Geminate recombination in excited-state proton transfer reactions: Numerical solution of the Debye–Smoluchowski equation with backreaction and comparison with experimental results

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The well-known phenomenon of proton dissociation from excited-state hydroxy-arenes is analyzed by the Debye–Smoluchowski equation which is solved numerically with boundary conditions which account for the reversibility of the reaction. The numerical solution is then compared with the measured dissociation profiles which were obtained by picosecond time-resolved fluorescence spectroscopy. The intrinsic rate constants thus determined are used to predict steady-state rates, yields, and pK values, in agreement with experiment.

I. INTRODUCTION

Proton transfer reactions are among the most common and important chemical processes in aqueous solutions.1–4 In recent years, intermolecular proton transfer in the excited state has been the subject of intensive theoretical and experimental investigations as they provide valuable information about the mechanism and the nature of acid-base reactions in aqueous solutions.5–7

To initiate these reactions, aqueous solutions of suitable organic molecules are irradiated by very short (picosecond) laser pulses.8–10 Consequently, the excited-state molecules dissociate very rapidly by transferring a proton to nearby water molecules.

The overall dissociation process can be subdivided into two consecutive steps of reaction and diffusion. In the reactive stage, a rapid short range charge separation occurs, and a solvent-stabilized ion pair is formed. This is followed by a diffusive stage, when the two ions withdraw from each other due to their thermal random motion. The reverse process is geminate recombination (neutralization) of the two separated ions, either by the direct collapse of the ion pair, or following a geminate reencounter of the solvated “free” ions.

A simple and straightforward description of such a process was given by Eigen:4

\[
\text{RO}^- + \text{H}^+ \xrightarrow{k_p} \text{[RO}^- \cdot \cdot \cdot \text{H}^+] \xrightarrow{k_2} k\text{ROH,}\tag{1}
\]

where R is an organic radical and [RO\(^-\) \cdot \cdot \cdot \text{H}^+] is the ion pair formed between the molecular anion RO\(^-\) and the proton H\(^+\). \(k_p\) and \(k_2\) are the forward and reverse diffusion-controlled rate constants, obtained from a steady-state solution of the Debye–Smoluchowski equation (DSE).11 \(k_2\) and \(k_1\) are the ion-pair recombination and molecular dissociation rate constants.

In the above model all four rate coefficients are assumed to be independent of time. The model has proved to be very useful in describing fast homogeneous (as opposed to gemin-
combination in solution would serve as a good test case, but it was soon found that this system is complicated by effects such as electronic and vibrational relaxation, and it was concluded that the DSE is not a useful approach for this system. In fluorescence quenching the parameters derived from fitting the transient nanosecond kinetics to a solution of the DSE are in conflict with those obtained from the steady-state Stern–Volmer plots. For charge-recombination reactions there is evidence for agreement with the transient solution of the DSE in a Coulomb potential, however, the experimental results are presently only semiquantitative.

The HPTS dissociation and recombination is one or two orders of magnitude slower than the corresponding processes for I\(_\text{3}^-\). The longer diffusional times, which are more than an order of magnitude slower than the dielectric relaxation of water, allow the proton to explore large distances (see Fig. 8), which justifies the usage of the continuous DSE approach. In addition, fluorescence measurements are easier to interpret as compared with absorption measurements, where absorption from both ground and excited states must be considered. We find (see Sec. IV) that the present system is free of other possible complications, and therefore constitutes a suitable example of geminate recombination.

It is also interesting to compare the present system with the situation in the charge-recombination experiments. These differ in two respects: the initial and boundary conditions. When a molecule is ionized, an electron flies off "ballistically," and thermalizes at rather large distances. Only then does its motion become diffusive. Therefore, the initial condition is that of separated charges. In contrast, when a proton dissociates its excess kinetic energy is small (see Sec. IV). In addition, its mass is much larger than that of an electron, so that it is not ejected further away than the "contact distance," from where its motion is diffusive. The initial conditions are of the undissociated phenol molecule, the dissociation step being described by the backreaction boundary conditions.

The other difference is in the fate after recombination. Recombination with an electron immediately quenches any excitation in the molecular cation. No secondary dissociation is possible, and the ultimate fate is that of neutralization. Therefore, an absorbing or "radiation" boundary condition suffices: \( \kappa_t \) in Eq. (3) may be taken as zero. This is in general not the case for proton recombination in the excited state and in particular with excited state HPTS, which is not quenched to its ground state. It is shown below that proton recombination to HPTS is a reversible reaction, hence the backreaction boundary conditions are indispensable for a quantitative comparison of the DSE with experiment.

In the present work we compare new and more accurate experimental results on the survival probability of the excited HPTS molecule following a picosecond laser pulse, with the exact numerical solution of the DSE with backreaction boundary conditions. The rate parameters \( \kappa_p \) and \( \kappa_t \) thus determined give access to the factors which control the reactivity on the molecular level. These parameters determine the steady-state RO\(^-\) yield, recombination rate, and \( pK^* \) values. Unlike the case of fluorescence quenching, we find good agreement with independent steady-state experiments. In a subsequent paper the calculation is extended to nanoseconds and fits, with no additional free parameters, the ground-state recombination yields. To our knowledge, this comprises the first quantitative, comprehensive example for the adequacy of the time-dependent DSE description of fast chemical reactions.

II. EXPERIMENTAL

A. Materials

The sodium salt of 8-hydroxypyrene 1,3,6-trisulfonate (HPTS) was Laser Grade by Kodak and used without further purification. The HPTS molecule has in the ground state a \( pK = 7.7 \pm 0.1 \). Estimates of \( pK^* \) for the excited singlet state \( (S_1) \) vary between 1.4 and 0.5. Both anion (RO\(^-\)) and acid (ROH\(^+\)) forms of HPTS have a fluorescence lifetime of 5–6 ns in the excited \( S_1 \) state. \( \lambda_{\text{max}} \) for ROH\(^+\) and RO\(^-\) fluorescence are 445 and 510 nm, respectively. \( \lambda_{\text{max}} \) of the ground-state absorbance of these species are 403 and 454 nm, respectively. The excitation wavelength used was 354 nm, where the absorbance of the RO\(^-\) is only 15% of that of ROH \( (e(ROH) = 1.2 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}) \).

The experiments were carried out at \( pH = 5.5–6.0 \), where mostly the acid (ROH) form exists (RO\(^-\) concentration is less than 1%). This bulk pH is comparable to the \( pH \) induced by ROH\(^+\) dissociation. The low concentration of HPTS used, \( 5 \times 10^{-5} \text{ M} \), ensures (see Sec. IV) the predominance of geminate over homogeneous recombination. This also minimizes the salt effects on the reaction rates. Water was filtered and ion exchanged, so that its resistivity was larger than 2 MΩ. Deuterated HPTS was prepared by incubating the protonated HPTS in \( \geq 99.5\% \text{ D}_2\text{O} \) (Merk).

B. Experimental setup

The schematics of the optical arrangement are described elsewhere. A Nd\(^3+\)/YAG oscillator was passively mode locked to yield a 1.06 μm pulse train. A single pulse was extracted with a pulse selector (Laser Metrics) and amplified with a Nd\(^3+\)/YAG amplifier, partially converted to 532 nm with a KDP-type I crystal and to 354 nm with a KDP-type II crystal. A small portion of the 532 nm light was collimated into a vacuum photodiode to generate a streak camera trigger pulse \( ~ 20 \) ns before the sample emission reached the streak camera (Hamamatsu model C979, resolution 10 ps) entrance slit. The streak camera output was imaged onto an intensified silicon vidicon optical multichannel analyzer (PAR 1205D). The records were averaged and analyzed by a microcomputer system.

Samples (at concentrations of \( 5 \times 10^{-5} \text{ M} \)) were irradiated by a 354 nm 25 ps FWHM pulse, with intensity of \( 10 \mu\text{J/mm}^2 \). The fluorescence was collected from the front surface at angle of 15°. A polarizer set at 54.7° (the "magic angle") to eliminate polarization effects, was situated in front of the streak camera entrance slit. Colored glass filters were used to select and pass only the proper fluorescence band, i.e., ROH\(^+\) (blue, 400–460 nm) or RO\(^-\) (green) fluorescence. The blue band was collected after passing the
fluorescence signal through Schott filters BG-3 (2 nm) and GG-420, which together have a maximum transmission at 430 nm, while the green band was collected behind a Schott KV-550 filter, which has its maximum transmission at 550 nm.

In order to check whether the filters used for monitoring ROH* fluorescence pass any of the RO- fluence, we have monitored the fluorescence also under basic conditions, where RO- is excited directly. It was found that the signal after filtration was small. Taking into account the differences in excitation probabilities of the two species (see above) we conclude that in acidic conditions, where RO- is formed from the dissociation of ROH*, the anion contributes 0.6% of the blue fluorescence amplitude, 1 ns after excitation. This agrees with steady-state fluorescence measurements, where the intensity of the RO- band at the maximum of the ROH* band (445 nm) is only 0.5% of its peak intensity at 510 nm. Since both species have the same radiative lifetime (hence both bands have the same molar fluorescence intensities) this is also the contribution of the RO- fluorescence to the ROH* band at 445 nm.

III. NUMERICAL PROCEDURE

We describe an efficient algorithm for solving the spherically symmetric DSE in three dimensions:

\[
\frac{\partial p(r,t)}{\partial t} = -(4\pi r^2)^{-1} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} De^{-\nu} r^2 \frac{\partial}{\partial r} e^\nu p,
\]

where \(p(r,t)\) is a probability density function, \(t\) is time, \(r>\bar{a}\) is distance, \(D\) a diffusion coefficient (taken here as a constant), and \(V(r)\) is a potential function divided by \(\kappa_0 T\). \(J\) is the diffusional flux.

The boundary condition at the “contact distance” \(a\), is that of backreaction 16:

\[
J(a,t) = \kappa_d [1 - Q(t)] - \kappa_d 4\pi r^2 p(a,t),
\]

where

\[
Q(t) = \int_a^\infty q(r,t)dr,
\]

\[
q(r,0) = 0.
\]

We shall solve Eq. (8), subject to conditions (5') and (7').

The numerical algorithm begins with discretizing the coordinate \(r\), from \(a\) to some maximal value, \(r_{\text{max}}\), so that there are \(m+1\) evenly spaced points \(r_i\). Hence \(r_i = a + r_{i+1} - r_i\), and \(\Delta r = (r_{\text{max}} - a)/m\). A function, such as \(g(r,t)\), becomes a vector \(q_i(t), ..., q_{m+1}(t)\). To account for the “trap,” namely the dissociated ROH*, we add another point, say \(r_0 = a - \Delta r\), so that \(q_0(t)\Delta r = 1 - Q(t)\). Normalization now holds for the augmented set of points

\[
\sum_{i=0}^{m+1} q_i(t)\Delta r = 1.
\]

The algorithm involves two central steps: Evaluation of the operator and propagation in time of the probability density.

(i) Operator evaluation: We discretize the diffusion operator \(L\) so that Eq. (8) becomes a Master equation, 25(b),26 or Markov chain, with nearest-neighbor transitions:

\[
(Lq)_i = q_{i-1} \Omega(i|i-1) + q_{i-1} \Omega(i|i+1) - q_{i-1} \Omega(i-1|i) - q_{i-1} \Omega(i+1|i),
\]

\[
\Omega(i|j)\text{ are transition probabilities per unit time from }j \text{ to } l.
\]

The discretization of the one-dimensional DSE (8) gives

\[
\Omega(i|j) = \frac{D}{\Delta r^2} \exp \left(-\frac{\Delta U}{2}\right), \quad i,j \geq 1
\]

where \(\Delta U = U_i - U_j\) and \(\Delta V = V_i - V_j\). The preexponential factor in Eq. (11) favors transitions which increase \(r\), in accordance with the volume element \(4\pi r^2 dr\).

The merits of this approach over the conventional finite-difference discretization are discussed in detail in Ref. 25(b). For example, the transition probabilities obey detailed balance, \(\Omega(i|j)/\Omega(j|i) = \exp (-\Delta V)\). As compared with the fast Fourier transform method, 27 in the present procedure it is easier to introduce boundary conditions. This is done by noting that the flux is given by

\[
J_{i+1/2}(q) = q_i \Omega(i+1|i) - q_{i+1} \Omega(i|i+1) \Delta r.
\]

For transitions between the boundary at \(r_i = a\) and the trap, we replace Eq. (11) by

\[
\Omega(1|0) = \kappa_d, \quad \Omega(0|1) = \kappa_d/\Delta r
\]

which is obtained by comparing Eqs. (5') and (12). The radiation boundary condition 17 is a special case of Eq. (13), when \(\kappa_d = 0\). The transition frequencies are calculated once when initializing the program, and stored as the three vectors needed to evaluate the operator, Eq. (10).

\(r_{\text{max}}\) is taken large enough, so that only a negligible fraction of the population reaches this outer boundary during the propagation time. The boundary condition at \(r_{m+1} = r_{\text{max}}\) is therefore immaterial. In practice we set an absorbing boundary there, by reassigning \(\Omega(m|m+1) = 0\). We


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use the population accumulated at $r_{m+1}$ as a test for the choice of $r_{\text{max}}$.

Another advantage of the present algorithm is that it is easy to solve for an initial delta function probability density, which is

\[ q_0(0)\Delta r = 1, \quad q_i = 0 \quad \text{for} \quad i > 1. \quad (7^*) \]

The only numerical problem is due to the fact that, for an adequate representation of a delta function, $\Delta r$ should be small.

(ii) Propagation scheme: The propagation in time is based on the formal solution of Eq. (8):

\[ q(L,r + \Delta t) = \exp \left( -\Delta t \frac{L}{\nu} \right) q(r,t). \quad (14) \]

Following Ref. 28, we expand the exponent in a Chebyshev series. This series converges uniformly in the interval $[-1,1]$, which allows for relatively large propagation time steps. A similar propagation procedure has been used\(^\text{29}\) for solving the time-dependent Schrödinger equation. The Chebyshev expansion used is

\[ e^{\Delta A} = e^{-\nu \Delta t / 2} \sum_{n=0}^{N} a_n T_n \left( 2L/\nu + 1 \right), \quad (15) \]

where $a_0 = I_0(\nu \Delta t / 2)$ and $a_n = 2I_n(\nu \Delta t / 2)$ for $n > 0$. $I_n$ is the $n$th modified Bessel function of the first kind. $\nu$ is the highest frequency in the expansion. It is the upper bound for the range of eigenvalues of the operator $L$ on the 1D grid

\[ \nu = D \left[ \frac{\pi^2}{\Delta r^2} + \frac{\partial^2 U}{\partial \xi^2} \right]_{\text{max}}. \quad (16) \]

Since all the eigenvalues of $L$ are negative, those of $L/\nu$ are in $[-1,0]$. These are shifted in Eq. (15), so that they are distributed in $[-1,1]$. $T_n$ is the $n$th Chebyshev polynomial,\(^\text{30}\)

\[ T_n \left( \cos \theta \right) = \cos \left( n\theta \right) \quad (17) \]

calculated by its recursion relation:

\[ T_n \left( X \right) = 2XT_{n-1} \left( X \right) - T_{n-2} \left( X \right), \quad (18) \]

where $T_0(X) = 1$ is the identity operator, $T_1(X) = X$ and $X = 2L/\nu + 1$.

The number of terms in the Chebyshev expansion is determined by the Bessel function $I_n$ which decays exponentially if $n > \sqrt{\nu \Delta t}$. This means that for every propagation time step $\Delta t$, the number of terms is chosen to bring the accuracy of the calculation below a certain predetermined limit. We typically use 40 to 100 such terms. It is also clear that for longer time steps the procedure becomes more efficient.

The program was compared with analytic solutions\(^\text{31}\) for spherically symmetric free diffusion in 3D with absorbing, reflecting, and radiation boundary conditions. In 1D it was compared [after deleting the term $r_j/r_i$ in the transition frequencies, Eq. (11)] with the exact solution\(^\text{16(d)}\) for free diffusion with absorbing, reflecting, and back-reaction boundary conditions at $r = a$, as well as with those for diffusion in a linear potential with radiation boundary conditions. In all cases initial delta-function conditions were used.

IV. RESULTS AND DISCUSSION

A. Proofs for the validity of the proposed mechanism

The species involved in the HPTS (scheme I) excited-state deprotonation process, Eq. (3), are easily observed by time-resolved fluorescence spectroscopy. Figure 1 shows the emission of both ROH* and ROH−. Note the nonexponentiality of these curves, as manifested by their long-time tails. Following are some experimental proofs that this observed behavior is due to a simple dissociation–recombination reaction in the excited state.

(i) Excitation is a simple one-photon process: To verify this point, we have varied the laser intensity in the range of 2 to 50 $\mu J/mm^2$. We have found that within the dynamic range of the streak camera the total integrated fluorescence signal is linear in intensity, and the decay profile is unchanged. In addition, we have carried out a measurement of the time-resolved emission of ROH* and ROH− using a very low-power (pJ/pulse), high repetition rate (82 MHz) cw mode-locked argon pumped dye laser with a synchronscan streak camera (Hamamatsu), again finding an almost identical decay profile. The 96% quantum yield\(^\text{32}\) also attests to a one-photon process.

(ii) Excitation does not cause photodegradation: The HPTS molecule was found to be very stable under conditions of N$_2$ laser excitation at 337 nm. After 10$^6$ pulses, each ~1 ns long and 5 $\mu J/mm^2$ in intensity, no apparent change

![FIG. 1. ROH* (blue) fluorescence decay at ~340 nm and ROH− (green) fluorescence rise at ~550 nm, corresponding to the proton-transfer reaction ROH* (blue) → ROH− (green) + H+. The fluorescence was monitored by a streak camera, following laser excitation at 354 nm of 5 × 10$^{-8}$ M HPTS solution in water.](image)
was found in the ground-state diffusion-controlled kinetics of the HPTS anion.  

(iii) The initial state is that of ROH*: This is clearly seen from the temporal profile in Fig. 1, which (save for the rise-time which is due to the finite width of the laser pulse) is monotonically decreasing. It contrasts with the photodetachment experiments, where the electron is ejected ballistically, probably in the subpicosecond time scale, to very large distances.

(iv) The fast decay of the ROH* fluorescence is due to the deprotonation process: As can be seen from Fig. 1, the ROH* decay fits well with the rise time of the RO−* fluorescence, both of about 100 ps duration. This observation, combined with the known total quantum yield for ROH* and RO−* formation which is close to unity (4% and 96%, respectively) leads us to conclude that nonreactive processes contribute negligibly to the observed decay profile.

(v) Excess photon energy does not affect the kinetics: The experimental results obtained by using the fourth harmonic of a Nd^{3+}/YAG laser, 37 600 cm⁻¹, were the same as those obtained with the third harmonic, 28 200 cm⁻¹, which is the frequency used throughout this work. Since the maximum in the S<T₂−>S₁ absorption band is at 27 700 cm⁻¹, this shows that the kinetics is insensitive to excess energy (above the S₁ zero-point energy) between 3500 and 13 000 cm⁻¹. We conclude, as is usually assumed in such cases, that ultrafast vibrational relaxation is taking place prior to the photon transfer.

It follows that the excess vibrational energy is transferred to the solvent as heat. Using the heat capacity and the density of water, we calculate that for an excess photon energy of 3500 cm⁻¹ (excitation with the third Nd^{3+}/YAG harmonic used in this work) the temperature in a sphere of 15 Å around an excited HPTS molecule would increase by only 1 °C. Moreover, using the diffusional heat transfer coefficient a = 1.46 × 10⁻⁴ cm² s⁻¹, which is more than an order of magnitude larger than the protic diffusion coefficient, we find that the time needed for the heat to be transferred to a distance r = 15 Å is ā of 0.1 ps. Thus, heat transfer away from the reaction center is faster than proton dissociation. We conclude that the proton dissociates to the contact distance, and that its excess energy above thermal is negligible, so that its motion is diffusive from the outset.

(vi) The long tail in the ROH* emission is due to recombination of RO−* with the geminate proton: There are two arguments showing that it is not due to recombination with homogeneous protons. First, for the low concentrations (3 × 10⁻⁶ M) of protons used, the average distance between protons is almost 800 Å. For typical values of the protic diffusion constant, D = 930 Å²/ns, there would be little homogeneous recombination during the fluorescence lifetime of the RO−* (6 ns), and practically none during the time of measurement (1.5 ns). Second, there was no apparent dependence of the dissociation kinetics on the laser intensity, hence on the transient pH induced by photolysis, nor on HPTS concentration in the range 1–100 μM.

To check this point further, we have measured the ROH* time-resolved fluorescence in several aqueous solutions, containing increasing concentrations of acid (HClO₄). As can be seen from Fig. 2, the long-lived component is independent of the pH at small acid concentrations (1–100 μM). It is only at higher acid concentrations that we observe an increase in its amplitude with decreasing pH. This is a kinetic (as opposed to a steady state) fluorimetric titration. The increase in the amplitude of the tail above its value at low acid concentrations is due to the increasing role of homogeneous recombination. A quantitative treatment of the concomitant geminate-homogeneous processes is postponed to future work.

(vii) Reprotonation does not cause deexcitation: A question arises whether the reprotonation causes a radiolysis transition of the excited species to the ground state, namely RO−* + H⁺ → ROH. Steady-state fluorescence analysis revealed that the sulfonate derivatives of 2-naphthol react with excess protons with diffusion-controlled rates, and that the excited species, ROH* and RO−*, remain in the excited state. Deactivation, if it occurs at all in these molecules, should be negligible, as was found in the case of 2-naphthol itself, where protonation is two orders of magnitude faster than deactivation. Dynamic measurements of 2-naphthol 6-sulfonate gave similar results. An exception to this general trend is 1-naphthol: It was found both from steady-state and transient measurements, that in this molecule reprotonation does cause a radiolysis transition to the ground state. This is typical to the α position of naphthalene derivatives. As for the HPTS molecule, deactivation was not observed in either the steady-state or transient measurements. This can be seen from Fig. 2, where the tail of the observed ROH* fluorescence preserves its 6 ns lifetime, and is unaffected by the addition of concentrated acids (pH = 1.3).

Finally, we argue that a continuous dissipation scheme is appropriate for the present system because this fast chemical reaction is still slow (> 100 ps) not only as compared with vibrational relaxation and heat-transfer time scales (see above), but also compared to the dielectric relaxation
time of the solvent (9.4 ps for water at 25 °C). The longitudinal relaxation time is obtained by multiplying the above by \( \frac{\epsilon_0}{\epsilon} (\epsilon = \text{dielectric constant at a frequency } f) \). Hence it takes 250 fs for the solvent to rearrange around a point charge. In addition, the initial dissociation step (to the contact distance \( a \), see below) separates the proton from the anion by about two water layers. We assume that the hydrated dissociated proton at this distance already exhibits transport properties of the bulk hydrated proton, hence that molecular effects on \( D \) or \( \epsilon \) are small, and using their bulk values is justified.

B. Effect of the parameters in the diffusional scheme

The above discussion suggests that the simple reversible DSE, described in Sec. III, is an appropriate model for HPTS picosecond dissociation kinetics. The solution of the diffusion equation is determined by several parameters, which we wish to discuss below:

(i) The unscreened Coulomb potential \( V(r) = -R_D/r \), which is governed by the “Debye radius”

\[
R_D = \frac{|z_1 z_2| e^2}{\epsilon k_B T}
\]

(19)
determined by the charges \( z_1 \) and \( z_2 \) of the proton and anion (1 and -4 for HPTS), the dielectric constant \( \epsilon \) of the solvent, and the absolute temperature \( T \). (\( e \) is the electronic charge and \( k_B \) is Boltzmann’s constant.) The use of the unscreened potential is justified by the low ionic strength (\( \approx 0.3 \) mM) and the large average distance between the sodium cations (about 150 Å for the \( 5 \times 10^{-5} \) M tri-sodium salt of HPTS).

(ii) The contact distance \( a \), which is the center-to-center distance in the few water molecules separated ion pair. The motion is assumed diffusive for \( r > a \).

(iii) The relative anion–proton diffusion constant \( D \), which is almost the same as the (very large) proton diffusion constant.21

(iv) The initial separation of the proton after thermalization, \( r_0 \). Here we assume that \( r_0 \) is that of the bound proton, so that this parameter plays no role in our analysis.

(v) The intrinsic dissociation and recombination rate constants to and from contact, designated \( \kappa_d \) and \( \kappa_r \), respectively [cf. Eq. (5)].

In Figs. 3 and 4 we plot the calculated survival probability for ROH\(^+\) as a function of time for several values of the abovementioned parameters. In each panel the second curve from the bottom is similar to the best fit for the experimental fluorescence of HPTS in water at 20 °C (see below). In each panel, we hold all parameters at their best-fit values except for one (denoted in each panel) which has been changed.

In Fig. 3 one sees that an increase in \( R_D \) is somewhat equivalent to a decrease in \( a \); both result in a more intense Coulomb field at contact, hence in faster recombination. The effect in \( D \) is milder but, as can be expected, slower diffusion also results in enhanced geminate recombination. From the panel at the lower right we see that if at \( t = 0 \) the proton is already dissociated and located even 1 Å away from contact, a completely different profile is expected: [ROH\(^+\)] is initially zero, rises to a small value due to recombination, and finally decays by dissociation and diffusion.

In Fig. 4 we see that \( \kappa_d \) determines the initial slope of the decay curves: The larger \( \kappa_d \), the faster the initial exponential drop. The intrinsic recombination rate constant \( \kappa_r \), does not effect the behavior at \( t \to 0 \), but determines the magnitude of the long-time tail. The effect of increasing \( \kappa_r \) is somewhat similar to decreasing \( D \). It differs from the effect of changing \( R_D \) or \( a \) in the curvature of these plots.

C. Fitting the experimental results

The parameters for the numerical solution of the DSE (4) were taken from the literature,27,28 when available: \( R_D(T) \) was calculated [cf. Eq. (19)] from the experimental values of \( \epsilon(T) \).27 The mutual proton–anion diffusion coefficient \( D(T) \) is mainly due to the proton diffusion coefficient,28 to which we have added 0.06 or 0.05 Å\(^2\)/ps as the contribution from the anion diffusion coefficient in \( \text{H}_2\text{O} \) or \( \text{D}_2\text{O} \), respectively. The contact radius \( a = 6.5 \) Å is similar to the value recommended in the literature.39,40 This value is slightly larger than the molecular spherical gyration radius (4.5–5.5 Å) obtained from measurements of HPTS ro-

![FIG. 3. Effect of variations in the different parameters on the ROH\(^+\) survival probability. In each panel only one parameter is varied (marked) while the others are kept at their values for HPTS in water at 20 °C (Table 1). Note the change in the time scale for \( r_0 \) variations (bottom right panel).](image)

![FIG. 4. Effect of varying the intrinsic rate constants on the survival probability of ROH\(^+\). See legend of Fig. 3.](image)
TABLE I. Parameters for fitting the HPTS fluorescence decay in water shown in Fig. 5.

<table>
<thead>
<tr>
<th>Parameter*</th>
<th>80 °C</th>
<th>20 °C</th>
<th>2 °C</th>
<th>−12 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>( D(A^2 \text{ps}^{-1}) )</td>
<td>1.68</td>
<td>0.91</td>
<td>0.61</td>
<td>0.41</td>
</tr>
<tr>
<td>( R_0 (\text{Å}) )</td>
<td>31.0</td>
<td>28.4</td>
<td>27.9</td>
<td>27.6</td>
</tr>
<tr>
<td>( \alpha (\text{Å}) )</td>
<td>6.5</td>
<td>6.5</td>
<td>6.5</td>
<td>6.5</td>
</tr>
<tr>
<td>( 10^3 \times \kappa_d (\text{ps}^{-1}) )</td>
<td>10</td>
<td>9.2</td>
<td>7.5</td>
<td>6.0</td>
</tr>
<tr>
<td>( 10^5 \times \kappa_r (\text{Å ps}^{-1}) )</td>
<td>9</td>
<td>9.3</td>
<td>6</td>
<td>3</td>
</tr>
<tr>
<td>( r_{\text{max}} (\text{Å}) )</td>
<td>280</td>
<td>250</td>
<td>200</td>
<td>170</td>
</tr>
<tr>
<td>( m )</td>
<td>480</td>
<td>500</td>
<td>400</td>
<td>240</td>
</tr>
<tr>
<td>( \Delta r (\text{Å}) )</td>
<td>0.57</td>
<td>0.48</td>
<td>0.48</td>
<td>0.63</td>
</tr>
<tr>
<td>( N )</td>
<td>76</td>
<td>87</td>
<td>72</td>
<td>47</td>
</tr>
<tr>
<td>( \Delta t (\text{ps}) )</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>( \sigma (\text{ps}) )</td>
<td>50</td>
<td>47</td>
<td>47</td>
<td>47</td>
</tr>
<tr>
<td>Shift (ps)</td>
<td>−3</td>
<td>0</td>
<td>0</td>
<td>5</td>
</tr>
<tr>
<td>( 10^r \text{ rmsd} )</td>
<td>4.1</td>
<td>4.2</td>
<td>5.4</td>
<td>12</td>
</tr>
</tbody>
</table>

* \( m \) and \( N \) are number of grid points and Chebyshev terms, Eq. (15). \( \alpha \) is the full width of the Gaussian instrument response function at half-height. Shift is temporal shift between maxima of experimental and theoretical curves. rmsd is the root mean square deviation.

Such a fit involves a third parameter, namely the ratio of the amplitudes of the two components, which in turn determines the curvature of the plot at intermediate times. However, a biexponential cannot fit the decay profile over an extended time regime. This is clearly demonstrated in a subsequent work. \(^{11(a)}\)

In addition to the abovementioned parameters, there are parameters which are due to the experimental setup. Most important is the width of the overall instrumental response function. For example, the response function for the streak camera in the scale of 1500 ps with the entrance optics used for HPTS in water has a width of 33 ps FWHM (full width at half-height). Combined with the laser profile of 25 ps FWHM, we conclude that the total width of the line shape with which the calculated kinetics must be convoluted is at least 41 ps FWHM for the \( H_2 O \) results. The number used in our fits is (Table I) 45–50 ps. In addition, the relative intensity of the experimental profiles was normalized to the maximum of the theoretical profile, and \( t = 0 \) was set at the maximum of the profiles.

Figures 5 and 6 show the result of the above fitting procedure to our time-resolved ROH* and ROD* fluorescence emission. (These were measured in \( H_2 O \) and \( D_2 O \), respectively.) As can be seen, the fits at room temperature and above are excellent. As \( T \) is lowered, there is an increasing discrepancy at intermediate times, where the calculated curves underestimate the experimental decay.

One possible explanation is demonstrated by Fig. 7, where a much larger value for the contact distance \( \sigma = 20 \text{ Å} \) is used. This suggests that at low temperatures there may be an increase in the “local order” around the anion.

An alternative explanation invokes competition between geminate recombination and rotation of the HPTS

![Figure 5](image-url)

FIG. 5. Comparison of the experimental decay (dots) of the excited \( (S_1) \) HPTS molecule in water, at four different temperatures, with the numerical integration (full curve) of Eq. (4), corrected for the 0.6% of RO* fluorescence, multiplied by \( \exp ( -t/\tau ) \) and convoluted with the experimental response function (dashed curve). Parameters for the fits are given in Table I.
anion. This is determined by the relative time constants for (proton) translational diffusion vs (anion) rotational diffusion. If the rotational time constant $\tau_R$ is much larger than the geminate recombination time scale, the proton is likely to return to the hydroxy-group side of the HPTS anion, resulting in a large, time-independent value for $\kappa$. If, on the other hand, $\tau_R$ is much smaller than the typical recombination time, the returning proton is likely to find the hydroxy group uniformly distributed on a sphere of radius $a$. This would result in a smaller, but time-independent value of $\kappa$. When the two time constants are of similar magnitude, one expects $\kappa$ to decrease with time. As a result, the tail at intermediate times would be larger than predicted from fitting a constant $\kappa$ to the long-time behavior.

The typical time when the contribution of geminate recombination to the observed fluorescence decay in H$_2$O becomes appreciable can be estimated from the location of maximal curvature in the plots of Fig. 5, to be 300–400 ps. It can be seen that this value depends only weakly on temperature: First, due to the anomalous proton mobility, the proton diffusion coefficient $D$ decreases only by a factor of 2 between room temperature and $-12$ °C. Second, the decrease in $R_D$ with decreasing $T$ operates in the opposite direction to the decrease in $D$ (cf. Fig. 3).

Values for the measured $\tau_R$ are found$^{39(a),40}$ to be in the range of 100–160 ps at room temperature [an exception is the value reported in Ref. 39(b)]. The most reliable value is perhaps $^{40(b)} \tau_R \approx 150$ ps which is fast compared with the translational diffusion. Let us assume, as in the Einstein–Stokes relation, that $\tau_R$ is proportional to $\eta / T$, where $\eta$ is the solvent's shear viscosity. $\eta$ depends exponentially on $1/T$. Extrapolating the observed viscosity of water$^{37}$ to $-12$ °C gives $\tau_R$ ( $-12$ °C) = 450 ps. At this low temperature molecular rotation is slowed down to the time scale of proton geminate recombination, so that an accurate solution would have to include both translational and rotational diffusion.

The temporal evolution of the proton and deuteron distribution functions, obtained as a numerical solution of Eq. (4), is shown in Fig. 8. At $t = 0$ all the protons are bound to ROH*. According to our model, the protons are discharged from ROH* at the contact distance $a = 6.5$ Å with a time constant of about 100 ps at 20 °C. At short times, the proton distribution is almost exponential: Due to the relative slowness of the protic diffusion process, protons are located near the contact distance. At longer times, diffusion sets in and the shape of the distribution changes. At still longer times it achieves a quasiequilibrium shape, with the famous minimum$^{41}$ which is due to the attractive Coulomb forces. In D$_2$O this temporal evolution is slower than in H$_2$O. This is due to the larger mass, which results$^{38}$ in a D$^+$ diffusion coefficient which is smaller by 30% compared with that of H$^+$.

It is interesting to consider the values of the intrinsic rate parameters obtained, as shown in Tables I and II. We estimate the accuracy in $\kappa$ to be 10%. Because of the difficulty in obtaining a reliable long-time tail, the determination of $\kappa$ is accurate only to 20%–30%. Both parameters are insensitive to temperature in the high $T$ range (80–20 °C for

![FIG. 6. Same as Fig. 5 for deuterated HPTS. Parameters collected in Table II.](image)

![FIG. 7. An improved fit to the fluorescence decay in supercooled solvents, compare with Figs. 5 and 6. The fit was achieved by substantially increasing the contact distance (to $a = 20$ Å) and $\kappa$ (to $9 \times 10^{-3}$ Å/ps for H$_2$O and $25 \times 10^{-3}$ Å/ps in D$_2$O). Other parameters are unchanged.](image)
parameters are determined from fitting the transient experiments. \( \tau \) is the fluorescence lifetime of both species. We have extended the numerical integration of Eq. (4) to 20 ns using the parameters of Table I, and performed the integration in Eq. (20) numerically to an accuracy of at least 1%. We find for \( \phi(\text{ROH}^*) \) values ranging from \( 3.2 \times 10^{-2} \) for \( \tau = 6.0 \) ns to \( 3.7 \times 10^{-2} \) for \( \tau = 5.4 \) ns. Taking into account errors in both intrinsic rate constants and radiative lifetime \( \tau \), we get \( \phi = 3.5 \pm 0.7 \times 10^{-2} \).

(ii) Off rate constant: The overall steady-state rate coefficient for proton detachment,

\[
\frac{k_{\text{off}}}{k_{\text{on}}} = \frac{\text{ROH}^*}{\text{ROH}^- + \text{H}^+}
\]

designated here as \( k_{\text{off}} \), can be determined by integrating the excited-state ROH* survival probability for an infinite radiative lifetime

\[
\tau_{\text{off}} = k_{\text{off}}^{-1} = \int_0^\infty [1 - Q(t)] dt
\]

or from the simple relation

\[
k_{\text{off}} = k_d / \left( 1 + a^2 \kappa_r \left[ \exp \left( R_D / a \right) - 1 \right] / DR_D \right). \tag{21b}
\]

From a numerical integration to 25 ns we find \( \tau_{\text{off}} = 234 \pm 5 \) ps at \( 20^\circ \text{C} \). From Eq. (21b), \( k_{\text{off}} = 4.2 \pm 0.5 \times 10^8 \) s\(^{-1}\).

Approximating \( 1 - Q(t) \) in Eq. (20) by \( \exp \left( -t/\tau_{\text{off}} \right) \), gives for the fluorescence yield

\[
\phi(\text{ROH}^*) \approx \frac{\tau_{\text{off}}}{\tau_{\text{off}} + \tau}. \tag{20'}
\]

Traditionally,\(^{22}\) Eq. (20') has been used for calculating \( k_{\text{off}} \) from the measured values of \( \tau \) and \( \phi \). Using \( \tau_{\text{off}} = 238 \) ps, we find for \( \phi(\text{ROH}^*) \) values between \( 3.8 \times 10^{-2} \) for \( \tau = 6.0 \) ns and \( 4.2 \times 10^{-2} \) for \( \tau = 5.4 \) ns. These values are within 15% of the values obtained from Eq. (20).

(iii) On rate constant: The on rate constant, which is the overall homogeneous protonation rate under steady-state conditions, has been measured\(^{30}\) by fluorimetric titration (steady-state fluorescence spectrum as a function of pH)\(^{3} \) to be \( k_{\text{on}} = 5 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1} \). The steady-state diffusion boundary condition at a \( [\text{H}_2 \text{O}] = 0 \) in Eq. (5) is given by\(^{4,12}\)

\[
k_{\text{on}} = \frac{4 \pi DR_D}{1 + \left[ DR_D / a^2 \kappa_r \left( DR_D / a^2 \kappa_r - 1 \right) \right] \exp \left( -R_D / a \right)}. \tag{22}
\]

Inserting the parameters for HPTS in water at 20 °C (Table I), we find \( k_{\text{on}} = (1.1 \pm 0.2) \times 10^{11} \text{ M}^{-1} \text{ s}^{-1} \). (The numerator in units of cm\(^2\)/s×molecule was multiplied by \( N_A / 1000 \), where \( N_A \) is Avogadro’s number.)

\( k_{\text{on}} \) can also be estimated from the analysis of the time-resolved proton titration data presented in Fig. 2. As a first approximation, we have subtracted the contribution of geminate recombination to the long-time tail of the ROH* fluorescence. From simple kinetic considerations, the ratio of the short- and long-time components is proportional to \( \left( k_{\text{off}} / k_{\text{on}} \right) \), where \( c \) is the homogeneous proton concentration. Taking into account the effect of ionic strength, the analysis gives \( k_{\text{on}} = (1.2 \pm 0.15) \times 10^{11} \text{ M}^{-1} \text{ s}^{-1} \).

**D. Comparison with steady-state results**

We compare below the parameters obtained from fitting the transient picosecond kinetics, with results measured at room temperature by steady-state fluorescence using a continuous rather than a pulsed light source. The various results are summarized in Table III.

(i) Fluorescence yields: The steady-state fluorescence spectrum of HPTS shows\(^{3} \) a small peak for ROH*, centered at 445 nm, and a very large peak for ROO* which is centered at 510 nm. We have measured the fluorescence spectrum in an expanded scale and under the same conditions as in the transient experiments. From the area under the two peaks (taking account of their overlap) we find, in agreement with Ref. 22, that the ROH* peak occupies 4.5 ± 1% of the total area for HPTS in water at 20°C. Since the total ROH* + ROO* quantum yield is nearly unity,\(^{22}\) this represents the absolute ROH* quantum yield.

On the other hand, this absolute fluorescence yield can be calculated as

\[
\phi(\text{ROH}^*) = \tau_{\text{off}}^{-1} \int_0^\infty [1 - Q(t)] \exp \left( -t/\tau_{\text{off}} \right) dt, \tag{20}
\]

where \( Q(t) \) is obtained from the solution of Eq. (4), and the

**TABLE III. Steady-state results: A comparison of their determination by the present transient measurements (= pw) and previous measurements of steady-state HPTS fluorescence in water at room temperature.**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Present work</th>
<th>Steady-state exp</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \phi ) (%)</td>
<td>3.5 ± 0.7</td>
<td>4.5 ± 1</td>
<td>pw, 6, 22</td>
</tr>
<tr>
<td>( k_{\text{on}} ) (10^10 M(^{-1}) s(^{-1}))</td>
<td>11 ± 2</td>
<td>5.0 ± 0.2</td>
<td>3(b)</td>
</tr>
<tr>
<td>( k_{\text{off}} ) (10^8 s(^{-1}))</td>
<td>4.2 ± 0.5</td>
<td>2.1 ± 1.4</td>
<td>22</td>
</tr>
<tr>
<td>( pK^* )</td>
<td>1.41 ± 0.07</td>
<td>1.38 ± 0.05</td>
<td>3(b)</td>
</tr>
</tbody>
</table>

(iv) \( pK^* \) determination: Excited-state \( pK^* \) values at infinite dilution (conventionally denoted \( pK^* \)) can be determined from [see also Ref. 13(b)]

\[
K^* = k_{\text{off}}/k_{\text{on}} = \frac{\kappa_d \exp\left(-R_D/a\right)}{4\pi a^2 \kappa_r}.
\]

(23)

Using the parameters of Table I (and converting to units of molaras above) we find \( pK^* = 1.41 \pm 0.07 \), in agreement with the value of \( 1.38 \pm 0.05 \) obtained by Weller. 3(b)

(v) Isotope effects: Discussion of the room-temperature isotope effects is deferred to a later publication, 13(a) where we reexamine both isotopic reactions at 23 °C.

(vi) Number of rebindings: The average number of times a proton rebinds to the anion prior to its ultimate escape (i.e., the number of returns of the origin of the random walk) can be evaluated as follows: The average number of times a proton dissociates is \( \kappa_d/k_{\text{off}} \), therefore the number of returns is simply

\[
N_r = \frac{\kappa_d}{k_{\text{off}}} - 1.
\]

(24)

This can also be written as \( \left(\tau_{\text{off}} - \tau_d\right)/\tau_d \), where \( \tau_d \equiv 1/\kappa_d \).

Hence \( N_r \) is just the area of the tail divided by the area under the exponential part of the kinetic trace. In water at 20 °C we find \( N_r = 1.15 \).

V. CONCLUSION

We have studied by picosecond transient fluorescence methods the phenomenon of proton dissociation from an electronically excited state of 8-hydroxypyrene 1,3,6-trisulfonate (HPTS). We have shown that this system is free of many complications encountered in other systems which were studied in the past, 18-20 and hence represents an ideal case of geminate recombination. The deprotonated species ROH* is four times charged, and therefore exhibits a large Coulomb attraction to the geminate solvated proton. This results in enhanced geminate recombination, which is manifested in the long-time nonexponential tail of the ROH* fluorescence decay.

The conventional rate-equation approach is insufficient for explaining the observed kinetics, 13(a) which has to be analyzed by the exact numerical solution of the transient Debye-Smoluchowski equation (DSE). To account for multiple dissociation-recombination cycles, we have utilized, for the first time in this field, the "backreaction" boundary condition. Excellent agreement with our transient fluorescence decay curves was obtained at the higher temperatures. At low temperatures one possibly needs to take into account the effect of anionic rotational diffusion. The observed discrepancy under these conditions may therefore be due to a transient steric effect. This is a subject for future investigations.

From the intrinsic rate parameters obtained we could generate, with no additional free parameters, the fluorescence yield, overall dissociation and recombination rates and \( pK^* \) values, generally in good accord with steady-state experiments. In a following publication, 13(c) we show that the ground-state ROH yields are also correctly determined from these parameters. Together this presents a comprehensive test to the validity of the DSE for fast reactions in solution.

Our results demonstrate how many important features in excited-state dissociation are influenced by the geminate-recombination process. It seems justified to speculate that the role of geminate recombination can be even larger in volume-limited diffusion, 6,13(b) such as in micelles or in the cavity of an enzyme. A particularly large effect of geminate recombination is anticipated in cases of a small diffusion coefficient or a large Coulomb attraction. Such cases are encountered at low temperatures or in mixed water/organic solvent solutions.

ACKNOWLEDGMENTS

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