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interaction and that perhaps only full quantum chemical calculations of ^{17}O chemical shifts can provide the desired insight on the origins and determining factors of the ^{17}O chemical shifts in these compounds.²⁵

(25) Changing bond lengths and bond angles in a quantum chemical calculations of the ^{17}O chemical shifts in model compounds did not show the trends observed in the experimental values. This may be due to the method and basis set used in the calculations and/or the model compounds selected for the study.

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Dynamics of Proton Transfer from Photon-Initiated Acids in Alcohol/Water Mixtures

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Proton transfer from the excited state of 8-hydroxypyrene-1,3,6-trisulfonate (HOPTS) to water is studied in water/alcohol mixtures. The very fast time-dependent decay observed in water becomes slower as the concentration of alcohol is increased, and the decay is single exponential in pure alcohol. The addition of CaCl_2 and urea to the solvent mixture is observed to enhance the dissociation rate of excited HOPTS. These results have been explained by two mechanisms, the geminate dissociation-recombination model and the effect of the water structure. Both mechanisms are believed to contribute to the decay rate of aromatic acids in water/alcohol mixtures.

Introduction

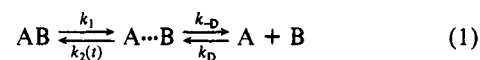
The study of reactions of acids and bases is a fundamental part of chemistry. Although this subject has been under study for a long time,¹⁻⁵ the exact nature of the process and the role played by the surrounding solvent molecules are often only speculations. Picosecond and femtosecond spectroscopic methods have now made it possible to study these proton-transfer reactions during the very first moments of dissociation and to discuss in more detail the mechanisms of the proton-transfer process. For example, measurements of the rates of proton transfer to the water have revealed the importance of the solvent structure at very short time scales.^{6,7}

The acid-base equilibrium constant of the electronically excited state molecules, $K^* = k_1/k_2$, as defined in scheme 1, can be significantly different from that in the ground state, $K_g = k_a/k_b$. The rate of deprotonation may increase by several orders of magnitude upon electronic excitation where it is known that in some cases $\Delta pK_a = pK^* - pK_g$ may reach 29 units.²

A lot of work has been done on weak aromatic acids such as 1-naphthol⁷ and 2-naphthol^{6,8,9} where the pK^* is between 2.5 and 3.5. However, the lower the pK^* value, the faster is the deprotonation which may, in turn, give more insight into the deprotonation mechanism and the interaction with the solvent molecules. In this paper we present part of our results on 8-hydroxypyrene-1,3,6-trisulfonate (HOPTS) shown in Figure 1, having a pK^* value between 1.4 and 0.5.¹⁰ Therefore, HOPTS is possibly a better candidate than 2-naphthol for this type of study and hence is expected to give a clearer understanding of the nature of the deprotonation process. The fast deprotonation of HOPTS could be the reason for its different observed decay profile from that of 2-naphthol. In fact, contrary to 2-naphthol, which shows a monoexponential decay in aqueous solutions, HOPTS exhibits a nonexponential decay profile.

In a recent series of publications, Pines et al.^{10,11} and Agmon^{12,13} have, comprehensively, analyzed the behavior of HOPTS in aqueous media using the time-dependent diffusion equation.

On one hand, for the reaction scheme I, the fast decay has been explained by the geminate dissociation-recombination mechanism.



In this case k_1 is the intrinsic dissociation rate of the acid at the contact distance " r_{AB} ". The value of k_1 is assumed to be time independent and depends only on the type of solvent. Within a certain distance R_∞ from the deprotonated species, which is the radius of the Coulomb cage for the ions, the proton may recombine geminately with the anion. k_2 is the geminate recombination rate which is, therefore, a function of time. Outside the Coulomb cage, the process can be described as a diffusion of the proton with k_D and k_{-D} rate parameters. On the other hand, the decay at longer times is explained by the diffusion scheme giving rise to a $t^{-3/2}$ dependence.

In this paper, we present our work on HOPTS in water/methanol and water/propanol mixtures. The effect of the addition of CaCl_2 and urea to the water/methanol mixtures has also been investigated and analyzed.

Our experimental results in a pure water solvent agree quite well with the model proposed by Pines et al.^{10,11} However, in light of our results in the water/alcohol mixtures and the CaCl_2 and urea effects, we believe that the assumption of constant k_1 is not well justified. In this paper, we try to relate k_1 to the activity of

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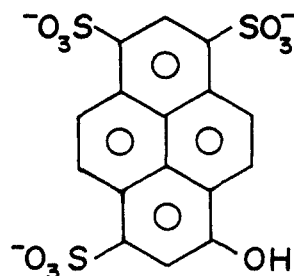


Figure 1. Molecular structure of HOPTS.

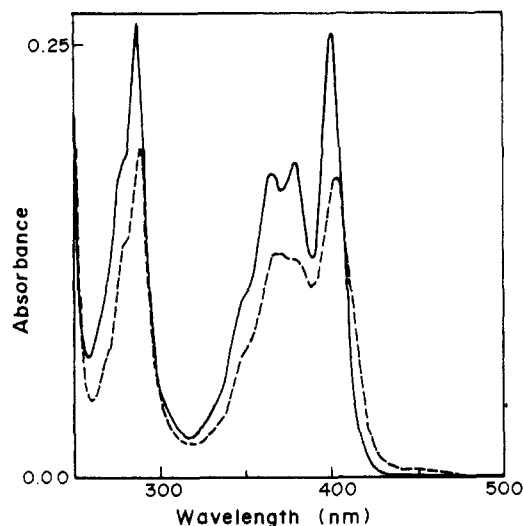


Figure 2. Absorption spectra of HOPTS in methanol (—) and (---) water.

the solvent and show the important role of the water structure in the deprotonation reactions in the fast time domain.

Experimental Section

Materials. The sodium salt of 8-hydroxypyrene-1,3,6-trisulfonate (HOPTS) supplied through the Institute of Physical Chemistry, Stuttgart, was used without further purification. Methanol and propanol were of spectral grade. Urea and CaCl_2 were purchased from Aldrich Chemical Co. Alcohol/water mixtures having alcohol concentrations of 0%, 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80%, 90%, and 100% were prepared in volume fractions. The pH values of around 5 for the solutions were not affected in any of the experiments to be reported here, except in the CaCl_2 experiment. When CaCl_2 is added to the HOPTS in methanol/water mixtures, the color has slightly changed to green which cleared after the addition of a drop of very dilute HCl. In all experiments, concentrations of HOPTS were kept at 10^{-5} M. The temperature at which all experiments were done was around 23.5°C , i.e., the room temperature.

Apparatus and Procedure. Absorption spectra were recorded with a Bausch and Lomb Spectronic 2000 spectrophotometer. Extra care was taken in recording the base line of spectra. Fluorescence spectra were recorded with a SPF-500 spectrofluorimeter from SLM Instruments Inc. The excitation wavelength was slightly changed from one sample to another to ensure that the absorbance value is the same. Fluorescence spectra were also corrected for lamp intensity and photomultiplier sensitivity. Lifetimes were measured by using the picosecond Applied Photophysics photon counting system described elsewhere.¹⁴ In most of the experiments, the excitation wavelength was around 283 nm, using the picosecond cavity-dumped synchronously pumped dye laser system with Rhodamine 110 dye described before.¹⁴ To study whether the excess energy supplied to the system at this excitation wavelength has an effect on the kinetics of the decay, the excitation wavelength was later changed to around 403 nm. Laser pulses of shorter than 1 ps from a Styryl 9 dye laser pumped

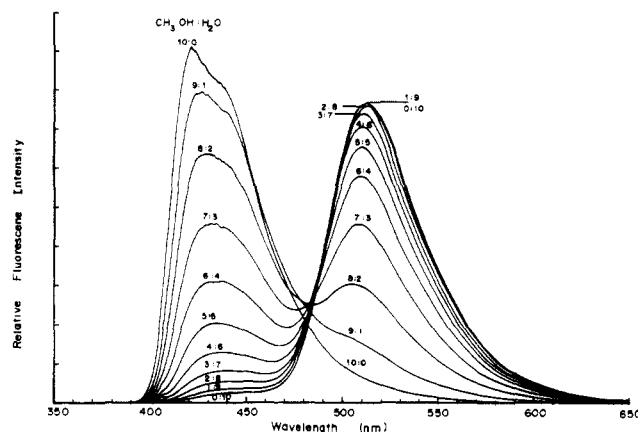


Figure 3. Fluorescence spectra in water/methanol mixtures.

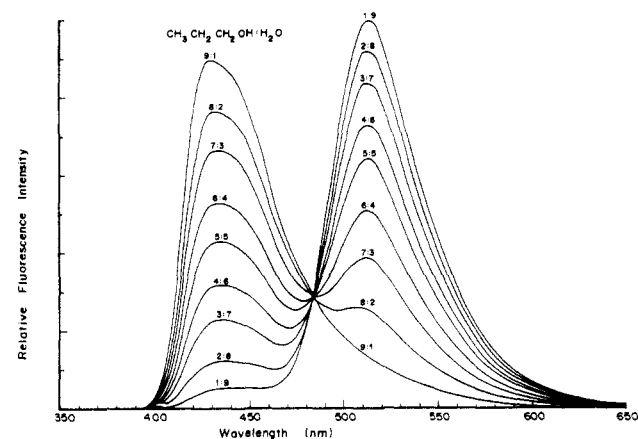


Figure 4. Fluorescence spectra in water/propanol mixtures.

with a Spectra-Physics Model 3800 Nd:YAG femtosecond laser system (with Model 451 mode locker and Model 3695 pulse compressor) were used. Decay of the acid was recorded at 410 nm and of the base at 540 nm.

Results and Discussion

(i) **Absorption and Fluorescence Spectra.** The absorption spectra of HOPTS are only very slightly sensitive to the relative concentrations of water and methanol or propanol in the solvent mixture. Figure 2 shows the absorption spectra of HOPTS in water and methanol. The positions of the peak maxima are the same in the two solvents. The spectrum is, however, better resolved in methanol. A similar result is also obtained in propanol. Solubility in pure propanol is very poor, around 10^{-7} M, but increases considerably upon addition of a few percent of water.

Fluorescence spectra, on the other hand, are very sensitive to the fraction of water in the solvent as shown in Figures 3 and 4. In a pure methanol solvent, the fluorescence spectrum shows an intense band at about 420 nm. On addition of water, the intensity of this band decreases and a new band grows at 515 nm. The short-wavelength emission is attributed to the triply charged acidic form of HOPTS and the long-wavelength emission to the deprotonated quadruply charged anion. The type of alcoholic solvent, methanol or propanol, does not affect the shape or position of the fluorescence band.

However, a basic difference between the two mixtures of water/methanol and water/propanol is that the quantum yields are not the same. It is found that, in water/propanol mixtures, addition of up to 90% water increases the intensity of the anion fluorescence at the same rate of decrease in the intensity of fluorescence from the acidic form of HOPTS and that

$$\Phi_a/\Phi_{a0} + \Phi_b/\Phi_{b0} = 1 \quad (2)$$

as shown in Figure 5. Φ_a is the quantum yield of the acidic form of HOPTS, and Φ_{a0} is the quantum yield in acidic medium when the fluorescence is purely from the acidic form of HOPTS. Φ_b

TABLE I: Values for Lifetimes (τ_i) and Normalized Preexponential Factors (A_i) from Deconvoluted Experimental Decays

[H ₂ O], mol/L	A_1	τ_1 , ps	A_2	τ_2 , ps	A_3	τ_3 , ps	A_4	τ_4 , ps
0.0	1.000	3873						
5.5	0.734	3983	0.065	3335	0.200	761		
11.1	0.417	4083	0.266	1941	0.317	224		
16.6	0.399	3570	0.296	1301	0.416	155		
22.2	0.227	3037	0.340	924	0.433	123		
27.7	0.158	2820	0.422	1069	0.419	213		
33.2	0.087	2654	0.310	827	0.602	234		
38.8	0.047	2693	0.170	902	0.784	276		
44.3	0.022	2927	0.022	943	0.871	224		
49.9	0.012	3197	0.068	867	0.921	154		
55.4	0.003	4989	0.019	1300	0.050	433	0.928	96

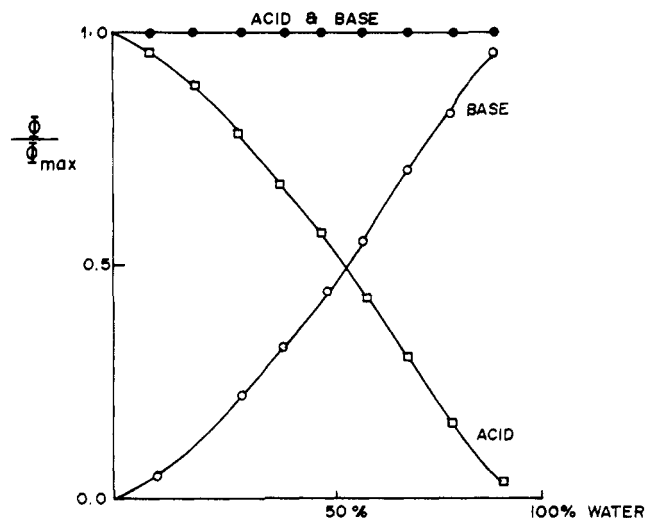


Figure 5. Quantum yield of acidic fluorescence of HOPTS as a function of water concentration in water/propanol mixtures.

is the quantum yield of the anionic form of HOPTS, and Φ_{b0} is the quantum yield in basic medium when the fluorescence is purely from the anion. In water/methanol mixtures, on the other hand, it is found that the addition of more than 70% water does not affect the intensity of the anion fluorescence to the same extent it changes the fluorescence of the acidic form. It is found that in water/methanol mixtures

$$\Phi_a/\Phi_{a0} + \Phi_b/\Phi_{b0} < 1 \quad (3)$$

as shown in Figure 6.

This result is in disagreement with the previously reported result¹⁵ of a total quantum yield close to unity (4% for the acidic form of HOPTS and 96% for the anion). This probably indicates that a certain quenching process is active in water/methanol mixtures but not active in water/propanol mixtures. In terms of the geminate recombination model suggested by Pines et al.,^{10,11} this result means that for methanol solutions the correction factor $\exp(-t/\tau)$ includes both the radiative and nonradiative decays.

(ii) *Decay Curves.* Decay curves in water/methanol and water/propanol mixtures are shown in Figure 7. A similar set of decay curves have also been obtained for water/propanol mixtures. Decay of HOPTS in methanol can be nicely fit to a single-exponential decay with a lifetime of $\tau = 3.873 \pm 0.020$ ns. Exactly the same lifetime was obtained for HOPTS in propanol. However, in both cases, upon addition of water, the decay becomes much faster and the decay curve can no longer be fitted even to biexponential decay. For example, the decay in a water/methanol mixture of 30% water can be fitted to a three-exponential decay with lifetimes $\tau_1 = 155 \pm 101$ ps, $\tau_2 = 1301 \pm 274$ ps, and $\tau_3 = 3570 \pm 215$ ps. The same data can also be fitted to a four-exponential decay. It is found that, depending on the range used for fitting and the initial starting fitting values, different values

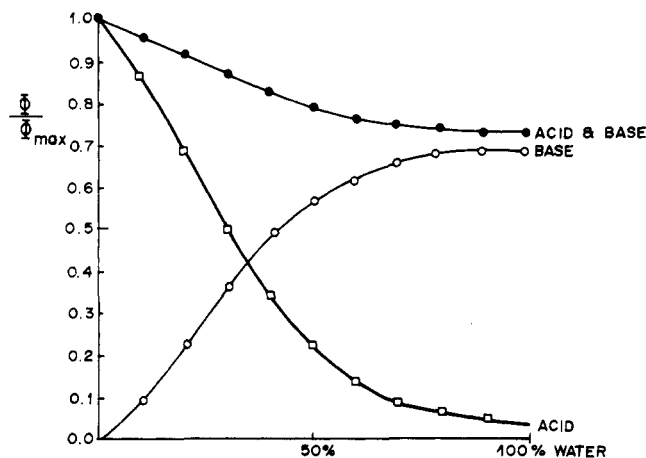


Figure 6. Quantum yield of acidic fluorescence of HOPTS as a function of water concentration in water/methanol mixtures.

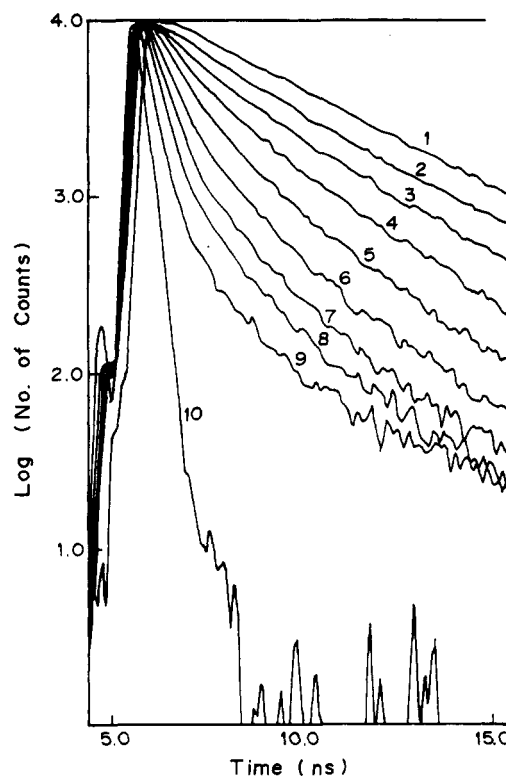


Figure 7. Decay curves of HOPTS in water/methanol mixtures: 1, 0%; 2, 20%; 3, 30%; 4, 40%; 5, 50%; 6, 60%; 7, 70%; 8, 80%; 9, 100% water; 10, laser pulse.

of lifetimes and preexponential factors are obtained. By integration of the respective decays between $t = 0$ and $t = \infty$, a criterion is obtained to select the best set of lifetimes. That is when $(\sum A_i \tau_i)/A \tau_0$ is equal to Φ_a/Φ_{a0} , where A_i are the normalized preexponential factors ($\sum A_i = 1$), τ_i is the lifetime of decay

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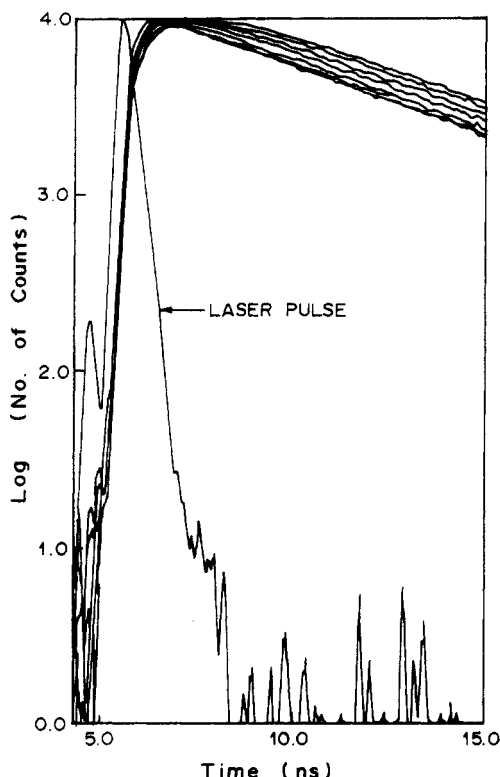


Figure 8. Decay curves of base in water/methanol mixtures.

component i , A is equal to one, τ_0 is the fluorescence lifetime in pure methanol, and Φ_a/Φ_{a0} is obtained from the fluorescence spectra as in Figure 6. Results of lifetimes (τ_i) and normalized preexponential factors (A_i) from deconvoluted experimental decays are summarized in Table I.

Figure 8 shows decay curves of the base for various water/methanol mixtures. Clearly, decay at longer times is the same for all mixtures, i.e., the decay of the pure base. The description of the rise of the base fluorescence is more complex than the acid decay. It might be explained by models for acid decay described later in this paper. However, this will be dealt with in a subsequent publication.

(iii) *Excess Photon Energy Does Not Affect the Kinetics.* Most of our experimental results were obtained by using the frequency-doubled Rhodamine 110 dye laser excitation at a wavelength of 283 nm corresponding to the S_0 - S_2 transition. The same results were obtained when frequency-doubled Styryl 9 dye laser femtosecond excitation pulses at a wavelength of 403 nm corresponding to the S_0 - S_1 transition are used. This shows that the kinetics of this reaction is insensitive to excess energy¹¹ and in agreement with quantum yields with either 283- or 403-nm excitation.

(iv) *Fitting Experimental Data to Geminate Dissociation Recombination Model.* (a) *Rate Equations.* In deriving the rate equations, Pines et al.¹¹ have not included the decay rate of the base. If there is a recombination reaction, i.e., an equilibrium between the acid and the base in the excited state, one cannot ignore the influence of the lifetime of the base on the observed rate of decay of the acid. When the decay of the base is considered, the rate equation should be written as

$$d[A\cdots B]/dt = k_1[AB] - (k_2 + k_{-D} + K'_f)[A\cdots B] \quad (4)$$

where K'_f is the rate constant of the fluorescence of the base. However, for the time being, we use the equations derived by Pines et al.^{10,11} for comparison with our experimental results. The rate coefficients are given by

$$k_1 = k_d \quad (5)$$

$$k_{-D} = 3DR_D[R_{cc}^3 - r_{AB}^3]^{-1}[\exp(R_D/R_{cc}) - 1]^{-1} \quad (6)$$

$$k_2 = (3DR_D/(R_{cc}^3 - r_{AB}^3)) \exp(-R_D/R_{cc})[\exp(-R_D/R_{cc}) - \exp(R_D/r_{AB}) + (DR_D/r_{AB}^2 k_r) \exp(-R_D/r_{AB})]^{-1} \quad (7)$$

TABLE II: Comparison of the Intensities of Fluorescence in Water Calculated Using the Pines et al.^{10,11} Model and Our Values of Fluorescence Intensities Obtained from a Four-Exponential Fit to Deconvoluted Experimental Decays

time, ns	fluorescence intensity	
	calcd using the Pine's et al. model	calcd using a four-exponential fit to exptl decays
0.05	0.620	0.615
0.10	0.385	0.386
0.15	0.254	0.263
0.20	0.177	0.165

TABLE III: Variables Used in the Decay Curves Fitting

[H ₂ O], mol/L	wt % H ₂ O	ϵ	η_w/η_{mix}	D , Å ² /ns	R_D , Å	k_1
0.0	0.00	32.68	1.709	1606	68.74	0.000
5.5	12.28	38.29	1.128	1060	58.58	0.480
11.1	23.96	43.52	0.822	772	51.54	1.540
16.6	35.08	48.30	0.677	636	46.44	2.720
22.2	45.66	53.32	0.586	551	42.07	3.740
27.7	55.76	57.62	0.550	517	38.93	4.050
33.2	65.41	61.94	0.548	515	36.22	2.880
38.8	74.63	66.42	0.584	548	33.77	3.040
44.3	83.45	70.82	0.661	621	31.67	3.960
49.9	91.90	74.82	0.792	744	29.98	6.370
55.4	100.00	78.71	1.000	940	28.50	10.000

where k_d and k_r are the intrinsic dissociation and recombination rates, respectively, R_D is the Debye radius, R_{cc} is the Coulomb cage radius, and D is the diffusion coefficient of the ions involved in the solution.

(b) *Short Time Behavior.* Pines et al.^{10,11} have suggested some values to be used in fitting the decay in pure water. We have tried to compare our experimental results with their model. A nice correlation has been obtained for the results in pure water as shown in Table II. We also have extended the work to water/methanol mixtures, and results are summarized in Table III. The different parameters have been derived for water/methanol mixtures in the following way. The dielectric constant of the solution, ϵ_{mix} , is calculated from the formula¹⁶

$$\epsilon_{mix} = [V_w \epsilon_w^{1.5} + (1 - V_w) \epsilon_m^{1.5}]^{1/1.5} \quad (8)$$

where V_w is the volume fraction of water, ϵ_w is the dielectric constant of pure water¹⁷ ($\epsilon = 78.54$), and ϵ_m is the dielectric constant of pure methanol¹⁷ ($\epsilon = 32.63$) at 25 °C. The Debye radius (R_D) is then calculated from the equation¹⁰

$$R_D = |z_1 z_2| e^2 / (\epsilon_{mix} k_B T) \quad (9)$$

where z_1 and z_2 are the charges of the proton and the anion (1 and -4 for HOPTS), ϵ_{mix} is the dielectric constant of the solvent mixture, T is the absolute temperature, e is the electric charge, and k_B is the Boltzmann constant. The diffusion coefficient in the mixture D is calculated from the formula

$$D = D_w \eta_w / \eta_{mix} \quad (10)$$

where D_w is the diffusion coefficient in water¹¹ ($=940$ Å²/ns) and η_w/η_{mix} is the viscosity of water over the viscosity of the water/methanol mixture and is obtained from the *CRC Handbook of Chemistry and Physics*.¹⁸

The contact distance¹¹ $r_{AB} = 6.5$ Å, the Coulomb radius R_{cc} is considered almost equal to R_D , and k_r is constant in all mixtures ($k_r = 8$ Å/ns). All the values that have been used in the calculations are summarized in Table III.

We have assumed as a first trial that the value of k_1 is proportional to the water concentration only and have calculated the intensity of fluorescence accordingly. When comparing the in-

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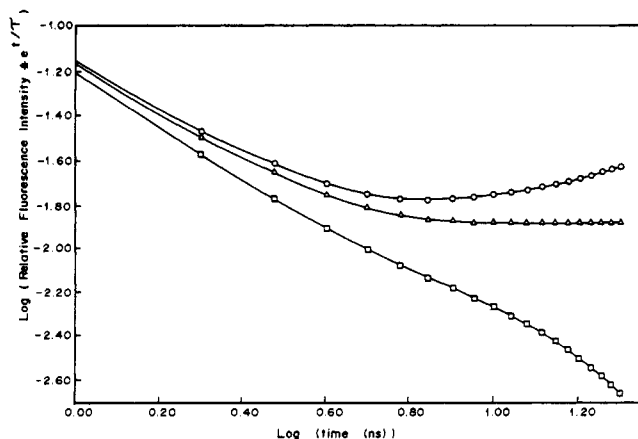


Figure 9. Calculated long-time decay behavior of HOPTS in water for different values of τ : (O) $\tau = 6.0$; (Δ) $\tau = 3.9$; (\square) $\tau = 3.5$.

tensities of fluorescence calculated by using the above-mentioned procedure with the experimental values, a discrepancy is found. k_1 is then varied by an iteration procedure until the experimental and calculated intensities of fluorescence match each other in the first 250 ps. Values of k_1 are summarized in Table III. One cannot calculate the value of k_1 simply from the concentration of water in the mixture. The discrepancy could be probably because k_1 is not only related to the solvent but is also time dependent.

(c) *Long Time Behavior.* Pines et al.^{10,11} have described the long time decay according to a $t^{-3/2}$ law as

$$I(t) = (((\pi r_{AB}^2 k_r \exp(R_D/r_{AB})) / (2k_d(\pi D t)^{3/2})) \exp(-t/\tau)) \quad (11)$$

where $\exp(-t/\tau)$ is a correction factor due to the radiative lifetime of the acid. While Pines et al.^{10,11} have used $\tau = 6$ ns, we find that the shape of the decay curve very strongly depends on the choice of τ as shown in Figure 9. Unfortunately, their results cover only times up to about 4 ns. However, the $t^{-3/2}$ behavior is only observed, if it is there, in a very small time range. Actually, when τ is chosen to be 3.9 ns, the intensity becomes constant at longer times as shown in Figure 9. This time of 3.9 ns corresponds to the lifetime of HOPTS in methanol; i.e., no dissociation has occurred. This results clearly show the important role played by the solvent and its effect on the decay of HOPTS. It seems that for "longer times" the acid cannot dissociate at all. In addition to the mechanism of the geminate dissociation-recombination, the solvent type and the availability of enough number of proton acceptor solvent molecules should be considered in the description of the decay of HOPTS in water and water/methanol mixtures.

(v) *Effect of CaCl_2 .* It is found that addition of CaCl_2 has a significant effect on the fluorescence spectra and decay curves as shown in Figures 10 and 11. The quantum yield of the acidic form of HOPTS dramatically decreases in the presence of 0.13 M CaCl_2 . The quantum yield of the anion, on the other hand, dramatically increases. The quenching of the excited acidic form of HOPTS by CaCl_2 cannot explain this observation because quenching would not be accompanied by an increase in the anion quantum yield. This observation means that the dissociation rate is enhanced by CaCl_2 and can for example be explained by the increase in the number of acceptor molecules free to accept a proton in the system. CaCl_2 has been known for a long time to be a good water structure breaker. The effect of the addition of CaCl_2 could, therefore, be probably explained by the increase of the concentration of "free" water molecules in the system. The increase in the concentration of free water molecules being the acceptor of the dissociated proton enhances the rate of dissociation.

However, this observation can also be explained by the geminate dissociation-recombination model of Pines et al.^{10,11} The effect of the salt could be understood by the reduction of the Coulomb cage radius of the anion, R_{cc} . The added ions will shield the dissociated proton from the attractive potential of the anion which will result in a faster decay.

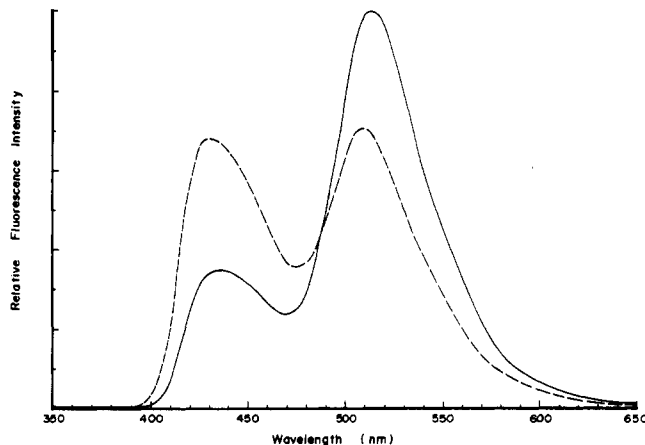


Figure 10. Fluorescence spectrum of HOPTS in 30% water/70% methanol with CaCl_2 : (---) 0.0 M CaCl_2 ; (—) 0.13 M CaCl_2 .

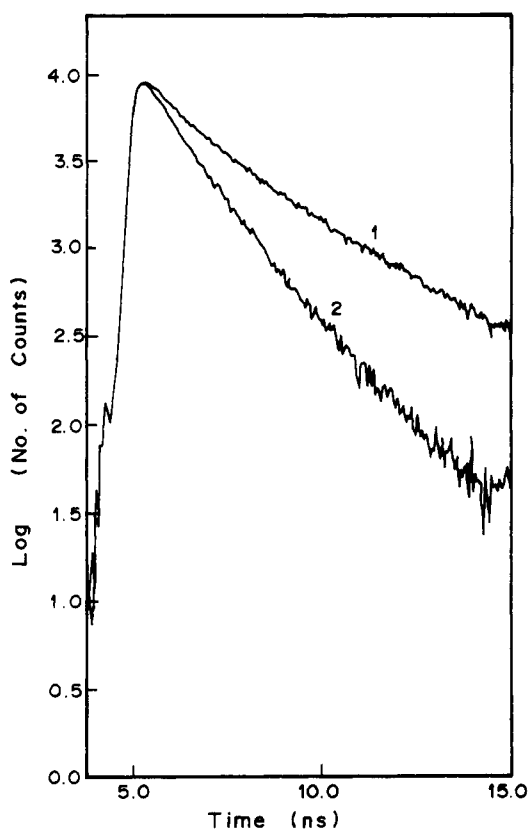


Figure 11. Decay curve of HOPTS in 30% water/70% methanol with CaCl_2 : 1, 0.0 M CaCl_2 ; 2, 0.13 M CaCl_2 .

(vi) *Effect of Urea.* Similar to the effects of addition of CaCl_2 but to a lesser extent, addition of urea reduces the quantum yield of the acidic form of HOPTS, increases the quantum yield of the base, and makes the decay faster as shown in Figures 12 and 13. This result is very crucial because urea is not ionic. It probably has a negligible effect on the Coulomb cage radius, R_{cc} . It also has been known, on the other hand, to be a good water structure breaker⁸ which will increase the concentration of free water molecules in the system. The observed effect of adding urea is a decisive experiment for the importance of considering the water structure in explaining the decay of excited HOPTS in water/alcohol mixtures.

Therefore, these experiments show that both the two effects of the geminate dissociation-recombination and the water structure contribute to the dissociation of HOPTS in water/alcohol mixtures.

(vii) *Proposed Model of the Effect of Free Water on the Decay of HOPTS Fluorescence.* We think that the dissociation "constant", k_1 , in the geminate recombination model of Pines et

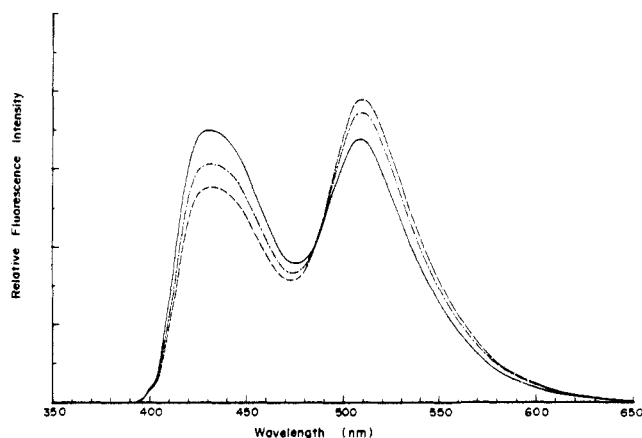


Figure 12. Fluorescence spectrum of HOPTS in 30% water/70% methanol with urea: (—) 0.0 M urea; (---) 0.13 M urea; (- - -) 0.25 M urea.

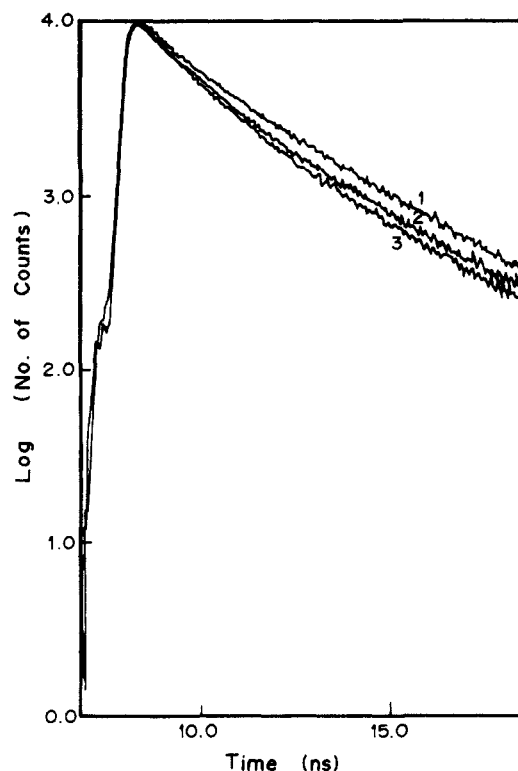


Figure 13. Decay curve of HOPTS in 30% water/70% methanol with urea: 1, 0.0 M urea; 2, 0.13 M urea; 3, 0.25 M urea.

al.^{10,11} is not actually constant. The time dependence of k_1 may be shown if the reaction between water molecules and excited HOPTS molecules is thought of as a diffusion-controlled reaction. Birks et al. have made an excellent review¹⁹ of the theory of diffusion-controlled reactions in solutions which was originally developed by Smoluchowski. In this model, the time-dependent rate parameter of the diffusion-controlled reaction is given by the relation

$$k_1(t) = 4\pi N' r_{AB} D_{AB} p C_{0,q} [1 + r_{AB}/(\pi D_{AB} t)^{1/2}] \quad (12)$$

where N' is the number of molecules per millimole, r_{AB} is the contact distance between the two reacting species, D_{AB} is the sum of diffusion coefficients of the two species ($D_{AB} = D_A + D_B$), p is the fraction of collisions effective in quenching, $C_{0,q}$ is the initial concentration of the quencher in mol/L. Substituting the following values in eq 2, $D_{AB} = 2.54 \times 10^{-5}$ cm²/s which is actually the diffusion coefficient of water at this temperature,²⁰ $r_{AB} = 6.5 \times$

10^{-8} cm, $C_{0,q} = 55.5$ mol/L assuming all water molecules are involved in the reaction, and $p = 1$, eq 12 reduces to

$$k_1(t) = 6.93 \times 10^2 (1 + 0.23/t^{1/2}) \text{ ns}^{-1} \quad (13)$$

where t is in nanoseconds.

It is obvious that there is a clear time dependence of the rate "constant" in the first nanosecond after which it becomes almost constant. This could be the reason why the time dependence of the dissociation constant has not been observed in molecules of slower dissociation rate such as 1-naphthol and 2-naphthol.

If one assumes n molecules of water form a free water cluster, the following relation is obtained:

$$k_1(t) = (6.93 \times 10^2/n)(1 + 0.23/t^{1/2}) \text{ ns}^{-1} \quad (14)$$

Using the value of $k_1 = 10 \text{ ns}^{-1}$ suggested by Pines et al.,^{10,11} n takes the value 70; i.e., about 70 "free" water molecules are involved in the dissociation process. However, this cluster is not thermodynamically in equilibrium, and it is believed that this cluster eventually breaks to a smaller size. Probably this is the reason why a cluster size of four has been suggested for the longer time scales in the range of micro- and nanoseconds.

Huppert et al.²¹ have studied proton transfer from several aromatic alcohols and amines in water/alcohol mixtures. A water cluster model ($\text{H}_3\text{O}^+[\text{H}_2\text{O}]_n$, $n > 1$) was proposed to interpret their results. Recently, Robinson et al.⁶ have suggested an average hydration number of four for proton in methanol/water mixtures, based on Markov random-walk analysis of solvent composition effects of the lifetime of 1-naphthol⁷ and 2-naphthol.⁶

Scandola et al.²² have studied the proton-transfer processes of *cis*-dicyanobis(2,2'-bipyridine)ruthenium(II) in acetonitrile/water solvent mixtures and have also suggested an average hydration number of 3.

Deviation of the observed decays from their theoretical rates of decay have been observed by Robinson et al.⁷ and have been assumed to exist in the cases where the reaction is diffusion controlled, i.e., low water concentration and high alcohol concentration. Deviations have also been observed in the cases of the most rapid electron transfers.^{23,24}

Lee⁹ has emphasized that proton hydration requires four properly oriented molecules, not any four water molecules having unspecified orientation. Therefore, in a large number of water molecules, e.g., 70, there is a high probability of having four properly oriented water molecules.

Our results indicate that there are at least two processes involved in the deprotonation reaction. One is the dissociation of the acid, and the second is the reorientation of the water solvent molecules. In the case of fast deprotonation processes such as in the case of HOPTS with very small pK^* values, these two processes occur at comparable rates and, therefore, a large number of water molecules are involved. However, in slower cases such as 2-naphthol, water reorientation occurs at much faster rate than acid dissociation. In the latter case, the experimentally deduced number of water molecules is determined by the dissociation rate of the acid and not by the rate of reorientation of solvent water molecules. Therefore, in the case of slow deprotonation it looks as if a small number of water molecules were involved. However, the initial number of water molecules involved in the slow deprotonation reaction is probably the same as in the fast deprotonation, but it does not significantly contribute to the observed overall rate of the dissociation.

Conclusion

In this paper, we have studied the proton transfer from the excited state of HOPTS in water/alcohol mixtures. The geminate dissociation-recombination model proposed by Pines et al.^{10,11} has

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been applied to our results. It is found that this model in both the short- and long-time domains cannot explain all the observed results. We have tried to show the importance of considering the role of the solvent acceptor molecules. Both mechanisms of the Coulomb cage effect and acceptor properties seem to contribute to the decay of HOPTS in water/alcohol mixtures.

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Fluorescence of Gaseous Tetraenes and Pentaenes

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Fluorescence, fluorescence excitation, and absorption spectra of room temperature vapors of 1,3,5,7-octatetraene, 1,3,5,7-nonatetraene, 2,4,6,8-decatetraene, and 2,4,6,8,10-dodecapentaene have been obtained. All four polyenes show dual ($S_1 \rightarrow S_0$ and $S_2 \rightarrow S_0$) fluorescences with the ratios of the two emissions ($2^1A_g \rightarrow 1^1A_g$ and $1^1B_u \rightarrow 1^1A_g$) being sensitive to the extent of substitution. For example, the $(S_1 \rightarrow S_0)/(S_2 \rightarrow S_0)$ fluorescence yield ratio increases from 0.06 to 0.7 when terminal methyl groups are added to octatetraene. The gas-phase S_2-S_1 energy gaps are almost identical for these two molecules (6600 cm^{-1} for octatetraene versus 6300 cm^{-1} for decatetraene), suggesting that the apparent difference in internal conversion efficiencies is due to the larger density of vibronic states in the methyl-substituted compounds. This is supported by an even larger $(S_1 \rightarrow S_0)/(S_2 \rightarrow S_0)$ yield ratio (1.4) in dodecapentaene, for which the gas-phase S_2-S_1 energy difference is 7200 cm^{-1} . The fluorescence excitation spectrum of decatetraene has been measured in the 34 600–37 450- cm^{-1} region ($S_0 \rightarrow S_2$) in a supersonic expansion. Vibronic line widths have been used to estimate a lifetime of 0.25 ps for the zero-point level of 1^1B_u and indicate coupling between the 1^1B_u and 2^1A_g manifolds in the statistical limit. These results are discussed in relation to the previous gas-phase spectroscopy of octatetraene and shorter polyenes.

Introduction

Linear polyenes have received experimental and theoretical attention for several decades because of their relevance in several photobiological processes, such as vision and photosynthesis, and their usefulness as models for developing descriptions of the electronic states of conjugated π -electron systems.¹ The optical spectroscopy of simple, unsubstituted polyenes in low-temperature solutions¹⁻³ and mixed crystals⁴⁻⁶ has established (for simple, unsubstituted polyenes with four or more double bonds) the presence of a 2^1A_g (S_1) state between the ground 1^1A_g (S_0) and first one-photon-allowed excited state 1^1B_u (S_2). Absorption into S_2 typically is followed by a Stokes-shifted emission from S_1 , though the fluorescence yields are sensitive to details of molecular structure. For example, the high emission yields of certain long polyenes (~ 0.6 in frozen solutions of octatetraene)⁷ contrast the absence of fluorescence in shorter analogues such as hexatriene under identical experimental conditions.

Low-temperature optical measurements in glasses and mixed crystals have been supplemented by recent studies of polyenes in supersonic jets.⁸⁻¹¹ Most of this work has focused on the spectroscopy of diphenyl-substituted compounds.¹²⁻¹⁹ These compounds not only are commercially available but also are both highly fluorescent and relatively stable. Absorption, fluorescence, and fluorescence excitation spectra have provided additional information on the electronic structures and dynamics of these polyene systems and for diphenylhexatriene and diphenylbutadiene suggest intermediate case coupling between the 2^1A_g and 1^1B_u excited states.

The high fluorescence quantum yields of the diphenylpolyenes contrast the immeasurably weak fluorescences of butadiene and

hexatriene, indicating that the results obtained for the short diphenylpolyenes are not applicable to polyenes without phenyl substituents. Octatetraene is the shortest unsubstituted polyene with detectable fluorescence and thus has been the subject of a

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