

Water Structure Affected by a Weak Base

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Abstract: The behavior of the photon-initiated weak base 6-methoxyquinoline was compared in the neat solvents heptane, cyclohexane, acetonitrile, alcohols, and water and also in aqueous two-component-solvent mixtures containing alcohol, dioxane, and acetonitrile. In water, the strong intramolecular nonradiative decay rate k_{nr} competes with the intermolecular proton abstraction rate k_{ab} . Lifetime and quantum yield measurements at various temperatures show that k_{ab} in aqueous solutions is not measurably sensitive to temperature, while k_{nr} has an activation energy ΔE of about 1.25 kcal/mol. From the mixed-solvent studies, a water cluster $(H_2O)_{4\pm 1}$ is found to be the effective proton donor. The significance of this specific water cluster as a proton donor and acceptor is discussed in terms of the microscopic structure of liquid water and the hydration of $OH^-(H_2O)_3$ associated with the weak base. Surprising, perhaps, is the fact that proton transfer from a weak acid to water exactly parallels the mechanism of proton transfer to a weak base from water.

I. Introduction

Three of the most fundamental ionic constituents in chemistry are the electron, the proton, and the hydroxyl ion. Despite the fact that their static structural and dynamic properties have been comprehensively studied and characterized in terms of X-ray structure, mobility, activity coefficient, etc.,¹⁻³ there is still not a good understanding of these fundamental ions on a molecular basis.

In previous work, we have studied the influence of water structure on electron⁴⁻⁶ and proton^{6,7} transfer processes using photon-initiated e^- and H^+ donors and have shown that the presence of a cluster containing no less than 3-4 water molecules is essential for efficient activation of the e^- ejection or the H^+ dissociation process. This same kind of effect has now been observed in proton-transfer experiments employing isolated molecular clusters.⁸ To see if a common picture exists among the fundamental ions in water, it is the interest of this paper to study aqueous phase OH^- with use of photon-initiated proton extraction.

The molecule 6-methoxyquinoline (6MQ) in aqueous solutions has been found to increase its basicity substantially upon photoexcitation ($pK_a = 5.2$, $pK_a^* = 11.8$).⁹ It is capable of producing OH^- by abstracting a proton from water in its electronic excited state. The absorption and emission spectra of 6MQ and $6MQH^+$ are well separated.¹⁰ Thus 6MQ becomes an ideal molecular precursor for studying the aqueous OH^- structure without interference from ground-state processes or from congestion caused by spectral overlap.

II. Experimental Section

The 6MQ having 98% purity and 99.9% spectrophotometric grade methyl alcohol were purchased from Aldrich Chemical Co. HPLC grade

acetonitrile (ACN), heptane, and cyclohexane were purchased from the J. T. Baker Chemical Co. Ethyl alcohol of 200 proof was purchased from AAPER Alcohol and Chemical Co. Distilled water was deionized and passed through a NANOpure three-cartridge system and a 0.2 μm type FG Millipore filter. The measured resistivity of the filtered water is above 15 $M\Omega/cm$. All other chemicals and solvents were used without further purification. Concentrations of 6MQ were kept below 1×10^{-5} M. System temperatures between 0 and 80 $^\circ C$ were controlled by a Borg-Warner LHP-150 solid-state heat pump and a TC-108 temperature controller.

Absorption and emission spectra were measured on a Perkin-Elmer 559D UV-vis spectrophotometer and a MPF-44B spectrofluorimeter with a DCSU-2 intensity correction unit. A 15-ps second harmonic generated synchronously pumped dye laser pulse was used to excite 6MQ at 305 nm. The fluorescence lifetimes of the excited states $6MQ^*$ and $6MQH^{*+}$ were measured at 360 and 470 nm respectively with use of a time-correlated single-photon-counting apparatus and a standard reconvolution data analysis procedure.⁴⁻⁷

III. Results

Ground-state 6MQ shows a neutral absorption spectrum in aqueous and nonaqueous neat solvents. The excited-state molecule $6MQ^*$ emits weakly in heptane and cyclohexane, having a lifetime τ of about 320 ps at 360 nm. This relatively rapid excited-state decay is caused by the presence of a fast nonradiative intersystem crossing process in this molecule.¹¹ The lifetime τ and emission quantum yield Φ of $6MQ^*$ increase as the polarity and dielectric constant ϵ of the solvents increase. As is the case for its parent molecule quinoline,¹¹ the rapid intersystem crossing rate in $6MQ^*$ is retarded when the unpaired electrons on the nitrogen atom become involved in hydrogen bonding with proton-donating solvents.

In water, a new band from $6MQH^{*+}$ at 450 nm appears (Figure 1). The lifetime curve for $6MQH^{*+}$ exhibits a risetime τ'_{rise} corresponding to the decay time τ (1.8 ns, at room temperature) of $6MQ^*$ and a long decay time τ' of about 23 ns (Figure 2). Furthermore, excitation spectra monitored at 360 and 450 nm coincide with the absorption spectrum of 6MQ. Thus $6MQH^{*+}$ is produced from $6MQ^*$ by an excited-state proton-abstraction process. The additional intermolecular proton-abstraction rate k_{ab} in aqueous solution shortens the lifetime of 6MQ, thus reversing the τ vs ϵ correlation in other polar solvents.

Increasing the temperature reduces the intensity of the emission spectrum of $6MQH^{*+}$ weakly but moderately quenches that of $6MQ^*$ with an activation energy of about 1.25 kcal/mol. Figure 1 shows emission spectra of $6MQ^*$ in water at 0 and 60 $^\circ C$. Since $6MQH^{*+}$ emission is insensitive to temperature, the temperature dependence of the $6MQ^*$ kinetics is attributed to its intramolecular k_{nr} rate. Confirming this is the fact that a similar temperature

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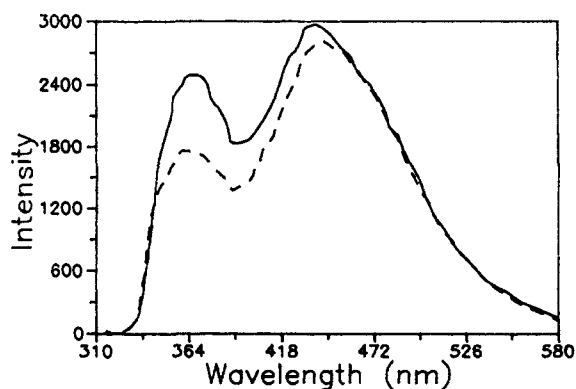


Figure 1. 6MQ* emission spectra in water at 0 °C (solid line) and 60 °C (dashed line). The peak near 360 nm is from the neutral molecule 6MQ*, while the peak near 450 nm is from the cation 6MQH**.

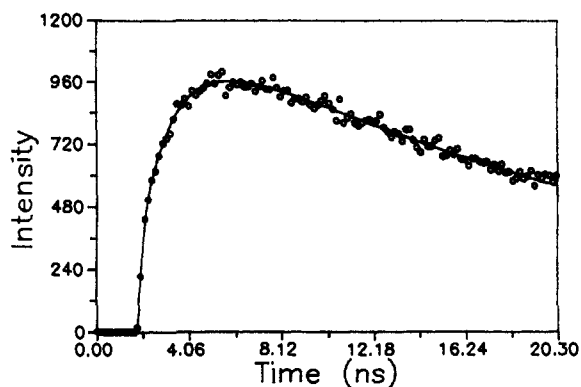


Figure 2. The rise (1.7 ns) and decay (23 ns) of 6MQH** in water at room temperature. The circles represent the experimental data. The solid line represents the fitted curve.

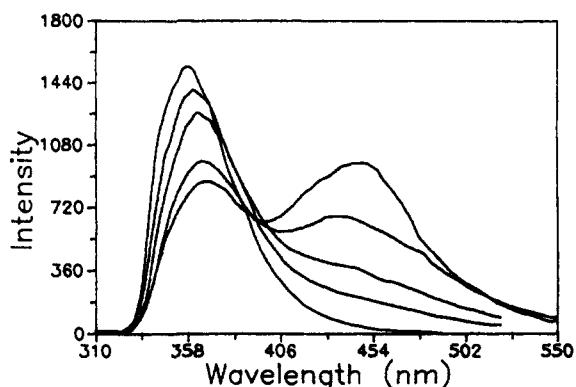


Figure 3. 6MQ* and 6MQH** emission spectra in ethanol-water mixtures at room temperature. The spectra of 6MQH** at 450 nm correspond to 0, 10, 20, 30, and 50% ethanol volume fractions from top to bottom, respectively. The corresponding spectra of neutral 6MQ* at 360 nm increase in intensity from bottom to top. The curves are automatically normalized, since a constant concentration of 6MQ (1×10^5 M) was used for all mixtures.

dependence was observed for 6MQ* emission in methyl and ethyl alcohol solvents. Adding alcohol or ACN to water retards the production of 6MQH** from 6MQ*. The 6MQ* emission spectra in 0, 10, 20, 30, and 50% ethanol-water mixtures at room temperature are plotted in Figure 3. The 6MQH** band decreases nonlinearly as a function of ethanol, dioxane, or ACN concentrations and is almost completely absent when a concentration of 50% of these solvents is reached. It is worthwhile to point out that an analogous nonlinear behavior has been observed for e^- and H^+ donating molecules in aqueous alcohol mixtures.⁴⁻⁷

IV. Rate Constants and Quantum Yields

The extremely large k_{nr} for quinoline and its derivatives in non-hydrogen-bonded solvents has been extensively studied and

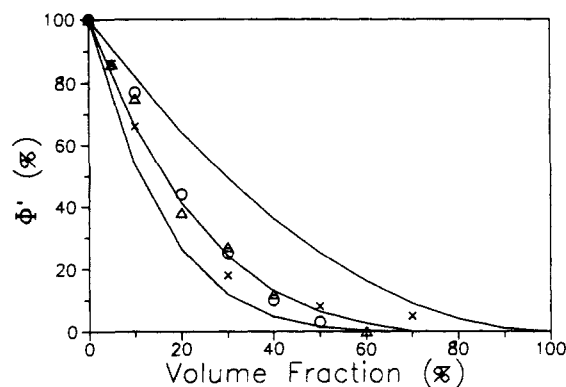


Figure 4. Normalized quantum yields of 6MQH** as a function of ethanol (O), dioxane (Δ), and ACN (x) volume fractions. The solid lines from top to bottom correspond to calculated data for cluster sizes 2, 4, and 6, respectively.

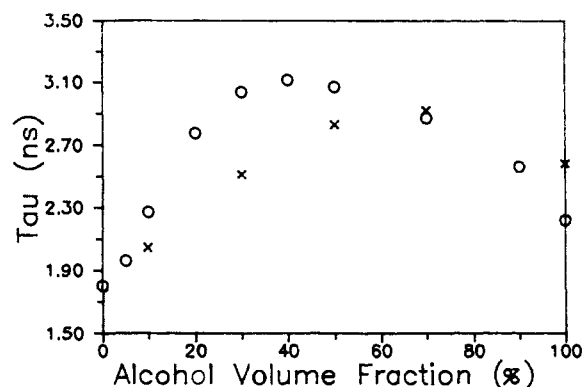


Figure 5. The decay lifetime of 6MQ* as a function of ethanol (O) and methanol (x) volume fractions at room temperature.

attributed to the instability of the unpaired electron at the nitrogen atom.¹¹ On the other hand, the rate k_{nr} decreases in solvents where $N \cdots H-O$ hydrogen bonding stabilizes the unpaired electron and retards the intersystem crossing process. In aqueous solutions, the intermolecular hydrogen bond of 6MQ in its electronic excited state becomes strong enough to abstract a proton from the solvent and the molecule relaxes through both its cationic⁹ and neutral states.

A quantum yield Φ' of 6MQH** can be obtained by comparing the integrated intensity of 6MQH** with that of the total emission intensity from 6MQH** and 6MQ*. The needed information at various ethanol, dioxane, and ACN concentrations is contained in plots such as those shown in Figure 3. Relative Φ' values normalized to that in pure water can then be plotted against solvent concentration as in Figure 4. In contrast to the sharp decrease of Φ' noted in Figure 4, the decay lifetime τ of 6MQ* shows only a slight increase upon addition of the nonaqueous solvent (Figure 5). This is a result of the fact that $k_{nr} \gg k_{ab}$ in aqueous solvents. The large intramolecular nonradiative rate causes the lifetime data for the proton abstraction by 6MQ* to be relatively insensitive to the composition of the solvent mixtures, and these data are thus of less interest in the analysis of the proton-abstraction process.

The phenomenological rate equations for [6MQ*] and [6MQH**] can be written in terms of k_{ab} and the proton dissociation rate constant k_{dis} in the following way

$$\frac{d[6MQ^*]}{dt} = -(k_0 + k_{ab})[6MQ^*] + k_{dis}[6MQH^{**}] \quad (1a)$$

$$\frac{d[6MQH^{**}]}{dt} = -(k_0' + k_{dis})[6MQH^{**}] + k_{ab}[6MQ^*] \quad (1b)$$

where k_0 (k_0') is the intramolecular rate constant for the neutral (cationic) excited-state molecule 6MQ* (6MQH**). To agree with the experimental observations (1) that in neutral water 6MQ* decays exponentially and (2) that 6MQH** has a rise time

Table I. Rate Parameters^a for 6MQ*

k_r , ns ⁻¹	k_{ab} , ns ⁻¹	k_{nr}^0 , ns ⁻¹	ΔE , kcal/mol
0.046	0.12	3.88	1.25

^aTotal rate = $k_r + k_{ab} + k_{nr}^0 \exp[-\Delta E/k_B T]$.

corresponding to the decay of 6MQ*, $k_{dis}[6MQH^{**}]$ in eqs 1 and 2 must be negligibly small. With this simplifying condition, solutions for eqs 1a and 1b are readily found,

$$[6MQ^*] = [6MQ^*]_0 e^{-(k_0+k_{ab})t} \quad (2a)$$

$$[6MQH^{**}] = \frac{k_{ab}[6MQ^*]_0}{k_0 + k_{ab} - k_0'} [e^{-k_0't} - e^{-(k_0+k_{ab})t}] \quad (2b)$$

Integrating eqs 2a and 2b, $t = 0$ to $+\infty$, yields theoretical expressions for the quantum yields Φ and Φ' of 6MQ* and 6MQH^{**}

$$\Phi = \frac{[6MQ^*]_0}{k_0 + k_{ab}} \quad (3a)$$

$$\Phi' = \frac{[6MQ^*]_0 k_{ab}}{k_0'(k_0 + k_{ab})} \quad (3b)$$

where $[6MQ^*]_0$ is the initial 6MQ* concentration. The only parameters to be determined in these two equations are k_0 and k_{ab} . Their values are 0.45 and 0.12 ns⁻¹, respectively. In a pH 13 aqueous solution, where proton abstraction is unimportant, the measured τ for 6MQ* is about 2.3 ns. The agreement between τ (pH 13) and $1/k_0$ determined from eqs 3a and 3b is very good. However, 0.12 ns⁻¹ is not in very good agreement with the 0.2 ns⁻¹ for k_{ab} obtained indirectly from pOH jump measurements.¹² The discrepancy may be caused by the fact that k_0 is rather larger than k_{ab} . This creates an uncertainty when attempting to extract k_{ab} from the sum $(k_0 + k_{ab})$. The determined kinetic constants are summarized in Table I.

V. Water Clusters

Adding alcohol, dioxane, or ACN to water retards the proton-abstraction process of 6MQ*. Furthermore, the degree of retardation is nonlinearly dependent on the concentration of the nonaqueous solvent (Figures 3 and 4). As mentioned earlier, a similar retardation process has been found for electron⁴⁻⁶ and proton^{6,7} donor systems. With use of a transfer matrix rate scheme,⁴ a water cluster $(H_2O)_{4\pm 1}$ was found to be the e⁻ and H⁺ acceptor. The necessary formation of this cluster is responsible for the nonlinear dependence on the concentration of the nonaqueous solvent.

This transfer matrix scheme can be applied to the present proton-abstraction process and requires only knowledge of the rate constants in the appropriate neat solvents. The rate constants of the neutral species 6MQ in mixtures are linearly scaled with the intramolecular rate constants in the neat solvents. The intermolecular proton abstraction is assumed to be k_{ab} for the pure water cluster of size N and 0 for hybrid clusters containing fewer water molecules. By adjusting the matrix size, thus the water cluster size N, this scheme is then capable of fitting both the time decay and the steady state quantum yield data as a function of mixed solvent concentrations.⁴ The matrix size that gives the best agreement with the experimental results provides the most probable minimum water cluster size needed to solvate OH⁻.

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Since the lifetime of 6MQ* increases only slightly from water to alcohol (Figure 5), the calculated decay lifetimes in water-alcohol mixtures are rather insensitive to the cluster size and are thus incapable of identifying the correct solvent structure. However, the drastic change of the 6MQH^{**} quantum yield Φ' as a function of alcohol, dioxane, or ACN concentrations provides a useful parameter for this purpose. The calculated results using cluster size 2, 4, and 6 are shown as solid curves in Figure 4. A water cluster of four members is seen to give the best agreement with the experiment. Consequently, in order for 6MQ* to abstract a proton rapidly from water, a structure $(H_2O)_4$ with specific geometry is needed, suggesting that $OH^-(H_2O)_3$ forms the core of the final solvation structure of OH⁻ in water. Put another way, no proton can dissociate from liquid water, at least on the time scale of the 6MQ* lifetime, unless this specific water cluster exists in the neighborhood of 6MQ*.

Although there is no activation barrier associated with k_{ab} , the highly structured $OH^-(H_2O)_3$ imposes a large entropy barrier to the proton-transfer process and reduces the magnitude of k_{ab} appreciably. The transformation of a loosely bound group of liquid water molecules into the rather stiffly structured $OH^-(H_2O)_3$ causes this entropy change. If the rate-limiting step for the formation of $OH^-(H_2O)_3$ is similar to that for the formation of $H_3O^+(H_2O)_3$, this rate depends on the Debye orientation time of water molecules.^{7,13} With these assumptions, an activation entropy of about -6 cal·(mol/K)⁻¹ can be estimated.

VI. Conclusions

Photoexcited 6MQ can abstract a proton from water, and this system can thus act as a molecular precursor for the ultrafast formation of hydrated OH⁻. The small proton-abstraction rate for 6MQ* is attributed to the fact that a large entropy is required for the formation of highly structured $OH^-(H_2O)_3$ from free water molecules in the liquid state. Replacing water with alcohol, dioxane, or ACN does not affect the decay lifetime of 6MQ* appreciably. On the other hand, the emission intensity of the cation 6MQH^{**} is very sensitive to the presence of these nonaqueous solvents. The nonlinear decrease in the quantum yield of 6MQH^{**} as a function of alcohol, dioxane, or ACN concentration supports the idea of a special water cluster being involved in the dynamics. In fact, the behavior for OH⁻ is surprisingly similar to that found for proton dissociation in photon-initiated weak acids and for electron dissociation in indole,^{5,15} 8,1-ANS,^{5,15} TNS,⁴ and 2-AN.¹⁴ With use of a random walk transfer matrix scheme, the dynamics of all these charge-transfer systems can be analyzed in an analogous manner. A water cluster containing about four members is shown to provide the minimum requirement for triggering the charge-transfer process and concomitant hydration of e⁻, H⁺, or OH⁻.

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(15) Good correlations between rates, using extremely intense light, and quantum yields, using extremely weak light, of precursors, and the hydration properties of aqueous e⁻, H⁺, and now OH⁻, rule out two-photon effects in these aqueous studies. However, some workers still insist that hydrated electrons are not produced from precursors such as 8,1-ANS in aqueous systems by one-photon excitation. See, for example: Ebbesen, T. W.; Ghiron, C. A. *J. Phys. Chem.* **1989**, *93*, 7139. While we have no arguments with this interpretation in nonaqueous systems, current direct detection studies being carried out in our laboratory have settled this point once and for all for aqueous systems.