

Hydrolysis Kinetics of Photoexcited 6-Methoxyquinoline in Aqueous Acetonitrile Solutions

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6-Methoxyquinoline undergoes pseudo-first-order hydrolysis and its conjugate acid, second-order proton abstraction by hydroxide ion, in the lowest excited singlet state. The proton transfer kinetics in water containing acetonitrile up to a mole fraction of about 0.1 have been evaluated as a function of acetonitrile concentration. At mole fractions above 0.13 of acetonitrile, proton transfer does not occur. At mole fractions below 0.1 steady-state and pulsed-source fluorimetries show the rate constant for hydrolysis to decrease exponentially with the mole fraction of acetonitrile. This is believed to be due to penetration of the aqueous solvent cage of the 6-methoxyquinoline by acetonitrile rather than to specific solvation by the organic cosolvent. The rate of neutralization of the conjugate acid by hydroxide ion is found to vary only slightly and depends on the bulk dielectric properties of the solvent.

KEY WORDS: 6-Methoxyquinoline; aqueous acetonitrile; hydrolysis kinetics.

INTRODUCTION

Mixed organic-aqueous solvents are used to enhance solubilities of substances sparingly soluble in water, chemical properties (e.g., acidity) for analytical purposes, and separation of complex mixtures in liquid chromatography. Often it is desired to extrapolate properties determined in mixed solvents to the values they would have in pure water. This is difficult because solvation and molecular transport can be far more complicated in mixed solvents than in pure solvents. The kinetics of proton transfer of electronically excited acids and bases are affected by the solvent composition in ways which reflect the solvations of the reactants and products and the influences of their structures upon ionic or molecular diffusion. Moreover, excited-state proton transfer occurs in organic solvents only when a substantial amount of water is present [1-3], suggesting that

water structure plays a major role in fast proton transfer. If the relationships between solvent composition and proton transfer rate constants can be accurately evaluated, a greater understanding of the nature of solvent-solvent and solvent-solute interactions and better predictability of properties of solutes in aqueous solutions may result. In particular, it may be possible to determine the activities of the components of binary solvent systems.

Fluorimetric, steady-state pH titrations [4,5] coupled with fluorescence decay time measurements may be used to determine rate constants k_b and k_a for pseudo-first-order base hydrolysis and second-order proton abstraction by OH^- . To date, however, the influence of solvent composition on the hydrolysis of weak bases in the lowest excited singlet state has been studied only in aqueous ethanol solutions and no study of the reverse reaction, the abstraction of H^+ from the conjugate acid by OH^- , has been undertaken in any mixed solvent. Because of our interest in the role the solvent composition might play in the kinetics of hydrolysis and proton abstraction, the present study of the photohydrolysis of 6-methoxyquinoline was undertaken.

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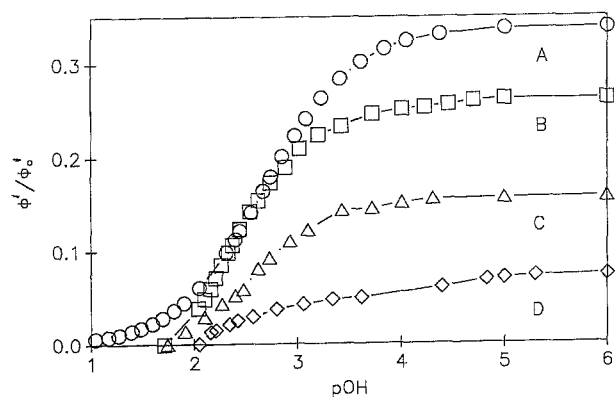


Fig. 1. Variation of the relative quantum yield of fluorescence (ϕ'/ϕ_o) of 6-methoxyquinolinium cation with the logarithm of hydroxide ion concentration ($[\text{OH}^-]$) at various mole fractions of acetonitrile (X_{MeCN}) in aqueous acetonitrile: A ($X_{\text{MeCN}} = 0$); B ($X_{\text{MeCN}} = 0.037$); C ($X_{\text{MeCN}} = 0.079$); D ($X_{\text{MeCN}} = 0.128$).

EXPERIMENTAL

Materials

6-Methoxyquinoline was purchased from Pfaltz and Bauer, Inc., Westbury, CT, and purified by vacuum distillation. Acetonitrile (HPLC grade) was stored over Davison 4-Å molecular sieves; 5.0 M sodium hydroxide and perchloric acid (analytical grade) were purchased from Fisher Scientific Co., Fairlawn, NJ.

Absorption measurements were made on a Cary Model 219 spectrophotometer. Steady-state fluorescence measurements were made at 25°C on a Perkin Elmer LS-5 fluorescence spectrophotometer whose monochromators were calibrated against the xenon line emission spectrum. A Lauda K-4R water bath was used in association with the spectrophotometers to maintain the temperature constant at 25°C. Fluorescence decay times were measured on a TRW Model 31B decay time fluorometer. A Gilmont Pipetman micropipet was used to deliver water and cosolvent mixtures.

Methods

A 10^{-2} M ethanolic stock solution of 6-methoxyquinoline was prepared prior to experimentation. A known volume of the stock solution was then micropipetted into a series of 10-ml volumetric flasks and the aliquot was evaporated under a stream of nitrogen gas. The residue was brought to volume by the addition of a known concentration of acid or base along with a specific volume of organic cosolvent to give the mole fraction of interest. The final concentration of 6-methoxy-

quinoline in each test solution was 5×10^{-6} M. The probe concentration was chosen to keep the absorbance at the excitation wavelengths below 0.02 absorbance unit, thereby minimizing the nonlinearity of fluorescence with concentration dependent absorbance changes.

Titrations were performed as follows:

(1) Two milliliters of a test solution of known mole fraction of organic cosolvent was pipetted into a 1-cm² cuvette having a 3 ml volume and the emission spectrum was obtained.

(2) The above solution was titrated with an aqueous acetonitrile solution, 1.00 M in sodium hydroxide and 5×10^{-6} M in 6-methoxyquinoline, so that the concentration of the latter remained constant throughout the titration. Fluorescence spectra were scanned immediately after each increment of titrant was added to minimize acetonitrile hydrolysis catalyzed by the alkaline medium and the titration was carried out until the fluorescence of the 6-methoxyquinolinium cation could no longer be observed. Calculation of the ionic strength at each point in the titration was carried out using the formal concentration of the sodium hydroxide at each point. Activity coefficients were calculated using dielectric constants for acetonitrile water solutions found in the literature [6–8].

RESULTS AND DISCUSSION

The dependences of the relative quantum yields of fluorescence of 6-methoxyquinoline, in solvents containing varying molar ratios of acetonitrile and water, on the formal hydroxide ion concentration $[\text{OH}^-]$ are shown in Fig. 1. At formal hydrogen ion concentrations greater than 1×10^{-4} M, the cation is the sole absorbing and emitting species. In the interval 1×10^{-5} M $> [\text{OH}^-] > 1 \times 10^{-9}$ M, the neutral molecule is the sole absorber. However, fluorescence is observed from the cation as well as from the neutral molecule. This results from the protonation, in the lowest excited singlet state, of the nitrogen atom of the directly excited neutral molecule [9]. In this region of acidity or alkalinity, the relative quantum yields of fluorescence of the neutral molecule, ϕ/ϕ_o , and of the cation, ϕ'/ϕ'_o , are invariant with respect to $[\text{H}^+]$ and $[\text{OH}^-]$ and are related to the kinetics of protonation in the excited state, in mixed aqueous organic solvents as well as in water, by [5, 9]

$$\left(\frac{\phi'/\phi'_o}{\phi/\phi_o}\right) = k_b \tau_o \quad (1)$$

where k_b is the rate constant for protonation of 6-meth-

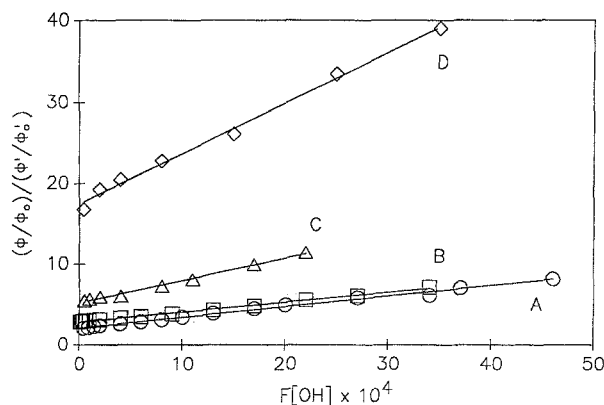


Fig. 2. Plots of $(\phi/\phi_0)/(\phi'/\phi'_0)$ vs $F[\text{OH}^-]$ for 6-methoxyquinoline in aqueous acetonitrile. A ($X_{\text{MeCN}} = 0$); B ($X_{\text{MeCN}} = 0.037$); C ($X_{\text{MeCN}} = 0.079$); D ($X_{\text{MeCN}} = 0.128$).

oxyquinoline in, and τ_0 the lifetime of, the excited state. It was previously shown for 6-methoxyquinoline in aqueous ethanol that $(\phi'/\phi'_0)/(\phi/\phi_0)$ and, therefore, $k_b\tau_0$ vary exponentially with the mole fraction of organic cosolvent [5] and that the slope of the plot of $\log k_b\tau_0$ against X_c , the mole fraction of cosolvent, is a function of the activity of water and the distance separating the fully hydrated hydrogen ion and the fully hydrated conjugate base in the encounter complex [5] (or solvent separated ion pair).

At $[\text{OH}^-] \geq 1 \times 10^{-5} M$, the fluorescence of the neutral 6-methoxyquinoline increased with increasing $[\text{OH}^-]$ in all solvent mixtures, becoming maximal in about 0.1 M NaOH. At the same time, the fluorescence of the conjugate acid decreased and eventually disappeared, concomitant with the increase in fluorescence from the neutral molecule. This behavior is typical of an *N*-heterocyclic compound and corresponds to deprotonation of the excited conjugate acid subsequent to hydrolysis of the conjugate base [9]. At $[\text{OH}^-] < 1 \times 10^{-5} M$, the kinetics of deprotonation are such that there is not enough $[\text{OH}^-]$ present to deprotonate the cation measurably, during the lifetime of the excited state, τ'_0 . In the alkaline region where ϕ/ϕ_0 and ϕ'/ϕ'_0 vary with $[\text{OH}^-]$ (Fig. 2), the relationship between them is given by [5,9]

$$\frac{\phi/\phi_0}{\phi'/\phi'_0} = \frac{1}{k_b\tau_0} + \frac{k_a\tau'_0}{k_b\tau_0} F[\text{OH}^-] \quad (2)$$

where k_a is the rate constant for deprotonation of the 6-methoxyquinoline cation (BH^+) in the excited state and F is the Bronsted kinetic activity factor [10,11], which corrects each experimental value of k_a to zero ionic strength in the solvent mixture chosen and is given by

$$-\log F = \frac{2A\sqrt{\mu}}{1 + aB\sqrt{\mu}} \quad (3)$$

where μ is the ionic strength. A is related to the dielectric constant ϵ and the absolute temperature T by [12,13]

$$A = 1.826 \times 10^6 (\epsilon T)^{-3/2} \quad (4)$$

B is related to ϵ by

$$B = 5.031 \times 10^9 (\epsilon T)^{-1/2} \quad (5)$$

and a is the mean distance of closest approach of the fully solvated $[\text{OH}^-]$ and the 6-methoxyquinoline cation, which when calculated from the slope of $\log k_b\tau_0$ versus X_{MeCN} was found to be 8.0 Å [14].

Values of ϵ , A , and B for various acetonitrile water mixtures at 25°C, in which fluorimetric titrations were carried out, are given in Table I. As shown in Fig. 2, plots of $(\phi/\phi_0)/(\phi'/\phi'_0)$ versus $F[\text{OH}^-]$ are linear up to at least $[\text{OH}^-] = 0.004 M$. The ordinate intercepts of these lines, which according to Eq. (2), should correspond to $(k_b\tau_0)^{-1}$, agree well with the corresponding terms calculated from Eq. (1). Although $k_b\tau_0$ is extremely solvent dependent, $k_a\tau'_0$ (Table I) is virtually independent of the mole fraction of acetonitrile in the solvent up to $X_{\text{MeCN}} = 0.128$, the highest amount of acetonitrile that could be present and still allow a reasonable fluorimetric titration with OH^- to be evaluated (at higher X_{MeCN} excited-state proton transfer is almost nonexistent).

The fluorescence decay times of 6-methoxyquinoline and its protonated form were found to be 10.8 ± 0.7 and 23.7 ± 0.4 ns in water [14] and were invariant in the water-alcohol solutions up to a mole fraction of acetonitrile (X_{MeCN}) of about 0.13. These lifetimes and the values of $k_a\tau'_0$ taken from Fig. 2 were used to calculate the rate constants k_b and k_a listed in Table I.

A plot of $\log k_b$ vs X_{MeCN} , shown in Fig. 3, is linear with a slope m of -10.7 ± 0.2 and has the equation

$$\log k_b = \log k_b(0) + mX_{\text{MeCN}} \quad (6)$$

which transforms directly to

$$k_b/k_b(0) = e^{2.303 m X_{\text{MeCN}}} \quad (7)$$

where $k_b(0)$ is the pseudo-first order rate constant for photohydrolysis in pure water. In Eq. (7) the term $k_b/k_b(0)$ may be taken as the probability that acetonitrile will not interfere with the hydrolysis reaction, an assumption that allows a physical interpretation of the slope m .

The probability P_n that n acetonitrile molecules penetrate a sphere of radius R around a reactant (excited

Table I. Rate Constants k_b and k_a for the Pseudo-First-Order Hydrolysis and Second-Order Proton Abstraction by Hydroxide Ion of 6-Methoxyquinoline and Its Conjugate Acid, Respectively, in Partially Aqueous Solutions Containing Various Mole Fractions (X_{MeCN}) of Acetonitrile

Volume percentage acetonitrile	X_{MeCN}	k_b ($\text{s}^{-1} \times 10^{-7}$) ^a	k_b ($\text{s}^{-1} \times 10^{-7}$) ^b	k_a ($M^{-1} \text{s}^{-1} \times 10^{-10}$)
0	0	4.6 ± 0.3	4.3 ± 0.3	2.4 ± 0.2
10	0.037	3.3 ± 0.2	3.3 ± 0.2	1.8 ± 0.2
20	0.079	1.7 ± 0.1	1.8 ± 0.1	2.2 ± 0.2
30	0.128	0.78 ± 0.06	0.55 ± 0.04	1.7 ± 0.1

^aCalculated with the aid of Eq. (1).

^bCalculated from the ordinate intercepts in Fig. 2.

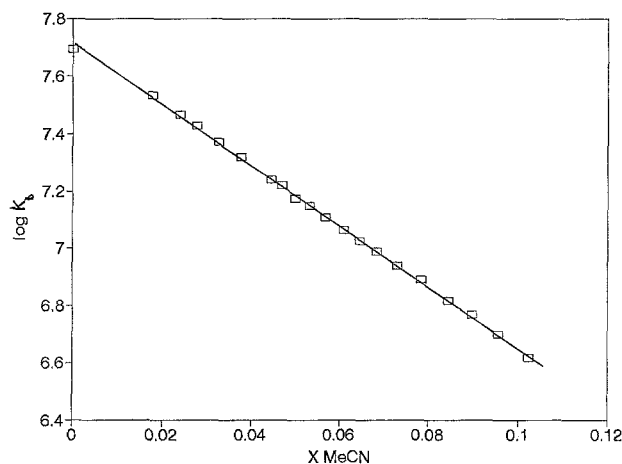


Fig. 3. Plot of the variation of the logarithm of the photohydrolysis rate constant k_b of 6-methoxyquinoline with the mole fraction of acetonitrile, X_{MeCN} , in acetonitrile-water solutions.

6-methoxyquinoline) molecule is given by the Poisson distribution [15].

$$P_n = \frac{\lambda^n}{n!} e^{-\lambda} \quad (8)$$

where

$$\lambda = \frac{4/3\pi R^3 N_0 X_{\text{MeCN}}}{V_{\text{MeCN}}} \quad (9)$$

N_0 is Avogadro's number and V_{MeCN} is the partial molar volume of acetonitrile, which may be approximated as the ratio of its molecular weight to its density ($V_{\text{MeCN}} = 52.2 \text{ cm}^3$). λ is therefore the product of the mole fraction of acetonitrile and the ratio of the volume of the hydration "sphere of action" to the molecular volume of acetonitrile. If $k_b/k_b(o)$ is taken as the probability that no acetonitrile has entered the "sphere of action" of excited 6-methoxyquinoline, then $n = 0$ and

$$k_b/k_b(o) = P_0 = e^{-\lambda} \quad (10)$$

It follows from Eqs. (9) and (10) that

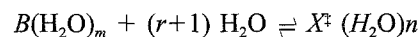
$$2.303m = [-4/3\pi R^3 N_0] / V_{\text{MeCN}} \quad (11)$$

and if $m = 10.7 \pm 0.2$, we can calculate that

$$R = 8.0 \times 10^{-8} \text{ cm}$$

This result is quite close to the $7.5 \times 10^{-8} \text{ cm}$ usually taken as a mean value for the interionic separation in an encounter complex or solvent separated ion pair in a proton transfer reaction [16]. We may therefore interpret R as the distance through which the proton must travel from a water molecule to an accepting 6-methoxyquinoline molecule, unimpeded by the interruption of water structure in the vicinity of the base by acetonitrile.

The slope of the plot of $\log k_b$ vs X_{MeCN} also appears to be related to the activities of water in the various solvents. If the hydrolysis proceeds through a transition state (or encounter complex) $X^\ddagger(\text{H}_2\text{O})_n$ according to



where $r + 1 = n - m$ (one water molecule splits to protonate B and form the hydroxide ion), then, if the activity coefficients of $B(\text{H}_2\text{O})_m$ and $X^\ddagger(\text{H}_2\text{O})_n$ can be assumed to be equal, the rate of the hydrolysis reaction is given by

$$k_b[\text{BH}^+] = k_b(o)[\text{BH}^+]a_w^{r+1} \quad (12)$$

or

$$\log k_b = \log k_b(o) + (rH)\log a_w \quad (13)$$

A plot of $\log k_b = \log k_b$ vs $\log a_w$ is shown in Fig. 4 and has a slope of 7, suggesting that a cluster of six water molecules intervenes between the conjugate acid and the hydroxide ion in the encounter complex $\text{BH}^+//\text{OH}^-$.

Interestingly, the rate constant for proton abstraction from the excited 6-methoxyquinolinium cation by

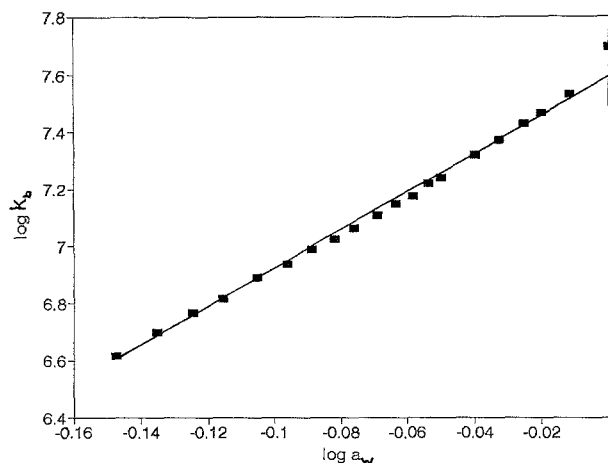


Fig. 4. Plot of the variation of the logarithm of the photohydrolysis rate constant k_b of 6-methoxyquinoline with the logarithm of the activity of water in acetonitrile-water solutions.

hydroxide ion is minimally influenced by the mole fraction of acetonitrile over the range of solvent composition in which the reaction was amenable to study. This reaction appears to be diffusion controlled and is affected by the solvent only insofar as the dielectric behavior of the latter permits. The implication of this is that the ability of the organic cosolvent to “structure” water around it has a substantially greater effect upon the rate of hydrolysis, which is governed largely by the rates of desolvation and resolvation of the participant species, than upon the rate of proton abstraction, which depends, in the main, on the existence of an extended network of hydrogen bonds between the water molecules. This is probably the result of the OH^- ion requiring electronic translational motion to “hop” across hydrogen bonds,

whereas the resolvation of B and H_2O requires rotational motions of water molecules, which are much more influenced by the “tightness” of hydrogen bonds caused by structuring. Further experiments are being carried out to assess the role of the organic cosolvent in the proton transfer process.

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