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Self-Exchange Reaction Kinetics of Metallocenes Revisited: Insights from the Decamethylferricenium–Decamethylferrocene Reaction at Variable Pressure

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Rate constants k_{ex} and volumes of activation $\Delta V_{ex}^{\ddagger}$ have been obtained using ^{1}H NMR for the self-exchange reaction of the $[(\eta^5\text{-}C_5(CH_3)_5)_2Fe]^+$ hexafluorophosphate and tetrafluoroborate with $[(\eta^5\text{-}C_5(CH_3)_5)_2Fe]$ in acetone-*d*$_6$ ($\Delta V_{ex}^{\ddagger} = -8.6 \pm 0.3$ cm^3 mol^{-1}), dichloromethane-*d*$_2$, and (semiquantitatively) in acetonitrile-*d*$_3$. Under the experimental conditions, ion pairing was significant only in CD_2Cl_2, but even that produced only a minor reduction in k_{ex} and so had a negligible effect on $\Delta V_{ex}^{\ddagger}$ ($= -6.4 \pm 0.2$ cm^3 mol^{-1} with PF_6^-). In all cases, $\Delta V_{ex}^{\ddagger}$ is negative and consistent with a simple two-sphere activation model, rather than with that of Weaver et al. (Nielson, R. M.; McManis, G. E.; Safford, L. K.; Weaver, M. J. *J. Phys. Chem.* **1989**, *93*, 2152) in which the barrier crossing rate is limited by solvent dynamics. Similarly, the ∼5-fold increase in k_{ex} on going from $[(\eta^5\text{-}C_5H_5)_2Fe]^{+/0}$ to $[(\eta^5\text{-}C_5(CH_3)_5)_2Fe]^{+/0}$ in acetone can be explained with the two-sphere model on the basis of the effects of reactant size on the solvent reorganization energy, without reference to solvent dynamics.

The kinetics and mechanism of electron transfer in metallocene couples in nonaqueous solution[1−7] continue to attract attention.[8] We report here an investigation of the effect of pressure on the kinetics of the decamethylferricenium/decamethylferrocene self-exchange reaction in three organic solvents, carried out in support of a high-pressure study of the corresponding electrode reaction in 10 solvents[9] but with the additional purpose of testing the applicability of a successful treatment of pressure effects on aqueous electron transfer reactions[10] to nonaqueous systems. Whereas recent theoretical discourse[6−8] has focused on the electronic coupling between between the donor and acceptor centers, pressure dependences of the self-exchange rate constants k_{ex} provide special insights into solvent effects on electron transfer rates.[10] The solvent can influence k_{ex} through its contribution to the activation barrier height[11] but also possibly through solvent dynamical control of the barrier-crossing frequency (solvent "friction").

The effect of pressure P on k_{ex} for adiabatic outer-sphere self-exchange electron transfer reactions of metal complexes in aqueous solution can be accounted for quantitatively in terms of a simple extension[10] of Marcus−Hush theory,[11] and indeed, significant deviations of measured volumes of activation $\Delta V_{ex}^{\ddagger}$ from the predicted values can serve as evidence for mechanistic alternatives such as inner-sphere pathways[10] or catalysis by counterions.[12]

$$\Delta V_{ex}^{\ddagger} = -RT(\partial \ln k_{ex}/\partial P)_T \qquad (1)$$

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The success of these calculations is due in part to the smallness of the contribution $\Delta V_{IR}^{\ddagger}$ for internal reorganization of the reactants[13] (in the absence of major structural effects due to spin-multiplicity changes[10]) and the fortuitous near-cancellation at practical values of the ionic strength I of the contributions of Coulombic work of precursor complex formation ($\Delta V_{COUL}^{\ddagger}$) and Debye−Hückel-type ion activity terms ($\Delta V_{DH}^{\ddagger}$). In water, then, $\Delta V_{ex}^{\ddagger}$ is governed largely by the negative solvent reorganization term $\Delta V_{SR}^{\ddagger}$, with a very small positive contribution from the pressure dependence of the non-Coulombic part of the precursor complex formation constant ($\Delta V_{PREC}^{\ddagger}$):

$$\Delta V_{ex}^{\ddagger} = \Delta V_{IR}^{\ddagger} + \Delta V_{SR}^{\ddagger} + \Delta V_{DH}^{\ddagger} + \Delta V_{COUL}^{\ddagger} + \Delta V_{PREC}^{\ddagger} \tag{2}$$

In contrast, for ion−ion electron transfer reactions in nonaqueous solvents with relatively low dielectric constants ϵ, $\Delta V_{DH}^{\ddagger}$ and $\Delta V_{COUL}^{\ddagger}$ can become numerically very large, so that even if they roughly cancel the theoretical calculation of $\Delta V_{ex}^{\ddagger}$ becomes highly susceptible to imperfections in the model.[10,14] Furthermore, the calculations are likely to be invalidated by extensive ion-pair formation between the reactants and the counterions, the kinetic consequences of which are not readily predictable.[15] Applications of the theory to nonaqueous systems are therefore most likely to succeed when one reactant is electrically neutral, so that $\Delta V_{DH}^{\ddagger} = \Delta V_{COUL}^{\ddagger} = 0$ and only the ionic reactant is subject to ion pairing which, for singly charged ions, will be minimal. With these considerations in mind, the pressure dependences of the kinetics of the $[Ru(hfac)_3]^{0/-}$ [16,17] (hfac$^-$ = $CF_3COCHCOCF_3^-$) and $Fc^{+/0}$ [3] (Fc = ferrocene, $[(\eta^5\text{-}C_5H_5)_2Fe]$) self-exchange reactions have previously been examined in organic solvents.

In this same vein, as part of a wider study[9,18−24] that attempts to relate the kinetic parameters of electrode reactions (particularly the volumes of activation $\Delta V_{el}^{\ddagger}$) to those of the corresponding self-exchange reactions, we have measured $\Delta V_{ex}^{\ddagger}$ for the obligate-outer-sphere self-exchange reaction of decamethylferrocene (DmFc, $[(\eta^5\text{-}C_5(CH_3)_5)_2Fe]$) with its cation in three nonaqueous solvents. Although the familiar $Fc^{+/0}$ couple, traditionally a standard for nonaqueous electrochemistry, might seem a more obvious choice, the Fc^+ cation is subject to side reactions and to possible redox reactions with impurities leaking from the pressurizing fluid over the time scale (several hours) of a cycle of measurements at high pressures, and indeed, we were unable to obtain reliable values of $\Delta V_{el}^{\ddagger}$ for the $Fc^{+/0}$ electrode reaction in acetonitrile.[24] Furthermore, for the $Fc^{+/0}$ self-exchange reaction in acetonitrile, Hunt et al.[3] suspected a systematic error in the k_{ex} values of the pioneering study by Wahl et al.,[1] in which context Weaver et al.[4,5] noted difficulties in the extraction of reliable k_{ex} values from ^{1}H NMR line width data in the "fast exchange" regime. Nevertheless, Hunt and co-workers[3] were able to obtain $\Delta V_{ex}^{\ddagger} = -7.0 \pm 2.0$ cm^3 mol^{-1} for $Fc^{+/0}$ in CD_3CN by working at 0 °C with careful exclusion of moisture and oxygen but remarked that a more negative value would be predicted by the model[10] based on Marcus−Hush theory. Moreover, Weaver et al.[4−6] have argued that k_{ex} for $Fc^{+/0}$ in organic solvents is limited by both nonadiabaticity and solvent dynamical effects. Thus, the $Fc^{+/0}$ system is fraught with both experimental and interpretational difficulties.

Lay et al.,[25] however, have pointed out that the $DmFc^{+/0}$ couple is much to be preferred to $Fc^{+/0}$ as a redox-stable electrochemical standard, particularly in connection with studies involving solvent effects on electron transfer, as is the case in our work. Indeed, the self-exchange kinetics have been previously mapped out at variable temperature by ^{1}H NMR in CD_3CN, $(CD_3)_2CO$, CD_2Cl_2, and C_6H_5CN by Wahl et al.[2] and Weaver et al.,[5] and we have found the electrode kinetics to be reproducible over lengthy pressure cycles in 10 solvents.[9] The high-pressure study of the $DmFc^{+/0}$ self-exchange reaction reported here gave excellent reproducibility but was limited to solutions in $(CD_3)_2CO$ and CD_2Cl_2, with only semiquantitative results in CD_3CN, by the low solubility of DmFc in most polar solvents, because the sensitivity of static high-pressure NMR probes is relatively low and is subject to a ^{1}H background from impurities in the pressurizing fluid.

A special feature of high-pressure kinetic studies is that reaction rate control by organic solvent dynamics is associated with a strongly positive contribution to $\Delta V_{ex}^{\ddagger}$,[21,23,24] whereas the conventional treatment of outer-sphere electron transfer kinetics based on transition-state theory predicts that $\Delta V_{ex}^{\ddagger}$ should be moderately negative.[10,14] The "signature" of solvent dynamical control is an approximate inverse dependence of rate constant on solvent viscosity η, which, for organic solvents (unlike water at near-ambient temperatures), rises roughly exponentially with increasing pressure.[21] Thus, any incursion of solvent dynamics in metallocene self-exchange kinetics in organic solvents, as proposed by Weaver et al.,[4−6] would be revealed experimentally by observation of a substantially positive value of $\Delta V_{ex}^{\ddagger}$.

Experimental Section

Materials. Tetrabutylammonium phosphate (Fluka electrochemical grade, >99%), acetone-d_6 (Deutero GmbH, Kastellaun, 99.8%),

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and dichloromethane-d_2 (Euriso-top, Saclay, HDO + D_2O < 0.05%) were used as received; acetonitrile-d_3 (Euriso-top, 99.6% D, H_2O < 0.01%) was stored over dehydrated 3A molecular sieves. Decamethylferrocene (Aldrich, 97%) was purified by vacuum sublimation twice at 140 °C, followed by recrystallization from acetone; ^1H NMR at 400 MHz in acetone-d_6, dichloromethane-d_2, and acetonitrile-d_3 showed only a single solute peak at ~650 Hz. [DmFc]PF_6 and [DmFc]BF_4 were made by the method of Hendrickson et al.[26] and checked for purity by CHN microanalysis; they showed only a single, broad ^1H NMR resonance at −14750 to −14790 Hz.

High-Pressure NMR Measurements. The solutions were prepared by weight, and the concentrations converted to the molar scale with estimated solution densities. Each sample was sealed in a cut-down 5 mm o.d. commercial NMR tube with a floating Kel-F piston with two O-rings of EPDM ethylene−propylene polymer for use with CD_3CN and CD_2Cl_2, or NBR acrylonitrile polymer for use with $(CD_3)_2CO$, and placed in a home-built high-pressure static NMR probehead[27] resonating at 400.13 MHz for ^1H. Sample temperature was monitored through a Pt-100 resistor and was held constant (±0.5 °C) with circulating fluid. The chemical shifts (calibrated against residual proton resonances in the solvents) and line widths of the single ^1H resonances of DmFc, $DmFc^+$, and their mixtures in solution were measured at selected pressures in the range 1−150 MPa with a Bruker AVANCE DRX-400 spectrometer equipped with a wide-bore magnet. Field homogeneities better than 6×10^{-9} were achieved by shimming on the ^1H FID with the BOSS I shim system. The ^1H 90° pulse width was 16 μs, and the sweep width was varied between 6000 and 20000 Hz. A relaxation delay of 2 s was applied in a single 30° pulse experiment, with accumulation of up to 256 scans. Line widths of some very broad resonances (>1500 Hz) of the chemically exchanging DmFc/$DmFc^+$ mixtures in the shift region −8 to +5 ppm could not be determined precisely because of a broad background signal from the probehead or pressurizing fluid, but in such cases, acceptable accuracy was achieved by digitally subtracting the background signal obtained from a pure solvent sample.

Results

Measurements were made of the ^1H resonance chemical shifts ν_D, ν_P, and ν_{DP} and line widths at half-maximum W_D, W_P, and W_{DP} of solutions containing only diamagnetic DmFc, paramagnetic $DmFc^+$ salts, and the chemically exchanging mixtures $DmFc^{+/0}$, respectively, over an ascending and then descending range of pressures. The mole fractions f_D of DmFc and f_P of $DmFc^+$ were calculated from the solute weights and also from ν_{DP} relative to ν_D and ν_P; agreement was excellent except in cases where the weights were very small, and then, the latter method was taken as definitive. In general, the chemical shifts and hence the overall shifts $\delta\nu$ (= $\nu_D - \nu_P$) were almost independent of pressure, but increasing pressure caused W_P to increase (cf. Fc^+ in CD_3CN[3]) and W_{DP} to decrease substantially, while W_D was sufficiently small (7.5−10 Hz) that the barely discernible decrease was often negligible. Full details are given in the Supporting Information. Second-order rate constants k_{ex} were calculated from the formula[1]

$$k_{ex} = 4\pi f_D f_P (\delta\nu)^2/(W_{DP} - f_D W_D - f_P W_P)c \qquad (3)$$

where c is the total metallocene molar concentration; the W_P and W_D values used were smoothed on the basis of an empirical linear dependence on pressure. For solutions in acetone-d_6 and dichloromethane-d_2, the pressure dependences of ln k_{ex} were accurately linear within the experimental error (eq 4 and Figure 1); i.e., $\Delta V_{ex}^{\ddagger}$ was effectively constant over the pressure range 0−150 MPa. The results are summarized in Table 1.

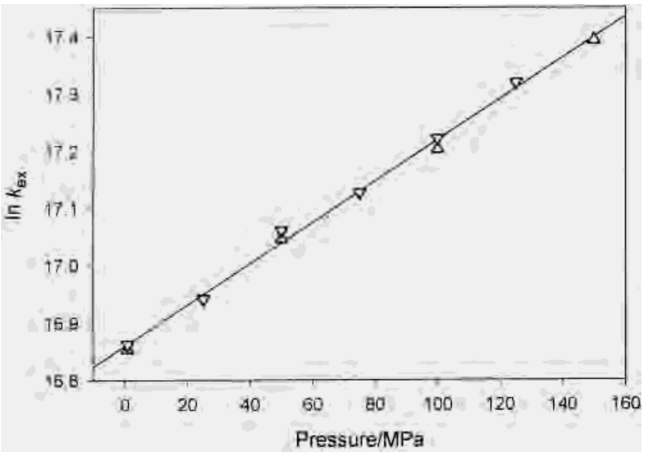

Figure 1. Pressure dependence of ln k_{ex} for $DmFc^{+/0}$ in acetone-d_6 at 25.0 °C; anion is BF_4^-, no added electrolyte. Concentrations as in Table 1. Measurements taken with upward pressure steps (△) and downward pressure steps (▽) are shown.

Table 1. Volumes of Activation for the Self-Exchange Reaction of Decamethylferrocene and Decamethylferricenium Ion in Different Solvents[a]

solvent	anion[b]	[DmFc]/ mmol L^{-1}	[$DmFc^+$]/ mmol L^{-1}	$k_{ex}^0/10^7$ L mol^{-1} s^{-1}	$\Delta V_{ex}^{\ddagger}$/cm^3 mol^{-1}
$(CD_3)_2CO$	PF_6^-	14.5	9.29	2.24 ± 0.02	−8.5 ± 0.3
	PF_6^- [c]	11.5	5.63	2.24 ± 0.02	−8.7 ± 0.3
	BF_4^-	14.6	6.44	2.12 ± 0.01	−8.9 ± 0.2
CD_2Cl_2	PF_6^-	25.4	11.4	9.58 ± 0.05	−6.5 ± 0.2
	PF_6^- [d]	29.1	12.5	8.24 ± 0.08	−6.3 ± 0.3
	BF_4^-	27.5	9.66	8.87 ± 0.08	−7.2 ± 0.3
CD_3CN	PF_6^-	3.26	0.583	(7 ± 2)[e]	(−5 ± 2)[e]

[a] At 25.0 °C; except as noted, error limits are standard deviations of fit to eq 4. [b] Anion concentration = [$DmFc^+$] except as noted. [c] Using newly constructed high-pressure probehead. [d] In presence of 0.099 mol L^{-1} [$(n\text{-}C_4H_9)_4N$]PF_6. [e] Provisional result based on 75−150 MPa data only; error limits are subjective.

$$\ln k_{ex} = \ln k_{ex}^0 - P\Delta V_{ex}^{\ddagger}/RT \qquad (4)$$

For acetone-d_6 and dichloromethane-d_2 as solvents, k_{ex} showed good reproducibility and may be considered accurate to within ±5%. For acetone-d_6, k_{ex} showed no significant dependence on the anion and was in excellent agreement with Wahl's value,[2] which was also adopted by Weaver et al.[5] For CD_2Cl_2, however, anion effects are evident (Table 1), and Wahl et al.[2] gave a value lower than any of ours (k_{ex} = 4.4×10^7 L mol^{-1} s^{-1} at 25 °C) for $DmFc^{+/0}$/PF_6^-, albeit at higher c. Weaver et al.[5] expressed concern that some of

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the k_{ex} values of Wahl et al.[1,2] could be too low and, perhaps significantly, chose to disregard this particular result. We found that addition of a swamping concentration of PF_6^- (0.1 mol L^{-1}) to force complete ion pairing with $DmFc^+$ produced only a small reduction in k_{ex} (Table 1), so the discrepancy for CD_2Cl_2 solutions cannot be ascribed entirely to anion effects. The consistency of the CD_2Cl_2 data of Table 1 lends credibility to the present results.

It is important to note that ln k_{ex} values on the upward leg of each pressure cycle agreed within the experimental uncertainty with those on the subsequent downward leg at a particular pressure, i.e., that there was no drift in k_{ex} with time, as this could have produced a false slope of the ln k_{ex} versus P plot and hence an erroneous value of $\Delta V_{ex}^‡$.

The solubility of DmFc in methanol, dimethyl sulfoxide, and other polar organic solvents was too low for high-pressure NMR, and that in CD_3CN (1.32 mg per g solvent at 22 °C) was barely sufficient. In practice, W_{DP} in acetonitrile was too broad to measure except with a limited choice of f_P (which unfortunately placed ν_{DP} in a region with substantial background from the high-pressure probe) and an elevated pressure range 75−150 MPa where k_{ex} was high enough to give tractable line widths (cf. eq 3). Thus, the provisional atmospheric pressure k_{ex} value for CD_3CN in Table 1 is the result of a long, uncertain extrapolation from high pressures, and as such, its disagreement with Wahl's value (3.8×10^7 L mol^{-1} s^{-1})[2] is not serious; the extent of ion pairing was <1%, according to calculations based on Fuoss theory,[28] and would not affect this comparison. The essential point is that $\Delta V_{ex}^‡$ for CD_3CN, though only approximate, is clearly negative and is at least semiquantitatively consistent with the values for the other two solvents.

Discussion

The atmospheric pressure value of k_{ex} for the $DmFc^{+/0}$ exchange in acetone-d_6 at 25 °C shows no significant dependence on the nature or concentration of the anion under the conditions of our experiments and confirms the result of Wahl et al.[2] at roughly comparable concentrations. A Fuoss-type calculation[28] (see Supporting Information) indicated that only about 2.5% of the $DmFc^+$ would be paired with PF_6^- at 0.1 MPa, and 1.7% at 150 MPa. Thus, the $DmFc^+$ exchange is 4−5 times faster than that of $Fc^{+/0}$ in acetone at 25 °C,[2] even allowing for a possible 30% error in k_{ex} for the latter as suggested by Hunt et al.[3] Weaver et al.[5] interpreted differences in k_{ex} for various metallocene couples in several solvents to barrier-crossing frequency control by donor−acceptor coupling and solvent dynamics, particularly in the case of $Fc^{+/0}$, but for the DmFc−Fc comparison at least the explanation may be simpler. (The cobalticenium/cobaltocene couple that Weaver et al.[4,5] attempted to include under the same rubric is a mechanistically different "hole transfer" case[7] which involves significant internal reorganization.[8]) Theoretically,[11] k_{ex} is given in L mol^{-1} s^{-1} by the SI expression

$$k_{ex} = 4000\pi N\sigma^2\kappa_e\nu_n\delta\sigma \exp(-\Delta G_{ex}^‡/RT) \qquad (5)$$

where σ is the closest separation of the metal centers (which may be approximated to the sum of the effective radii r_1 and r_2 of the reactants), κ_e is the electronic transmission coefficient (=1 for a fully adiabatic reaction, otherwise <1), ν_n is the nuclear frequency factor, $\delta\sigma$ is the range of σ over which electron transfer rate is substantial, and $\Delta G_{ex}^‡$ is the free energy of activation. It is difficult, however, to evaluate ν_n and $\delta\sigma$ precisely,[4] so we will use eq 5 to predict relative rather than absolute values of k_{ex} (indeed, $\Delta V_{ex}^‡$ is derived from relative values of k_{ex}). The contributions of internal reorganization to $\Delta G_{ex}^‡$ are small and about the same (~0.6 kJ mol^{-1})[6] for $DmFc^{+/0}$ and $Fc^{+/0}$, and the Coulombic and Debye−Hückel contributions are effectively nil,[29] so the difference in $\Delta G_{ex}^‡$ for the two couples is the difference in the solvent reorganization energies $\Delta G_{SR}^‡$:

$$\Delta G_{SR}^‡ = (Ne^2/16\pi\epsilon_0)[(1/2r_1) + (1/2r_2) - (1/\sigma)](\epsilon_{op}^{-1} - \epsilon^{-1}) \qquad (6)$$

where the optical dielectric constant ϵ_{op} may be approximated to the square of the refractive index of the solvent.[30] Taking σ for $DmFc^{+/0}$ to be about 960 pm (the close-contact Fe−Fe distance in solid DmFc[31]) and for $Fc^{+/0}$ to be about 800 pm,[3] and putting $r_1 \approx r_2 = \sigma/2$ [31−34] while assuming $\delta\sigma$ to be proportional to σ, we calculate k_{ex} for $DmFc^{+/0}$ to be about $7k_{ex}$ for $Fc^{+/0}$ in acetone (cf. $4-5k_{ex}$, observed), if κ_e and ν_n are the same for the two couples. Since DmFc is bulkier than Fc, close-contact electronic coupling in $DmFc^{+/0}$ may be expected to be weaker than in $Fc^{+/0}$, and so, any contribution through κ_{el} to the rate difference should be in the opposite direction. Thus, reactant size differences can account for this kinetic difference, through solvent reorganization energetics. Weaver et al.[4−6] did not consider this possibility.

A similar calculation predicts that k_{ex} for the $DmFc^{+/0}$ exchange in CD_2Cl_2 should be 5.4 times faster than in $(CD_3)_2CO$, in the absence of complications such as anion−cation pairing. In fact, the kinetic effect of ion pairing is quite small in this case; Fuoss-type calculations[28] indicate 48% $DmFc^+$/

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(29) A reviewer has pointed out that quadrupolar interactions in the $Fc^{+/0}$ and the $DmFc^{+/0}$ couples may become significant in the encounter pair involved in electron transfer, leading to enhanced precursor complex formation constants and thus somewhat higher k_{ex}, more so for the former couple. This would result in a smaller difference in k_{ex} between the two couples than is predicted from the simple two-sphere model, as is in fact observed. Quadrupolar effects may also lead to preferred orientations of the reactants within the transition states and as such may affect the kinetic parameters of the self-exchange process. However, this is beyond the scope of the two-sphere model presented here. Any quadrupolar effects on $\Delta V_{ex}^‡$ through $\Delta V_{COUL}^‡$ and $\Delta V_{PREC}^‡$ (which are opposite in sign) are expected to be at least an order of magnitude smaller than for ion−ion interactions and may, therefore, be neglected.

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PF_6^- ion pairs with [anion] = [$DmFc^+$] ≈ 0.01 mol L^{-1} at 0.1 MPa, falling to 34% at 150 MPa, yet addition of 0.1 mol L^{-1} [Bu_4N]PF_6 to force virtually complete ion pairing of $DmFc^+$ caused only a 14% diminution in k_{ex} (Table 1). Presumably, BF_4^- will pair with $DmFc^+$ more strongly than does the larger PF_6^- ion, and indeed, k_{ex} for $DmFc^{+/0}/BF_4^-$ without added electrolyte falls between the values for $DmFc^{+/0}/PF_6^-$ with and without [Bu_4N]PF_6 (Table 1). These results are in accordance with Wherland's general observation[15] that ion pairing of reactants tends to reduce electron transfer rates in nonaqueous systems; the effect is small in this case because, if one reactant is uncharged, it matters little whether the effective charge on its reaction partner is reduced by ion-pairing or not, so long as the pairing counterion has no specific role to play (contrast cation catalysis of anion−anion exchange in water[12]). From the data with PF_6^-, one can estimate $k_{ex} \approx 1.1 \times 10^8$ L mol^{-1} s^{-1} for $DmFc^{+/0}$ couple in CD_2Cl_2 at 25 °C with no ion pairing, i.e., 4.9 times larger than in $(CD_3)_2CO$ and in good agreement with the foregoing prediction for adiabatic electron transfer in the absence of solvent friction.

Theoretical values of $\Delta V_{ex}^{\ddagger}$ at selected pressures were obtained by solving eqs 1, 5, and 6 simultaneously over small (1 MPa) increments at each pressure, allowing σ and $\delta\sigma$ to vary with pressure with linear compressibility $\beta/3$, where β is the isothermal volume compressibility of the solvent (see Supporting Information for computational procedure). In practice, whether σ and $\delta\sigma$ are taken as pressure-dependent or not is inconsequential for an adiabatic reaction, as the effects on $\Delta V_{SR}^{\ddagger}$ and $\Delta V_{PREC}^{\ddagger}$ (eq 5) are small, roughly equal in magnitude, and opposite in sign.[30] For nonadiabatic electron transfer, although the donor−acceptor coupling matrix element H_{if} falls off essentially exponentially with increasing σ beyond the adiabatic limit, the interaction energy (which includes the repulsive potential) for the $Fc^{+/0}$ couple and presumably also for $DmFc^{+/0}$ varies only slowly with σ in the near-approach region;[8] consequently, contrary to earlier expectations that focused on H_{if},[30] nonadiabatic contributions to the apparent $\Delta V_{ex}^{\ddagger}$ can be small, in this case, negligible (≤ 0.1 cm^3 mol^{-1}). Thus, in the absence of solvent dynamical rate control, $\Delta V_{SR}^{\ddagger}$ must be by far the dominant component of $\Delta V_{ex}^{\ddagger}$ for the couples considered here.

Because the pressure dependences of the key variables ϵ and ϵ_{op} in eq 6 are closely related to β, which, for organic solvents, is itself quite strongly pressure dependent,[10,14,30] the predicted $\Delta V_{ex}^{\ddagger}$ values at 25 °C for $DmFc^{+/0}$ in acetone and dichloromethane, respectively, vary from −16.8 and −7.9 cm^3 mol^{-1} at atmospheric pressure to −9.5 and −5.9 cm^3 mol^{-1} at 75 MPa, and to −6.7 and −4.6 cm^3 mol^{-1} at 150 MPa. In fact, no significant curvature of the experimental ln k_{ex} versus P plots is discernible for $DmFc^{+/0}$ in these solvents (see, e.g., Figure 1), but the measured $\Delta V_{ex}^{\ddagger}$ values in Table 1 correspond well to the average or midrange (75 MPa) theoretical values. In the case of dichloromethane as solvent, the partial breaking-up of ion pairs by increasing pressure should lead to a somewhat more negative apparent $\Delta V_{ex}^{\ddagger}$ when no swamping concentration of added anion is present, given that the ion pair is less reactive than the free ion, but because the free $DmFc^+$ ion reacts only some 31% faster than its ion pair with PF_6^-, this effect does not emerge above the experimental error limits in Table 1. Thus, it is acceptable to compare experimental $\Delta V_{ex}^{\ddagger}$ values for $DmFc^{+/0}$ in CD_2Cl_2 with the theoretical value ignoring ion pairing, and indeed, the three experimental values for CD_2Cl_2 are effectively the same, but about 2 cm^3 mol^{-1} less negative than for acetone-d_6 solutions, as theory[10,30] predicts.

In summary, the value of k_{ex} for $DmFc^{+/0}$ relative to that for $Fc^{+/0}$ in acetone-d_6 is consistent with a simple two-sphere Marcus−Hush-type model without significant influence of solvent friction; the difference between these rate constants can be attributed to the fact that the effective radii of the DmFc species are about 20% larger than those of the Fc couple. Furthermore, the consistency of $\Delta V_{ex}^{\ddagger}$ for $DmFc^{+/0}$ in acetone-d_6 and in CD_2Cl_2 with the theoretical predictions for the simple model is strong evidence against rate control by solvent friction, which is associated with strongly positive contributions to $\Delta V^{\ddagger}$ that overwhelm other components.[9,10,21−24,30] Such a positive contribution to $\Delta V_{ex}^{\ddagger}$ might conceivably be reduced somewhat[23,34] by a negative one due to nonadiabaticity,[10,28,30] but as already noted, nonadiabaticity should have a negligible effect on $\Delta V_{ex}^{\ddagger}$ for the $Fc^{+/0}$ and presumably also the $DmFc^{+/0}$ exchanges. In the limiting case of extreme nonadiabaticity, according to the Sumi−Marcus model,[35] solvent frictional effects would disappear anyway.

The same considerations apply to $\Delta V_{ex}^{\ddagger}$ for the $Fc^{+/0}$ couple in acetonitrile. Hunt et al.[3] considered the measured $\Delta V_{ex}^{\ddagger}$ (−7 ± 2 cm^3 mol^{-1} at 0°C) to be less negative than that predicted from the simple theory, but it seems that their prediction was for 0.1 MPa (−17.5 cm^3 mol^{-1}, by our calculation), whereas at the midrange pressure of 100 MPa the predicted $\Delta V_{ex}^{\ddagger}$ is −9.6 cm^3 mol^{-1}, which is a fair match given the experimental difficulties with the $Fc^{+/0}$ couple and pressure dependence of the theoretical value. We were unable to obtain a reliable experimental $\Delta V_{ex}^{\ddagger}$ value for the $DmFc^{+/0}$ exchange in acetonitrile because excessive NMR line widths at low pressures limited useful measurements to the pressure range 75−150 MPa, over which the average predicted $\Delta V_{ex}^{\ddagger}$ value is about −7.5 cm^3 mol^{-1} at 100 MPa; the approximate experimental value given in Table 1 is in fair agreement with this, in view of the large experimental uncertainty, and at least is unmistakably negative, again militating against any major influence of solvent dynamics.

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Supporting Information Available: Tables S1−S6 containing NMR measurements and rate constants as functions of pressure; outline of computational procedure. This material is available free of charge via the Internet at http://pubs.acs.org.

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