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Non-Exponential Smoluchowski Dynamics in Fast Acid−Base Reaction

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Acid−base reactions are among the most fundamental processes in chemistry. Numerous liquid-phase reactions are known to be acid- or base-catalyzed. In biology, the proton appears as a substrate, product, or intermediate in nearly all enzymatic reactions. Acid−base reactions can be extremely fast,[1] and thus diffusion may lead to strong deviations from simple exponential kinetics. Yet fast direct proton transfer (PT) between acid (AH) and base (B),

$$\mathrm{AH} + \mathrm{B} \rightarrow \mathrm{A} + \mathrm{BH}$$

have hardly been studied in the time domain. Such studies require a fast trigger to initiate the reaction.

Ultrafast laser initiation is possible for photoacids (e.g., hydroxyaryls, which exhibit enhanced acidity in their excited S_1 state[2]), leading to ultrafast PT to solvent (PTTS).[3] We have studied such reactions, finding that they behave reversibly during their excited-state lifetime.[4−6]

$$\mathrm{AH} \overset{1/\tau_d}{\rightleftharpoons} \mathrm{A}^- + \mathrm{H}^+ \text{ (solv.)}$$

As to excited-state PT from AH to B, only the limits of small or large [B] were investigated.[7,8] Small amounts of base scavenge the diffusing proton[7] but do not react directly with AH. At very large B-concentrations, AH···B complexes form already in the ground-state, reacting irreversibly with rates which exceed those of PTTS.[8] The present work investigates the regime of intermediate [B], when the direct AH + B reaction occurs in preference to PTTS.

Bimolecular irreversible diffusion influenced reactions,[9] in the pseudo-unimolecular limit when one reactant (say, B) is in excess, are the subject of the celebrated “Smoluchowski theory”.[10] In the limit that the proton donor (AH) is static this theory is exact.[11,12] It is an excellent approximation also when both donor and acceptor move.[13] The initial decay is faster than exponential due to the excess of B molecules at close proximity to AH.[14] As this density approaches its steady-state limit, the reaction becomes exponential, $\exp(-k_\infty t)$. This theory has been applied predominantly to fluorescence quenching,[15] but it proved difficult to find conclusive experimental evidence for the predicted initial non-exponential regime in the quenching kinetics.[16]

Table 1. Literature and Derived Data for Glycerol/Water Mixtures

vol % glycerol	ϵ[a]	(η/η_0)[b]	τ_d (ns)[c]	D (10^{-5} cm^2/s)[d]	b[e]
0	78	1.00	1.2	0.97	0.0042
10	74	2.27	2.1	0.45	0.0085
20	71	2.98	3.3	0.26	0.0029
30	68	3.87	5.0	0.17	0.0010
40	65	6.21	7.7	0.115	0.0056
50	61	11.1	12	0.067	0.0022
60	58	21.7	20	0.040	0.017
70	53	43.1	33	0.023	0.0095

[a] Static dielectric constant.[18] [b] Solution viscosity relative to 0 M glycerol (η_0), after adding 2 M CH_3COONa. [c] Proton dissociation times measured with 2 M $NaClO_4$. [d] Sum of 2N6S + CH_3COO^- diffusion coefficients from our dynamic measurements. [e] Background subtracted in eq 1.

The present work is unique in (a) observing non-exponential kinetic data for a direct acid−base reaction and (b) demonstrating that it quantitatively conforms with the Smoluchowski theory. Using time-resolved fluorescence, we monitor excited-state proton-transfer from 2-naphthol-6-sulfonate (2N6S) to an acetate (Ac) anion in water/glycerol mixtures of varying compositions (at room temperature). The solution pH was adjusted to around 7 by adding small amounts of acetic acid. The relative acid−base diffusion coefficient varies (by a factor of 40) with the solvent viscosity, η, which we measure independently using an Ostwald viscosimeter (see Table 1). This, we show, is the major cause for the large changes in the AH + B kinetics.

Details of the experimental setup[6] and steady-state fluorescence spectra are available as Supporting Information. The absence of spectral shifts with solvent composition indicates that negligible ground-state ion pairing takes place. Indeed, with acid and base both negatively charged, such pairing is not expected, so that PT must occur by their relative diffusion. Transient fluorescence was recorded near the peak of the acid emission band (360 nm). The width of the instrument response function (IRF) was about 50 ps (fwhm). It has parasitic after-spikes at 0.4 and 1.5 ns delay (Figure 1, dashed curve), and this adds nondesired bumps to fast-decaying profiles. We account for the IRF by convoluting it with the theoretical results prior to comparison with experiment.

For each water/glycerol mixture we have made three time-resolved measurements: (a) with both 2N6S and NaAc present, (b) with acetate only, and (c) with 2N6S and 2 M $NaClO_4$ replacing the NaAc. Measurement (b) gave us a small fluorescence background from the solvent, which was subtracted from (a) to produce the observed intensity, I_{obs}. The latter was further corrected for the excited-state lifetime, τ_0, and a constant background, b, according to

$$I_{\mathrm{corr}}(t) = I_{\mathrm{obs}}(t)\exp(t/\tau_0) - b \tag{1}$$

$\tau_0 = 10$ ns was assumed invariant of glycerol content. The 0.1−1% background is almost unavoidable in sensitive fluorescence measurements. It might arise from a small degree of dimerization

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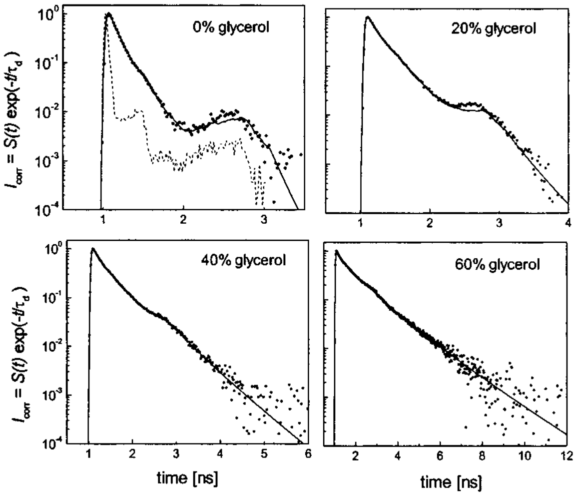

Figure 1. Time-resolved emission of 2N6S in water/glycerol mixtures (vol % indicated) containing 2 M NaAc. Circles are the corrected intensities according to eq 1. Lines depict the Smoluchowski model, eqs 2−4, calculated using the SSDP software.[19] Both were normalized to unity at the peak. $a = 7$ Å, $k_{PT} = 8 \times 10^9$ M^{-1} s^{-1}, $\tau_0 = 10$ ns, and other parameters in Table 1. Normalized IRF is shown as the dashed curve (upper left panel). Time zero is arbitrary.

or degradation of the photoacid. Figure 1 shows I_{corr} (circles) for four out of eight different water/glycerol compositions. Measurement (c) yielded the PTTS times (τ_d, Table 1) under conditions of identical ionic strength but no direct PT to the acetate base. These increase considerably with increasing organic cosolvent[17] and salt concentration. Below we multiply the survival probability, $S(t)$, of the 2N6S acid by $\exp(-t/\tau_d)$ to account for the (small) contribution from PTTS.

According to the Smoluchowski theory,[9−12] the survival probability of the donor (here, AH) due to its irreversible reaction with a concentration $c \equiv [B]$ of acceptors is given by

$$S(t) = \exp\left(-c\int_0^t k(t')\mathrm{d}t'\right) \qquad (2)$$

where $k(t)$ is the time-dependent rate coefficient (i.e., the reactive flux at the contact distance $r = a$) for the donor−acceptor pair

$$k(t) = k_{PT}p(a, t) = 4\pi Da^2\, e^{-\beta U(a)}\, \frac{\partial}{\partial r}\, e^{\beta U(r)} p(r, t)|_{r=a} \qquad (3)$$

The pair density distribution, $p(r, t)$, is governed by a Smoluchowski equation (diffusion in a potential $U(r)$) in three dimensions

$$\frac{\partial p(r, t)}{\partial t} = Dr^{-2}\, \frac{\partial}{\partial r}\, r^2 e^{-\beta U(r)} \frac{\partial}{\partial r}\, e^{\beta U(r)} p(r, t) \qquad (4)$$

with an equilibrium initial distribution at temperature T ($\beta \equiv 1/k_BT$), $p(r, 0) = \exp[-\beta U(r)]$, and the "radiation" boundary condition, eq 3. D is the relative acid−base diffusion coefficient.

There are several input parameters for this model. As customary,[2] a is taken as 7 Å. The bimolecular PT rate coefficient is $k_{PT} = 8 \times 10^9$ M^{-1} s^{-1} in all solvent compositions. $U(r)$ is taken as the Debye−Hückel (DH) screened Coulomb potential,

$$\beta U(r) = (R_D/r)\, e^{-\kappa(r-a)}/(1 + \kappa a) \qquad (5)$$

for the electrostatic repulsion between the univalent 2N6S and acetate anions, whereas the screening is due to the NaAc salt. At room temperature, R_D and κ may be calculated from the solvent's static dielectric constant,[18] ϵ, according to $R_D = 554/\epsilon$ Å; $\kappa = 2.90\sqrt{c/\epsilon}$ Å^{-1} (c in molar). Although the DH theory is inaccurate at high salt concentrations, for $c = 2$ M the DH screening length, $1/\kappa \approx 2$ Å, is so small that the effect of the potential is only marginal.

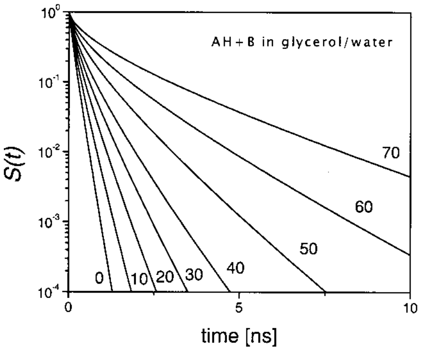

Figure 2. Acid survival probability toward proton transfer to 2 M NaAc in various water/glycerol mixtures (vol % glycerol indicated) obtained by fitting the time-resolved fluorescence data in Figure 1 to the Smoluchowski theory, eqs 2−6. Note the semilog scale.

We have solved eq 4 numerically, using a user-friendly Windows application (SSDP, ver 2.6).[19] The calculated $S(t)$ $\exp(-t/\tau_d)$, convoluted with the independently measured IRF, are displayed in Figure 1 as bold curves. These fit the (corrected) data for nearly 4 decades in intensity. Essentially, D was the only solvent-dependent adjustable parameter (also the background b, but it influences only the final part of the decay). In water/acetate (0% glycerol) we find $D \approx 1 \times 10^{-5}$ cm^2/s. Indeed, the diffusion coefficient for each ion should be[20] 0.5−1 × 10^{-5} cm^2/s (less at high salt concentration), thus $D = D_{AH} + D_B = 1 \times 10^{-5}$ cm^2/s is a reasonable number. It decreases by a factor of about 40 in 70 vol % glycerol. As Table 1 shows, the solvent dependence of D matches quite nicely with Stokes' law using our independently measured viscosities (η_0/η).

Finally, Figure 2 shows the fitted survival probabilities for the various solvent mixtures. These may be viewed as the background-corrected, deconvoluted AH + B kinetics. With increasing glycerol content, these kinetics become increasingly nonexponential. (In comparison, the non-exponentiality revealed in the classical fluorescence quenching work of Nemzek and Ware[15] is minute.) This means that the time-dependent rate-coefficient, $k(t)$, is indeed time-dependent, decreasing from its initially high value of $k_{PT}\exp[-\beta U(a)]$ (cf. eq 3) to $k_\infty = (k_{PT}^{-1} + k_D^{-1})^{-1}$, where k_D is the diffusion-control rate, $k_D = 4\pi Da_{eff}$.[9,14] The non-exponentiality thus depends on their ratio. In water it is nearly 2, increasing to about 80 for 70% (vol) glycerol.

To our knowledge, this is a first measurement of fast bimolecular acid−base reaction in the time domain. It shows clear evidence for diffusion-controlled many-body reactivity conforming to the Smoluchowski model. 85 years after his seminal work, and following countless efforts to verify the theory for fluorescence quenching reactions,[16] a clear example is provided for a real chemical reaction.

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Supporting Information Available: A listing of experimental procedures and steady-state fluorescence spectra (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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