Experimental Determination of the Long-Time Behavior in Reversible Binary Chemical Reactions

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A new asymptotic behavior of reversible pseudo first-order binary chemical reactions is revealed by time-resolved fluorescence measurements of excited-state proton transfer. The asymptotic behavior is a power-law rather than the exponential decay expected from the chemical rate equations. Unlike the conclusion from mean-field approximations, the power seems to increase with concentration.

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Bimolecular chemical reactions in solution are essentially a many-body problem. The conventional rate equation approach [1], which neglects the spatial distribution of the reacting particles, is satisfactory for intrinsically slow reactions. When the reaction is diffusion controlled, competition between reacting particles introduces correlations in their diffusive motion. This should be manifested in the long-time dependence of the reactive concentrations. Specifically, we consider a recombination-dissociation reaction written symbolically as

$$A + B \underset{\kappa_d}{\overset{\kappa_r}{\rightleftarrows}} AB \,.$$

When $[A] \ll [B] \equiv c$, the reaction is pseudo first order. B particles from a homogeneous concentration c compete for binding to an A particle. B may be a proton which binds to a base, A, to produce an acid AB, a substrate binding to an enzyme to form an enzyme-substrate complex, and so on. A and B diffuse in solution (diffusion coefficients D_A and D_B), though $D_A \ll D_B$. Upon reaching a contact distance, $r = a$, they recombine with an intrinsic rate coefficient κ_r. The bound AB molecule is reflecting towards additional B particles, so that no more than one B is bound at any given instant. AB may in turn dissociate (with a probability κ_d per unit time), producing an $A \cdots B$ pair at contact.

The case $\kappa_r = 0$ is uninteresting since this leads to unimolecular dissociation, characterized by an exponential decay of the initial AB population. The case $\kappa_d = 0$ (but $\kappa_r > 0$) represents irreversible many-body recombination. The conventional rate equations of chemical kinetics [1] predict an exponential decay of the initial concentrations, except for the case of equal initial concentrations which produces a $1/t$ decay. Classical works concerning the many-body aspects of this irreversible reaction include those of Smoluchowski [2], Waite [3], Noyes [4], and others. When the reaction is pseudo first order and the initial distribution of B particles is random, the Smoluchowski approximation applies [2]. When, in addition, A is stationary ($D_A = 0$) it is exact [5, 6], and may be extended to a mobile A by using a density expansion [7]. In three dimensions (but not in lower dimensionalities) the Smoluchowski theory predicts an ultimate exponential decay for the survival probability of the minority species, i.e., the A particles. This coincides with the rate-equation prediction, albeit with an effective rate coefficient which approaches κ_r only for intrinsically slow reactions.

The study of bimolecular reactions as a many-body problem has been pursued by physicists, treating primarily the equal concentration and diffusion coefficient case, $[A] = [B]$ and $D_A = D_B$ [8]. It has been shown, by numerical simulations [9], scaling arguments [10], and other methods, that the long-time behavior is determined by the initial distribution. Fluctuations in the initially random B-particle density lead to an ultimate power-law decay of the survival probability, as summarized in recent reviews [11, 12]. To our knowledge, these interesting predictions have not been tested by experiment, since monitoring populations over many orders of magnitude is required. Additionally, it is difficult to prepare a sample containing precisely equal concentrations of (uncorrelated) A and B.

The situation is more complex when both rate parameters exceed zero ("reversible competitive binding"). The rate equations predict an exponential approach to equilibrium [1]. Extensions of the scaling argument to reversible reactions [10] has led to a power-law decay. Unfortunately, such extensions overlook the fundamental difference between the two situations: In the irreversible case, the process ends with the first binding event, while for a reversible reaction a recently bound AB molecule may subsequently dissociate to reproduce the $A \cdots B$ partners, thus altering their spatial distribution. After a few cycles of recombination and dissociation the initial distribution becomes irrelevant. One expects the densities to approach equilibrium, independently of the initial condition and by following an asymptotic law which itself should be independent of the initial distribution.

In the present Letter we deal with the pseudo first-order case. The binding probability, $1-\mathcal{S}(t)$, is expected to approach

$$1-\mathcal{S}(\infty)=cK_{\mathrm{eq}}/(1+cK_{\mathrm{eq}}) \tag{1}$$

as $t\to\infty$. Here $\mathcal{S}$ is the (many-body) "separation probability" [13] and K_{eq} is the recombination equilibrium coefficient

$$K_{\mathrm{eq}} = 4\pi a^2 \kappa_r \, e^{-V(a)}/\kappa_d . \tag{2}$$

The A-B interaction potential (in units of the thermal energy, k_BT) is denoted by $V(r)$.

Approximate (mean-field) treatments of the many-body effect in reversible reactions have recently been considered [13–26]. Some of these are nicely reviewed by Szabo [25]. A power-law asymptotic decay was first demonstrated in a one-dimensional (1D) Brownian simulation involving a "bimolecular boundary condition" [23]. Using the "superposition approximation," a corrected and simplified version of a theory by Lee and Karplus [15], one finds [[25], Eq. (5.16)] that the binding probability for reactions in 3D behaves at long times ($t\to\infty$) as

$$\frac{\mathcal{S}(\infty)-\mathcal{S}(t)}{\mathcal{S}(\infty)-\mathcal{S}(0)} \sim \frac{K_{\mathrm{eq}}}{1+cK_{\mathrm{eq}}}\,\frac{1}{(4\pi Dt)^{3/2}}\,, \tag{3}$$

where $D\equiv D_A+D_B$ is the relative diffusion coefficient. A similar result has been obtained by Burlatsky, Oshanin, and Ovchinnikov [22]. Equation (3) is valid irrespective of the initial distribution and for an arbitrary spherically symmetric potential which vanishes at large separations.

Equation (3) generalizes the asymptotic behavior derived earlier [13, 27(b)] for a reversible geminate pair ($c=0$) whose relative motion may be treated as spherically symmetric diffusion [28]. This reflects the probability of return to the origin of a random walker in 3D. We have studied isolated pair kinetics experimentally in a nearly ideal system [27]. The experiments involve laser excitation of a solvated ROH dye molecule (8-hydroxypyrene 1,3,6-trisulfonate, HPTS), which dissociates in the excited state to produce a geminate proton–excited anion pair. Thus $\mathcal{S}(0)=0$. The solvated proton is attracted by the quadruply charged excited anion and recombines with it reversibly, without quenching it to the ground state. This increases the fluorescence signal from the excited ROH acid above that expected from a single-step exponential dissociation process. The proton subsequently redissociates and, after several dissociation-recombination cycles, diffuses to such large distances that further recombination becomes unobservable.

Using time-correlated single photon counting (TCSPC), it is possible to follow the blue ROH fluorescence signal to long times with good signal-to-noise ratio. As can be seen from the log-log plot in Fig. 1, the data in water cover more than 3 orders of magnitude. These are in excellent agreement with the exact numerical solution (solid line) of the time-dependent, spherically symmetric Debye-Smoluchowski equation for a Coulomb potential and a back-reaction (reversible) boundary condition at contact [27]. It can be shown analytically [13] that this theory exhibits an asymptotic power-law decay with a power of $-d/2$ in d dimensions. Thus, under the experimental conditions, the excited-state kinetics reflect primarily the effect of proton diffusion. Dynamics in other degrees of freedom (vibrational, dielectric or solvent relaxation) occur faster than the ca. 100 psec dissociation time and are averaged out.

We now extend this study to the pseudounimolecular case. By adding controlled amounts of acid the concentration c of homogeneous protons can be varied. Unlike the geminate case, where multiple dissociation cycles lead to ultimate escape of the geminate proton, we expect the low pH fluorescence signal to approach the finite equilibrium limit of Eq. (1). By carefully subtracting the $t\to\infty$ plateau, we hope to obtain an experimental indication for the ultimate approach to equilibrium. This will produce a first experimental proof for deviations from conventional rate equations for bimolecular (nongeminate) reactions in excited-state proton transfer to solvent [30, 31] and test the long-time behavior in Eq. (3).

In order to obtain meaningful results, careful background subtraction has been applied and optimized to the high pH data of Fig. 1. It was subsequently utilized

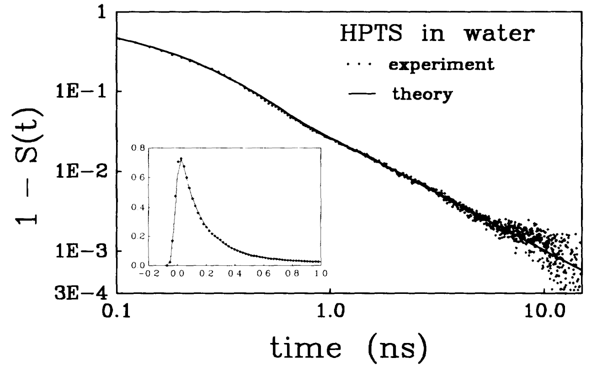

FIG. 1. Fluorescence decay of HPTS in water at pH≈6. Points are TCSPC data [29], after background subtraction using $b=2.2\times10^{-4}$, $g=9.5\times10^{-4}$, $\tau_g=5.5$ nsec, and $\tau_f=5.1$ nsec in Eq. (4). The solid line is a numerical solution to the Debye-Smoluchowski equation with parameters [cf. Eq. (2)] similar to those of Ref. [27]: $a=7$ Å, $\kappa_d^{-1}=125$ psec, $\kappa_r=7.4$ Å/nsec, $V(r)=-R_D/r$ (i.e., no screening at high pH), $R_D=28.3$ Å, and $D=930$ Å^2/nsec. The numerical solution has been convoluted with the instrument response function determined in Ref. [27(f)]. Inset: The same data on a linear scale, emphasizing the short-time behavior.

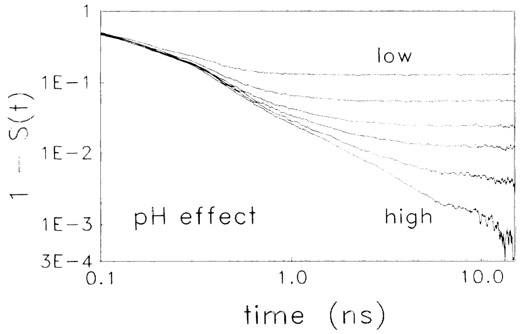

FIG. 2. The pH effect on HPTS fluorescence signal. Approximate proton concentrations are (bottom to top): 0.001, 0.3, 0.7, 1.5, 4, and 15 mM. Data [29] are shown after background subtraction, lifetime correction, and numerical smoothing as described in text. Thus the lowest curve represents the data of Fig. 1 after smoothing.

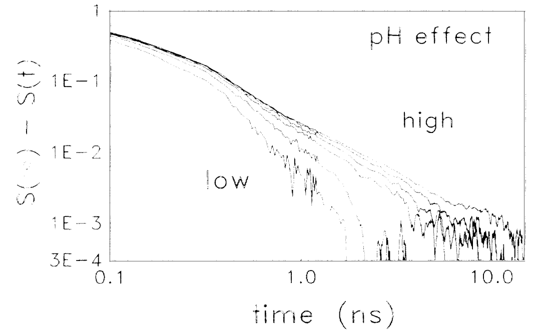

FIG. 3. Long-time approach to equilibrium in excited-state HPTS dissociation in aqueous solutions of various pH values. Obtained from the data in Fig. 2 by subtracting the following equilibrium values (top to bottom), $1 - \mathcal{S}(\infty) = 0$, 0.004, 0.012, 0.023, 0.054, and 0.126.

without change at the lower pH values. This small background, ignored under normal operating conditions, is important when probing over many decades in intensity. It results from remnants of the green anion fluorescence (a fraction g with a lifetime τ_g), not completely eliminated by the blue filter, and from fluorescing impurities (fraction b) in the HPTS sample (Kodak, > 99% chemically pure). Given the TCSPC signal $I(t)$, whose maximum (near $t = 0$) is $I_m \approx 60\,000$ counts/channel, we calculate the binding probability from

$$1 - \mathcal{S}(t) = h\,[I(t)/I_m - b - g\mathcal{S}(t)e^{-t/\tau_g}]\,e^{t/\tau_f}. \qquad (4)$$

The correction for the ROH fluorescence lifetime, τ_f, allows us to consider the reactants as if they live forever in the excited state. The data are normalized so that their height ($h = 0.73$) coincides with the peak of the theoretical curve, after its convolution with the measured [27(f)] instrument response function (FWHM≈55 ps). Finally, we have applied a numerical (25 point) data smoothing routine effective in white-noise filtering.

The solution pH has been lowered by adding $HClO_4$ from a micropipette and subsequently verified by a pH meter. With the addition of homogeneous protons, an equilibrium plateau indeed develops (Fig. 2). As expected, $1 - \mathcal{S}(\infty)$ is higher the larger the proton concentration. The excited-state equilibrium coefficient can be calculated from this value via Eq. (1). K_{eq} decreases with increasing c due to self-screening by the protons. We have found [27(g)] that this "equilibrium salt effect" is well described by the Debye-Hückel theory. This demonstrates that a true (quasi)equilibrium state is achieved in this reaction, limited only by the finite radiative lifetime.

The approach to equilibrium is obtained by subtraction of $1 - \mathcal{S}(\infty)$, as determined by averaging the data numerically between 10 and 15 nsec, from the transient decay. Results shown in a log-log scale (Fig. 3) clearly exhibit a power-law approach to equilibrium. The surprise is that the asymptotic power α is not independent of concentration: It is 3/2 at infinite dilution and seems to increase with c

$$[\mathcal{S}(\infty) - \mathcal{S}(t)]/[\mathcal{S}(\infty) - \mathcal{S}(0)] \sim A/t^{\alpha}. \qquad (5)$$

A dependence of the asymptotic behavior on concentration has been observed in a different reversible system [17] namely, $B + B \leftrightarrow B$. For the reaction under consideration, a variable α has not been predicted by the approximate theories. To verify that the observed effect is reproducible, experiments have been repeated a year later yielding similar results. Figure 4 shows values of the asymptotic slope obtained by linear regression in the range 0.3–3.0 nsec (0.3–5.0 nsec for pure water), with a correlation coefficient 0.990–0.998. There is a nice agreement between both sets of data, though the absolute values of α depend on the range chosen for linear regression. The decrease in the intercept of the linear fits to the data of Fig. 3 is attributed by Eq. (3), in the small c limit, to the decrease of K_{eq} with screening. We indeed find a

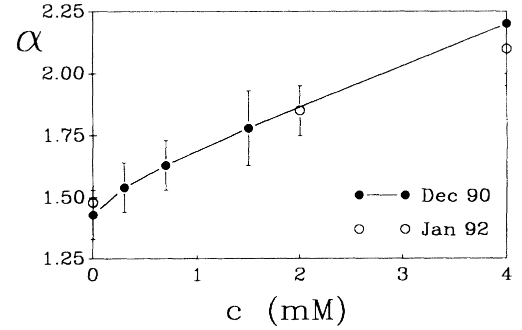

FIG. 4. Dependence of the asymptotic slope, Eq. (5), on proton concentration. Solid circles were obtained from the data of Fig. 3, while open circles represent a more recent set of measurements.

qualitative agreement with the values of K_{eq} determined [27(g)] from $\mathcal{S}(\infty)$.

Since an increase of α with c has not been predicted by any of the mean-field approximations, we have tried to detect it in 1D Brownian simulations [23]. In these simulations, n noninteracting random walkers on a linear lattice of l sites compete for reversible binding to a static, single-particle saturable trap. When the concentration, $c = n/l$, is increased by decreasing l we find that α increases above its infinite-dilution value of $\frac{1}{2}$, but as n is varied for fixed l there are no detectable changes in α. This suggests that in the thermodynamic limit of an infinitely large lattice, α for noninteracting random walkers in 1D is independent of concentration. It could be that proton-proton repulsions in 3D are in some sense analogous to limiting the diffusion space to a finite domain, thus leading to variations in α. This, as well as other possible sources for such variations, remains under investigation.

In conclusion, a new asymptotic behavior of reversible binary chemical reactions in solution has been revealed by experiment. While the short-time behavior is affected by the initial distribution and the interaction potential, the long-time behavior carries the imprint of the equation of motion governing the time evolution, which is the fundamental reason justifying its study.

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