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Geminate Recombination in Excited State Proton Transfer Reactions: Picosecond Dynamics in Electrolyte Solutions

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1. INTRODUCTION

Geminate recombination plays an important role in proton dissociation reactions [1]. We have recently shown [2] that excited-state acids dissociate via a number of reversible dissociation-geminate recombination cycles. The dissociation profiles of such excited acids are nonexponential, having a t⁻¹/² dependence at long times. These nonexponential tails are affected by temperature and isotopic (H/D) substitution [3].

As a model molecule we have used [4] 8-hydroxy pyrene 1,3,6-trisulfonate (HPTS). Having a 4-fold negative charge after dissociation, this molecule recombines readily in the excited singlet state with its geminate proton. The intrinsic "chemical" dissociation rate, as determined from the slope of the decay curve, is initially 10⁹ s⁻¹ in water. After Insec it is slowed down due to geminate recombination by an order of magnitude. As a result, the observed steady-state dissociation rate, namely the reciprocal area under the dissociation profile, is much slower than the true "intrinsic" chemical rate.

The reversibility of the excited state proton dissociation can be further demonstrated by carrying out the experiment in strong acidic media [4] or in volume limited environments [6]. In both cases a steady-state amplitude of the undissociated HPTS is created.

The dissociation profiles can be accurately reproduced by assuming that the dynamics of the separated ion-pair obeys the Debye-Smoluchowski equation (DSE) with reversible "back-reaction" boundary conditions. The two "intrinsic" rate-coefficients (κₐ, κ₋) for dissociation to and recombination from the contact distance, a, are taken as free parameters. For the actual numerical solution we have applied an efficient Chebyshev propagation algorithm which allows for large time-steps. Agreement with experiment deteriorates for supercooled water. We think that rotational diffusion of the anion, which becomes comparable to κ₋ at low temperatures, leads to a "dynamic static effect". At the higher temperatures, our treatment [5] is superior over the conventional two-state rate-equation models, such as the classical Eigen scheme [7], whose asymptotic temporal decay is exponential rather than a power-law.


From the rate-parameters of the transient measurements we estimate [4] the steady-state dissociation rate and $pK_a$ value, with encouraging agreement to older fluorimetric (constant illumination) measurements [8].

In the present work we utilize the excited HPTS molecule as a microscopic probe for the study of electrolyte solutions in the time-domain, with a resolution of ca. 100ps. This timescale is short compared to the diffusional times but longer than the characteristic relaxation of the solvent (water). Therefore the DSE is valid over the entire experimental time-range.
2. EXPERIMENTAL AND METHOD

Solutions of 5x10^-5 M HPTS in 2:1(v) water-methanol mixtures at 60°C were irradiated by the 3rd harmonic, 25 ps pulse, of a mode-locked Nd:Yag laser. The ps time resolved fluorescence of the acidic HPTS form was detected by a streak camera.

The composition of the solution was chosen to maximize the geminate recombination yield. The pH of the solutions was between 5.5 and 6.0 assuring that homogeneous recombination was insignificant in the experimental time-range. The temperature of the solution was raised to 60°C to eliminate the abovementioned "dynamic steric effect". Under present conditions the average number of geminate proton rebindings to the HPTS anion, before ultimate escape to the bulk, is calculated to be 2.7, twice as much as in pure water [4]. Hence geminate recombination is the main process which determines the apparent HPTS dissociation rate in this environment.

3. RESULTS AND DISCUSSION

Fig. 1 shows the effect of an added electrolyte (NaNO₃) on the transient dissociation profile of HPTS. The averaged streak camera records clearly show a suppression of the long-time fluorescence tail by the added salt. This is explained by a nonequilibrium screening effect which reduces the Coulombic attraction in the ion pair.

The relaxation time of the ionic atmosphere around a central ion suddenly formed in solution is [9] 2De⁻¹, where D is the relative diffusion coefficient between the ions and 1/κ is the ionic atmosphere radius. In water at room temperature a solution of 150mM univalent electrolyte will have a relaxation time of 350ps. This is roughly an order of magnitude slower than the time needed for the proton to reach the nearest neighbor ion. The much faster proton can thus be pictured as moving through a largely unrelaxed ionic atmosphere which still has much of its predissociation characteristics. Only when the proton covers the nearest neighbor distance, Rₚ, would it be influenced by the screening of the other ions [10]. This model was found by us to be very simple to use and yet superior to the conventional Debye-Hückel approach, which fails in our case both because of the relatively high electrolyte concentrations (0.01-0.6M) and the nonrelaxed nature of the ionic atmosphere.

![Graph showing the effect of NaNO₃ concentration on HPTS fluorescence decay](image)

**Fig. 1.** Averaged streak camera recordings of the HPTS fluorescence decay at 440nm at various salt (NaNO₃) concentrations. Top to bottom: 0, 0.3, 1.50M.

In conclusion, geminate dissociation gives access to solutions. Further work will be necessary to achieve the best fit in Fig. 2 for the model value of 14A.

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Fig. 2 shows the analysis of the HPTS fluorescence decay in the presence of 150mM NaNO₃. The numerical calculation was carried out assuming that no screening of the Coulombic potential exists until the proton has reached the nearest neighbor distance $R_{av} = 3000/4\pi c n_A$ where $n_A$ is Avogadro's number and $c$ is the concentration of the oppositely charged ion in moles/liter. At larger distances the Coulombic potential is assumed to be totally screened. Although a good fit could be achieved without any adjustable parameters, we allowed ourselves some freedom in order to achieve the best fit. In Fig. 2 $R_{av}$ is taken as 16Å compared to a calculated value of 14Å.

In conclusion, geminate recombination of protons in excited-state acid dissociation gives access to the dynamical properties of electrolyte solutions. Further work is in progress aiming to bring new experimental and theoretical insights into this much investigated yet largely unresolved research field.

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