Proton-Transfer Kinetics of Photoexcited 7-Hydroxy-1-Naphthalenesulfonic Acid in Aqueous Formamide Solutions

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The monoanion of 7-hydroxy-1-naphthalenesulfonic acid (HNS) undergoes pseudo-first order dissociation and its conjugate base, second order protonation in the lowest excited singlet state. The proton transfer kinetics in water containing formamide up to a mole fraction of about 0.95 have been evaluated as a function of formamide concentration. At mole fractions above 0.95 of formamide, proton-transfer does not measurably occur. At mole fractions below 0.95, steady state and pulsed-source fluorimetries show the rate constant for dissociation to decrease exponentially with increasing mole fraction of formamide. This is believed to be due to penetration and disruption of the aqueous solvent cage of the HNS by formamide, resulting in impairment of the Grotthus proton-transfer mechanism.

KEY WORDS: hydroxynaphthalenesulfonic acid; proton transfer kinetics; formamide.

INTRODUCTION

The kinetics of proton transfer of electronically excited acids and bases are affected by solvent composition in ways which reflect the solvations of the reactants and products and the influences of solvent association upon ionic or molecular diffusion. Excited state intermolecular proton transfer, has up to now, been shown to occur 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 and the pH of binary solvent systems. Recently, it was observed in this laboratory that photo-dissociation of hydroxyaromatics occurred in formamide-water solutions up to a mole fraction of about 0.95 of formamide, a considerably less aqueous solvent than any observed to sustain proton transfer on the nano-second time scale, to date.

The present study is a continuation on the formamide-water system with 7-hydroxy-1-naphthalenesulfonic acid (HNS) as the model hydroxyaromatic. As shown in Scheme 1, HNS has two possible proton dissociation processes in both ground and excited states. When the solvent was pure water, we have found that the pKa value for proton dissociation from monoanion to dianion in the ground state was 9.47 ± 0.02 (unpublished data); while in the excited state in pure water, rate constant of protonation from dianion to monoanion, k_b was calculated to be $2.8 \pm 0.2 \times 10^{10} \text{ s}^{-1} \text{ M}^{-1}$, based on the life time of dianion in alkaline solution measured to be 13.5 ± 0.5 nanosecond and $k_b \tau_0$ being 381 ± 6.

Because of our interest in the role that the solvent composition might play in the kinetics of proton

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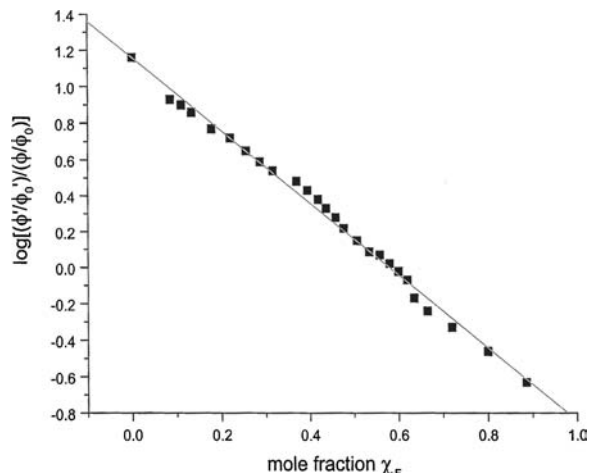
ground state proton dissociation of 7-hydroxy 1-naphthalenesulfonic acid (HNS)

excited state proton dissociation of 7-hydroxy 1-naphthalenesulfonic acid (HNS)

Scheme 1. Proton dissociations of 7-hydroxy 1-naphthalenesulfonic acid.

transfer, the dependence of the fluorescence and the photodissociation of HNS in different formamide-water compositions was measured.

EXPERIMENTAL

Materials

Potassium salt of 7-hydroxy-1-naphthalenesulfonic acid (HNS, 99^+%) was purchased from TCI Organic Chemicals, Inc., Portland, OR and used as received. Formamide (HPLC grade), was stored over Davison 4 Å molecular sieves. 5.0 M sodium hydroxide and sulfuric 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-50 fluorescence spectrophotometer whose monochromators were calibrated against the Xenon line emission spectrum. A Lauda K-4/R water bath was used in association with the spectrophotometers to maintain constant temperature at 25°C. Fluorescence decay times were measured on a PRA (Oak Ridge, TN) model 510C time-correlated, single-photon counting, decay-time fluorometer interfaced with a computer to deconvolute the fluorescence decay from the lamp-pulse characteristics. A Gilmont Pipetman micropipette was used to deliver water and cosolvent mixtures.

Methods

Fluorimetric steady-state pH titrations [4,5] with fluorescence excited at an isosbestic point (so that intensity is proportional to fluorescence quantum yield), coupled with fluorescence decay time measurements was used to determine rate constants k_a for pseudo-first order dissociation (shown in Scheme 1).

A 10^{-3} M methanolic stock solution of HNS 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 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 HNS in each test solution was 2×10^{-6} M. The probe concentration and excitation wavelength were chosen to keep the absorbance at the excitation wavelength below 0.02 absorbance unit.

Titrations were performed as follows:

1. Two milliliters of a test solution of known mole fraction of formamide (X_F) were pipetted into a 1 cm^2 cuvette having a 3 mL volume and the emission spectrum was obtained.

2. The above solution was titrated with an aqueous formamide solution, 0.83 M in sulfuric acid and 2×10^{-6} M in HNS, so that the concentration of the latter remained constant throughout the titration. Fluorescence spectra were scanned immediately after each increment of titrant was added and the titration was carried out until the fluorescence of the HNS dianion could no longer be observed. Because in this work we were interested only in the dissociation rate constant, k_a, effort was concentrated on the 1×10^{-4} M > [H$^+$] > 1×10^{-7} M region where fluorescence efficiency is independent of [H$^+$], so that k_a could be evaluated.

Fig. 1. Variation of log $(\phi'/\phi'_o)/(\phi/\phi_o)$, the ratio of the relative fluorescence efficiencies of the dianion to that of the monoanion derived from 7-hydroxy-1-naphthalenesulfonic acid with the mole fraction of the formamide X_F in formamide-water solutions where 1×10^{-4} M > $[H^+]$ > 1×10^{-7} M.

RESULTS AND DISCUSSION

In the $[H^+]$ concentration interval of interest here, 1×10^{-4} M > $[H^+]$ > 1×10^{-7} M, the monoanion is the sole absorber. However, fluorescence is observed from the dianion as well as from the monoanion. This results from the dissociation, in the lowest excited singlet state, of the hydroxy group of the directly excited monoanion [4,5]. In this region of acidity the relative quantum yields of fluorescence of the monoanion, ϕ/ϕ_o, where ϕ is the quantum yield of fluorescence at intermediate $[H^+]$ and ϕ_o, that at high $[H^+]$ ($[H^+] > 0.2$ M, where the monoanion is the sole emitting species) and of dianion, ϕ'/ϕ'_o, where ϕ' is the quantum yield of fluorescence at intermediate $[H^+]$ and ϕ'_o that at high $[OH^-]$ ($[OH^-] > 1 \times 10^{-2}$ M, where the dianion is the sole emitting species) are invariant with respect to $[H^+]$ and are related to the kinetics of dissociation in the excited state, in mixed aqueous organic solvents as well as in water, by [4,5]:

$$\frac{\phi'/\phi'_0}{\phi/\phi_0} = k_a \tau_0 \qquad (1)$$

where k_a is the rate constant for dissociation of HNS, and τ_0 the lifetime of the HNS monoanion in the lowest excited singlet state. It was previously shown for 2-hydroxybiphenyl in aqueous alcohols that $(\phi'/\phi'_o)/(\varphi/\varphi_o)$ and therefore $k_a\tau_0$ varies exponentially with the mole fraction of organic cosolvent [3].

At $[H^+] \geq 1 \times 10^{-4}$ M, the fluorescence of the monoanion HNS increased with increasing $[H^+]$ in all sol-

vent mixtures becoming maximal in about 0.2 M H_2SO_4. The ratio of the fluorescence intensity in neutral solution to that in 0.2 M H_2SO_4 is ϕ/ϕ_o. At the same time, the fluorescence of the dianion decreased and eventually disappeared, concomitant with the increase in fluorescence from the monoanion. This behavior is typical of a hydroxyaromatic compound and corresponds to protonation of the excited conjugate base subsequent to dissociation of the conjugate acid [4]. At $[H^+] < 1 \times 10^{-4}$ M, the kinetics of protonation are such that there isn't enough H^+ present to protonate the dianion measureably, during the lifetime of its excited state, τ'_0. The fluorescence decay-time of monoanionic HNS is 7.03 ± 0.06 ns and is virtually invariant in the interval $0 < X_F < 0.95$. This lifetime and the values of $k_a\tau_0$ calculated from Eq. (1) and the experimental values of the relative quantum yields of fluorescence of the dianion and monoanion, respectively, were used to calculate the rate constants, k_a, listed in Table I.

A plot of log k_a vs X_F (Fig. 1) is linear with a slope m, of -2.2 ± 0.1 and has the equation:

$$\log k_a = \log k_a(o) + m X_F \qquad (2)$$

which transforms directly to

$$k_a/k_a(o) = \exp(2.303 \times m X_F) \qquad (3)$$

where $k_a(o)$ is the pseudo-first order rate constant for photo-dissociation in pure water. In Eq. (3), the term k_a/k_a(o) may be taken as the probability that formamide will not interfere with the dissociation reaction, an assumption that allows a physical interpretation of the slope m.

Table I. Variation of the Relative Fluorescence Efficiency ϕ'/ϕ'_o of the Dianion Derived from 7-Hydroxy-1-Naphthalenesulfonate and the Ratio of the Relative Fluorescence Efficiency of the Dianion to that of the Monoanion $[k_a\tau_0 = (\phi'/\phi'_o)/(\phi/\phi_o)]$ with the Mole Fraction of Formamide X_F in Solution where 1×10^{-4} M > $[H^+]$ > 1×10^{-7} M

X_F	ϕ'/ϕ'_o	$k_a\tau_0 =$ $(\phi'/\phi'_o)/(\phi/\phi_o)$	$k_a \times 10^{-9}$ (s^{-1})
0	0.95 ± 0.03	18.2 ± 0.6	2.6 ± 0.1
0.10	0.87 ± 0.03	6.92 ± 0.2	0.98 ± 0.05
0.20	0.85 ± 0.03	5.75 ± 0.2	0.82 ± 0.04
0.30	0.77 ± 0.02	3.39 ± 0.1	0.48 ± 0.03
0.40	0.72 ± 0.02	2.51 ± 0.08	0.36 ± 0.02
0.50	0.60 ± 0.02	1.51 ± 0.04	0.21 ± 0.01
0.60	0.49 ± 0.02	0.95 ± 0.03	0.14 ± 0.01
0.70	0.35 ± 0.01	0.55 ± 0.02	0.078 ±0.01
0.80	0.26 ± 0.01	0.35 ± 0.01	0.050 ± 0.01
0.90	0.19 ± 0.01	0.23 ± 0.01	0.033 ± 0.01
0.95	0.08 ± 0.01	0.09 ± 0.03	0.01 ± 0.01

Note. k_a is the rate constant for photo-dissociation and τ_0 is the decay time of the monoanion in S_1 state.

The probability, P_n that n formamide molecules penetrate a sphere of radius R around a reactant (excited monoanionic HNS) molecule is given by the Poisson distribution [6]

$$P_n = \frac{\lambda^n}{n! e^{-\lambda}} \qquad (4)$$

where

$$\lambda = \frac{(4/3)\pi R^3 N_o X_F}{V_F} \qquad (5)$$

N_0 is Avogadro's number, and V_F is the partial molar volume of formamide, which may be approximated as the ratio of its molecular weight to its density ($V_F = 39.7$ mL/mol). λ is therefore, the product of the mole fraction of formamide and the ratio of the volume of the hydration "sphere of action" to the molecular volume of formamide. If $k_a/k_a(o)$ is taken as the probability that no formamide has entered the "sphere of action" of excited monoanionic HNS, then $n = 0$ and

$$k_a/k_a(o) = P_0 = e^{-\lambda} \qquad (6)$$

It follows from Eqs. (5) and (6) that

$$2.303 \, m = [-4/3\pi R^3 N_0]/V_F \qquad (7)$$

and if $m = -2.2 \pm 0.1$, we can calculate that

$$R = 4.3 \times 10^{-8} \text{ cm.}$$

This result is reasonably close to the $(6.5–7.5) \times 10^{-8}$ 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 [7]. We may therefore, interpret R as the mean distance through which the proton must travel to the proton-accepting water molecule which becomes resolvated as a hydronium ion, from a dissociating monoanionic HNS molecule, unimpeded by the interruption of water structure in the vicinity of the excited acid by formamide.

CONCLUSION

The range of formamide-water composition over which excited state proton transfer can be quantitated ($0 \le X_F \le 0.95$) is the widest yet observed for any cosolvent mixed with water. Previously, acetonitrile-water and methanol-water [3,5] showed the highest range over which excited state proton transfer could be observed (up to a mole fraction of the organic cosolvent of 0.51). This is most likely related with the smaller collision diameter R in formamide-water than in the other two mixed solvents, which probably allows more efficient separation of dianion from the conjugate base. The molecular details are not yet well understood and work is continuing in this area to elucidate the details.

REFERENCES

1. N. M. Trieff and B. R. Sundheim (1965). The effect of solvent on the acid-base kinetics of the excited state of .beta.-naphthol. *J. Phys. Chem.* **69**, 2044–2059.
2. D. Huppert and E. Kolodney (1981). Picosecond proton transfer studies in water-alcohols solutions. *Chem. Phys.* **63**, 401–410.
3. S. G. Schulman and R. W. Townsend (1993). Determination of accurate and thermodynamically significant pH in alcohol/water solutions. *J. Pharm. Sci.* **82**, 771–775.
4. A. Weller (1952). Fluorescence shifts of naphthols. *Z. Elektrochem & Ang. Phys. Chemie* **56**, 662–668.
5. R. W. Townsend and S. G. Schulman (1992). Acidity of hydroxybiphenyls in the lowest excited singlet state: the influence of substituent orientation. *Chimica Oggi.* **10**, 49–52.
6. J. M. Frank and S. I. Vavilov (1931). Effective spheres in the extinction process in the fluorescent liquids. *Z. Phys.* **69**, 100–110.
7. M. Eigen (1954). Ionic reactions in aqueous solutions with half-times as short as 10^{-9} s. Applications to neutralization and hydrolysis reactions. *Disc. Faraday Soc.* **17**, 194–205.