Kinetics of Excited-State Proton Transfer of Doubly Protonated 2-Aminoacridine

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2-Aminoacridine has been used to extend the quantitation of excited-state proton-transfer kinetics in concentrated acid media to $\cong 13\ M$ sulfuric acid. The reasons for the large discrepancy between the excited-state dissociation constant determined from kinetic measurements and that calculated from a thermodynamic cycle are discussed.

INTRODUCTION

It has been about 50 years since Weller [1,2] first elucidated the quantitative relationship between the acidity dependences of the fluorescence of aromatic acids and bases and the kinetics and equilibria of their proton transfers in both the ground and the excited states. Weller's equations accurately describe the reactions of interest only when they occur in dilute, aqueous solutions. A treatment using a Hammett acidity function and taking account of water as a reactant [3], however, has been successfully used to quantitate the excited-state proton-transfer kinetics of molecules which have neutral conjugate bases and singly charged conjugate acids and which ionize in concentrated acid media (pH $\ll$1) [3,4]. The derivation in ref. 3 may be applied to molecules with monocationic conjugate bases and dicationic conjugate acids by modifying the derivation to include H_+ instead of H_0 (the Hammett acidity function for molecules with neutral conjugate bases and monocationic conjugate acids). When this is done, the relationship between the relative quantum yields of fluorescence of conjugate acid and base and the acidity function becomes

$$\frac{\Phi/\Phi_0}{\Phi'/\Phi_0' - \alpha_b} a_w^r = \frac{1}{k_a(0)\tau_0} + \frac{k_b(0)\tau_0'}{k_a(0)\tau_0} \times h_+ a_w^n \frac{\Phi'/\Phi_0'}{\Phi'/\Phi_0' - \alpha_b}$$

(1)

which, when the ground- and excited-state inflection regions are well separated, so that $\alpha_b = 0$, as is the case here, becomes

$$(\Phi/\Phi_0/\Phi'/\Phi_0')a_w^r = 1/k_a(0)\tau_0 + \frac{k_b(0)\tau_0'}{k_a(0)\tau_0} h_+ a_w^n \quad (2)$$

where a_w is the activity of water, $h_+ = \text{antilog}(-H_+)$, and α_b is that fraction of the ground-state population which is found as the conjugate base. The relative quantum yield of fluorescence of the conjugate acid, Φ/Φ_0, is given as the quotient of Φ, the fluorescence efficiency of the conjugate acid under the occurrence of excited-state proton transfer, and Φ_0, the fluorescence efficiency of the isolated conjugate acid ($\Phi = \Phi_0$ when $H_+ \ll pK_a^*$). The relative quantum yield of fluorescence of the conjugate base, Φ'/Φ_0', is analogous to Φ/Φ_0. The lifetimes τ_0 and τ_0' are, respectively, the fluorescence decay times of the conjugate acid and base. The exponent n represents the number of water molecules which are required in the deprotonation reactions for the Hammett indicator used to determine the H_+ scale over that region of acidity in which the excited-state reaction of interest occurs. The exponent r is the number of water molecules which react

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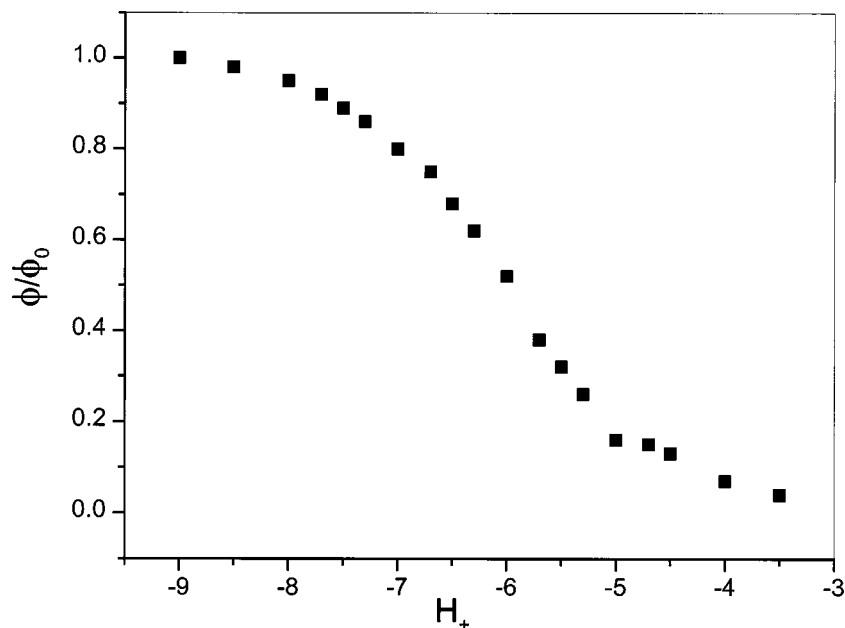[2] To whom correspondence should be addressed. Fax: 352-392-9455.

Fig. 1. Relative quantum yield of fluorescence (Φ/Φ_0) of 2-aminoacridine as a function of H_+.

with the excited conjugate acid to form the transition-state or activated complex species which is common to the excited-state protonation and deprotonation reactions. The rate constants $k_a(0)$ and $k_b(0)$ correspond to the pseudo-first-order deprotonation of the conjugate acid and the second-order protonation of the conjugate base, respectively, as if the reaction were occurring at infinite dilution in pure water.

The present work demonstrates the applicability of Eq. (2) to the excited-state proton transfer of 2-aminoacridine.

EXPERIMENTAL

A sample of 2-aminoacridine was a gift from Dr. D. Jackman (Utah State University). Pure 2-aminoacridine was obtained with atmospheric-pressure liquid chromatography using silica as the stationary phase. The com-pound was gradient eluted from the column with methanol:chloroform (5 vol% MeOH in $CHCl_3$ to 40 vol% MeOH in $CHCl_3$). Purity was confirmed by thin-layer chromatography on silical gel using 5 vol% MeOH in $CHCl_3$ as the mobile phase, which was alkalinized by the addition of 1 drop of NH_4OH.

A description of the instrumentation used may be found elsewhere [3]. A 1.9×10^{-5} M solution of 2-aminoacridine was used for all uv–visible absorption studies and for the determination of the fluorescence life-times. The solution used for the fluorescence titration was 1.9×10^{-6} M in 2-aminoacridine. Fluorescence was excited at 349 nm (an isosbestic point in the absorption spectrum), and an analytical wavelength of 495 nm was used in the analysis of the fluorescence spectra.

Sulfuric acid solutions were made with analytical-grade H_2SO_4 and deionized, distilled water. All acid solu-tions were checked for spurious emission prior to being used.

Table I. Low-Frequency Absorption (ν_a) and Fluorescence (ν_a) Maxima and Fluorescence Decay Times (τ_0) and Ground-State pK_a [15] of Doubly and Singly Protonated 2-Aminoacridine

	$\bar{\nu}_a$ (cm$^{-1} \times 10^{-4}$)	$\bar{\nu}_f$ (cm$^{-1} \times 10^{-4}$)	$\bar{\nu}_{0-0}$ (cm$^{-1} \times 10^{-4}$)[a]	τ_0 (ns)	pK_a
Dication	2.49	2.11	2.30	7.8 ± 0.1	1.1
Monocation	2.17	1.69	1.93	7.9 ± 0.3	

[a] The estimated frequencies of the 0–0 bands (pure electronic transitions) are obtained for each species by averaging the low-frequency absorption and fluorescence maxima for each species.

Table II. Rate Constants and pK_a^* of the Prototropic Dissociation 2-Aminoacridine Dication in the Lowest Excited Singlet State

$k_a(0)$ (s^{-1})	$k_b(0)$ (M^{-1} s^{-1})	pK_a^* (25°C)
$1.2 + 0.1 \times 10^{10}$	$4.9 \pm 0.5 \times 10^5$	$-4.39 + 0.06^a$
		$-6.7 + 0.3^b$

[a] Calculated as $pK_a^*(0) = -\log[k_a(0)/k_b(0)]$.
[b] Estimated from the Förster cycle [12] and the data in Table I.

Values of a_w were taken from Refs. 6 and 7. Values of H_+ up to 7 M H_2SO_4 were taken from Ref. 8. Lovell and Schulman [9], in a redetermination of the H_+ scale in H_2SO_4, have shown that the values of H_+ in Ref. 8 for $H_2SO_4 > 7$ M are in error. H_+ data for $H_2SO_4 > 7$ M should, therefore, be taken from Ref. 9. Lovell and Schulman also observed that H_+ and H_0 are identical when $H_2SO_4 > 7$ M, and hence, the H_0 data found in Refs. 10 and 11 could be used as H_+ over the applicable concentration range.

The fluorescence lifetimes of mono- and diprotonated 2-aminoacridine were measured at pH = 4.01 and $H_+ = -8.7$, respectively.

RESULTS AND DISCUSSION

The relative quantum yield of fluorescence of dicationic 2-aminoacridine is shown in Fig. 1 as a function of H_+. The inflection region of the titration occurs in sulfuric acid between the concentrations of $\cong 8$ M H_2SO_4 and $\cong 15$ M H_2SO_4. Table I lists the spectral maxima and fluorescence decay times of the conjugate acid and base.

According to Eq. (1), a plot of $[(\Phi/\Phi_0)/(\Phi'/\Phi_0')]$ a_w^r vs $h_+ a_w^n$ should be linear and have a slope of $k_b(0)\tau_0'/k_a(0)\tau_0$ and an ordinate intercept of $1/k_a(0)\tau_0$. Figure 2 is a plot of this type for 2-aminoacridine, with $n = 2$ and $r = 1$ (other values of n and r do not fit the data because the plots are not linear). Thus, one molecule of water enters into the ground-state indicator reaction and two into the excited-state 2-aminoacridine dication dissociation reaction. Several other molecules [3] have reactions with hydration requirements of three or four water molecules, but those reactions occur in acid such that $[H_2SO_4] \le 6$ M (in which $a_w \ge 0.48$). The relatively low hydration requirement of the 2-aminoacridine reaction may be due to the relative scarcity of water in the medium ($0.15 \ge a_w \ge 0.008$) over the inflection region of the titration and may reflect less than the extent of hydration that would be observed in dilute acidic aqueous solutions.

Table I lists the low-frequency absorption and fluorescence maxima as well as the ground-state pK_a of the dication and monocation derived from 2-aminoacridine.

Table II presents $k_a(0)$, $k_b(0)$, and $pK_a^*(0) = -\log k_a(0)/k_b(0)$ as calculated from the slope and intercept of the line in Fig. 2. Also included in Table II is pK_a^*(F.C.), which is pK_a^* calculated from the Förster
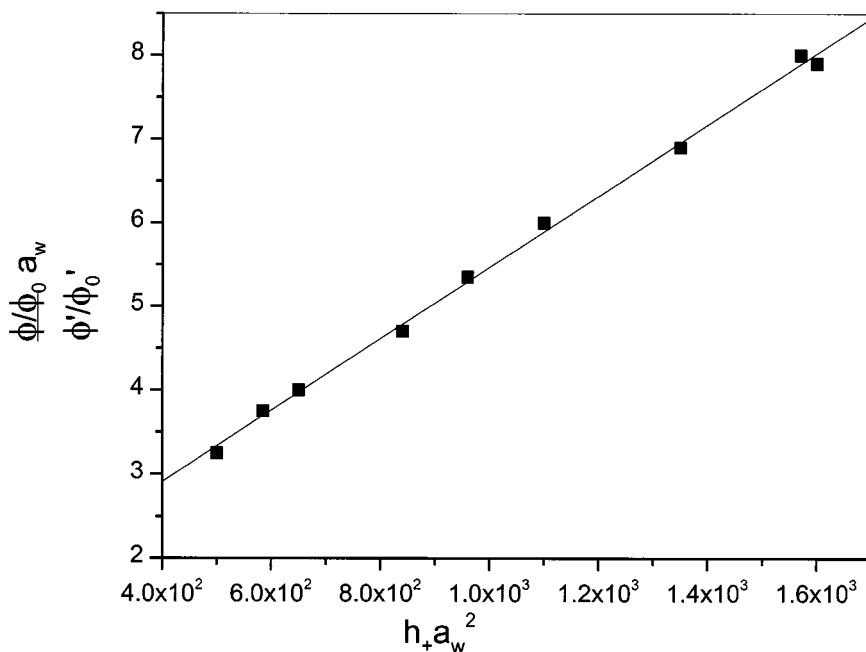
Fig. 2. Plot of $[(\Phi/\Phi_0)/\Phi'/\Phi_0')]$ a_w^r vs $h_+ a_w^n$ for 2-aminoacridine, with $n = 2$ and $r = 1$.

cycle) [12] and the data in Table I. The agreement between pK_a^*(0) and pK_a^*(F.C.) is poor, showing a disparity of 2.3 log units. Normally a discrepancy of no more than 0.3 log unit is observed between excited-state equilibrium constants measured by both methods. The discrepancy is likely due to differences in hydration numbers between the species extant in concentrated acid, where the kinetic measurements were made, and in dilute aqueous solutions, where the spectra of the monocation were taken. These difference can lead to increments in the entropy of dissociation [13] and in the enthalpies of hydration and solvent relaxation which are not reflected in the Förster cycle calculation. This subject is currently under study in this laboratory.

An earlier study [14] showed that for proton-transfer reactions to reach equilibrium during the lifetime of the lowest excited singlet state, the rate of the dissociation reaction must be much higher than the rate of photophysical deactivation of the excited conjugate acid. The product of the dissociation rate constant and the lifetime of the lowest excited singlet state of the dication is 91, suggesting that excited-state proton transfer is much faster $(1.2 \times 10^{10}$ s$^{-1})$ than photophysical deactivation of the excited dication $(1.3 \times 10^8$ s$^{-1} = 1/\tau_0)$ and that 2-aminoacridine does attain a near-equilibrium situation between its photoexcited dication and monocation. The attainment of prototypic equilibrium in the lowest excited singlet state appears to be considerably more common in reactions represented by fluorimetric titration curves whose inflection regions lie in acidity regions corresponding to concentrated mineral acid solutions than in those corresponding to dilute aqueous solutions. This is undoubtedly a reflection of the greater acidity of the conjugate acids of the reactions occurring in concentrated acidic media.

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