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The Effects of Donor-Acceptor Electronic Interactions on the Rates of Gas-Phase Metallocene Electron-Exchange Reactions

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ABSTRACT

Rate constants for electron self exchange, k_{ex}, of five cobaltocenium-cobaltocene and ferrocenium-ferrocene couples in the gas phase have been measured by means of Fourier transform ion cyclotron resonance mass spectrometry in order to explore the possible effects of donor-acceptor electronic coupling on gas-phase redox reactivity. The systems studied: $\mathrm{Cp_2Co^{+/o}}$, $\mathrm{Cp_2Fe^{+/o}}$ (Cp=cyclopentadienyl), the decamethyl derivative $\mathrm{Cp'_2Fe^{+/o}}$, carboxymethyl(cobaltocenium-cobaltocene) ($\mathrm{Cp^*_2Co^{+/o}}$) and hydroxymethyl (ferrocenium-ferrocene) ($\mathrm{HMFc^{+/o}}$), were selected in view of the substantial variations in electronic coupling inferred on the basis of their solvent-dependent reactivities (ref. 3) and on theoretical grounds (ref. 6). The sequence of k_{ex} values determined in the gas phase, $\mathrm{Cp^*_2Co^{+/o}} \approx \mathrm{Cp_2Co^{+/o}} > \mathrm{Cp'_2Fe^{+/o}} > \mathrm{HMFc^{+/o}} > \mathrm{Cp_2Fe^{+/o}}$, is roughly similar to that observed in solution, although the magnitude (up to 5 fold) of the k_{ex} variations is smaller in the former case. The likely origins of these differences in gas-phase reactivity are discussed in light of the known variations in the electronic coupling matrix element H_{12}, inner-shell reorganization energy ΔE^* and gas-phase ion-molecule interaction energy ΔE_w extracted from solution-phase rates, structural data, and theoretical calculations. It is concluded that the observed variations in gas-phase k_{ex} values, especially for $\mathrm{Cp_2Fe^{+/o}}$ versus $\mathrm{Cp_2Co^{+/o}}$, arise predominantly from the presence of weaker donor-acceptor orbital overlap for the ferrocene couples, yielding inefficient electron tunneling (i.e. reaction nonadiabaticity) for a substantial fraction of the gas-phase ion-molecule encounters. The anticipated differences as well as similarities of such nonadiabatic effects for gas-phase and solution electron-transfer processes are briefly outlined.

A central issue in electron-transfer kinetics concerns the manner and extent to which the observed rates are influenced by the nature, and the spatial proximity, of the donor and acceptor redox orbitals. The "orbital overlap", as described fundamentally by the electronic matrix coupling element, H_{12}, can affect electron-transfer rates both by altering the barrier height and the degree of electronic reaction adiabaticity.[1,2] (The latter refers to the fractional probability, κ_{el}, that electron transfer will occur once the nuclear transition state has been formed). The magnitude of H_{12} should be sufficiently sensitive to the molecular electronic structure as well as to the reaction geometry such that a wide range of experimental behavior is expected, spanning strongly nonadiabatic ($\kappa_{el} << 1$) to adiabatic processes ($\kappa_{el} \approx 1$).[1,2]

At least for thermal electron-transfer processes, however, the experimental diagnosis of electronic coupling effects has remained largely elusive. An interesting recent exception is provided by a study of the solvent-dependent rate constants, k_{ex}, for metallocenium-metallocene self-exchange reactions.[3a] The solvents were chosen so to yield substantial variations in the nuclear frequency factor, ν_n, as engendered by alterations in the solvent longitudinal relaxation time, τ_L ("solvent friction"). In a given solvent, up to ca 100 fold differences in k_{ex} are observed between the six metallocene couples studied, which were traced primarily to variations in H_{12} and hence in κ_{el}.[3,4] An illuminating spectrum of rate-solvent friction dependencies was observed.[3] For the most facile cobaltocene couples, a strong dependence of k_{ex} (corrected for the solvent-dependent barrier) on τ_L^{-1} was obtained, indicative of near-adiabatic behavior. In contrast, k_{ex} is largely independent of τ_L^{-1} for the least facile ferrocene couples, signaling the presence of largely nonadiabatic pathways.[3,5] These varying rate-solvent friction dependencies enable approximate estimates of H_{12} to be extracted.[3a]

Interestingly, these H_{12} values (between ca 0.1 and 1 kcal mol^{-1}) are roughly in accordance with recent theoretical calculations.[6]

In view of this instructive kinetic behavior in solution, and the resulting detailed information on reactant electronic coupling, it is of interest to ascertain if related effects are present for the corresponding reactions in the absence of solvent, i.e. in the gas phase. Richardson and coworkers have recently evaluated electron self-exchange rate constants, k_{ex}, for a number of metallocenium-metallocene couples in the gas phase by means of Fourier transform ion cyclotron resonance mass spectrometry (FTICR).[7] While some of the k_{ex} values approximate the limiting values prescribed by collision theory, significant rate variations are nonetheless obtained. Particularly interesting in the present context is their report that k_{ex} for cobaltocenium-cobaltocene ($Cp_2Co^{+/o}$) is ca 3 fold faster than for ferrocenium-ferrocene ($Cp_2Fe^{+/o}$) under these conditions.[7a] On the basis of the theoretical and solution-phase experimental results noted above,[3,6] this finding is suggestive of a higher degree of donor-acceptor electronic coupling for the $Cp_2Co^{+/o}$ system.

Reported here are gas-phase rate constants evaluated by the FTICR technique for five metallocenium-metallocene self-exchange reactions. In addition to a careful reevaluation of k_{ex} for $Cp_2Co^{+/o}$ relative to $Cp_2Fe^{+/o}$, values are given for the decamethyl derivative $Cp'_2Fe^{+/o}$ (Cp′ = pentamethylcyclopentadienyl), and for carboxymethyl(cobaltocenium-cobaltocene), and hydroxymethyl(ferrocenium-ferrocene), abbreviated here as $Cp^e_2Co^{+/o}$ (e=ester) and $HMFe^{+/o}$, respectively (cf ref. 3a). These systems were chosen in view of their previous detailed examination in solution, yielding a large (ca tenfold) variation in effective H_{12} values.[3a] In addition, theoretical values of H_{12} and gas-phase well depths for $Cp_2Fe^{+/o}$ and $Cp_2Co^{+/o}$ ion-molecule pairs have been obtained recently for a range of internuclear geometries.[6b] The present results support the somewhat novel contention that orbital-overlap factors can indeed influence gas-phase electron-transfer reactivities, at least for such relatively large polyatomic systems.

Experimental Section

A Nicolet FTMS-2000 Fourier transform ion cyclotron resonance mass spectrometer was used for all kinetic measurements. This instrument was configured with a single analysis cell (4.8 cm x 4.8 cm x 9.6 cm) situated in a 3 T superconducting magnet with the long axis of the cell oriented parallel to the magnetic field.

A previously described double-resonance technique was used to obtain data for the pseudo-first order self-exchange reactions.[7a] Ionization was achieved by electron impact at 10-12 eV. These low electron energies minimize potential excitation of the ions generated. Following a 500 ms cooling period, the metallocenium ion population was isotopically enriched by ejecting the principal isotope of the molecular metallocene ion, and swept double-resonance pulses were used to remove any metallocene fragment ions formed during ionization. The isotopically enriched ions were then permitted to react with the neutral metallocene through electron transfer, resulting in regeneration of the original ion isotope distribution. The reaction time was varied over a range from 3 ms to at least 500 ms and not longer than several seconds. Finally, ions were detected using broad-band excitation and transient digitization.

The neutral metallocenes were synthesized as outlined in refs. 3a and 4a. The compounds were introduced into the spectrometer on the end of a temperature-controlled solids probe; the low vapor pressure of most of the metallocenes used here precluded the use of controlled leak valves. Following insertion of the probe, the system was permitted to pump down for three hours to achieve a low and well-known constant background pressure before performing experiments. During this period the sample was continuously cooled by flowing liquid-nitrogen-cooled nitrogen gas through the probe. This was necessary to prevent the more volatile metallocenes (especially ferrocene) from vaporizing completely while the background pressure was reduced to a stable value. Once a stable background pressure had been achieved (~10^{-8} torr), the chamber was heated to 150°C to reduce the condensation of low vapor pressure metallocenes during data collection. Heating the chamber (along with tubes leading to the ionization gauge) improved pressure stability considerably during the experiment. The pressure of the metallocene vapor in the chamber was adjusted by changing the temperature of the probe tip to an appropriate value. Experiments were typically conducted with metallocene pressures from 10^{-7} to 10^{-6} torr.

Efforts taken to ensure that nonthermal ions did not affect the observed rates include the low ionization energies mentioned above. In addition, data were collected with and without argon buffer gas, which was introduced through a Varian controlled leak valve; the observed rates were essentially unaltered under these conditions.

Pressures were measured by using a Bayard-Alpert ionization gauge which was calibrated over the range of values used in this experiment by obtaining kinetically the actual pressure of $Cp_2Co^{+/o}$ (based on the rate constant reported in ref. 7a) as a function of the observed gauge reading. Since one of the FTMS-2000 diffusion pumps is located between the ion gauge and the analysis cell, this procedure was required to achieve a pressure-dependent geometry correction to the observed gauge pressure. In addition, the observed ion gauge pressures were corrected for the differences in ionization cross section expected for the various metallocenes. The ionization gauge sensitivity, R_x, has been related to the polarizability, $\alpha(\text{Å}^3)$, via the empirical equation $R_x = 0.36\ \alpha + 0.30$ ($R_x = 1.00$ for N_2).[8] The experimental polarizability of ferrocene has been measured as 19.0 Å^3.[9] Cobaltocene was assumed to have the same polarizability as ferrocene; the polarizabilities of the other metallocenes were determined empirically using the method of Miller and Savchik.[10] (See Table I).

Rate data were analyzed using the method of Richardson et al.[7b] Self-exchange rate constants were obtained from equation 1,

$$\ln(R_t - (f'_0/f_0)/(R_t + 1) = -k_{ex}Pt \qquad (1)$$

Here P is the metallocene gas pressure, f'_0 and f_0 are the initial fractions (natural abundances) of nonejected and ejected isotopes, respectively, and $R_t = f'/f$, where f' and f are the measured fractions of nonejected and ejected isotopes at time t after ejection. The masses of the different metallocene isotopes are sufficiently close and the total reaction times employed here are sufficiently short that corrections for the mass-dependent diffusional loss of ions from the trapping cell were not required.

Except for the $Cp_2^*Co^{+/0}$ rate constant, which was measured only three times (due to a shortage of the compound), each rate study was replicated at least ten times. On any given day replicate runs for a particular metallocene were performed over a series of pressures, and rate constants varied typically by less than 10%. The ion gauge was recalibrated each time the series of compounds was studied. The overall statistical variation in each of the rate constants is approximately 30% or less.

Results and Discussion

The relative k_{ex} values for the five metallocene redox couples evaluated here are summarized in Table I. Although the differences in rate between these systems are not enormous, in most cases they are clearly beyond the range of experimental uncertainty. In particular, k_{ex} for $Cp_2Co^{+/0}$ is about fivefold larger than for $Cp_2Fe^{+/0}$. This rate ratio is somewhat larger than that (ca 3) observed by Richardson et al[7a]; numerous replicate measurements nonetheless yielded rate ratios persistently within 10-20% of the former value. The other two ferrocene-based redox couples, $Cp'_2Fe^{+/0}$ and $HMFc^{+/0}$, exhibit k_{ex} values intermediate between those for $Cp_2Fe^{+/0}$ and $Cp_2Co^{+/0}$, whereas k_{ex} for the one cobaltocene derivative examined, $Cp^*_2Co^{+/0}$, is within experimental error of that for $Cp_2Co^{+/0}$.

Interestingly, these gas-phase reactivity trends roughly parallel those seen for these self-exchange reactions in a given solvent, although larger variations are typically obtained in the latter case, at least in low-friction media (vide infra).[3a] This is illustrated by the relative k_{ex} values obtained in acetonitrile, labelled k_{ex}^{sol}(rel) in Table I, which are extracted from ref. 3a. Given that these condensed-phase reactivity differences are due predominantly to differences in the donor-acceptor electronic coupling (i.e. in H_{12}), it is tempting to suggest that this factor is also responsible for the rate variations observed in the gas phase. Before exploring this possibility further, however, it is necessary to consider carefully the factors that are normally considered to affect ion-molecule reactivities in the gas phase.

It is generally useful to normalize the measured k_{ex} values to the "capture rate constant", k_{cap}, evaluated by using collisional models.[12] In the simplest, Langevin, treatment

$$k_{cap} = 2\pi e(\alpha/\mu)^{\frac{1}{2}} \qquad (1)$$

where e is the electronic charge, α is the molecular polarizability, and μ is the reduced mass of the reacting partners. The resulting estimates of k_{cap} for each redox couple are listed in Table I. These are seen to vary by only ca 10% or less between the different reactions. For $Cp^*_2Co^{+/0}$ and $HMFc^{+/0}$, the effect of a permanent dipole moment (due to the methoxy and hydroxy substituents, respectively) should also be considered. The lower pair of k_{cap} estimates listed for these reactions in Table I were obtained instead by using the parameterized trajectory equation of Su and Chesnavich,[11] which accounts for such ion-dipole interactions. While k_{cap} is necessarily enhanced in the presence of a permanent dipole, the predicted effect here is relatively small (ca 20-30%). The influence of ion-quadrupole interactions upon k_{cap} can also be significant. Although convenient parameterized formulae are apparently not available, on the basis of the closely similar quadrupole moments of ferrocene and benzene[13] together with model calculations for the latter[14] the influence of this factor on k_{cap} appears to be small.[15]

Also included in Table I are ratios of the observed rate constants for each reaction to the corresponding capture rate constant, k_{ex}/k_{cap}, i.e. the "reaction efficiency." Since only relative k_{ex} values were determined here due to the absence of a reliable absolute pressure calibration, the k_{ex} value for $Cp_2Co^{+/0}$ quoted by Richardson et al[7a] (7.8×10^{-10} cm^3 molecule^{-1} s^{-1}) was utilized to scale the remaining values. Although these absolute k_{ex} values (and hence the k_{ex}/k_{cap} ratios) are somewhat less reliable (possibly ± 50%), this nonetheless provides a convenient scale with which to discuss the structure-dependent reactivities.

As noted by Richardson et al,[7a] $Cp_2Co^{+/0}$ self exchange exhibits a reaction efficiency (0.74) which is comparable to, although perhaps significantly larger than, that corresponding to the maximum anticipated value, $k_{ex}/k_{cap} = 0.5$. This latter value corresponds to the occurrence of efficient electron exchange during the lifetime of each ion-molecule encounter pair. The present observation of a similar reaction efficiency for $Cp_2Co^{+/0}$ and $Cp^{*}_2Co^{+/0}$ is unsurprising on this basis given that the latter couple exhibits even stronger electronic coupling in solution than for the former.[3a]

Irrespective of the uncertainties in the absolute reaction efficiencies, the fivefold smaller k_{ex}/k_{cap} value obtained for $Cp_2Fe^{+/0}$ versus $Cp_2Co^{+/0}$, and the milder yet significant corresponding differences observed for $Cp'_2Fe^{+/0}$

and $HMFc^{+/o}$ versus $Cp_2Co^{+/o}$ (Table I), provide enticing evidence that the structural sensitivity of k_{ex} arises from factors beyond those contained in k_{cap}. At least on the basis of the Langevin treatment, then, the present rate variations are most simply interpreted as reflecting differences in the properties of the ion-molecule encounter pair.

Such an overall situation is encountered commonly for electron transfer in both gas- and solution-phase environments. The interpretation of such rate differences within structurally related series for these two cases, however, is usually quite different. For solution-phase reactions, variations in both the activation barrier and the dynamics of barrier crossing have commonly been invoked to account for the observed reactivity trends.[1-3] Most observed rate variations in the gas phase, for electron transfer[7] and related charge and atom transfers,[15] have been considered instead to arise primarily from differences in the height of the central barrier, ΔE^*, together with variations in the energy stabilization for the precursor complex versus the separated reactants, i.e. the "well depth" ΔE_w.[15] For clarification, a labelled potential energy-reaction coordinate diagram is shown in Fig. 1.

For the present metallocene self exchanges in solution, ΔE_w is probably small or negligible, whereas ΔE^* is substantial, ca 5-6 kcal mol^{-1}, arising predominantly from solvent repolarization.[3,4] For the corresponding gas-phase reactions, by contrast, ΔE^* should be small since in the absence of solvent the central barrier arises only from inner-shell (i.e. reactant intramolecular) reorganization. From structural and vibrational spectroscopic data, the central barrier in the absence of electronic coupling, ΔE^*_c, (i.e. "cusp" barrier, see Fig. 1) equals ca 1.4 and 0.8 kcal mol^{-1} for $Cp_2Co^{+/o}$ and $Cp_2Fe^{+/o}$, respectively, with comparable (or smaller) barriers being likely for the substituted metallocene couples.[16] Theoretical complexities notwithstanding,[17] the presence of significant electronic coupling (i.e. nonzero H_{12}) will diminish ΔE^* somewhat. Given the substantially (ca 0.5-

1.0 kcal mol^{-1}) larger H_{12} values inferred experimentally[3a] as well as computationally[6] for $Cp_2Co^{+/o}$ versus $Cp_2Fe^{+/o}$ (vide infra), ΔE^* is likely to be comparably small, $\leq$ 1 kcal mol^{-1}, for the present self-exchange reactions. Variations in the barrier height therefore appear unlikely to account for the present rate differences.

A more compelling, albeit less conventional, interpretation for the differences in the gas-phase k_{ex} values involves variations in the degree of reaction adiabaticity. As mentioned above, the rate differences observed for the present metallocene couples in a given solvent can be traced primarily to variations in the electronic transmission coefficient κ_{el} caused by differences in H_{12}.[3] The extent of the rate demarcation depends upon the solvent, being largest in low friction (small τ_L) media. (This sensitivity to the solvent dynamics arises since τ_L^{-1} determines the effective net velocity through the transition-state region; κ_{el} for these systems tends to decrease, and the sensitivity of κ_{el} and hence k_{ex} to H_{12} increases, as τ_L^{-1} increases[3]). The dynamical reasoning involved is well developed on the basis of Landau-Zener theory combined with contemporary solvent friction treatments.[3b]

The interpretation of the present gas-phase kinetic data in terms of donor-acceptor electronic coupling is necessarily different from this picture due to the dissimilar energetics of gas- and solution-phase ion-molecule reactions. Most importantly, as noted above the ion-molecule "encounter complex" in the gas phase is typically characterized by substantial attractive interactions, yielding large well depths, in contrast to the solution phase where these interactions are effectively screened by the solvent. The average gas-phase encounter-complex lifetime is commonly thought to be much (several orders of magnitude) longer than that associated with translational motion. (ca 10^{-12} s).[18] Combined with the small anticipated central barriers for the present gas-phase systems, one might expect that electron exchange should be consummated easily within the encounter-complex lifetime, even for donor-acceptor pairs featuring only very weak electronic coupling, thereby yielding persistently $k_{ex} \approx 0.5\ k_{cap}$.

This point can be illustrated most simply with reference to the unimolecular rate constant for electron transfer within the precursor complex, $k_{et}(s^{-1})$, commonly considered in solution-phase reactions. If ΔE^* for the gas-phase processes is small, k_{et} should approach (at least within ca 10 fold) the corresponding frequency factor for barrier passage, $\kappa_{el}\nu_n$, where ν_n is the nuclear frequency factor.[19] For the present reactions, $\nu_n \approx 1 \times 10^{13}\ s^{-1}$ since the central barrier involves a change in metal-Cp distance.[16] Providing the average precursor lifetime, τ, is longer than $\sim(10^{12}\kappa_{el})^{-1}$ s, electron exchange therefore should occur usually prior to ion-molecule dissociation, yielding $k_{ex} \approx 0.5\ k_{cap}$. In solution, on the other hand, a continuous (near-random) distribution of ion-molecule geometries is envisaged, with a defined statistical probability of forming an encounter pair with the reaction partners in suitably close proximity for electron transfer. This probability distribution, together with the likely weak nonspecific interactions between the reaction partners, largely obviates the need for explicit consideration of precursor lifetimes for the solution-phase processes. Consequently, then, in contrast to solution reactions one might expect that gas-phase electron transfer would commonly be unaffected by reaction nonadiabaticity ($\kappa_{el} < 1$) within the encounter complex, at least for systems featuring small central barriers.

A closer examination, however, reveals at least a plausible rationale for the observed metallocene reactivity differences. Little experimental information is available regarding ΔE_w for metallocenium-metallocene pairs, although $-\Delta E_w$ for ferrocene has been reported to be less than 13 kcal mol^{-1}.[20] Newton, however, has recently calculated interaction energies associated with electrostatic and van der Waals interactions for various internuclear configurations of $Cp_2Fe^{+/0}$ and $Cp_2Co^{+/0}$.[6b] Interestingly, ΔE_w

is sensitive to the symmetry of the ion-molecule contact pair, even though approximately the same values are obtained for $Cp_2Fe^{+/o}$ and $Cp_2Co^{+/o}$. The energetically most favorable encounter complex configuration involves D_{5h} symmetry (i.e. with the Cp rings forming a common fivefold axis), for which $-\Delta E_w \approx 5.8$ kcal mol^{-1}. For the alternative D_{2h} ("side-by-side") symmetrical geometry, $-\Delta E_w$ is much smaller, ca 1 kcal mol^{-1}. Newton has also obtained estimates of H_{12} by means of INDO calculations for these and other internuclear geometries.[6] The largest (i.e. most favorable) H_{12} values are also obtained for the D_{5h} configuration: 2.6 and 0.4 kcal mol^{-1} for $Cp_2Co^{+/o}$ and $Cp_2Fe^{+/o}$, respectively. Markedly smaller values are extracted for the D_{2h} geometry: 0.08 and 0.03 kcal mol^{-1}, respectively. Other internuclear geometries yield intermediate values of both $-\Delta E_w$ and H_{12}.[6b] These calculations show clearly that electron transfer will take place preferentially through reaction channels featuring very specific geometric configurations.

The magnitude of the well depth can exert an important influence on the effective lifetime, τ, that the ion-molecule pair remains in that geometry. A relation between τ and ΔE_w is[18]

$$\tau \approx \tau_o \left[\frac{-\Delta E_w + (s + 1)\, k_B T}{(s + 1)\, k_B T}\right]^{\alpha - 1} \qquad (2)$$

where τ_o is the timescale of energy redistribution, k_B is the Boltzmann constant, α is the number of degrees of freedom of the ion-molecule complex, and sk_BT is the average vibrational energy in the two reactants prior to association. Even though α and s are somewhat ill-defined for the large polyatomic reactants considered here, from Eq(2) it is likely that τ is several orders of magnitude longer than τ_o (ca 10^{-13} - 10^{-12} s[18]) for large well depths, say $-\Delta E_w \geq 10$ kcal mol^{-1} (cf above discussion). Equation (2) actually represents a classical limit to the quantum expression:

$$\tau = \tau_o \left[\prod_{k=1}^{s-1} \left(1 - \frac{m}{j + k}\right)\right]^{-1} \qquad (3)$$

Here it is assumed that j quanta of energy are distributed among s identical oscillators. This latter expression tends to yield lifetimes that are somewhat shorter than those given by Eq. (2). Nonetheless, on the basis of these arguments, k_{et} for $Cp_2Fe^{+/o}$ as well as $Cp_2Co^{+/o}$ should be sufficiently large under these circumstances so to provide efficient electron exchange on the above timescales. (For example, for $H_{12} = 0.4$ kcal mol^{-1}, appropriate for $Cp_2Fe^{+/o}$ in the D_{5h} configuration, κ_{el} is estimated to be ca 0.5, so that $\kappa_{el}\nu_n \approx 5 \times 10^{12}$ s^{-1}[21]).

A rather different situation can be encountered, however, for energetically less favorable encounter geometries. For example, for $Cp_2Fe^{+/o}$ in the D_{2h} configuration, where $H_{12} \approx 0.03$ kcal mol^{-1}, κ_{el} is estimated to be only 0.02.[21] Much smaller κ_{el} values are predicted for the range of other "loose" encounter geometries anticipated to be formed, having larger donor-acceptor separations. Given that the collision complex lifetime is predicted to be very short (possibly even approaching τ_o) for small $-\Delta E_w$ [Eq(2)], one can envisage that only a moderate or even small fraction of the ion-molecule encounters might yield electron transfer prior to dissociation of the reactant pair. For $Cp_2Co^{+/o}$, however, the uniformly larger H_{12} values obtained for a given ion-molecule geometry should result in electron transfer occurring during a substantially higher fraction of such encounters, thereby accounting qualitatively for the larger k_{ex} and k_{ex}/k_{cap} values for this system.

This line of argument presumes that such energetically less favorable initial encounter states do not interconvert largely to more stable, and therefore longer-lived, geometries prior to dissociation of the ion-molecule complex. Such an interconversion might be hindered in part by the conservation of angular momentum within a given encounter complex. Unfortunately, theoretical and/or computational guidance regarding ion-molecule encounter dynamics is conspicuous by its absence for larger polyatomic systems such are of interest here. Some evidence exists that relatively inefficient ion-molecule capture can arise in a related situation where the ion-molecule interactions are strongly anisotropic due to the presence of a permanent dipole.[22] A similar circumstance is expected in the present ion-molecule partners, in that they involve strongly anisotropic ion-quadropole interactions[6b](vide supra). In addition, it is possible that systems such as $Cp_2Co^{+/0}$ exhibit sufficient donor-acceptor coupling so to enable electron transfer to take place via "close encounters" of the reacting pair without even transitory formation of a trapped ion-molecule pair. Such "longer-range" electron transfer contributions can account further for the rate-electronic structural demarcations observed here.

Irrespective of the detailed dynamics, then, the present results are considered to provide direct evidence that donor-acceptor electronic coupling as well as nuclear reorganization (i.e. ΔE^*) can retard the rates of some gas-phase electron-transfer processes. The relative k_{ex} values for the other metallocenes considered here are also roughly consistent with this interpretation. In particular, the larger gas-phase k_{ex} value for $Cp'_2Fe^{+/0}$ versus $Cp_2Fe^{+/0}$ is in harmony with the corresponding solution-phase rates (Table I), consistent with the expectation that the methyl substituents engender greater donor-acceptor electronic coupling.[3,6b]

The diagnosis of electronic-coupling effects on gas-phase electron-transfer reactivity is probably masked in many cases by uncertainties in the reaction energetics, especially in ΔE^*. Even in the present examples, uncertainties in both ΔE^* and ΔE_w restrict the interpretation to a largely qualitative one. Nevertheless, given that the cusp barrier height ΔE_c^* is probably *larger* for $Cp_2Co^{+/o}$ than for $Cp_2Fe^{+/o}$ (vide supra), there seems little doubt that the faster kinetics observed for the former couple are due to electronic coupling factors. These may influence k_{ex} perhaps by decreasing ΔE^* and by increasing ΔE_w as well as by enhancing the reaction adiabaticity within the encounter complex.

Other documented examples of electronic coupling effects in gas-phase electron transfer are hard to find. A recent study of gas-phase electron transfer between substituted nitrobenzene molecule-radical anion pairs suggests that electronic coupling plays a role in the observed rate variations.[23] Richardson et al have reported a very small k_{ex}/k_{cap} value, 0.03, for $Ru(hfac)_3^{0/-}$ gas-phase self exchange[7b] (hfac = hexafluoroacetylacetonate). A recent analysis indicates that this reaction is impeded by marked nonadiabaticity both in homogeneous solution and at electrode surfaces.[24] The weak electronic coupling for this system is understandable in view of the "insulation" provided by the fluorinated organic ligand. It seems plausible, then, that the small gas-phase reaction efficiency for $Ru(hfac)_3^{0/-}$ is also due to the presence of substantially nonadiabatic pathways within the encounter complex, especially since ΔE^* is likely to be small or moderate.[23]

Even given the complications wrought in the gas-phase processes by the uncertainties in the dynamics and energetics of encounter complex formation, the further examination of such reactions characterized previously in solution with regard to electronic coupling factors would appear to be well worthwhile.

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TABLE I Relative Rate Constants for Gas-Phase Electron Self Exchange for Some Metallocene Redox Couples.

Redox Couple[a]	k_{ex}(rel)[b]	k_{ex}^{sol}(rel)[c]	α[d] Å^3	10^{10} k_{cap}[e] cm^3 mol^{-1} s^{-1}	k_{ex}/k_{cap}[g]
$\mathrm{Cp_2Co^{+/o}}$	(1.0)	(1.0)	19	10.5	0.74
$\mathrm{Cp^*_2Co^{+/o}}$	1.0	4.4	29	10.2 13.4[f]	0.78 0.59[f]
$\mathrm{Cp'_2Fe^{+/o}}$	0.60	0.78	41	11.8	0.40
$\mathrm{Cp_2Fe^{+/o}}$	0.19	0.20	19.0	10.5	0.14
$\mathrm{HMFc^{+/o}}$	0.52	0.12	21.5	10.6 12.7[f]	0.39 0.32[f]

[a] Cp - cyclopentadienyl, Cp* - mono(carboxymethyl)cyclopentadienyl, Cp' - pentamethylcyclopentadienyl, HMFc - hydroxymethylferrocene.

[b] Rate constant for gas-phase electron self exchange, ratioed to that for $\mathrm{Cp_2Co^{+/o}}$. Reproducibility was typically ca 10-30%.

[c] Rate constant for electron self exchange in acetonitrile at 25°C, ratioed to that for $\mathrm{Cp_2Co^{+/o}}$; taken from ref. 3a.

[d] Polarizability of metallocene molecule. Value for ferrocene from ref. 9; other values estimated by procedure based on ref. 10 (see text).

[e] Capture rate constant, determined from Langevin equation [Eq(1)] using α values listed alongside, except where noted for $\mathrm{Cp^*_2Co^{+/o}}$ and $\mathrm{HMFc^{+/o}}$.

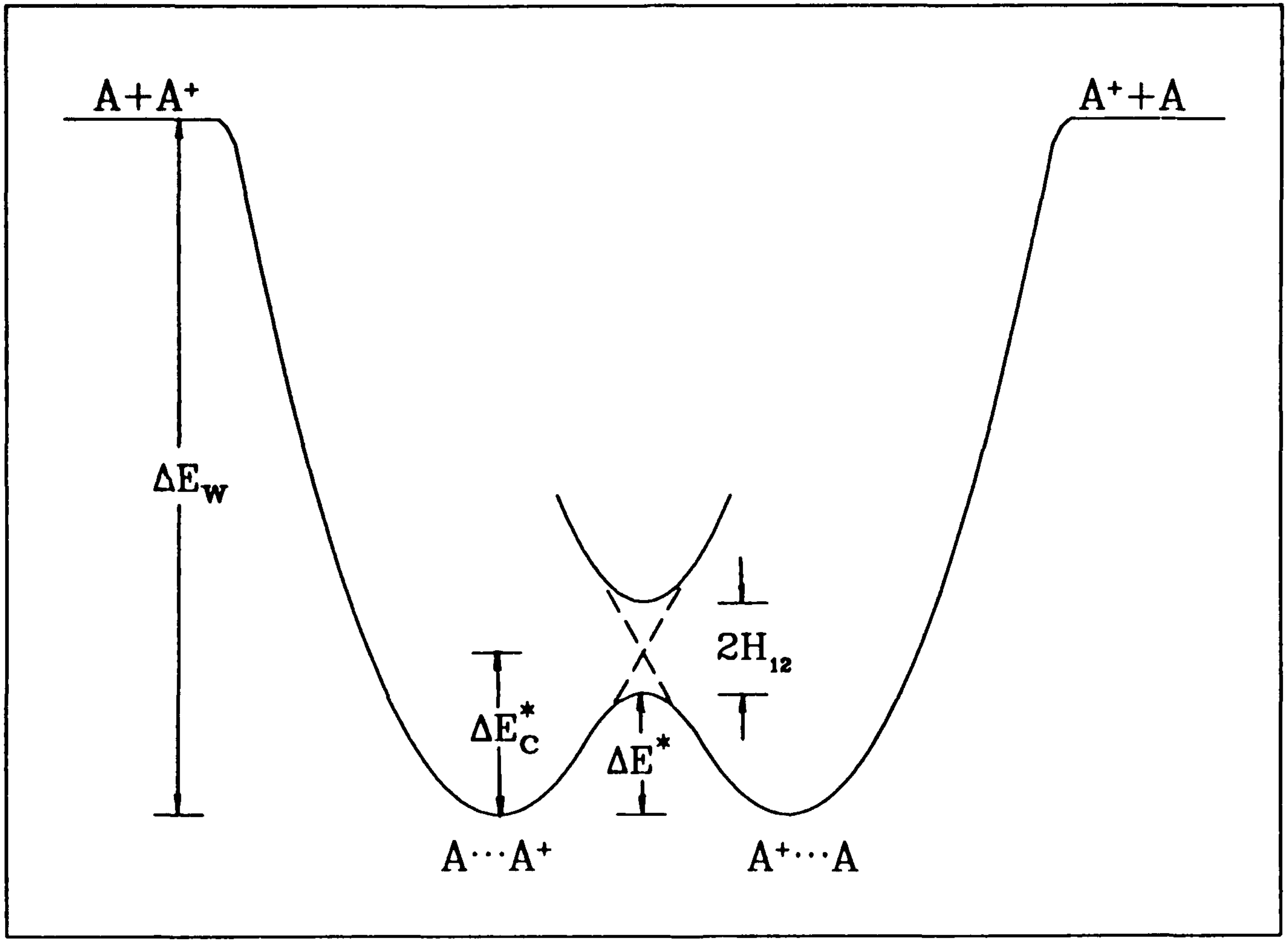
[f] Capture rate constants obtained from parametrized trajectory equation of Su and Chesnavich[11]. Required dipole moments were estimated to be 2.6 and 1.7 Debye for $\mathrm{Cp^*_2Co}$ and HMFc, respectively.

[g] Ratio of self-exchange rate constant to estimated capture rate constant. Absolute k_{ex} values were obtained from the relative values listed by employing the k_{ex} value for $\mathrm{Cp_2Co^{+/o}}$, 7.8 x 10^{-10} cm^3 molecule^{-1} s^{-1}, given in ref. 7a.

FIGURE CAPTION

Fig. 1

Schematic potential energy-reaction coordinate profile for gas-phase electron self-exchange reaction. Dashed line refers to "cusp-like" central barrier that would be obtained in the absence of donor-acceptor electronic coupling.


$A+A^+$
A^++A
ΔE_W
$2H_{12}$
ΔE_C^*
ΔE^*
$A\cdots A^+$
$A^+\cdots A$