

# Dynamical Solvent Effects on Electron-Transfer Processes: Recent Progress and Perspectives

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Received January 30, 1990 (Revised Manuscript Received May 21, 1990)

The last decade has seen a remarkable upsurge of interest in the dynamical role of the solvent in liquid-state chemical processes.<sup>1</sup> Along with the intrinsic importance of such phenomena in chemistry and biology, these activities have been fostered by substantial recent developments of both a theoretical and an experimental nature. The central concept of solvent "friction", whereby the collective solvent motion necessary to surmount the activation barrier slows the rate below that expected from transition-state theory (TST),<sup>1</sup> has spawned a myriad of theoretical treatments that attempt to describe the effective solvation dynamics. The ensuing interplay with experiment has considered chemical systems ranging from highly activated thermal reactions to ultrafast photoinduced processes where the solvation dynamics alone determine the reaction time scale.<sup>2</sup>

Although the range of chemical processes of significance in this context is necessarily wide, of particular interest are those involving electron or related charge transfers. For such systems, the solvent plays a pivotal role in determining the activation energetics and often also the reaction thermodynamics. Such energetic (or "static") factors, arising from the changes in solvent polarization that necessarily attend the transfer of charge, are well-known; they form central aspects of the Marcus and related kinetic treatments.<sup>3</sup> The recognition of an additional *dynamical* role of the solvent upon the charge-transfer kinetics, i.e., upon the frequency of barrier crossing, is of much more recent origin. The time scales for collective solvent dipole rotations and translations associated with progress along the reaction coordinate are known to be sensitive to the solvent structure, so that wide variations in the reaction dynamics can be anticipated.

Current experimental inquiries into solvent dynamical effects in electron transfer are, broadly speaking,

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George's death in October 1989 cut tragically short a truly promising scientific career. In addition to being an outstanding scientist, George was a remarkably unselfish, caring, and courageous person. His abounding energy, enthusiasm, scholarship, intrepidity, humor, and abiding love for science are qualities that will long be remembered by, and provide a continuing inspiration for, those who knew "The Elf" (M. J. W.).

of two types. The first involves measurements of time-dependent fluorescence Stokes shifts (TDFS) for chromophores forming suitable charge-transfer excited states.<sup>2,4,5</sup> Such measurements probe the real-time dynamics of polar solvent relaxation around a newly formed dipole. Recent instrumentation advances now enable relaxation times down to ca.  $10^{-13}$  s to be followed.<sup>2b,6</sup> In addition, measurements of electron-transfer (ET) rates themselves, either from photoexcited or ground states, can yield solvent dynamical information. Most intramolecular photoexcited ET processes examined so far in this regard yield reaction times comparable to the solvation times,  $\tau_S$ , extracted from TDFS measurements, indicating the presence of only small or negligible activation barriers ( $\lesssim k_B T$ , where  $k_B$  is the Boltzmann constant).<sup>2b,c</sup>

Such ultrafast TDFS and ET rate measurements provide direct information on charge-induced solvent relaxation and have justifiably been accorded considerable attention in the recent literature.<sup>2,4,5</sup> Most chemical ET processes, however, involve sizable activation barriers which can modify significantly the influence of solvent dynamics on the reaction rate. The dynamical description of such activated ET processes has attracted widespread recent theoretical attention (see, e.g., refs. 7-14 and below). While less abundant, related experimental studies have begun to delineate the nature and importance of dynamical solvent effects

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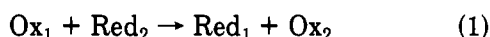
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on activated ET processes.<sup>15-18</sup>

The aim of this Account is to outline in straightforward terms current understanding on the manner and extent to which dynamical solvent properties can influence the kinetics of electron-transfer processes, drawing in part from recent experimental and calculational results from our laboratory. Although connections will be made to dynamical information extracted from ultrafast photoinduced processes, we focus here instead on activated reactions. While several recent reviews consider the former,<sup>2,4,5</sup> there is a dearth of transparent descriptions of the latter case. An important goal here is to demonstrate how the close interplay between theory and experimental kinetic studies along with related real-time information on solvent relaxation can yield substantial insight into the nature of dynamical factors in activated electron transfer.

### Conceptual Background and Pertinent Dynamical Information

We consider here outer-sphere electron-transfer reactions having the general form



The present discussion will focus primarily on bimolecular self-exchange (i.e., symmetrical) reactions, although most arguments apply with minor modification to nonsymmetrical homogeneous and to electrochemical processes. For reactions featuring significant ET barriers,  $\Delta G^* > (2-3)k_B T$ , the observed bimolecular rate constant can be expressed most simply as<sup>19</sup>

$$k_{\text{ob}} = K_p \kappa_{\text{el}} \nu_n \exp(-\Delta G^*/k_B T) \quad (2)$$

where  $K_p$  is a precursor preequilibrium constant,  $\kappa_{\text{el}}$  is the electronic transmission coefficient, and  $\nu_n$  is the nuclear frequency factor ( $\text{s}^{-1}$ ). Any influence of solvent dynamics is contained within  $\nu_n$ . In general,  $\nu_n$  will comprise appropriately weighted dynamical contributions from each of the nuclear motions that contribute to  $\Delta G^*$ . In the present context, the simplest case is where virtually the entire barrier arises from solvent reorganization, i.e., where the "inner-shell" contributions from reactant bond distortions are small. In this circumstance,  $\nu_n = \tau_{\text{eff}}^{-1}$ , where  $\tau_{\text{eff}}$  is the effective solvent relaxation time associated with ET barrier crossing.

Of central interest is the relationship between  $\tau_{\text{eff}}$  and observed solvent relaxation times. The simplest di-

electric continuum treatments<sup>7,8a,9a</sup> predict that roughly  $\tau_{\text{eff}} \sim \tau_L$  for cusp-like barriers, where  $\tau_L$  is the well-known longitudinal relaxation time extracted from dielectric loss spectra.<sup>20</sup> This quantity denotes the relaxation time for an isotropic dipolar fluid in response to a sudden change in charge, as will occur in ET processes. Significantly,  $\tau_L$  is known to be sensitive to the solvent structure, differing by at least ca. 50-fold (from ca. 0.2 to 10 ps at ambient temperatures) between common "Debye" solvents, i.e., those that exhibit only one dissipative relaxation in the dielectric loss spectrum.<sup>15c,16d</sup> Very crudely,  $\tau_L$  correlates with the solvent viscosity in some cases, although the physical origins of these quantities are quite different.<sup>22</sup>

The physical relevance of  $\tau_L$  to barrier crossings can be understood simply as follows. In ET processes, especially those featuring cusp barriers, electron tunneling can occur (essentially instantaneously) only upon the formation of a transition state featuring an intermediate, nonequilibrium, solvent polarization. In the presence of so-called dielectric friction, the collective solvent dipole reorientation necessary to both approach and traverse this intersection region of the reactant and product wells is impeded by irreversible energy dissipation from a given dipole to its surroundings (diffusive or "overdamped" motion).<sup>1a,8a</sup> Consequently, the time scale required for significant net progress along the reaction coordinate can be substantially longer than for small-amplitude dipole motion. The frequency of the latter ( $\omega_0$ ) is determined in part by the molecular moment of inertia and corresponds to the zero-friction (TST) limit. At energies within ca.  $k_B T$  of the transition state, thermal fluctuations can send the system back and forth over the barrier at frequencies close to  $\omega_0$ . Nevertheless, net progress to energies further below the transition state, so that the system becomes effectively trapped in the products' well, occurs on the longer time scale associated with the overdamped solvent motion. Diffusive solvent motion *within* the reactant and product wells can also provide a dominant contribution to the net barrier-crossing dynamics, especially for cusp-like barriers.<sup>9c,25</sup> Since  $\tau_L$  refers necessarily to such *dissipative* solvent relaxation,<sup>21,22</sup> it is not surprising that this quantity should provide a relevant description of the time scale for ET barrier crossing under overdamped conditions.

While there is strong experimental evidence that  $\nu_n$  at least correlates with  $\tau_L^{-1}$  under some conditions (vide infra), several factors that have come under recent theoretical scrutiny conspire to make the anticipated influence of solvent dynamics on the reaction rate rather more involved. In the remainder of this section, we consider briefly the most important of these.

(20) Generally,  $\tau_L$  is related to the Debye relaxation time,  $\tau_D$ , observed in dielectric loss spectra by  $\tau_L = (\epsilon_\infty/\epsilon_0)\tau_D$ , where  $\epsilon_\infty$  and  $\epsilon_0$  are the "infinite" and zero-frequency solvent dielectric constants, respectively. For an erudite discussion of the physical meaning of  $\tau_L$  in relation to  $\tau_D$ , see ref 21.

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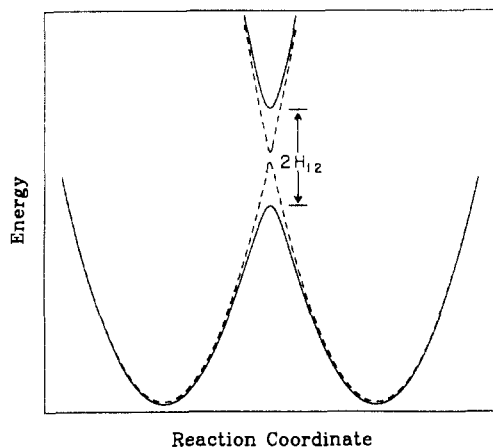
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**Figure 1.** Schematic free energy-reaction coordinate profiles for symmetrical electron-transfer processes having small and large electronic matrix coupling elements,  $H_{12}$  (dashed and solid curves, respectively). Reprinted with permission from ref 16d. Copyright 1989 American Chemical Society.

Most simply, even in the dielectric continuum/Debye limit  $\tau_L$  will only be a faithful description of the solvent dynamics if  $\tau_L^{-1} \ll \omega_0$  ("overdamped" limit).<sup>8a,23</sup> In low-friction media where  $\tau_L^{-1} \gtrsim \omega_0$  (e.g., acetonitrile), the TST limiting rate will be approached so that  $\nu_n \simeq \omega_0/2\pi$ ,<sup>8a</sup> whereupon solvent friction will play no role in the reaction dynamics. Largely overdamped solvent motion (i.e.,  $\tau_L^{-1} < \omega_0$ ), however, appears to be a more common circumstance.<sup>15b,23</sup>

Unlike the TST case, the overdamped barrier-crossing frequency is dependent upon both  $\Delta G^*$  and the shape of the barrier top.<sup>8a,9c,24,25</sup> As illustrated in Figure 1, the latter is influenced by the electronic coupling matrix element ( $H_{12}$ ), reflecting the degree of donor-acceptor orbital overlap. Roughly, one predicts that  $\nu_n \propto (\Delta G^*)^{1/2}$ ;  $\nu_n$  is generally expected to diminish as the barrier-top "roundedness" increases, i.e., as the barrier becomes less cusp-like (i.e., the solid rather than dashed profile in Figure 1). A simple rationalization of the latter effect is that barrier recrossings, yielding a lower frequency of successful diffusive passages through the intersection region and hence a smaller  $\nu_n$ , should become more prevalent as the barrier top becomes broader. For barrier shapes typical in activated ET, we anticipate  $\nu_n$  to be somewhat (ca. 2–5-fold) smaller than  $\tau_L^{-1}$ .<sup>24,25</sup>

There is considerable interest currently in the degree of which the actual relaxation times for polar solvation (and hence  $\tau_{\text{eff}}$ ) may differ from  $\tau_L$ , particularly as a result of "solvent molecularity" effects associated with the inevitable proximity of the reorienting solvent dipoles to the reacting solute particles.<sup>2,4,5</sup> One conceptually useful approach is to treat the solvent as a hard-sphere dipolar fluid using the "mean spherical approximation" (MSA). This treatment yields a distribution of solvent relaxation times, increasing from  $\tau_L$  for solvent molecules distant from the solute to values closer to the Debye relaxation time  $\tau_D$ <sup>20</sup> for nearby solvent.<sup>8b,26</sup> Interest in the MSA model was heightened originally by the observation of TDFS solvation times,  $\tau_S$ , that are somewhat longer than  $\tau_L$  along with multiexponential behavior (i.e., the presence of multiple  $\tau_S$  values), thereby in qualitative accordance

with the theoretical predictions.<sup>6,27</sup> The MSA model, however, appears to overestimate the extent of these noncontinuum effects;<sup>2a,27–29</sup>  $\tau_S$  values measured recently for a number of polar Debye-like solvents at ambient temperatures are mostly only ca. 1.5–2-fold longer than  $\tau_L$  (vide infra).<sup>2a</sup>

In addition to such longer  $\tau_S$  components, dynamical contributions having relaxation times shorter than  $\tau_L$  are often anticipated. Additional dispersions at higher frequencies in the dielectric loss spectra ("non-Debye" effects) are not uncommon (e.g., for alcohols<sup>30</sup>), indicating that faster relaxation components of the solvation dynamics can be expected even in the dielectric continuum limit. Some theoretical treatments have considered solvation dynamics in terms of wave vector ( $\mathbf{k}$ ) dependent dielectric properties, thereby including shorter range solvation effects arising from local field inhomogeneity.<sup>31,32</sup> These treatments predict the appearance of  $\tau_S$  components shorter than  $\tau_L$  even in Debye-like media. Although the observation of such faster relaxation components in TDFS measurements is limited by laser pulse width and other considerations, experimental evidence supporting their common presence is emerging from subpicosecond studies with Coumarin probes by Barbara et al.<sup>2b,6</sup>

A key issue for activated ET processes is the extent to which such faster versus slower relaxation components determine  $\tau_{\text{eff}}$  and hence the overall barrier-crossing frequency.<sup>33</sup> A theoretical treatment due to Hynes<sup>9c</sup> predicts that the faster time component(s) of dielectric loss spectra tend to provide important contributions to  $\tau_{\text{eff}}$  even for relatively small amplitude relaxations.<sup>25</sup> Other<sup>34,35</sup> but not all,<sup>12</sup> treatments yield comparable results.<sup>25</sup> Recent numerical simulations have confirmed the basic validity of Hynes's conclusions, at least for cusp-like barriers.<sup>36</sup> An experimental test is considered below. Such treatments can also be applied to the analysis of multiple relaxation times (or distributions thereof) arising from solvent molecularity effects.<sup>37</sup>

For reactions where  $\Delta G^*$  contains a substantial component associated with reactant bond distortions, such motions can provide significant accelerating contributions to  $\nu_n$  above that expected from overdamped solvent motion alone.<sup>10</sup> This is because the presence of a separate inner-shell reaction coordinate, associated typically with relatively rapid underdamped motion, can provide facile additional channels for barrier passage once the system has reached the vicinity of the

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(33) Note that the dynamics for activated ET processes are discernible in terms of a single effective  $\tau_{\text{eff}}$  value (and hence reaction rate) even if the solvation dynamics (such as TDFS) measurements exhibit multiple relaxation components,  $\tau_i$ , providing that  $\Delta G^*$  is sufficiently large so that the ET kinetic time scale is much longer than for  $\tau_i$ .

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intersection region. Nevertheless, numerical calculations predict that slower overdamped solvent motion typically can contribute importantly to  $\nu_n$  even for barriers composed of comparable solvent and inner-shell contributions.<sup>10b</sup> Some experimental data is roughly in accord with this prediction.<sup>15d</sup>

It is important to recognize that nuclear dynamics will control entirely the barrier-crossing frequency only if the donor-acceptor electronic coupling is sufficiently strong so that "reaction adiabaticity" is essentially achieved, i.e., when  $\kappa_{el} \rightarrow 1$  (eq 2). Physically, this implies that the splitting between the upper and lower potential-energy surfaces in the intersection region, equal to twice the electronic coupling matrix element  $H_{12}$  (Figure 1), is sufficiently large so that the system remains on the lower surface during its passage through the transition state. If  $H_{12}$  is small, on the other hand (Figure 1, dashed curves), the system is liable to traverse the intersection region by remaining on the reactant potential-energy surface, so that the probability of crossing to the product surface by electron tunneling is small (i.e.,  $\kappa_{el} \ll 1$ ).

An illustrative, albeit simplified, Landau-Zener expression for  $\kappa_{el}$  is<sup>19a,24a</sup>

$$\kappa_{el} = 2[1 - \exp(-\nu_{el}/2\nu_n)]/[2 - \exp(-\nu_{el}/2\nu_n)] \quad (3)$$

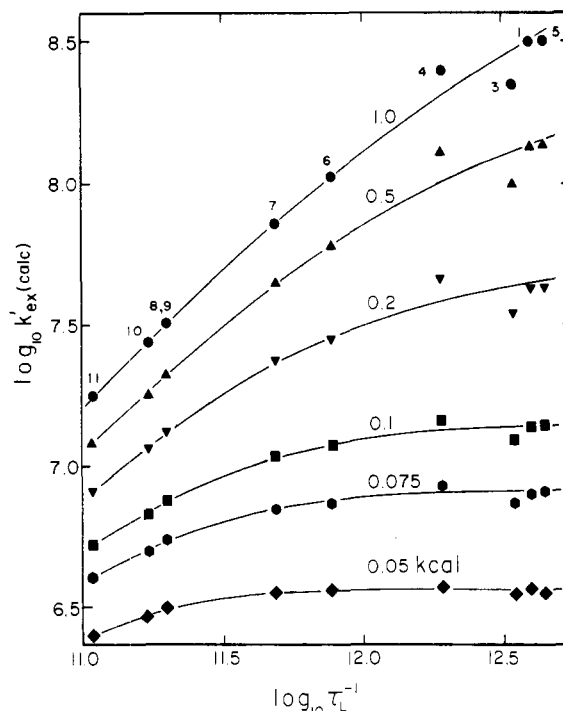
The "electronic frequency factor"  $\nu_{el}$  is given by

$$\nu_{el} = H_{12}^2(\pi^3/\Delta G^*h^2k_B T)^{1/2} \quad (3a)$$

While  $\kappa_{el} \rightarrow 1$  for strong electronic coupling (i.e., large  $H_{12}$ ) such that  $\nu_{el} \gg \nu_n$ , eq 3 reduces to  $\kappa_{el} \approx \nu_{el}/\nu_n$  for weaker coupling so that  $\nu_{el} \ll \nu_n$ . For such "nonadiabatic" processes ( $\kappa_{el} \ll 1$ ), then, the combined preexponential factor  $\kappa_{el}\nu_n$  (eq 2) will become independent of the nuclear dynamics and proportional to  $H_{12}^2$ <sup>19a,24a</sup> ("golden rule" limit). More sophisticated treatments of nonadiabatic effects have been developed.<sup>13,14c</sup> A formalism has also been outlined that accounts for barrier-shape effects (via  $H_{12}$ ) on the nuclear dynamics together with reaction nonadiabaticity and solvent inertial effects.<sup>24b</sup> These treatments employ the conventional assumption that  $\Delta G^*$  in the presence of substantial donor-acceptor orbital overlap is diminished by an amount equal to  $H_{12}$  (as in Figure 1).<sup>8a,9c,25</sup> A very recent quantum description of electronic coupling combined with solvent polarization predicts that the effect of  $H_{12}$  upon the barrier height can be substantially smaller than this,<sup>38</sup> however, the corresponding influence upon the reaction adiabaticity (i.e.,  $\kappa_{el}$ ) typically differs only slightly from the conventional Landau-Zener predictions.<sup>38</sup>

## Illustrative Comparisons with Experiment

**1. Rate-Solvent Friction Dependencies.** The most common experimental tactic utilized so far to explore solvent dynamical effects in activated ET processes involves evaluating rate constants for electron exchange,  $k_{ex}$ , in a sequence of solvents selected so to yield suitable alterations in the dielectric friction and thereby in  $\nu_n$ .<sup>15-18</sup> Choosing symmetrical reactions (self-exchange or electrochemical exchange) has the major virtue of eliminating solvent-dependent driving-



**Figure 2.** Logarithmic plots of calculated "barrier-corrected" rate constants ( $M^{-1} s^{-1}$ ) (for 5.0 kcal mol<sup>-1</sup> "cusp" barrier) for electron self-exchange versus inverse longitudinal relaxation time in 11 "Debye" solvents for the sequence of six electronic coupling matrix elements (at reactant contact) as indicated. See ref 16d for details; in particular, a spatial integration procedure<sup>24b,39</sup> was employed to evaluate the intermolecular rate constants. Key to solvents: 1, acetonitrile; 2, propionitrile; 3, acetone; 4, D<sub>2</sub>O; 5, nitromethane; 6, dimethylformamide; 7, dimethyl sulfoxide; 8, benzonitrile; 9, nitrobenzene; 10, tetramethylurea; 11, hexamethylphosphoramide. Reprinted with permission from ref 16d. Copyright 1989 American Chemical Society.

force contributions to the free energy barrier. After applying corrections for the solvent-dependent barrier height (yielding  $k'_{ex}$  values), any remaining  $k'_{ex}$ -solvent dependence can in principle be ascribed to variations in this dynamical term providing that  $K_p$  remains essentially constant (eq 2). The latter should be approximately the case, for example, for self-exchange reactions featuring weakly interacting solutes where one of the redox partners is uncharged.<sup>16</sup> Alternatively, estimates of the preexponential factor  $\kappa_{el}\nu_n$  can be obtained from  $k_{ob}$  and  $\Delta G^*$  by using eq 2 and the dependence on  $\tau_L^{-1}$  or other solvent dynamical parameters assessed.<sup>15d,16a-c</sup>

The form of the rate-solvent friction dependence is generally predicted from eq 3 to be sensitive to the donor-acceptor electronic coupling. As an illustration of this point, Figure 2 contains logarithmic plots of the calculated rate constant for a "model" self-exchange reaction,  $k'_{ex}$  (calc), in 11 "Debye" solvents against  $\tau_L^{-1}$  for a series of  $H_{12}$  values from 0.05 to 1.0 kcal mol<sup>-1</sup>, as indicated. The "cusp" barrier (i.e.,  $H_{12} \rightarrow 0$ ) is held constant at 5.0 kcal mol<sup>-1</sup>. Details of these calculations are given in ref 16d. The  $\log k'_{ex}$  (calc)- $\log \tau_L^{-1}$  dependencies in Figure 2 are seen to be sensitive to the solvent friction ( $\tau_L$ ) as well as to the electronic coupling ( $H_{12}$ ), the slopes increasing toward smaller  $\tau_L^{-1}$  values and with increasing  $H_{12}$ . These trends can be understood qualitatively in terms of eq 3; enlarging  $H_{12}$  and/or  $\tau_L$  will increase  $\kappa_{el}$  and hence the degree to which solvent dynamics, rather than electron tunneling, con-

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trols the barrier-crossing frequency. (The scatter seen in Figure 2 for some low-friction solvents is due to the variable influence of solvent inertial effects.<sup>16d,24b</sup>) Significantly, the occurrence of substantial solvent friction effects upon the reaction rate is predicted to require the presence of relatively strong electronic coupling ( $H_{12} \gtrsim 0.2$  kcal mol<sup>-1</sup>) for the typical range of  $\tau_L$  values in Figure 2. The additional presence of a substantial inner-shell component of the activation barrier is predicted to diminish further the rate-solvent friction dependence since the solvent dynamical influence on  $\nu_n$  will necessarily be muted.<sup>10</sup>

The strong sensitivity of the predicted rate-friction dependence to the electronic coupling seen in Figure 2 suggests that information on the latter might be discernible from suitable solvent-dependent rate studies. In practice, the reliable quantitative extraction of such information from solvent-dependent rate measurements is commonly thwarted by uncertainties in the corrections for the solvent-dependent barrier height.<sup>15b,c,16a</sup> An illuminating exception, however, is provided by some metallocene self-exchange reactions which have recently been examined in detail in our laboratory.<sup>16,41</sup> These reactions involve redox couples of the form Cp<sub>2</sub>M<sup>+0</sup>, where Cp = cyclopentadienyl and derivatives and M = Fe or Co. They have several virtues as solvent dynamical probes, including the presence of known small or negligible inner-shell barriers and suitability for self-exchange rate measurements by using proton NMR line broadening. Most importantly, reliable estimates of the solvent-dependent barrier heights are available from measurements of optical electron-transfer energies,  $E_{op}$ , for related biferrocene cations.<sup>40</sup> (Under suitable conditions,  $\Delta G^*_c = E_{op}/4$ , where  $\Delta G^*_c$  is the "cusp" barrier height, i.e., that referring to  $H_{12} \rightarrow 0$ ).

Significantly, the  $k_{ex}$  values in a given solvent are sensitive to the metallocene structure, varying by factors up to ca. 100-fold.<sup>16</sup> These rate differences have been traced primarily to variations in the donor-acceptor electronic coupling.<sup>16d,41</sup> Although not evident initially,<sup>16a</sup> a subsequent reevaluation of Cp<sub>2</sub>Fe<sup>+0</sup> kinetics<sup>16b</sup> together with further measurements yielded an interesting spectrum of barrier-corrected rate-solvent friction behavior.<sup>16d</sup> These experimental results, discussed in ref 16d, are closely reminiscent of the corresponding calculated traces (Figure 2) in that the more facile reactions (i.e., those with larger  $H_{12}$ ) display progressively greater dependencies of  $k'_{ex}$  upon  $\tau_L^{-1}$ . Comparison with Figure 2 enabled approximate estimates of  $H_{12}$  for each reaction to be obtained: these vary from about 0.1 kcal mol<sup>-1</sup> for Cp<sub>2</sub>Fe<sup>+0</sup> to 0.5 kcal mol<sup>-1</sup> for Cp<sub>2</sub>Co<sup>+0</sup> and 1.0 kcal mol<sup>-1</sup> for Cp'<sub>2</sub>Co<sup>+0</sup> (Cp' = pentamethylcyclopentadienyl). Interestingly, these  $H_{12}$  estimates are in approximate agreement with recent theoretical values obtained by Newton.<sup>42</sup> The greater electronic coupling for the cobalt versus the iron metallocenes, in particular, can be understood qualitatively in terms of the ligand- and metal-centered nature of the molecular orbitals, respectively, that participate in electron transfer.<sup>43</sup>

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Overall, these results indicate that  $\tau_L^{-1}$  can provide at least a semiquantitative description of the adiabatic barrier-crossing dynamics in Debye media.

Rate-solvent dependencies roughly consistent with this last conclusion have also been obtained for a number of other homogeneous-phase and electrochemical reactions.<sup>15-18</sup> On this basis, the latter type of process tends to occur via more adiabatic pathways than the former, although an interesting exception has been noted.<sup>15f</sup> In the absence of experimental optical information on the solvent-dependent barriers, it is conventional to utilize  $\Delta G^*$  estimates obtained from the Marcus and related dielectric continuum models. With due care, such procedures can at least provide a reliable diagnosis of solvent dynamical effects; i.e., the qualitative recognition of a solvent-friction-dependent preexponential factor.<sup>15b,c,16a</sup> An illustration of the limitations of this approach for *quantitative* rate-friction analyses, however, is provided by comparing optical electron-transfer energies for biferrocene cations with corresponding dielectric continuum predictions.<sup>40,45</sup> While the calculated barriers are largely within 10-20% of the measured values, these disparities depend systematically upon the magnitude of  $\Delta G^*$ ; moreover,  $\Delta G^*$  correlates roughly with  $\tau_L^{-1}$  in common Debye solvents.<sup>15c,16b</sup> These two factors can conspire to yield noticeably different inferred rate-solvent friction dependencies depending on whether the optical or the theoretical  $\Delta G^*$  values are used for the analysis.<sup>16b</sup>

**2. Non-Debye Solvent Relaxation.** Given the largely satisfactory picture noted above for metallocene self-exchange dynamics in Debye media, the examination of barrier-crossing frequencies in solvents featuring multiple relaxation times should provide an insightful test of the theoretical predictions noted above.<sup>16,25,50</sup> To this end, Table I compares inverse solvent relaxation times,  $\tau_L^{-1}$  and  $\tau_S^{-1}$ , obtained from dielectric loss and subpicosecond TDFS data, respectively (the latter from Barbara et al.<sup>2b,6a,49</sup>), in eight solvents with preexponential factors  $\kappa_{el}\nu_n$  for a pair of metallocene self-exchange reactions. The  $\kappa_{el}\nu_n$  values were extracted from measured  $k_{ex}$  and  $\Delta G^*$  values (see ref 16c and footnotes for details). The redox couples Cp<sup>e</sup><sub>2</sub>Co<sup>+0</sup> (Cp<sup>e</sup> = carbomethoxycyclopentadienyl) and HMFC<sup>+0</sup> [(hydroxymethyl)ferrocenium-(hydroxymethyl)ferrocene] are chosen here since they display largely adiabatic and nonadiabatic behavior, respectively,<sup>16d</sup> and can be examined in water as well as a range of nonaqueous solvents.<sup>16c</sup> Two of the solvents selected, propylene carbonate and methanol, exhibit non-Debye dielectric behavior,<sup>46,48</sup> also reflected in the pair of widely (ca. 10-fold) differing  $\tau_S$  values observed in both these me-

(43) The formulation of donor-acceptor electronic coupling in terms of reactant *molecular* orbitals, thereby considering metal-ligand orbital mixing, is equivalent to so-called electron "superexchange" mechanisms where the metal and ligand orbitals are considered separately.<sup>42,44</sup>

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**Table I**  
**Comparison between Inverse Solvent Relaxation Times from Dielectric Loss and TDFS Data with Effective Barrier-Crossing Frequencies for Metallocene Self-Exchanges**

solvent	$\Delta G^*$ , <sup>a</sup> kcal mol <sup>-1</sup>	$\tau_L^{-1}$ , <sup>b</sup> ps <sup>-1</sup>	$\tau_S^{-1}$ , <sup>c</sup> ps <sup>-1</sup>	$\kappa_{el}\nu_n$ , ps <sup>-1</sup> <sup>d</sup>	
				Cp <sup>e</sup> <sub>2</sub> Co <sup>+0/e</sup>	HMFc <sup>+0/f</sup>
acetonitrile	5.35	~2.5	1.8	2.5	0.2
acetone	5.4	3.5	1.0 (53%) 3.5 (47%)	2	0.25
nitromethane	5.3	4.5	4.0 (50%)	3	0.4
water	5.2	1.9	1.0 (50%) 4.0 (50%)	3.5 <sup>g</sup>	0.35 <sup>g</sup>
benzonitrile	4.55	0.17	0.16 (61%) 0.47 (39%)	0.3	0.15
nitrobenzene	4.55	0.19	0.24 (54%)	0.15	0.12
propylene carbonate	5.25	(0.3)	0.24 (54%) 2.3 (46%)	1.5	
methanol	5.2	(0.13)	0.10 (60%) 0.9 (40%)	1.5	0.45

<sup>a</sup> Cusp free energy barrier for self-exchange reactions, estimated from optical electron-transfer energies for ferrocenylacetylene cation in indicated solvent (see refs 16c,d and 40 for details). <sup>b</sup> Inverse longitudinal relaxation time for solvent indicated, obtained from dielectric loss spectra. See Table I of ref 16d for data sources, except for propylene carbonate (from ref 46) and acetonitrile (from ref 47, assuming Debye behavior). Values for propylene carbonate and methanol are given in parentheses since an additional higher frequency dispersion is also evident in the dielectric loss spectra.<sup>46,48</sup> <sup>c</sup> Inverse solvation times, along with percentage weighting factors, obtained from TDFS data for the coumarin C152 (refs 2b and 6a) except for water, which refers to C343 (ref 49). <sup>d</sup> Effective barrier-crossing frequency for metallocene self-exchange reaction indicated, obtained from experimental  $\kappa_{el}$  values together with listed  $\Delta G^*$  values, assuming that  $K_p = 0.25 \text{ M}^{-1}$  (Eq 2). See ref 16c for kinetic data and other details;  $\Delta G^*$  values for Cp<sup>e</sup><sub>2</sub>Co<sup>+0/e</sup> are taken to be 0.5 kcal mol<sup>-1</sup> smaller to allow for orbital overlap.<sup>16c</sup> <sup>e</sup> Cp<sup>e</sup><sub>2</sub>Co<sup>+0/e</sup> = carbomethoxycobaltocenium-carbomethoxycobaltocene [(CpCO<sub>2</sub>Me)<sub>2</sub>Co<sup>+0/e</sup>]. <sup>f</sup> HMFc<sup>+0/f</sup> = (hydroxymethyl)ferrocenium-(hydroxymethyl)ferrocene [Cp-CpCH<sub>2</sub>OH)Fe<sup>+0/f</sup>]. <sup>g</sup> Rate data refers to D<sub>2</sub>O.

dia.<sup>6</sup> Multiexponential TDFS decays are also seen for three other solvents in Table I.<sup>2b,6a,49</sup> Note, however, the good agreement between  $\tau_L$  and the average  $\tau_S$  values for all six Debye solvents in Table I, even though the relaxation times vary by ca. 20-fold.

The  $\kappa_{el}\nu_n$  values for HMFc<sup>+0</sup> are uniformly smaller than  $\tau_L^{-1}$  or  $\tau_S^{-1}$  and are roughly solvent independent, as expected for a largely nonadiabatic reaction (i.e.,  $\kappa_{el} \ll 1$ ).<sup>16d</sup> For Cp<sup>e</sup><sub>2</sub>Co<sup>+0/e</sup>, however, the  $\kappa_{el}\nu_n$  values not only correlate well with the solvent relaxation dynamics but also are close to (within 1.5-fold of) the larger  $\tau_S^{-1}$  value in all eight solvents. Although the agreement between the absolute  $\kappa_{el}\nu_n$  and  $\tau_S^{-1}$  values seen in Table I is probably fortuitous given the inevitable uncertainties in extracting the former, the close correlation nonetheless demonstrates the importance of the more rapid solvent dynamical component in accelerating electron transfer. This finding is in broad agreement with the theoretical predictions noted above,<sup>9c,25,34-36</sup> a more quantitative analysis yields solvent-dependent barrier-crossing frequencies that are largely consistent with the predictions of the Hynes model.<sup>50</sup>

The results in methanol and water are perhaps of greatest interest.<sup>16c</sup> The influence of the high-frequency relaxation component in methanol is particularly striking, yielding barrier-crossing frequencies that approach those in water and other low-friction media despite the presence of a markedly (10–30-fold) longer  $\tau_L$  value. The physical origin of such rapid relaxation modes is unclear at present, although the high-frequency dielectric-loss component in primary alcohols has been ascribed to OH group rotation.<sup>30</sup> Dipole translational relaxation may also contribute to the rapidity of the TDFS and barrier-crossing dynamics in methanol.<sup>16c,50</sup>

Comparable results have also been obtained for other adiabatic metallocene reactions,<sup>15c,16e,25,50</sup> although the presence of a rapid TDFS relaxation component is apparently not always reflected in accelerated ET dynamics.<sup>50</sup> Several factors may account for such observed

differences.<sup>50</sup> For example, the importance of rapid dynamical components associated with local solvation ("solvent molecularity") effects is generally expected to be sensitive to the solute size and structure. Moreover, some differences are always expected given that the TDFS and ET measurements refer to the solvation dynamics of dipolar and ionic solutes, respectively.<sup>51,52</sup>

### Other Approaches and Future Prospects

While solvent-dependent rates for bimolecular electron exchange, especially self-exchange, reactions constitute the bulk of the experimental information on activated solvent dynamical effects gathered so far, other approaches could be used to advantage. Examining the kinetics of unimolecular (preferably rigid intramolecular) electron-transfer processes would have the obvious virtue of eliminating uncertainties regarding the precursor-complex geometries and the energetics of their formation. Few such studies aimed at elucidating solvent dynamical effects for *activated* intramolecular ET have been reported so far, although as noted above there are a number of photoexcited intramolecular reactions examined that apparently feature small ( $\leq k_B T$ ) barriers.<sup>2b,53</sup>

Temperature-dependent rate studies should in some cases provide a useful means of diagnosing and examining solvent dynamical effects. This tactic has been utilized in several studies, again mostly involving small-barrier reactions.<sup>18d,54</sup> The procedure may also be useful for examining activated reactions. At least for bimolecular processes, however, the Arrhenius activation parameters can be distorted greatly by reactant

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intermolecular interactions.<sup>55</sup> Even for reactions involving monocharged cation/neutral pairs such as the metallocene self-exchanges considered above, unexpectedly low Arrhenius preexponential factors are usually obtained that probably reflect entropic contributions to the precursor-complex stability.<sup>16a</sup> This complication is absent, however, for intramolecular electron transfer, so that valuable dynamical insight should be forthcoming from temperature-dependent studies of such activated processes in various solvents.

A central issue, highlighted above, is the degree to which reaction adiabaticity is achieved, corresponding to rate control by solvent dynamics and other nuclear motion rather than by nonadiabatic electron hopping. The degree of electronic coupling that is evidently required to yield largely adiabatic barrier crossing, at least in low-friction media at ambient temperatures ( $H_{12} \geq 0.2$  kcal mol<sup>-1</sup>), should restrict the chemical variety of outer-sphere ET processes liable to be controlled by solvent dynamics under these conditions. Solvent dynamical effects should often be prevalent, however, for inner-sphere ET and other "strong overlap" reactions, providing that the bond formation between the reaction centers engenders sufficient donor-acceptor electronic coupling. While there is extensive theoretical work on some aspects of strong-overlap charge transfer,<sup>56</sup> corresponding experimental examinations of solvent-dependent dynamics are rare. One interesting recent example of the latter type, however, concerns the evaluation of primary kinetic isotope effects ( $k_H/k_D$ ) for hydride transfer.<sup>57</sup> A significant solvent dependence

of  $k_H/k_D$  was observed, from a maximum of ca. 5–5.5 in low-friction media to ca. 3.0 in some other solvents. Although a simple relationship between  $k_H/k_D$  and solvent friction was not established, the results are roughly consistent with a shift from virtually complete rate control by hydride tunneling to partial control by solvent relaxation.<sup>57</sup> This interpretation is closely analogous to the phenomenon of solvent friction dependent reaction adiabaticity for electron transfer, embodied in Figure 2.

Along with the anticipated experimental developments, molecular dynamics simulations should play a significant future role in delineating solvent effects in activated ET and related processes.<sup>56,58</sup> One hoped-for virtue of such simulations is that they should provide a common meeting ground between experimental results and relevant analytic theories of condensed-phase dynamics. As stressed above, the separation of energetic and dynamical factors remains a major stumbling block to the reliable interpretation of kinetic data in this vein. The concerted acquisition of parallel experimental and molecular simulation data could provide an insightful marriage for the future.

*Financial support from the Office of Naval Research is gratefully acknowledged. We are indebted to our co-workers Roger Nielson, Alex Gochev, Neal Golovin, and Don Phelps. We also thank a number of others, especially Drs. Paul Barbara, Graham Fleming, Casey Hynes, Marshall Newton, and Peter Wolynes, for their willingness to share data, ideas, and preprints, and for the patient longstanding tutelage offered by the last three.*

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