible for such nonlinearity.

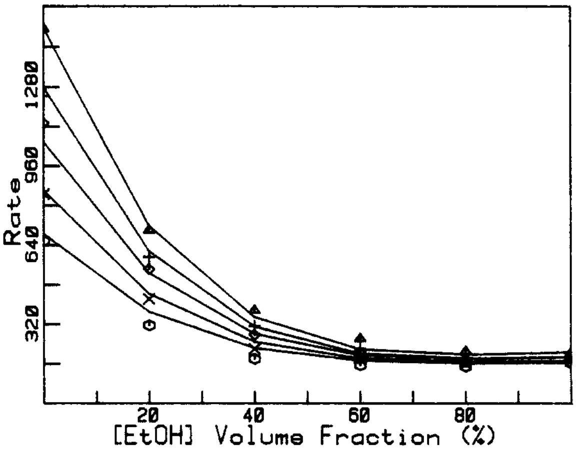

Figure 2. The total decay rate k of 1-ROH-2-S is plotted as a function of [EtOH]. The experimental values are shown by symbols. The calculated values using a water cluster of four members are shown by solid lines: (○), 273 K; (×) 293 K; (◇), 313 K; (+), 333 K; and (△), 353 K. The values along the vertical axis range from 0.32–1.28 ns^{-1}.

To explore more fully the structural effect of water on the 1-RO$^-$*-2-S proton recombination kinetics, the lifetimes of 1-ROH*-2-S and 1-RO$^-$*-2-S were measured as a function of pH. Within experimental error, the decay lifetime of 1-ROH*-2-S remains constant between pH 0 and 7. The anion 1-RO$^-$*-2-S shows a rise time $(1/\lambda_1)$ and a decay time $(1/\lambda_2)$. The rise time $1/\lambda_1$ of 1-RO$^-$*-2-S parallels the decay time of 1-ROH*-2-S. It does not change with pH. On the other hand, the decay time of 1-RO$^-$*-2-S continuously decreases as the pH decreases. Table I summarizes the values of λ_1 and λ_2 for 1-RO$^-$*-2-S at different pH and temperatures. It is worthwhile to point out that for pH $\lesssim 1$, where the 1-ROH*-2-S decay is longer than the 1-RO$^-$*-2-S decay, $1/\lambda_1$ switches with $1/\lambda_2$ to become the 1-RO$^-$*-2-S fall time, while $1/\lambda_2$ becomes the 1-RO$^-$*-2-S rise time. This is simply a mathematical consequence of combining the exponential decay of a reaction product with its buildup from a precursor to obtain the overall dynamics of the product. The shorter lived decay is always the risetime of the product. A similar effect has been observed for 1-RO$^-$*.[6]

Discussion

The Proton Acceptor, $(H_2O)_{4\pm1}$. In parallel with 1- and 2-ROH,[7-9] the evidence thus far strongly suggests that 1-ROH-2-S upon photoexcitation transfers a proton to a specific water structure in the surrounding solvent. Addition of ethanol causes this structure to be more difficult or impossible to form during the excited-state lifetime and thus reduces the proton dissociation rate k_{dis} (Figure 2). In comparison with 1-ROH*, 1-ROH*-2-S has a smaller k_{dis} and is temperature dependent. These differences may be the result of the intramolecular hydrogen bond, –OH···SO_3^- in 1-ROH-2-S, which may impose an activation barrier for the deprotonation channel. By using a transfer matrix rate scheme, it has been shown that a specific water cluster of a size at least as large as $(H_2O)_{4\pm1}$ is necessary to trigger the proton dissociation process of 1- and 2-ROH*.[7,9] It is of interest to see if a similar rate scheme applies here.

In this rate scheme, a critical cluster size of water is assumed. Knowing the rate constants at the end points, i.e., pure water and pure ethanol, the intermediate rate constants for the mixtures can be calculated without the use of further input data. The rate as a function of ethanol concentration would be expected to decrease linearly if the proton acceptor is a water monomer but nonlinearly

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if the proton acceptor is a water cluster. Comparing the calculated rates with the observed ones, a most probable cluster size can be determined. By using a cluster size of 4, the solid lines in Figure 2 give the calculated decay rates for 1-ROH*-2-S at 0, 20, 40, and 60, and 80 °C, respectively. The good agreement between experimental and calculated values is consistent with a water cluster having a minimum of four members being the effective proton acceptor for 1-ROH*-2-S. Despite the complications caused by intramolecular hydrogen bonding, 1-ROH*-2-S requires the same water configuration as 1- and 2-ROH* to activate the proton dissociation process. The agreement among these three proton donors further emphasizes the importance of microscopic water structures for solvent effects on chemical reactions in aqueous solutions.

Rate Equations. Equations 1 and 2 give the rate equations for neutral (ROH*) and anionic (RO^{-*}) species, respectively,

$$\frac{d[\mathrm{ROH}^*]}{dt} = [\mathrm{ROH}^*]_0 - \{k_0 + k_{\mathrm{dis}} + k_q[\mathrm{H}^+]\}[\mathrm{ROH}^*] + k_{\mathrm{rec}}[\mathrm{H}^+][\mathrm{RO}^{-*}] \quad (1)$$

$$\frac{d[\mathrm{RO}^{-*}]}{dt} = -\{k_0' + (k_{\mathrm{rec}} + k_q')[\mathrm{H}^+]\}[\mathrm{RO}^{-*}] + k_{\mathrm{dis}}[\mathrm{ROH}^*] \quad (2)$$

where k_0 and (k_0') and k_q (k_q') are the conventional intramolecular rate constant and the proton-induced quenching rate constant for ROH* (RO^{-*}), where ROH here means any of the three species 1-ROH, 2-ROH, or 1-ROH-2-S. k_0 (k_0') contains the radiative rate k_r (k_r') and the nonradiative rate k_{nr} (k_{nr}'). [ROH*]$_0$ is the initial concentration of ROH*. At neutral pH, where [H$^+$] is small, ROH* decays exponentially, and the decay rate can be approximated by its inverse lifetime, $\tau^{-1} = k_0 + k_{\mathrm{dis}}$. At low pH, a biexponential decay for both ROH* and RO^{-*} is expected

$$[\mathrm{ROH}^*] = \frac{[\mathrm{ROH}^*]_0}{\lambda_2 - \lambda_1}[(a - \lambda_1)e^{-\lambda_2 t} + (\lambda_2 - a)e^{-\lambda_1 t}] \quad (3)$$

$$[\mathrm{RO}^{-*}] = \frac{[\mathrm{ROH}^*]_0 k_{\mathrm{dis}}}{\lambda_2 - \lambda_1}[e^{-\lambda_1 t} - e^{-\lambda_2 t}] \quad (4)$$

where (upper sign corresponds to first subscript)

$$2\lambda_{2,1} = (a + a') \pm \{(a - a')^2 + 4k_{\mathrm{dis}}k_{\mathrm{rec}}[\mathrm{H}^+]\}^{1/2}$$

and the parameters a and a' are

$$a = k_0 + k_{\mathrm{dis}} + k_q[\mathrm{H}^+]$$

$$a' = k_0' + (k_{\mathrm{rec}} + k_q')[\mathrm{H}^+]$$

Although eq 3 predicts a biexponential decay, 1-ROH*-2-S decays exponentially for [H$^+$] ≤ 1 M. In contrast to Zaitsev's nonequilibrium argument, our result shows that the amplitude of the second component in eq 3 is too small to make any contribution to the rate process. In order to obtain accurate values of λ_1 and λ_2, eq 4 rather than eq 3 was used.[6,8] Furthermore, λ_1 measured from τ^{-1} of ROH* as well as $\tau_{\mathrm{rise}}^{-1}$ of RO^{-*} does not depend on [H$^+$] and remains relatively constant for [H$^+$] ≤ 1 M. This is caused by the accidental balance between k_{rec} and k_q. A similar phenomenon has been observed for 1-ROH.[6]

To determine k_{rec} the following equation was fitted:

$$\lambda_1 + \lambda_2 = k_0 + k_0' + k_{\mathrm{dis}} + (k_q + k_q' + k_{\mathrm{rec}})[\mathrm{H}^+]$$

Figure 3 shows the experimental (symbols) and the fitted (solid lines) data. The slopes k_s (= $k_q + k_q' + k_{\mathrm{rec}}$) for the five temperatures are summarized in Table II.

Further separation of k_q, k_q', and k_s requires steady-state quantum yield information

$$\frac{\Phi}{\Phi_0} = \frac{k_0 a'}{\lambda_1\lambda_2} \quad (5)$$

$$\frac{\Phi'}{\Phi_0'} = \frac{k_0' k_{\mathrm{dis}}}{\lambda_1\lambda_2} \quad (6)$$

Table I. λ_1 and λ_2 of 1-RO^{-*}-2-S as a Function of Temperature and pH

T (K)	pH	pH_f[a]	λ_1 (ns^{-1})	λ_2 (ns^{-1})
273	7	7	0.718	0.126
	5	5.006	0.713	0.124
	4	4.016	0.765	0.120
	2	2.136	0.783	0.352
	1	1.314	1.781	0.643[b]
	0	0.457	15.767	0.617[b]
293	7	7	1.054	0.127
	5	5.005	1.011	0.130
	4	4.015	0.965	0.132
	2	2.130	1.028	0.460
	1	1.299	2.516	0.817[b]
	0	0.432	22.195	0.714[b]
313	7	7	1.228	0.142
	5	5.005	1.291	0.145
	4	4.015	1.295	0.145
	2	2.124	1.349	0.618
	1	1.287	4.257	1.030[b]
	0	0.410	38.871	1.052[b]
333	7	7	1.392	0.158
	5	5.005	1.472	0.160
	4	4.014	1.478	0.161
	2	2.119	1.581	0.762
	1	1.276	6.687	1.127[b]
	0	0.390	62.342	1.200[b]
353	7	7	1.783	0.173
	5	5.005	1.580	0.181
	4	4.014	1.666	0.182
	2	2.115	2.262	0.821
	1	1.265	14.045	1.063[b]
	0	0.374	133.19	1.338[b]

[a] pH$_f$ is the pH corrected by the water activity and the Bronsted's kinetic activity coefficient.[6,8,13] [b] These values correspond to the decay rate of ROH.

The optimum values for k_q and k_q' and k_{rec} can be determined by the best fit of eq 5 and 6 for all the temperature and acid concentration measurements. The error in these fitted rate constants seem to be no more than 5%, but the correlations between these parameters in the fitting procedure make it difficult to assign precise error bars. The observed Φ/Φ_0 and Φ'/Φ_0' (symbols) at 20 °C are compared with the calculated values (solid lines) in Figure 4. The k_q and k_q' determined in this way are about 13 and 12 ns^{-1}, respectively, and they are included in Tables II and III for comparison. In contrast to 2-ROH*, where k_q is negligible, k_q for both 1-ROH* and 1-ROH*-2-S is of the same order of magnitude as k_{rec}. In fact, for 1-ROH*-2-S, $k_q \approx 0.4k_{\mathrm{rec}}$. The competition between k_q and k_{rec} makes the decay of neutral 1-ROH*[6] and 1-ROH*-2-S insensitive to pH variations, giving the single exponential decay.

τ_D vs τ_L Relaxation Times. Robinson et al. have presented a theory that correlates k_{dis} and k_{rec} of weak acids with the Debye relaxation time τ_D of water;[8,15] τ_D is proportional to experimental quantities such as the dielectric relaxation time τ_d. These rate expressions are described by the following equations

$$k_{\mathrm{dis}}(\mathrm{s}^{-1}) = \tau_D^{-1}\Omega e^{+\Delta S^\circ_i/R}e^{-\Delta H^\circ_i/RT} \quad (7)$$

$$k_{\mathrm{rec}}(\mathrm{M}^{-1}\,\mathrm{s}^{-1}) = \tau_D^{-1}\Omega \quad (8)$$

where reactants are at 1 M and where Ω is a steric/mobility factor introduced by Eigen and Kustin.[16] If the ionization enthalpy ΔH°_i is positive, both enthalpy and entropy factors create barriers for the dissociation reaction, and $\Delta G^\ddagger_{\mathrm{dis}} = \Delta G^\circ_i$. In comparison with Shapiro's result,[11] k_{dis} is much smaller for 1-ROH*-2-S than k_{dis}

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(15) Hasted, J. B. *Aqueous Dielectrics*; Chapman and Hall: London, 1973. On pp 21 and 22 of this reference, the difference between the dielectric relaxation time, which we label τ_d, and the microscopic or molecular relaxation time, which we label τ_D and call the Debye relaxation time, is discussed. The time τ_D is a molecular reorientational relaxation time in liquid water. It should also be noted in this discussion that the exact relationship between τ_d and τ_D, while linear, depends on the theoretical model used. Reference 8 briefly discusses the choice we have made here.

(16) Eigen, M.; Kustin, K. J. *J. Am. Chem. Soc.* **1960**, *82*, 5952.

Table II. Temperature Effects on k_{rec}

T (K)	$1/\tau_d$ (ns^{-1})	$1/\tau_D$^{a} (ns^{-1})	k_{rec}^{b} (calc)	k_{rec} (obs)	k_s (obs)	k_q^{c}	k'_q^{d}
273	55.86	63.37	15.16	16.75	32.38	8.13	7.39
293	107.52	121.98	29.18	22.67	43.67	11.00	10.00
298^e	123.46	140.06	33.50	26.73	51.49	12.97	11.79
313	172.41	195.59	46.79	38.91	74.96	18.88	17.17
333	256.41	290.89	69.59	61.00	117.50	29.60	26.91
353	333.33	378.15	90.46	127.50	245.60	61.86	56.24

[a] $1/\tau_D = 1/\tau_d \times 1.134$. This scaling factor is determined from τ_d (= 8.1 ps) and τ_D (= 7.1 ps) at 25 °C.[8,15] [b] k_{rec}(calc) = $0.24 \times 1/\tau_D$. Dimensions of k's are ns^{-1} M^{-1}. [c] $k_q = 0.25 \times k_s$(obs). The ratio 0.25 is determined from k_q/k_s(obs) at 293 K. [d] $k'_q = 0.23 \times k_s$(obs). The ratio 0.23 is determined from k'_q/k_s(obs) at 293 K. [e] The experimental k_s at this temperature is extrapolated from 293 K.

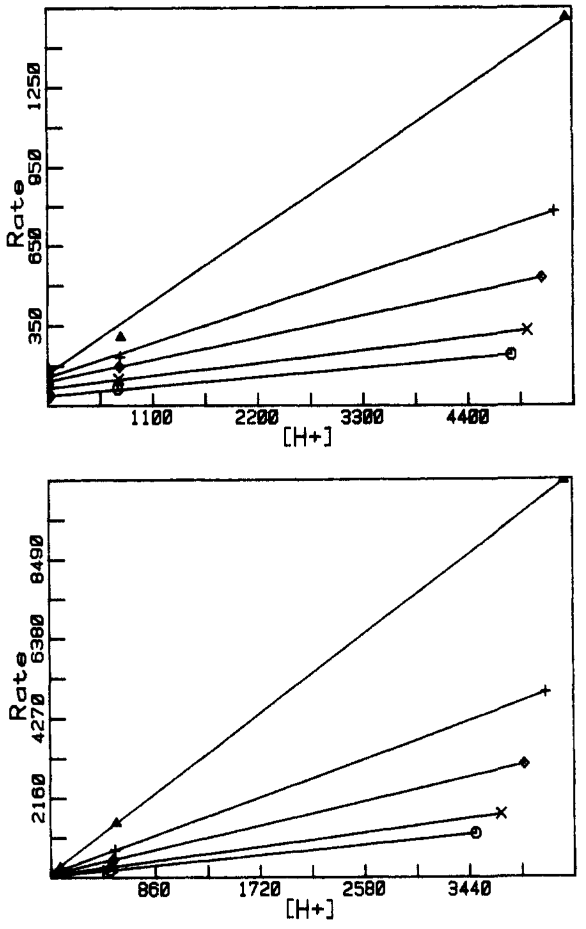

Figure 3. (a, top) $\lambda_1 + \lambda_2$ (s^{-1}) is plotted as a function of [H$^+$](M). Symbols represent the experimental values and solid lines represent the linear least-squares fitted results: (○), 273 K; (×), 293 K; (◇), 313 K; (+), 333 K; and (△), 353 K. The values on the horizontal and vertical axes are to be multiplied by 10^{-5} and 10^7, respectively. All data pH 1-7 are plotted, but only those at pH 1, 2, and 4 (from right to left) are discernible. (b, bottom) Another view of the $\lambda_1 + \lambda_2$ plot with the same units as in Figure 3a. The values on the x- and y-axes are to be multiplied by 10^{-4} and 10^7, respectively. The data here are plotted for pH 0-5. The slopes of the lines in Figure 3 (parts a and b) are the same.

for 1-ROH, while it is greater than k_{dis} for 2-ROH*. Meanwhile, k_q is the same order of magnitude as k_{rec}. On the other hand, no barriers stand in the way of the recombination reaction, and $\Delta G^{\ddagger}_{rec} = 0$. Experimental data for 2-ROH has given good agreement with this theory, showing that not only the magnitude of the prefactor for k_{dis} and k_{rec} matches τ_D^{-1} but also the temperature variations are the same.[8] In this theory, the longitudinal relaxation time τ_L plays no role in the rate-limiting process, though it is commonly used for many other types of chemical reactions in aqueous solutions.[17,18] It is of interest to see whether the rate-limiting step in 1-ROH-2-S is related to τ_D or to τ_L.

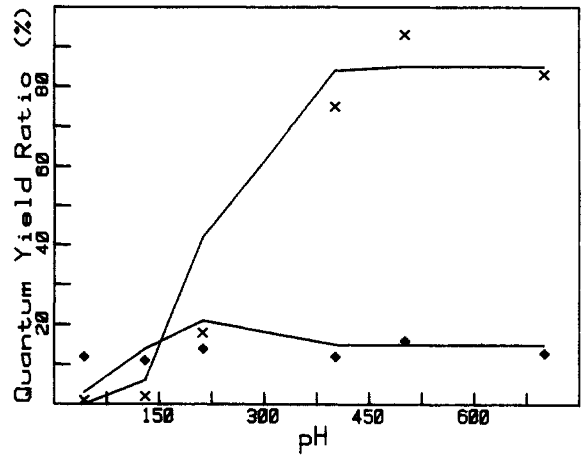

Figure 4. Φ/Φ_0 (◇) and Φ'/Φ_0' (×) are plotted as a function of [H$^+$]. Symbols represent the experimental values, and the solid lines are calculated from eq 5 and 6. The values on the horizontal axis are to be multiplied by 10^{-2}.

Table III. Rate Parameters[a] for 1-ROH, 1-ROH-2-S, and 2-ROH at 298 K

	1-ROH[b]	1-ROH-2-S	2-ROH[c]
k_0	6.8	0.143	0.115
k_0'	0.125	0.125	0.100
k_q	6	12.97	0
k_q'	33	11.79	22
k_{dis}	25	0.882	0.103
k_{rec}	68.00	33.50	58.00
k_{pf}	25.00	29.48	8.89
ΔE(kcal/mol)	0	2.08	2.64
ΔS(cal/mol/K)	−1.90	−0.25	−3.80
Ω	0.49	0.24	0.46
pK_a*	0.4	1.58	2.72

[a] The dimensions are ns^{-1} for k_0, k'_0, k_{dis}, and k_{pf} (prefactor); and ns^{-1} M^{-1} for k_{rec}, k_q, and k'_q. [b] Data for 1-ROH are obtained from ref 6, 8, and 9. [c] Data for 2-ROH are obtained from ref 4, 7, and 8.

Since k_{rec}, k_q, and k_q' represent parallel processes, their percent contribution to k_s should remain relatively constant for different temperatures. This feature provides a simplification in the analysis. Temperature effects on τ_d^{-1}, τ_D^{-1}, k_{rec}, k_q, and k_q' are summarized in Table II. It is found that $k_{rec} \ll \tau_L^{-1}$, and in fact that $k_{rec} = \Omega\tau_D^{-1}$, where $\Omega \approx 0.24$. The good agreement between calculated and observed k_{rec} for all temperatures verifies the validity of eq 8. It further supports the argument that the proton dissociation and recombination processes in 1-ROH*-2-S are controlled by the orientational motion of water molecules.

The temperature dependence of τ_D^{-1} should also affect eq 7. However, as pointed out in our previous work,[8] $\Delta G^{\circ}{}_i$ for a typical weak acid increases with increasing temperature. A near cancellation of the temperature effects on τ_D^{-1} and $\exp(\Delta S^{\circ}{}_i/R)$ is consistent with a fairly constant experimental $\Delta H^{\circ}{}_i$ over the temperature range of interest.

In a simple structureless polar solvent, theories predict that ionic hydration should relax exponentially with rate τ_L^{-1}.[17] Experiments on intramolecular charge transfer in several molecules have shown

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that these rates are indeed well correlated with τ_L^{-1}.[18] However, molecular solvation experiments[19] using time-resolved fluorescence spectroscopy have shown that this process is not controlled by τ_L. Furthermore, the relaxation is not a single exponential. Robinson et al. have suggested that using bulk water relaxation times to describe hydration dynamics of an ion depends on the ion involved.[8] For a large ion, the interaction between the ion and individual water molecules is not very specific, partly because of the large distance from the solvent to the generally delocalized charge on the ion. Little molecular reorientation of the water is required when this charge changes position or intensity, and the τ_D process is not dominant. On the other hand, for small ions, such as e^-, H^+, or OH^-, water physically wraps itself around the charge, and the ionic solvation process is more likely to be determined by τ_D. This picture is fully consistent with the 1-ROH*-2-S proton dissociation data presented here.

Table III compares the rate parameters for 1-ROH*, 2-ROH*, and 1-ROH*-2-S at 25 °C. The excited-state acidities (pK_a^*) determined from k_{dis} and k_{rec} are 0.4, 1.58, and 2.72 for 1-ROH*, 1-ROH*-2-S, and 2-ROH*, respectively. In comparison with 1-ROH*, 1-ROH*-2-S has an activation barrier that slows down proton dissociation. 1-ROH*-2-S also shows a somewhat smaller steric/mobility factor Ω than the other two molecules (0.24 vs ~0.5). This may be caused by the presence of the $-SO_3^-$ group, which could interfere with the dissociation/recombination path. In spite of these differences, all three of these excited-state weak acids require a water structure $(H_2O)_{4\pm1}$ to activate the proton dissociation channel, and furthermore the rate-limiting step is regulated by the Debye rotational time τ_D of water. The consistency between the experimental findings and the theoretical model indicates that specific structural and dynamic effects of water play an important role in these weak acid dissociations. Any sort of continuum solvent model must give an incomplete picture for these types of problems.

Conclusions

The excited-state proton dissociation/recombination in the excited state of 1-ROH-2-S has been explored in aqueous solutions. The results are compared with those from 1- and 2-ROH. The presence of intramolecular hydrogen bonding in 1-ROH-2-S causes this molecule to behave somewhat differently than 1- and 2-ROH. On the other hand, all three molecules reflect a common water structure $(H_2O)_{4\pm1}$ for accepting the dissociated proton H^+, and they reflect a common rate-limiting step, which is controlled by orientational motions in water on the time scale τ_D.

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Conformational Aspects of the Interaction of Bradykinin and Related Peptides with Sodium Dodecyl Sulfate

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Abstract: Conformational aspects of the interaction of SDS with bradykinin (BK) and related peptides were probed by CD, ^{1}H, ^{13}C, and ^{19}F NMR. The spectrum of [99% ^{13}C-2-Gly^6]bradykinin, pH 8.3, confirmed the high cis/trans ratio about the sixth peptide bond. Addition of 5.2 mM SDS broadened both the cis and trans ^{13}C resonances but only shifted the trans. Moreover, the cis/trans ratio increased substantially. Thus, the cis isomer is enhanced in the complex. ^{19}F NMR of [Gly^6,*p*-fluoro-Phe^8]bradykinin indicated that the *p*-fluoro-Phe^8 also sensed the cis and trans isomers of Pro^7. Addition of the same molar ratio of SDS:BK analogue as used for [^{13}C-2-Gly^6]BK gave a spectrum showing a similar increase in cis/trans ratio, but the cis ^{19}F NMR peak was shifted the most. The strong interactions of monomeric SDS with bradykinin and its C-terminal tetrapeptide fragment, SerProPheArg, were reflected in a generalized broadening of all ^{1}H signals accompanied by selective shifts and changes in coupling constants of some resonances. For the trans conformer of SerProPheArg the significantly shifted resonances were α- and β-Ser, β^t- and γ^t-Pro, and the ring protons of Phe. Previous and current CD spectra also indicated changes in conformation upon interaction with SDS. The presence of selective shifts of the NMR resonances bears upon the interpretation of the CD bands.

The aqueous solution structure of the peptide hormone bradykinin (BK, Arg^1-Pro^2-Pro^3-Gly^4-Phe^5-Ser^6-Pro^7-Phe^8-Arg^9) and selected analogues has been extensively investigated.[1-10] Those studies indicated that BK has, despite the three Pro residues,[6] <10% cis conformers based on the lack of multiple ^{1}H or ^{13}C peaks for a given resonance, and it has little, if any, peptide backbone hydrogen bonding (<20% of Ser^6-NH is H-bonded[6,10]) despite the predicted[10] high probabilities for γ-turns for the Pro^{2}Pro^{3}Gly^{4}Phe^5 and Ser^{6}Pro^{7}Phe^{8}Arg^9 sequences based on protein data. Those studies also showed little, if any, interaction between the Phe residues[1,4] and that all the side-chain atoms underwent rapid internal motions.[6] Consequently, in aqueous solutions BK appears to exist largely in a disordered state or at

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