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Solvent Relaxation in ~~E~~lectron-Transfer Reactions:
Comparisons Between Barrier-Crossing Dynamics in
Water and Polar Aprotic Media

by

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ABSTRACT

Rate constants, k_{ex} , for electron self exchange of three metallocene redox couples, carboxymethyl(cobaltocenium-cobaltocene) $[(CpCO_2Me)_2Co^{+/0}]$, hydroxymethyl(ferrocenium-ferrocene) $[(Cp \cdot CpCH_2OH)Fe^{+/0}]$, and trimethylaminomethyl(ferrocenium-ferrocene) $[(Cp \cdot CpCH_2NMe_3)Fe^{2+/+}]$, obtained using proton NMR line broadening, are utilized along with optical electron-transfer energies for the mixed-valence biferrocenylacetylene cation to obtain solvent-dependent frequencies, $\kappa_{01}\nu_n$, in water relative to those in methanol and six aprotic solvents. While $\kappa_{01}\nu_n$ for the ferrocene couples is insensitive to the solvent, indicative of nonadiabatic behavior ($\kappa_{01} < 1$), $\kappa_{01}\nu_n$ for the cobaltocene couple is responsive to the solvent dynamics. While rapid barrier-crossing dynamics are obtained in water, comparable to acetonitrile, acetone, and nitromethane, the influence of high-frequency relaxation components for water is less marked than for methanol.

There is currently considerable interest in elucidating the dynamical role of the solvent in electron-transfer (ET) reactions, as in other fundamental processes in condensed phases.^{1,2} An important and continuing impetus is provided by the evolution of theoretical treatments which emphasize the anticipated sensitivity of the barrier-crossing frequency to solvent dynamical properties. (A representative selection is refs. 3-9.) In addition, direct experimental information on the dynamics of polar solvation is being obtained from time-dependent fluorescence Stokes shifts (TDFS) for chromophores forming suitable charge-transfer excited states.^{2,10-12}

Corresponding experimental information on the role of the solvent in ET barrier-crossing dynamics has been obtained from rates of intramolecular charge transfer, k_{et} (s^{-1}), involving photoexcited states^{2b,12,13} or from the solvent-dependent kinetics of thermal electron-exchange processes.⁵⁻⁷ The barriers, ΔG^* , for the former reactions studied so far are apparently sufficiently small so that k_{et}^{-1} approaches the corresponding TDFS solvation times, τ_s .^{2b} While the larger barriers ($\Delta G^* \sim 5-10 k_B T$, k_B is the Boltzmann constant) characteristic of the latter processes complicate the extraction of solvent dynamical information from the measured kinetics,^{5,6} these systems are of particular interest since their barrier-crossing dynamics should be more characteristic of ordinary chemical reactions.

Experimental work on this topic in our laboratory has focused most recently on metallocene and related self-exchange processes, the kinetics being evaluated by proton NMR line broadening.^{14e,15} In particular, redox couples of the general form $Cp_2M^{+/0}$, where Cp = cyclopentadienyl (or derivatives) and M = Co or Fe, provide an invaluable set of self-exchange processes having uniformly small (or negligible) inner-shell barriers, yet marked differences in the donor-acceptor orbital overlap (i.e., in the electronic coupling matrix element

H_{12}).^{15,17,18} In addition, the solvent-dependent barrier heights may be estimated reliably from optical electron-transfer energies for related mixed-valence metallocenes.^{15,18-21} Together, these measurements enable the manner in which the dynamics of solvent reorganization influence the barrier-crossing frequency for differing degrees of orbital overlap to be explored in a range of polar nonaqueous media.^{14e,15} In particular, evidence has been garnered to support the influence upon the barrier-crossing frequency of faster "non-Debye" dynamical components in some solvents in addition to that described by the major longitudinal relaxation time, τ_L .^{14c,15a,22a} A transition from partly nonadiabatic to adiabatic behavior upon increasing τ_L and/or enhancing H_{12} has also been characterized (vide infra).^{15c}

As a consequence of probe solubility and other considerations, both the TDFS and ET solvent dynamical measurements reported so far involve almost exclusively nonaqueous media. It is of obvious interest to obtain such information also in aqueous solution in view of the unique properties and importance of water as a solvent. Very recently, the first TDFS measurements in water have been reported.^{11c} Presented here are some comparisons of the ET dynamics in deuterated water and aprotic media as derived from self-exchange rates for three water-soluble metallocene redox couples. The results support the presence of rapid yet overdamped solvent relaxation in aqueous media.

EXPERIMENTAL SECTION

Details of the preparation of the water-soluble metallocenes hydroxymethylferrocene $[(Cp \cdot CpCH_2OH)Fe]$, abbreviated here as "HMFc" and carboxymethylcobaltocene $[(CpCO_2Me)_2Co]$, referred to here as " Cp^*Co " (e = ester) will be given in ref. 15c. Briefly, the former was synthesized largely as in ref. 23; the ferrocenium form being obtained by $FeCl_3$ oxidation. The cobaltocenium salt of the latter was synthesized as outlined in ref. 24, and the

reduced form obtained by reaction with cobaltocene. The third water-soluble species, trimethylaminomethylferrocene $[(\text{Cp}^+\cdot\text{CpCH}_2\text{NMe}_3^+)\text{Fe}]$, "TMAFc⁺" was prepared as the iodide salt as in ref. 23, and converted into the BF_4^- salt by anion exchange. The methanol was removed under vacuum and the solid recrystallized from methanol. The oxidized form $(\text{Cp}^+\cdot\text{CpCH}_2\text{NMe})\text{Fe}(\text{BF}_4)_2$, was prepared by adding a stoichiometric quantity of AgBF_4 in nitromethane, filtering, and precipitation by addition of diethyl ether. Biferrocenylacetylene (BFA) was synthesized as described in ref. 25. The corresponding mixed-valence cation was usually generated in the appropriate solvent by adding an equimolar amount of $\text{Fe}(\text{bipyridine})_3^+(\text{PF}_6)_3$ to a BFA solution. Biferrocene was prepared according to ref. 26; the monocation was formed by Ag^+ oxidation, as above, and isolated as the BF_4^- salt.

Most details of the NMR sample preparation, measurements, and line-broadening data analysis are given in refs. 15a and b. Proton NMR spectra for the $\text{HMFc}^{+/0}$ and $\text{TMAFc}^{2+/+}$ systems, and the $\text{Cp}_2^+\text{Co}^{+/0}$ couple, were collected on Nicolet NT 200 and NT 400 instruments, respectively (operated at 200.0 and 469.5 MHz). The electron-exchange line broadening was probed using the methyl proton resonance for the latter two couples, and the $-\text{CH}_2-$ protons for the hydroxymethyl system.

RESULTS AND DATA ANALYSIS

Two of the three metallocene couples examined here, $\text{Cp}_2^+\text{Co}^{+/0}$ and $\text{HMFc}^{+/0}$, are of the same charge type (+/0) as the other cobaltocene and ferrocene couples previously examined in detail. Although there are significant effects of ion pairing upon the optical electron-transfer energies for mixed-valence biferrocenes,^{20,27} k_{ex} for $\text{Cp}_2\text{M}^{+/0}$ self exchange is typically insensitive to variations in the ionic strength.²⁸ The third water-soluble couple examined here, $\text{TMAFc}^{2+/+}$, carries a net positive charge on both reaction partners as a

result of the cationic amine group, so that the presence of a repulsive electrostatic work term is anticipated. However, k_{ex} for this couple in acetonitrile is also insensitive to ionic strength, μ , suggesting that the amine substituents are well separated in the precursor complex as anticipated on steric grounds.³⁰ Roughly comparable results were also obtained here for $\text{TMAFc}^{2+/+}$ in D_2O , although k_{ex} increases by about 2.5 fold as the ionic strength (as KPF_6) is increased from 0.03 to 0.5.

Values of k_{ex} for these three metallocene couples in D_2O , methanol, and in six aprotic solvents are summarized in Table I. The latter data were selected for inclusion here in part because they provide a significant variation in solvent dynamics (vide infra). The observed k_{ex} values can be related to the desired barrier-crossing dynamics most simply by^{14,15}

$$k_{ex} = K_p \kappa_{e1} \nu_n \exp(-\Delta G^*/k_B T) \quad (1)$$

where K_p is the effective equilibrium constant for forming the precursor complex (i.e. the reactant pair in the appropriate configuration for electron transfer), and κ_{e1} is the electronic transmission coefficient (i.e. the probability of electron transfer within the transition state).

The focus of attention here, as before,^{14,15} is the extraction of the net barrier-crossing frequency, $\kappa_{e1}\nu_n$, from k_{ex} . Obtaining absolute $\kappa_{e1}\nu_n$ values on this basis is clearly fraught with difficulty since absolute estimates of both K_p and ΔG^* are required. However, the problem is eased considerably if only the solvent dependence of $\kappa_{e1}\nu_n$ is required, partly because K_p is anticipated to be insensitive to the solvent (vide infra). Although the solvent dependence of ΔG^* is significant, it can be estimated from theoretical models.^{14c,15a} An alternative, and probably more reliable, procedure involves measuring the energies, E_{op} , for optical electron transfer within symmetrical mixed-valence compounds that are structurally similar to the thermal electron-transfer systems

of interest.¹⁵ Biferrocenylacetylene (BFA⁺) provides an optimal choice for the present purposes since the juxtaposition of the Cp₂Fe⁺/Cp₂Fe partners in the binuclear complex¹⁹ approximates that expected for the precursor complex for the present self-exchange reactions.^{15a} In addition, BFA⁺ approximates "class II" mixed-valence behavior,¹⁹ enabling the required thermal barrier in a given solvent to be obtained simply from³¹

$$\Delta G^* = E_{op}/4 \quad (2)$$

Values of the wavelength of maximum absorption for the intervalence transition, λ_{max} ($= E_{op}^{-1}$), of BFA⁺ in each solvent considered here are listed in Table I.³² The values are in good agreement with earlier data.¹⁹ Although BFA⁺ is insufficiently soluble in D₂O to enable E_{op} to be evaluated directly, the biferrocene cation, BF⁺, was found to be sufficiently soluble (ca 0.2-0.3 mM) as the BF₄⁻ salt in D₂O to enable λ_{max} , 1850 ($\pm$ 50) nm, to be obtained. (Essentially the same result was found by extrapolating λ_{max} values for BF⁺ in a series of D₂O/deuterated methanol mixtures.) By noting that the solvent dependence of E_{op} for BF⁺ and BFA⁺ is functionally almost identical, and especially that λ_{max} for BF⁺ in D₂O and methanol are very similar (1850 and 1875 nm, respectively), this enabled a reliable estimate of λ_{max} for BFA⁺ in D₂O, 1380 ($\pm$ 50) nm, to be extracted. The resulting estimates of ΔG^* , obtained from λ_{max} by using Eq. (2), are listed in Table II. The majority of these ΔG^* values are close to (within ca 0.3 kcal mol⁻¹ of) the corresponding dielectric continuum estimates, although some significant deviations are observed.²¹

Table II also summarizes solvent-dependent estimates of $\kappa_{e1}\nu_n$ (s⁻¹) for all three self-exchange reactions, resulting from the experimental k_{ex} value in Table I along with ΔG^* by using Eq. (1). [The ΔG^* values for Cp₂Co^{+1/0} were taken to be 0.5 kcal mol⁻¹ smaller, resulting from our estimate of H_{12} for this system^{15c} (vide supra).] The K_p value was taken as 0.25 M⁻¹; this approximate

estimate is appropriate for the present reactions provided they exhibit weakly adiabatic or nonadiabatic behavior.⁴¹ Even though the uncertainties in the values of both $\Delta G^\ddagger$ and K_p correspond to substantial uncertainties (probably as much as 5-10 fold) in these absolute estimates of $\kappa_{e1}\nu_n$, at least the solvent dependence of $\kappa_{e1}\nu_n$ for a given reaction, of central concern here, should be markedly more reliable.

DISCUSSION

Inspection of the $\kappa_{e1}\nu_n$ values in Table II reveals several interesting features. Most generally, while the barrier-crossing frequencies for the two ferrocenium-ferrocene couples are relatively insensitive to the solvent ($\kappa_{e1}\nu_n$ varying by 3 fold or less), those for $\text{Cp}_2^*\text{Co}^{+/0}$ are larger and vary to a markedly greater extent (up to ca 20 fold). These $\kappa_{e1}\nu_n$ variations correlate roughly with the literature τ_L^{-1} values, also given in Table II, at least in the supposed "Debye-like" solvents (i.e. τ_L^{-1} values given without parentheses). As discussed in more detail elsewhere^{15b,c} (utilizing a much larger data set^{15c}), these behavioral differences reflect the occurrence of largely nonadiabatic and adiabatic behavior for the present ferrocene and cobaltocene couples, respectively. For the former, the extent of orbital overlap is sufficiently small (around $H_{12} \sim 0.07 \text{ kcal mol}^{-1}$ ^{15c}) so that in most media $\kappa_{e1} < 1$; in the limiting case where $\kappa_{e1} \ll 1$, $\kappa_{e1} \propto \nu_n^{-1}$ so that $\kappa_{e1}\nu_n$ will be independent of ν_n and hence τ_L^{-1} . This behavior, which is also characteristic of some other ferrocene self-exchange reactions,^{15b,c} signals the relative insensitivity of the electron-transfer kinetics to solvent relaxation and other nuclear dynamical factors.⁴³ The more facile $\text{Cp}_2^*\text{Co}^{+/0}$ couple, on the other hand, apparently engenders sufficient orbital overlap so to display largely adiabatic behavior, whereupon $\kappa_{e1} \sim 1$ even in the most dynamically rapid solvents. (Indeed, we estimate that $H_{12} \sim 0.5 \text{ kcal mol}^{-1}$ for this reaction^{15c}). These differences in

H_{12} are consistent with the differing redox orbitals involved for the cobaltocene and ferrocene couples.^{15c,17,18}

This latter system therefore provides an interesting opportunity to examine how the adiabatic barrier-crossing frequency, ν_n , in water compares with that in other polar solvents in the absence of a substantial inner-shell contribution to ΔG^* . Comparison of the $\kappa_{e1}\nu_n$ values for $Cp_2^*Co^{+/0}$ in D_2O and nonaqueous media (Table II) reveals the former to be a dynamically "fast" solvent, yielding a frequency factor comparable to those in acetonitrile, acetone, and nitromethane. This finding is not entirely surprising since in Debye-like solvents it is expected that $\nu_n \approx \tau_L^{-1}$,^{3,4a} and the τ_L^{-1} value for deuterated water ($1.9 \times 10^{12} s^{-1}$ ⁴⁴) is close to, although ca twofold smaller than, τ_L^{-1} for these dynamically rapid aprotic media.

It is, nonetheless, worthwhile to examine more closely the $\kappa_{e1}\nu_n$ values for $Cp_2^*Co^{+/0}$ in water compared to methanol as well as aprotic media. It is noteworthy that while the major τ_L^{-1} value for methanol is substantially (15-30 fold) smaller than for water, acetonitrile, acetone, or nitromethane, the $\kappa_{e1}\nu_n$ value in methanol is comparable to (within 2 fold of) the values in these latter solvents (Table II). This considerable enhancement of the barrier-crossing dynamics in methanol has also been noted for other adiabatic reactions in primary alcohols,^{14c,15a,16e} and has been ascribed to the influence of higher-frequency components observed in the dielectric loss spectra.^{15a,22a} [The qualitatively similar, albeit milder, enhancement of $\kappa_{e1}\nu_n$ observed in propylene carbonate (Table II) can also be accounted for in this manner.^{15a,22a}] By comparison, the $\kappa_{e1}\nu_n$ value in water is only marginally (ca 2-3 fold) larger in relation to the corresponding values in acetonitrile, acetone, and nitromethane than anticipated on the basis of the relative τ_L^{-1} values (Table II). Besides the uncertainties in the $\kappa_{e1}\nu_n$ values themselves, this relatively small

difference may be due to solvent inertial effects (vide infra) and/or uncertainties in the effective τ_L values.²² Apparently, therefore, no marked enhancement of $\kappa_{01}\nu_n$ by "faster" dynamical components in water is occurring in the manner evident in methanol. One possibility is that dipole translational relaxation,⁴⁶ predicted to be significant in methanol but not in water,^{5c,47} is responsible for part of the dynamical enhancement observed in the former solvent.

It is of interest to compare briefly these findings with other pertinent dynamical information. Even though the dielectric loss behavior of water (and deuterated water) is remarkably Debye-like for such a strongly hydrogen-bound liquid, additional high-frequency components appear in the spectrum beyond the major Debye loss at 8.5 ps, most clearly a feature at 0.053 ps.⁴⁸ Recent molecular dynamics simulations of dielectric spectra for pure water⁴⁹ and charged-induced changes in aqueous solvation^{2d,50} also detect apparently similar high-frequency components. Although the assignment of the high-frequency dielectric loss feature has been controversial,⁵² it appears to be primarily resonant rather than dissipative in nature,⁴⁸ and therefore unlikely to diminish significantly the net solvent friction so as to enhance ν_n .^{5b,52}

Very recent subpicosecond TDFS measurements for water by Barbara et al indicate the presence of a biexponential decay with τ_s components of 0.16 and 1.2 ps.^{11c} Although a "fast" relaxation component is thereby identified, the overall dynamics are not greatly different from those, for example, in acetonitrile (monoexponential, $\tau_s \approx 0.55$ ps^{11b}), in harmony with the present results.⁵³ The recent observation of additional fast relaxation components in both methanol and propylene carbonate by means of TDFS^{11b} is also in harmony with the present results. Given the current emergence of subpicosecond TDFS data in a range of polar solvents,^{11,54} a more extensive comparison between the

solvent-dependent barrier-crossing frequencies and such microscopic real-time solvation dynamics is of obvious interest and will be pursued elsewhere.

Finally, it is worth noting that, unlike the other dynamically rapid solvents considered here (e.g. acetonitrile), the ET solvent dynamics in water are probably entirely overdamped in that τ_L^{-1} is well below the inertial limiting frequency, ca $5 \times 10^{13} \text{ s}^{-1}$ (estimated from a continuum model^{5a,22a}), which corresponds to the transition-state theory (TST) limit.^{1,4a,14b,52} Stated differently, even such rapid barrier-crossing dynamics ($\nu_n \sim 4 \times 10^{12} \text{ s}^{-1}$) correspond to the presence of substantial solvent friction in water, but not in acetonitrile. One interesting consequence is that the effective dynamics of electron-transfer reactions featuring substantial inner-shell distortions in water are more appropriately described by overdamped frictional treatments as in ref. 6 rather than by TST models which are usually employed. The numerical results in ref. 6b indicate that the solvent dynamics can exert an important influence upon ν_n even when the inner-and outer-shell contributions to ΔG^* are comparable.

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28. Thus typically k_{ex} for $Cp_2Fe^{+/0}$ and $Cp_2Co^{+/0}$ decreases by 30% or less as the ionic strength, μ , is increased over the range 0-0.25 M in several polar solvents, using PF_6^- , BF_4^- , or ClO_4^- as the added anion.^{15b} Significant ion-pairing effects upon k_{ex} are obtained, however, in the relatively nonpolar solvent dichloromethane,²⁹ mirroring the marked effects seen in the optical electron-transfer energies.²⁰
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41. Strictly speaking, even for spherical reaction partners the effective value of K_p will depend upon H_{12} and its sensitivity to the radial separation, tending to increase as H_{12} and/or r_1 increases.⁴² The assumption of a constant K_p value, however, is adequate for the present purposes.
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43. (a) McManis, G. E.; Mishra, A. K.; Weaver, M. J., *J. Chem. Phys.*, 1987, 86, 5550; (b) This conclusion differs from that in ref. 15a, which utilized literature k_{ex} values for $Cp_2Fe^{+/o}$ ³⁰ that we more recently found to contain systematic errors.^{15b}
44. It is worth noting that although the dielectric loss properties of D_2O are slightly different from those of H_2O ,³⁴ the τ_1 values are virtually identical, 5.2×10^{-13} s, based on data given in refs. 34 and 45.
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47. Note that the implication from Table 1 of ref. 5c that the relaxation dynamics in nitrobenzene as well as methanol should be accelerated by dipole translational relaxation is due to a typographical error (J. T. Hynes, personal communication). The diffusion coefficient and hence the quantity p for nitrobenzene are actually about tenfold smaller than the values listed in this Table.
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52. In this context, dissipation is distinguished conceptually from a resonance process in that the former involves irreversible energy loss from the system (e.g. a rotating dipole) to the surroundings, whereas the latter describes simple absorption with reversible energy transfer between the system and its surroundings. In a dielectric spectrum, a dissipative absorption is characterized by a "loss" (i.e. a net decrease in the real part of the complex dielectric constant towards the high-frequency side of the feature); no such loss accompanies a purely resonance absorption. Friction is inherently a dissipative process; resonant modes associated

with solvent inertia only influence the barrier-crossing dynamics in the absence of substantial friction, corresponding to the TST limit.^{1,4a}

53. Calculations of ν_n were undertaken utilizing these TDFS correlation function data in the non-Debye kinetic treatment of Hynes.^{5b} (The procedure is detailed in ref. 22.) Assuming an H_{12} value of 0.5 kcal mol⁻¹ and a barrier height of 5 kcal mol⁻¹, ν_n values of 1.0×10^{12} s⁻¹ and 5.5×10^{11} s⁻¹ were obtained in H₂O and acetonitrile, respectively.
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TABLE I. Self-Exchange Rate Constants and Optical Electron-Transfer Energies in Deuterated Water and Selected Organic Solvents at 25°C

Solvent	$\lambda_{\max}^b$ nm	$k_{ex} (M^{-1} s^{-1})^d$		
		$Cp_2^*Co^{+/0}{}^e$	$HMFc^{+/0}{}^f$	$TMAFc^{2+/+}{}^g$
Water ^a	(1380) ^c	3×10^8	1.4×10^7	9×10^6
Acetonitrile ^a	1330	1.9×10^8	5.4×10^6	2.1×10^6
Acetone ^a	1320	1.2×10^8	7.2×10^6	4.1×10^6
Nitromethane	1350	2.4×10^8	1.4×10^7	3.1×10^6
Methanol ^a	1380	$\sim 1.5 \times 10^8$	1.7×10^7	
Benzonitrile	1578	8×10^7	1.8×10^7	1.1×10^7
Nitrobenzene ^a	1570	4.4×10^7	1.4×10^7	1.0×10^7
Propylene Carbonate	1355	1.4×10^8		2.3×10^7

^a Deuterated solvents employed for both NMR and near-infrared measurements.

^b Wavelength of intervalence band maximum for BFA^+ in given solvent (see text and footnote 32). Values for benzonitrile and propylene carbonate taken from ref. 19a.

^c Value estimated from $\lambda_{\max}$ value (1850 nm) for biferrocene cation in D_2O relative to other solvents (see text).

^d Rate constant for self exchange in given solvent, obtained by proton NMR line broadening. For ferrocenium-ferrocene couples, concentrations of oxidized and reduced forms were ca 1-7 mM and ca 10-30 mM, respectively. For $Cp_2^*Co^{+/0}$, these concentrations were 10-30 mM and 3-10 mM, respectively. Data analysis was as described in ref. 15a,b. Rate constants reliable chiefly to within 10% for $HMFc^{+/0}$ and $TMAFc^{2+/+}$, and to within 10-25% for $Cp_2^*Co^{+/0}$.

^e Carboxymethyl(cobaltocenium-cobaltocene) [$(CpCO_2Me)_2Co^{+/0}$].

^f Hydroxymethyl(ferrocenium-ferrocene) [$(Cp \cdot CpCH_2OH)Fe^{+/0}$].

^g Trimethylaminomethyl(ferrocenium-ferrocene) [$(Cp \cdot CpCH_2NMe_3)Fe^{2+/+}$].

TABLE II. Estimated Barrier-Crossing Frequencies, $\kappa_{el}\nu_n$, for Metallocene Couples in Deuterated Water and Selected Organic Solvents at 25°C

Solvent	ΔG^* ^a kcal mol ⁻¹	τ_L^{-1} ^b s ⁻¹	$\kappa_{el}\nu_n$, s ⁻¹ ^c		
			Cp ₂ Co ^{+/0}	HMFC ^{+/0}	TMAFc ^{2+/+}
Water	5.2	1.9 x 10 ¹² ^d	3.5 x 10 ¹²	3.5 x 10 ¹¹	2 x 10 ¹¹
Acetonitrile	5.35	4 x 10 ¹² ^e	2.5 x 10 ¹²	2 x 10 ¹¹	7 x 10 ¹⁰
Acetone	5.4	3.5 x 10 ¹² ^f	2 x 10 ¹²	2.5 x 10 ¹¹	1.5 x 10 ¹¹
Nitromethane	5.3	4.5 x 10 ¹² ^g	3 x 10 ¹²	4 x 10 ¹¹	9 x 10 ¹⁰
Methanol	5.2	(1.35 x 10 ¹¹) ^h	1.5 x 10 ¹²	4.5 x 10 ¹¹	
Benzonitrile	4.55	1.7 x 10 ¹¹ ⁱ	3 x 10 ¹¹	1.5 x 10 ¹¹	9 x 10 ¹⁰
Nitrobenzene	4.55	1.9 x 10 ¹¹ ^j	1.5 x 10 ¹¹	1.2 x 10 ¹¹	9 x 10 ¹⁰
Propylene Carbonate	5.25	(4 x 10 ¹¹) ^k	1.5 x 10 ¹²		6 x 10 ¹¹

^a Free-energy barrier for self-exchange reactions, estimated from corresponding λ_{max} values for BFA⁺ listed in Table I by using Eq. (2) and noting that $\lambda_{max} = E_{op}^{-1}$.

^b Inverse of longitudinal relaxation time, extracted from dielectric loss measurements of the major Debye relaxation time, τ_D , together with corresponding "infinite" and zero-frequency dielectric constants, ϵ_∞ and ϵ_0 , respectively, using $\tau_L = \tau_D (\epsilon_\infty/\epsilon_0)$.^{14,15} Values in parentheses denote solvents for which additional, higher-frequency, relaxation components are apparent in the dielectric loss spectra. Sources of τ_D and ϵ_∞ as indicated; ϵ_0 values either from same source or from ref. 33 (see also refs. 14c, 15a).

^c Barrier-crossing frequency, obtained from values of k_{ex} (Table I) and ΔG^* listed alongside, assuming that $K_p = 0.25 \text{ M}^{-1}$. For Cp₂Co^{+/0}, ΔG^* values used are 0.5 kcal mol⁻¹ smaller than those listed to allow for effect of orbital overlap (see text and refs. 14c, 15a, 15c).

^d Ref. 34. ^e Estimated from average τ_D , obtained from data in ref. 35.

^f Ref. 36. ^g Ref. 37. ^h Ref. 38. ⁱ Ref. 39. ^j Ref. 39a. ^k Ref. 40.