Experimental Evidence for a Kinetic Transition in Reversible Reactions

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We provide a first experimental verification of a theoretical prediction of a kinetic transition in a reversible binding reaction, $AB \rightleftharpoons A + B$, driven by the difference in effective lifetimes of the bound and unbound states. We consider the kinetics of excited-state proton transfer to solvent from a photoacid whose conjugate anionic base possesses an extremely short unbound anion lifetime. Its solvent variation relative to the overall dissociation rate coefficient induces a transition in the kinetics, from power law to exponential.

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Physical phenomena normally vary smoothly as a function of their control parameters. Nevertheless, important examples of abrupt, discontinuous changes exist and are the subject of intensive research. In thermodynamic phase transitions, the many-particle structure of matter changes discontinuously as a function of thermodynamic parameters such as temperature and pressure. Dynamic phenomena may also show abrupt transitions, like those arising from the sensitivity of nonlinear differential equations to their initial conditions. For example, Hamiltonian trajectories for atom-diatom collisions terminate in different regions of coordinate space as initial conditions are varied [1,2]. Complex solution-phase reactions, obeying nonlinear chemical kinetic equations, may exhibit rich phase diagrams with transitions from oscillatory to nonoscillatory behavior [3]. It is less known that rather simple reactions, obeying linear diffusion-type equations, can also show discontinuous transitions. It is even rarer that a theoretical prediction of such behavior is actually verified experimentally, which is the subject of the present Letter.

We consider a simple dissociation/recombination reaction, $AB \rightleftharpoons A + B$, for the $A/B$ geminate pair in its excited electronic state, with different excited-state (ES) decay rate coefficients for $AB$ and $A$ ($k_0$ and $k_0'$, respectively). Our model reaction involves hydroxyaryl photolysis (ROH), which become strong acids in their first singlet ES ($R^*OH = AB$) [4–6], transferring their proton reversibly [7,8] to the solvent (S) on a ps–ns time scale, $R^*OH \rightleftharpoons R'O^- + H^+$. Figure 1(a) demonstrates the various reaction steps for a recently synthesized [9] “super” photoacid, S-(methanesulfonyl)-1-naphthol (5MS1N). Using time-resolved fluorescence, we follow the time dependence of the R'OH concentration. When $k_0 = k_0'$, the “corrected” acid concentration,

$$F(t) = [R^*OH]\exp(k_0't),$$

decays at long times with a $t^{-3/2}$ power law [10–14]. The same behavior is also expected for a ground-state reversible reaction ($k_0 = k_0' = 0$), so that $F(t)$ is a natural extension of the ground-state concentration, [ROH], to the ES. This asymptotic behavior, which differs drastically from elementary kinetics, reflects the relative diffusive motion of $A$ and $B$: Their probability to return to their initial contact distance goes as $t^{-3/2}$, the normalization of the fundamental Gaussian solution. In real ES reactions, $k_0 \neq k_0'$, yet measurements to date always produced the power-law decay [10–14].

FIG. 1. (a) Kinetic scheme for the protolytic dissociation of 5MS1N. The excited acid ($R^*OH = AB$) may either dissociate ($k_d$) or decay to its ground electronic state ($k_0$). The excited anion ($R'O^- = A$) can either recombine adiabatically ($k_a$) with a proton ($H^+ = B$) or decay nonadiabatically ($k_0' + k_q$). (b) Possible molecular mechanisms for deactivation of 1-naphtholates: Proton quenching and resonance stabilization.
It is tempting to conclude that the power-law behavior invariably characterizes reversible diffusive-influenced reactions. However, recent theoretical studies indicate that when the decay of the separated pair ($k_0'$) is fast compared with the overall decay of the bound pair ($k_a + k_{off}$, see below), a transition to an exponential asymptotic behavior should occur [15–19]. That the kinetics become exponential in the limit of $k_0' 	o \infty$ is hardly a surprise. The interesting observation is that the transition occurs already at a finite value of $k_0'$. Defining $\Delta k$ by

$$\Delta k \equiv k_0' - (k_a + k_{off})$$

it has been shown analytically [15–19] that three different asymptotic behaviors are expected [20]:

(i) The “$A$ regime” (the usual case): When the anion is relatively long-lived ($\Delta k < 0$), $F(t)$ decays rapidly and eventually switches into the ubiquitous $t^{-1/2}$ decay.

(ii) The transition regime: When $\Delta k = 0$, $F(t)$ decays only mildly and eventually switches into a $t^{-1/2}$ decay.

(iii) The “$AB$ regime” (previously unobserved): When the anion is relatively short-lived ($\Delta k > 0$), $F(t)$ rises exponentially, approximately as $\exp(\Delta k t)$ near $\Delta k = 0$. In this regime the characteristic power law disappears, and the exponential factor in the $[R^*OH]$ decay switches from the exclusively $A$-dependent form, $\exp(-k_0't)$, to one that depends predominantly on the kinetic properties of the $AB$ state.

The present work provides a first experimental verification of this transition, where a single photoacid shows the different types of behaviors in different solvents.

Mathematically, the reaction is modeled [13,14] as diffusion in the relative $A$-distance ($r$), in the attractive Coulombic potential $V(r) = -R_D/r$. The Debye radius, $R_D$, is estimated from the known dielectric constant of the solvent, whereas the relative anion-proton diffusion coefficient, $D$, is obtained from measured proton mobilities (plus a small additional contribution from the anion). When the $A-B$ pair reaches a critical “contact” distance ($a$), reversible binding in the excited state (association and dissociation rate coefficients $k_a$ and $k_d$, respectively) or a competing irreversible quenching reaction (rate coefficient $k_q$) may occur. The probability density, $p(r,t)$, for the $A-B$ pair to separate to a distance $r$ is assumed to obey a Smoluchowski equation, which is coupled to a kinetic equation for the probability $P(t)$ of observing the (excited) bound pair

$$\frac{\partial}{\partial t} P(r,t) = \left[ r^{-2} \frac{\partial}{\partial r} Dr^2 e^{-V(r)} \frac{\partial}{\partial r} e^{V(r)} - k_0' \right] p(r,t)$$

$$+ [k_d P(t) - (k_a + k_q)p(r,t)] \frac{\delta(r-a)}{4\pi a^2},$$

\[ (1a) \]

$$\frac{\partial}{\partial t} P(t) = k_a p(a,t) - (k_d + k_0) P(t).$$

\[ (1b) \]

The R$^*OH$ signal is then compared with $P(t)$, and R$^*O^-$ with $S(t) = 4\pi \int_0^\infty p(r,t) r^2 dr$. Note that our starting point is a microscopic equation for the stochastic translational motion of a pair of particles, and not a mean-field reaction-diffusion equation for their concentrations.

From the fundamental rate parameters in Eq. (1), one may define an effective, steady-state “off” rate coefficient [17]

$$k_{off} = \frac{k_d(k_D + k_a)}{k_a + k_D + k_q}.$$  \[ (2) \]

It is written in terms of the diffusional separation rate coefficient, $k_D = 4\pi D a_{off} e^{V(a)}$, where $a_{off} = \int_0^\infty e^{V(r)} r^{-2} dr$. The transition depends on $k_{off}$, which enters into the definition of $\Delta k$. For noninteracting pairs $[V(r) = 0]$, Eq. (1) can be solved exactly in both three dimensions [18] and one dimension [19]. Its Laplace transform gives rise to a cubic polynomial. The transition corresponds to one of the roots changing sign along the real axis [18], which occurs when $\Delta k$ changes sign. When $V(r) \neq 0$, Eq. (1) can be solved via an approximation, which becomes exact at asymptotically long times [16,17], except for the value of the exponent in the $AB$ regime, which is approximate.

Searching for a suitable ROH molecule which might exhibit the kinetic transition, we noticed that anan-substituted (1:5) naphthols possess a particularly short excited-state anion lifetime ($1/k_0' = 0.1–2$ ns, see below) [21,22]. We have chosen to study 5MSIN [Fig. 1(a)], a super photoacid recently synthesized by Tolbert and Haubrich [9]. Its excited-state $pK_a$ value is sufficiently low to promote proton transfer to pure organic solvents, such as dimethylsulfoxide (DMSO), methanol (MeOH), ethanol (EtOH), and other basic solvents. As previously described [13], the sample was excited by a ps dye laser at about 295 nm (the doubled frequency of the Rhodamine 6G dye laser, driven by a Nd:YAG laser), and the fluorescence of both R$^*OH$ (430 nm) and R$^*O^-$ (660 nm in alcohols, 715 nm in DMSO) was collected using a time-correlated single-photon-counting system with an instrument response function (IRF) of about 40 ps (full width at half maximum). In alcohols, the anion lifetime could be measured directly under high pH conditions, where the decay is single exponential giving $k_0' = 1.3$ ns$^{-1}$ (MeOH) and 1.0 ns$^{-1}$ (EtOH). $k_0'$ was estimated from R$^*OH$ decay in solvents (e.g., acetonitrile) where no dissociation occurs.

Figure 2 shows the excited-state proton-transfer kinetics for both R$^*OH$ and R$^*O^-$ in the three solvents under geminate conditions (low ROH concentrations and pH $\approx 6$). The obvious shortening of the R$^*O^-$ lifetime from DMSO to the alcohols suggests the possibility of a kinetic transition. To check for this possibility, the background-corrected R$^*OH$ data [23] are multiplied by $\exp(k_0't)$ and displayed, for the three solvents, in Fig. 3. Since $k_0'$ was
determined independently, from the fluorescence of pure R*O\(^-\) in basic solutions, no adjustable parameters are involved in this exposition. The theoretically predicted behavior is revealed: The data decay sharply in DMSO, only mildly in MeOH, while they exhibit a rapid rise in EtOH. The signal in the A regime disappears in the noise before approaching the asymptotic power law (dashed line). This limit is better demonstrated using longer-living anions [10–14]. In contrast, the (previously unobserved) exponential increase in the AB regime is unmistakable, because it starts early on, well before the onset of the \(t^{-3/2}\) asymptotic behavior in the A regime. We believe that this provides a first report of photochemical kinetics in the AB regime.

To check whether indeed \(\Delta k\) changes sign [15–19] between DMSO and ethanol, we determine the microscopic rate parameters by fitting the experimental data to Eq. (1), which is solved numerically using a publicly available Windows application (SSDP, VER. 2.6) [24], and convoluted with the measured IRF [25]. In doing so, we adjust the three rate parameters \((k_d, k_q, \text{and } k_q, q)\) thus obtaining the lines in Figs. 2 and 3. The various rate parameters are summarized in Table I, from which it is evident that indeed \(\Delta k\) changes sign between DMSO and EtOH. In MeOH, it is close to zero (though slightly negative), corroborating the observation that the kinetics here are close to the transition behavior.

The question arises, why do the ana-naphtholates [21,22] have such short lifetimes? For (unsubstituted) 1-naphthol, strong quenching by the geminate proton is observed [26,27]: It is manifested in low fluorescence quantum yields, a maximum in \([R*O^-]\) \(\exp(k_q t)\), and \(k_d\) which is similar in magnitude to \(k_a\). The quenching has been attributed [28] to proton attack on position 5 of the distal ring, leading to the ketonelike resonance structure of Fig. 1(b). The enhanced electron density in the 5 position is also manifested in marked preference for H/D substitution at that site in the ES [29]. For 5MS1N no maximum in the lifetime-corrected anion signal is observed, and \(k_q/k_a\) is considerably smaller (about 0.3 in DMSO, decreasing to 0.1 in EtOH). This suggests that the 5 substitution hinders proton attack while shortening the excited-state lifetime. It is possible that the sulfonyl substituent in position 5 gives rise to the resonance structure in Fig. 1(b), producing a keto form analogous to that obtained after the proton attack. Indeed, ROH photoacids which (by either intra- or intermolecular proton transfer) can isomerize into the keto form exhibit diminished lifetimes [30–32]. The other short-lived ana-naphtholates involved sulfonate [21] and cyano [22] substituents, which should also exhibit such resonance structures. It is expected that substituents (such as alkyls) which cannot support this resonance will protect against quenching in the 5 position without shortening the anionic lifetime (and their kinetics will thus be in the A regime).
Table I. Kinetic parameters for reactions initiated by photodissociating 5MS1N in three solvents. $R_D$ was calculated from dielectric data; $D$ was obtained from mobility data; $k_0$ was measured directly, at high pH; $k_d$, $k_a$, and $k_q$ were obtained by fitting Eq. (1) to the data of Fig. 2; $1/k_0$ was taken as 12 ns in all solvents and $\alpha = 5.5 \text{ Å}$. Change of sign in the last column is indicative of the kinetic transition.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$R_D$</th>
<th>$10^5 D$</th>
<th>$1/k_0$</th>
<th>$k_d$</th>
<th>$k_a$</th>
<th>$k_q$</th>
<th>$k_{d-}$</th>
<th>$k_{off}$</th>
<th>$\Delta k$</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMSO</td>
<td>12.1</td>
<td>1.0</td>
<td>1.85</td>
<td>1.7</td>
<td>0.96</td>
<td>0.27</td>
<td>1.15</td>
<td>1.01</td>
<td>$-0.55$, A regime</td>
</tr>
<tr>
<td>MeOH</td>
<td>17.2</td>
<td>3.7</td>
<td>0.78</td>
<td>2.8</td>
<td>3.09</td>
<td>0.39</td>
<td>2.2</td>
<td>1.27</td>
<td>$-0.07$, $\approx$transition</td>
</tr>
<tr>
<td>EtOH</td>
<td>23.1</td>
<td>1.94</td>
<td>1.0</td>
<td>2.0</td>
<td>3.15</td>
<td>0.32</td>
<td>0.52</td>
<td>0.42</td>
<td>$+0.50$, AB regime</td>
</tr>
</tbody>
</table>

Hence the case of “resonating” ana-naphthols provides a unique example of a kinetic transition promoted by solvent-induced shortening of the product lifetime as compared with the overall dissociation time. The theoretical prediction [15–18], which preceded our experimental work, has been verified in detail. Excited-state proton transfer is a convenient case study since light serves as an ultrafast trigger for initiating the reaction. However, the kinetic transition should not be limited to proton-transfer reactions or excited states. Any process which shortens the lifetime of the dissociation products may lead to a transition. For example, when acetylcholine is released from its nicotinic receptor in the neuromuscular junction, it may undergo many rebinding cycles (A regime) unless it is immediately hydrolyzed by acetylcholine esterase [33]. Here scavenging, with a rate constant proportional to scavenger (enzyme) concentration, provides an alternative mechanism for shortening the product’s lifetime. It is interesting to ask whether the concentration of the enzyme under physiological conditions is sufficiently large to promote the transition into the $AB$ regime.

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20. Theory requires [15–18] that the lifetime of the anion be used in F(t), even when correcting the acid signal.
23. A complication with most fluorescence work is that tiny amounts of fluorescing impurities can mask the long-time behavior. The <0.2% background leaves us with nearly 3 orders of magnitude of genuine data. Beyond this, the background should be corrected for by fitting a theoretical model to the data [see Eq. (1)]. This reveals a slowly decaying impurity with a lifetime between 10 ns (EtOH) and 18 ns (DMSO).
25. The “bump” around 2 ns in the data of Fig. 3 arises from a small after pulse, which is accounted for in the IRF.