

INVESTIGATION OF SOLVENT DEPENDENCE OF INTERMOLECULAR PROTON TRANSFER BY PICOSECOND ABSORPTION SPECTROSCOPY

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Abstract A picosecond absorption study on the intermolecular proton transfer of photoexcited 8-hydroxy-1,3,6-pyrene trisulfonate (HPTS) is presented. The time of formation of deprotonated excited HPTS was measured for various solvents. The dependence of this time of formation on the methanol fraction in water-methanol mixtures is discussed in terms of a simple cluster model. Proton transfer rates were determined in different micellar systems yielding information on the character of the micellar surrounding of the proton donor.

INTRODUCTION

Aromatic alcohols are known to form stronger acids in their excited electronic singlet state than in their ground state¹⁻⁴. This phenomenon is manifested in the fluorescence spectra of these compounds where two bands can be detected. The short wavelength band is assigned to the excited species ROH*, while the occurrence of the long wavelength band is due to the excited state proton transfer from the donor molecule to the molecular environment and can thus be assigned to the excited anion RO^{-*}. The proton transfer reaction, one of the fundamental and

fastest chemical reactions, is assumed to be of importance for a number of biological processes. Therefore various time resolved ps-fluorescence have been performed recently^{5,6}. The first ps-absorption experiments, described in this paper, have been performed in order to obtain information on the existence of transient absorbing states as well as to detect non-fluorescent states in protonation reactions.

In the present study 8-hydroxy-1,3,6-pyrene was used as proton donator in water-methanol mixtures. Further, it was embeded in various micellar structures. HPTS was used without further purification, all solvents were spectroscopic grade and triple distilled in an all-glass apparatus. Measurements were carried out on a ps-excite-and-probe spectrometer described in detail elsewhere⁷. HPTS was excited by the third harmonic radiation ($\lambda = 355$ nm; energy/pulse = 0.5 mJ; pulse duration = 5 ps) of a mode-locked Nd:phosphate glass laser.

PROTON TRANSFER IN WATER-METHANOL MIXTURES

In order to gain detailed information on the influence of the solvent environment (i. e. the proton acceptor) on the proton transfer rate the pure water surrounding was altered by addition of methanol⁴. A similar experiment was carried out on a ps-fluorescence spectrometer by Huppert and Kolodney⁵.

Figure 1 shows a typical example of transient spectra of changes in optical density of

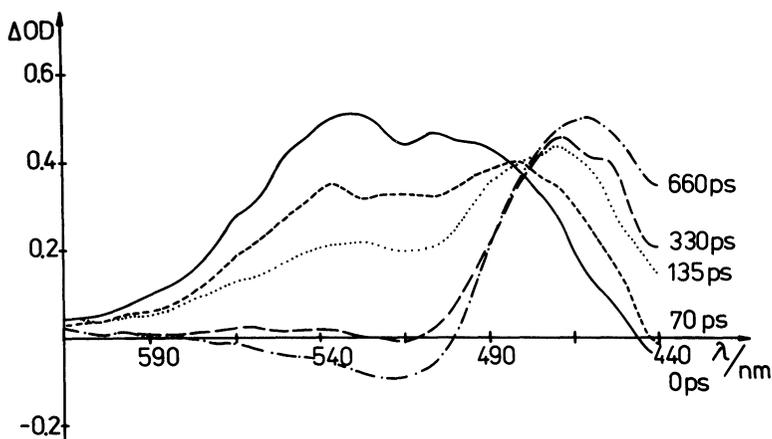


FIGURE 1. Transient absorption spectra of HPTS (10^{-3} mol/l) dissolved in a 1:1 water-methanol mixture after ps-THG excitation

THG excited HPTS in a water-methanol mixture. The $S_1 \rightarrow S_x$ absorption band of the protonated form ROH^* is seen for optical delay 0 ps in the wavelength range 450 ... 590 nm. This band is diminished through excited state proton transfer and $S_1 \rightarrow S_0$ transitions. The negative ΔOD values for delays $t_d \geq 330$ ps in the wavelength region 500 ... 565 nm are caused by amplification of the test light due to stimulated emission by the $RO^{-*} \rightarrow RO^-$ transition. The temporal rise of the amplification of the test light coincides with the evolution of the test light absorption in the region 440 ... 480 nm. This absorption is thus due to the $S_1 \rightarrow S_x$ absorption of the anion RO^{-*} . Kinetical curves for various methanol fractions

are plotted in figure 2. Risetimes of the deprotonated form (obtained from the build-up of the amplification) are summarized in table I.

TABLE I Risetimes t_r of deprotonation

solvent	methanol fraction Vol-%	Mol-%	risetime t_r in ps
H ₂ O	-	-	66 ± 8
H ₂ O-MeOH	33	18	422 ± 10
H ₂ O-MeOH	50	31	625 ± 12
H ₂ O-MeOH	66	48	877 ± 15
MeOH	100	100	no transfer

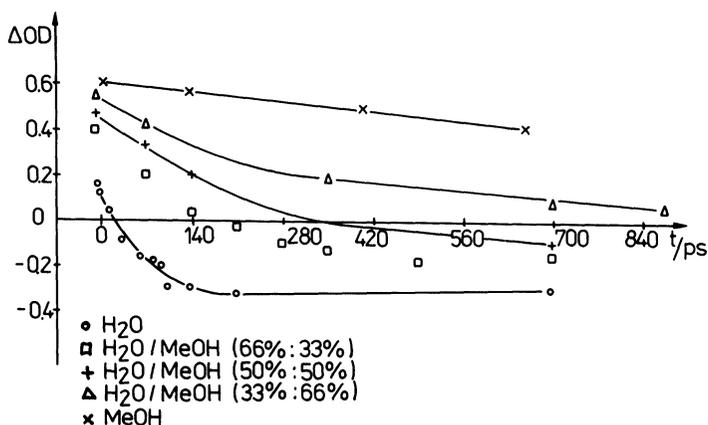


FIGURE 2. Transient absorption kinetics of HPTS in various water-methanol mixtures (probe wavelength 525 nm; $[HPTS] = 5 \cdot 10^{-4}$ mol/l).

The strong dependence of t_r on the methanol fraction can not be explained by the continuum theory of ionic reactions developed by Debye *et al.*⁸

The fact, that no proton transfer reaction takes place in pure methanol is not explicable, too. It must be assumed, that the structure of the water network surrounding of the proton donator has the decisive influence on the deprotonation rate⁴. Lee and Robinson⁹ proposed a water cluster model to interpret their results of electron transfer in Indole. The same model, based on a Markov random walk procedure was successfully applied to explain proton transfer rates of naphthol in water-methanol mixtures¹⁰. A slightly modified model is applicable to our problem. It is based on the following assumptions.

The OH-group of HPTS is surrounded by N solvent molecules (either water or methanol), N being the cluster size. Different assemblies of solvent molecules to form such clusters are possible, the relative concentrations of which are denoted by $S_{n,m}$; n being the number of water molecules, m the same of methanol ($n + m = N$).

These different cluster assemblies may transmute one into the other with a rate

$$W_{n,n'} = W(S_{n,m} \xrightarrow{\quad} S_{n',m-n'+n}). \quad (1)$$

In approximation it can be assumed, that

$$W_{n,n+i} = 0 \text{ for } i \geq 2, \quad (2)$$

i. e. only \overline{n} transitions to clusters with exchange of one solvent molecule are assumed to be likely. The rates can be related to the molar concentrations of the solvents according to

$$W_{n,n+1} = (N - n) \cdot P \cdot [H_2O] \quad (3)$$

$$W_{n,n-1} = n \cdot P \cdot [MeOH], \quad (4)$$

where P is the elementary exchange probability⁹,

which is assumed to be independent of the molecules exchanged. For intramolecular transitions $\text{ROH}^* \rightarrow \text{ROH}$ we assume the rate⁵

$k_{\text{int}} = k_r + k_{\text{nr}} = 1.6 \cdot 10^8 \text{ s}^{-1}$
to be valid for all cluster configurations.

The proton transfer rate for a given cluster configuration k_p is assumed to be the same as in pure water ($k_p = 2 \cdot 10^{10} \text{ s}^{-1}$)⁵, if the transfer is allowed at all in the given assembly of solvent molecules (see parameter N_M below).

Thus the following system of differential equation can be set up to describe the temporal evolution of the relative concentrations of cluster configurations:

$$\frac{d}{dt} S_{N,0} = W_{N-1,N} \cdot S_{N-1,1} - W_{N,N-1} \cdot S_{N,0} - k_{\text{int}} \cdot S_{N,0} - k_p \cdot S_{N,0} \quad (5a),$$

$$\frac{d}{dt} S_{N-1,N} = W_{N,N-1} \cdot S_{N,0} + W_{N-2,N-1} \cdot S_{N-2,2} - (W_{N-1,N} + W_{N-1,N-2}) \cdot S_{N-1,1} - k_{\text{int}} \cdot S_{N-1,1} \quad (5b),$$

⋮

$$\frac{d}{dt} S_{0,N} = W_{1,0} \cdot S_{1,N-1} - W_{0,1} \cdot S_{0,N} - k_{\text{int}} \cdot S_{0,N} \quad (5c),$$

$$\frac{d}{dt} [\text{RO}^*] = k_p \cdot S_{N,0} - k_{\text{int}} \cdot [\text{RO}^*] \quad (5d),$$

with $[\text{ROH}^*] = S_{N,0} + S_{N-1,1} + \dots + S_{0,N}$.

In establishing equation (5) it has been assumed, that only the pure water configuration allows de-

protonation. The initial relative concentrations $S_{n,m}(0)$ are given by:

$$S_{n,N-n}(0) = N! / n!(N-n)! \cdot [\text{MeOH}]^n \cdot [\text{H}_2\text{O}]^{N-n}. \quad (6)$$

The system of differential equations is solved numerically by means of a predictor-corrector procedure. Parameters to be varied in the calculations are given by N , P as well as the number of cluster configurations contributing to proton transfer. For the latter the maximum number of methanol molecules (N_M) in a solvent cluster still allowing proton transfer can be introduced as an equivalent parameter.

In order to fit our calculations to experimental data the calculations were performed for different fractions of methanol in a water-methanol mixture and compared with the experimental results depicted in figure 2. Results of these calculations are shown in figure 3, the best agreement with experimental data has been obtained for the parameter set

$$N = 4, P = 1 \cdot 10^{10} \text{ s}^{-1} \text{ and } N_M = 2,$$

whereas all other parameter sets yield significant deviations from the experimentally determined risetimes. Thus, we may conclude that a cluster composed of four solvent molecules seems very likely, which is in agreement with the results of Lee et al.⁹⁻¹¹. Moreover we can derive from our calculations that proton transfer is allowed only in cluster configurations composed of at least three water molecules.

The ability of protons ejected after ps-light

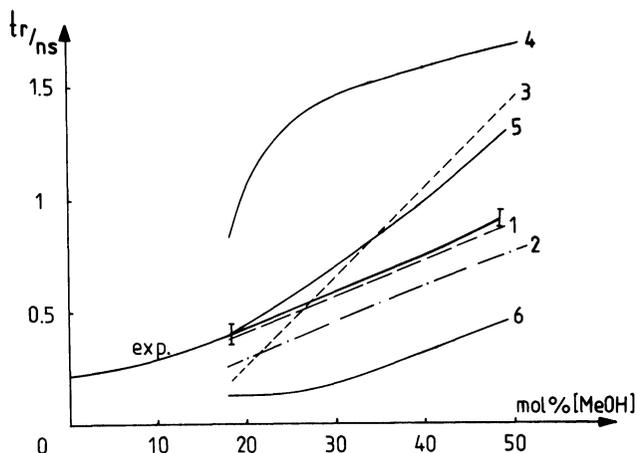


FIGURE 3. Calculation of RO^{-*} -formation time as a function of methanol fraction in $H_2O/MeOH$. 0 exp. curve obtained from fig. 2; 1-6 calcul. curves with parameters:

curve	N	N_M	P in $10^{10} s^{-1}$
1	4	2	1
2	2	1	1
3	6	2	1
4	6	1	1
5	3	1	1
6	4	2	5

irradiation, which are stabilized in such a solvent cage, to react with a suitable reactant can be demonstrated for instance by protonation of a polymethine dye⁴. In our case pinacyanol molecules (concentration 10^{-3} mol/l) were protonated by exciting HPTS molecules (same concentration) in a water-methanol mixture (1:1 volume %). The measurements revealed an irreversible decrease of the $S_0 \rightarrow S_1$ absorption band of pinacyanol as can be seen in figure 4 from the bleaching of the ab-

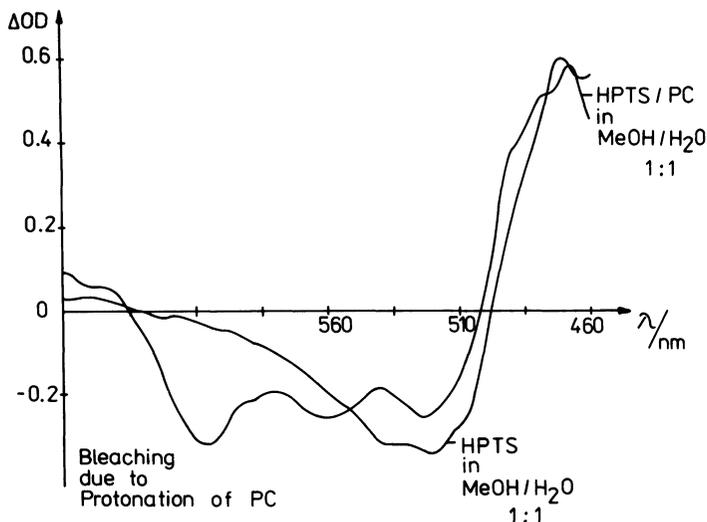


FIGURE 4. Protonation of the polymethine dye pinacyanol after THG excitation of HPTS. For comparison a transient spectra of HPTS in a water-methanol solution is shown.

sorption band of pinacyanol in the wavelength region 560 ... 630 nm. This result indicates that the bimolecular reaction $\text{dye} + \text{H}^+$ must effectively compete with the recombination reaction $\text{RO}^- + \text{H}^+$.⁴

PROTON TRANSFER IN MICELLAR SYSTEMS

Further experiments were carried out with micelles formed by cetyltrimethylammoniumbromid (CTAB) and sodium dodecylsulfate (SDS) in aqueous solution (aqueous micelles)¹⁶ and nonpolar solvents (reversed micelles)¹⁶. Both surfactants were pur-

chased from Merck and used without further purification.

Micelles represent an excellent tool for creating a special microenvironment for the proton transfer reaction. Recently several ps-fluorescence studies of such systems have been published 12-15.

The results of our ps-absorption measurements are shown in figure 5.

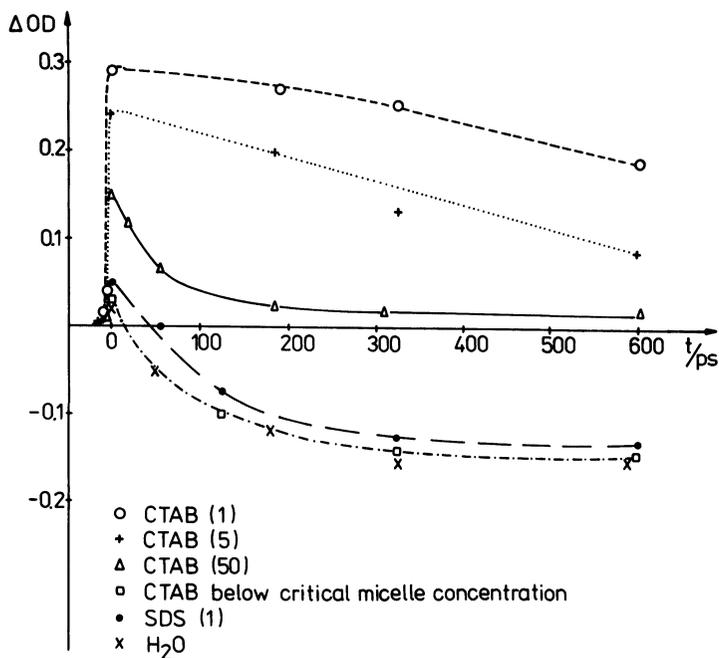


FIGURE 5. Kinetics of absorption changes ($\lambda_p = 520$ nm) of HPTS in various aqueous micelles after THG excitation

HPTS molecules are negatively charged ions. Therefore these molecules are not embedded into SDS mi-

celles (with their negative headgroups) and deprotonation proceeds analogously as in a bulk water environment (fig. 5, curves SDS(1) and H₂O; SDS(1) means one HPTS molecule per SDS micelle). HPTS ions can on the other hand move inside micelles with positively charged heads (e. g. CTAB) which results in an extreme deceleration of proton transfer (curve CTAB(1)). A weak deprotonation is observed for 5 and 50 HPTS molecules per micelle. This result can easily be explained by assuming that only part of the HPTS molecules are within micelles or that the micelle structure is disturbed by the large number of HPTS molecules. For CTAB concentrations below the critical micelle concentration¹⁶ the reaction coincides with the one in pure water, which gives evidence that micelle aggregation is the reason for the observed changes in the proton transfer reaction.

Measurements at various solvent temperatures were carried out to study stability of the micellar structures. As can be seen from figure 6 increasing solvent temperature in aqueous micellar solution of HPTS leads to an increased proton ejection rate, whereas the proton transfer in pure water solution is not influenced by temperature variation. A possible explanation seems to be the following. Since the HPTS has a very high solubility in water it is only loosely attached to the Stern layer⁴ of the ionic micelle. A temperature increase may loosen this link, locating the HPTS molecule in a more aqueous surrounding and thus increasing the deprotonation.

Further detailed studies are necessary to clarify these experimental findings.

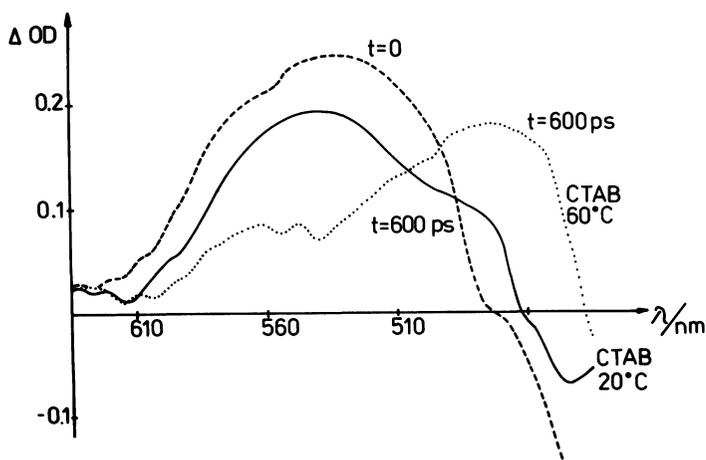


FIGURE 6. Transient absorption spectra of HPIS in aqueous CTAB(1) for various solvent temperature at delay zero (both temperatures yield the same curve) and delay 600 ps.

Further experiments were carried out with reversed micelles, in which certain amounts of water may be entrapped. These reversed micelles are formed by aggregation of a surfactant (CTAB) in a nonpolar solvent (chloroform)^{4,17}. The aim of our investigation was to clarify to what extent the surfactant entrapped water pools resemble a bulk water environment. Measurements were carried out for different sizes of the water pool given by the ratio R of entrapped water concentration to that of the surfactant (CTAB). Results of the measurement are shown in figure 7. It is obvious, that even for relatively large water pools the deprotonation reaction proceeds in a significant-

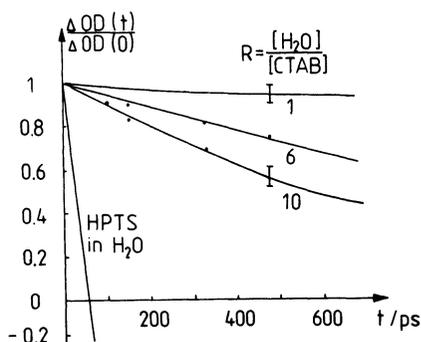


FIGURE 7. Kinetics of absorption changes ($\lambda_p = 525 \text{ nm}$) of HPTS ($5 \cdot 10^{-4} \text{ mol/l}$) in reversed micelles with different water pools.

ly different way than in a bulk water environment. This seems to be an indication that in small water pools[†] a strong interaction between ionic surfactant headgroups and solubilized water and HPTS molecules occurs, which does not allow the formation of water complexes promoting proton transfer. Our results hence support the experimental findings for AUT entrapped water pools¹⁴.

[†]Higher amounts of water can not be solubilized in CTAB micelles.

CONCLUSIONS

We have presented the first ps absorption measurement of intermolecular proton transfer of HPTS in different molecular environments. Strong excited-state absorptions have been detected. The observed variation of the deprotonation rates on methanol fraction in water-methanol mixtures has been explained by a simple cluster model. Our ps-absorption measurements in aqueous and reversed

micelles confirm the results obtained by fluorescence studies¹²⁻¹⁵. However, further detailed studies are necessary to clarify the reported temperature dependence of the transfer rates in aqueous micelles as well as the nature of the water structure in small surfactant entrapped water pools.

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REFERENCES

1. I. F. Ireland and P. A. A. Wyadd, Adv. Phys. Org. Chem. **12**, 131 (1976)
2. T. Foerster, Z. f. Elektrochemie, **54**, 531 (1950)
3. T. Foerster and S. Voelker, Z. f. Phys. Chemie, NF **97**, 79 (1975)
4. A. Granesz, M. Kaschke, D. Khechinashvili, and J. Kleinschmidt, Proc. V. Symposium Ultrafast Phenomena in Spectroscopy, Reinhardtbrunn (G.D.R.), October 1985
5. D. H. Huppert and E. Kolodney, Chem. Phys., **63**, 401 (1981)
6. D. H. Huppert, A. Jayaraman, R. G. Maines, D. W. Steyert, and P. M. Rentzepis, J. Chem. Phys., **81**, 5596 (1984)
7. T. Damm, M. Kaschke, M. Kresser, F. Noack, S. Rentsch, and W. Triebel, Exp. Techn. Phys. **33**, 49 (1985)
8. e. g. M. Eigen, Progr. React. Kin., **2**, 287 (1964)
9. J. Lee and G. W. Robinson, J. Chem. Phys., **81**, 1203 (1984)

10. J. Lee, R. D. Griffin and G. W. Robinson, J. Chem. Phys., 82, 4920 (1985)
11. R. Klein and I. Tatischeff, Chem. Phys. Lett., 51, 333 (1977)
12. J. R. Escabi-Perez and J. H. Fendler, J. Am. Chem. Soc., 100, 2234 (1978)
13. M. J. Politi and J. H. Fendler, J. Am. Chem. Soc., 106, 265 (1984)
14. M. J. Politi, O. Brand and J. H. Fendler, J. Phys. Chem., 89, 2345 (1985)
15. E. Bardez, E. Monnier, and B. Valeur, J. Phys. Chem., 89, 5031 (1985)
16. C. Tanford, in The Hydrophobic Effect, New York, p. 77 (1980)
17. A. Granesz, M. Kaschke, and A. Schlegel, to be published