oleanolate (**13a**) (36.1 mg), and the material from latter peak afforded methyl ursolate (**15a**) (39.4 mg). A phytosterol mixture (250 mg),[23] methyl 3-epimaslinate (180 mg), and a mixture of methyl maslinate and methyl 2α-hydroxyursolate (1.08 g) were also obtained by chromatography.[7]

Incubation of Sodium $[2\text{-}^{13}C^{2}H_3]$Acetate (1b). The suspension cultures of *R. japonica* were incubated in LS medium (9.0 L) containing 2,4-D (10^{-6} M) and sodium $[2\text{-}^{13}C^{2}H_3]$acetate (630 mg) and unlabeled sodium acetate (1.260 g) in 30 × 500 mL conical flasks for 4 weeks. The cells were collected, and the previously described procedure was used to isolate methyl ursolate (**13b**) (60 mg), methyl oleanolate (**15b**) (70 mg), methyl 3-epimaslinate (70 mg), a mixture of methyl 2α-hydroxyursolate and methyl maslinate, and a mixture of phytosterol (248 mg).[23]

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[23] This will be published elsewhere.

The Orbital-Overlap Factor in Electron Transfer: Sensitivity of Homogeneous Self-Exchange Kinetics for Some Metallocenes to Electronic Structure

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Abstract: Rate constants, k^{h}_{ex}, for the electron self-exchange of cobaltocenium–cobaltocene, $Cp_2Co^{+/0}$, and for the decamethyl derivative, $(Cp\text{-}Me_5)_2Co^{+/0}$, obtained by using the NMR line-broadening technique in acetonitrile and dimethyl sulfoxide are compared with corresponding data for the ferrocene couples $Cp_2Fe^{+/0}$ and $(Cp\text{-}Me_5)_2Fe^{+/0}$ and for bis(benzene)chromium(I)/(0). The rate constants in a given solvent display a marked sensitivity to the reactant structure, the k^{h}_{ex} values being about tenfold larger for $Cp_2Co^{+/0}$ relative to $Cp_2Fe^{+/0}$; decamethyl substitution yields tenfold increases in k^{h}_{ex} for both these couples. A relationship is established between these ca. 100-fold rate variations and the nature of the donor and acceptor orbitals. In particular, the markedly slower self-exchange kinetics observed for $Cp_2Fe^{+/0}$ relative to $Cp_2Co^{+/0}$ are consistent with the much greater ligand-delocalized character of the $4e_{1g}$ orbital involved in the latter electron transfer as compared with the $4e_2$ or $8a_{1g}$ orbital for the former reaction. The same argument is likely to account for the similar relative rates for $(Cp\text{-}Me_5)_2Fe^{+/0}$ versus $(Cp\text{-}Me_5)_2Co^{+/0}$. These rate differences are very unlikely to be due to variations in nuclear reorganization factors since the molecular structures of these couples are virtually identical, and they feature only small differences ($\lesssim$0.3 kcal mol^{-1}) in the inner-shell barriers. The results therefore provide unusually clear evidence for the influence of donor–acceptor electronic coupling in outer-sphere redox reactivity.

We have recently been examining the electrochemical electron-exchange kinetics of various metallocene redox couples as a function of the solvent in order to probe the possible role of solvent relaxation dynamics upon the barrier-crossing frequencies.[1] The couples selected include cobaltocenium–cobaltocene ($Cp_2Co^{+/0}$, where Cp = cyclopentadiene) and the decamethyl derivatives $(Cp\text{-}Me_5)_2Co^{+/0}$ (where Cp-Me$_5$ = pentamethylcyclopentadiene) and $(Cp\text{-}Me_5)_2Fe^{+/0}$.[1b] These as well as other structurally related metallocene and metal arene couples yield similar electrochemical reactivities in a given solvent, the small (ca. twofold or less) rate variations being consistent with the minor differences in the inner-shell (i.e., reactant bond distortional) barrier, ΔG^*_{is}, anticipated on the basis of structural data.[1b] A major virtue of these systems as model reactants for solvent dynamical studies is that the electron-transfer barrier is dominated by the reorganization of the surrounding solvent.[1b] In addition, the metallocenes approach the apparent spherical geometry desirable for theoretical comparisons.

Most recently, we have been expanding these studies to include measurements of the corresponding self-exchange kinetics in homogeneous solution by utilizing the NMR line-broadening technique.[2] A primary objective is to compare the form of the solvent-dependent kinetics at electrochemical interfaces and in homogeneous solution in order to ascertain if the nature and extent of the solvent dynamical effects are different in these two redox environments. During these studies it became clear that, in contrast to the electrochemical reactions, the homogeneous-phase systems display a notable sensitivity to the reactant electronic structure.

In the present paper we report some pertinent results for $Cp_2Co^{+/0}$ and $(Cp\text{-}Me_5)_2Co^{+/0}$ self-exchange in acetonitrile and dimethyl sulfoxide, which along with corresponding published data for $Cp_2Fe^{+/0}$, $(Cp\text{-}Me_5)_2Fe^{+/0}$,[3] and bis(benzene)Cr(I)/(0) $[(C_6H_5)_2Cr^{+/0}]$,[4] illustrate the dependence of the rate constants in a given solvent upon the nature of the metal as well as the ligand structure. A correlation is established here between the ca. 100-fold rate variations for these metallocene couples in a given solvent and the character of the orbitals involved in the electron transfer. The results implicate the importance of donor–acceptor orbital overlap to electron-transfer reactivity for such simple homogeneous-phase outer-sphere processes.

Experimental Section

Cobaltocene was obtained from Strem Chemicals. Cobaltocenium tetrafluoroborate was prepared by oxidation of Cp_2Co with tetrafluoroboric acid (Alfa); the corresponding decamethyl derivatives were synthesized as described in ref 5. Acetonitrile and dimethyl sulfoxide were "high-purity" grade from Burdick and Jackson; the former was purified further by distillation over phosphorus pentoxide. Deuteriated solvents were from Aldrich. All solutions for NMR measurements were prepared in 5-mm tubes in a nitrogen-filled glovebox. The $Cp_2Co^{+/0}$ system employed oxidized/reduced form concentrations of 0.02–0.12 M/0.7–20

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Table I. Rate Constants for Homogeneous Self-Exchange of Various Metallocene and Arene Redox Couples in Acetonitrile and Dimethyl Sulfoxide at 25 °C

	k^{h}_{ex},[b] $M^{-1}\ s^{-1}$		k^{th}_{ex},[g] $M^{-1}\ s^{-1}$	
redox couple[a]	ACN	DMSO	ACN	DMSO
$(Cp\text{-}Me_5)_2Co^{+/0}$	4.3 (±0.1) × 10^{8} [c]	1.8 (±0.3) × 10^{8} [c]	3.3 × 10^{7}	1.3 × 10^{7}
$Cp_2Co^{+/0}$	3.8 (±0.2) × 10^{7} [c]	2.4 (±0.3) × 10^{7} [c]	2.4 × 10^{7}	1.0 × 10^{7}
$(Cp\text{-}Me_5)_2Fe^{+/0}$	3.8 (±0.4) × 10^{7} [e]	*d*	5.0 × 10^{7}	2.0 × 10^{7}
$Cp_2Fe^{+/0}$	5.3 (±0.8) × 10^{6} [e]	1.6 (±0.6) × 10^{6} [e]	5.0 × 10^{7}	2.0 × 10^{7}
$(C_6H_6)_2Cr^{+/0}$		6.0 (±0.7) × 10^{7} [f]		1.4 × 10^{7}

[a] Cp = cyclopentadienyl. [b] Measured rate constant for homogeneous self-exchange of listed couple in acetonitrile (ACN) or dimethyl sulfoxide (DMSO), as indicated in column heading. [c] This work, obtained in 0.1 M tetraethylammonium tetrafluoroborate (see footnote 7 for details of NMR spectra). [d] Value could not be obtained due to insufficient solubility of ferrocene. [e] Values from ref 3, obtained in the absence of added electrolyte (values decreased by ca. 20% upon adding 0.1 M electrolyte[3]). [f] Value from ref 4, obtained in the absence of added electrolyte. [g] Rate constant for homogeneous self-exchange, derived from eq 1. Values of various parameters obtained as follows: K_p (0.26 M^{-1}) from eq 2 with $r = 7.6$ Å, $\delta r = 0.6$ Å; $\kappa_{el} = 1$; ν_n from "overdamped" solvent relaxation model (eq 9 of ref 1b); ΔG^*_{os} from dielectric continuum model (eq 19 of ref 1b); ΔG^*_{is} from bond distance and force constant data (see text) taken as follows: $(Cp\text{-}Me_5)_2Co^{+/0}$, 0.5 kcal mol^{-1}; $Cp_2Co^{+/0}$, 0.7 kcal mol^{-1}; $(Cp\text{-}Me_5)_2Fe^{+/0}$ and $Cp_2Fe^{+/0}$, 0.35 kcal mol^{-1}; $(C_6H_6)_2Cr^{+/0}$, 0.5 kcal mol^{-1}.

mM; for the $(Cp\text{-}Me_5)_2Co^{+/0}$ system these were 0.01–0.025 M/0.8–8 mM. The solutions also contained 1% tetramethylsilane as a chemical shift reference.

Proton NMR spectra were recorded on Nicolet NT 200 and NT 470 instruments. For data collection in protiated solvents, the interfering solvent proton peaks were diminished by homonuclear irradiation of undesirable resonances. The rate constants obtained in the protiated and deuteriated solvents generally agreed to within 10%. The NMR chemical shifts for the oxidized/reduced form mixtures equaled the weighted averages of those for the individual redox states measured separately. This indicates that the electron-transfer process conforms to the "fast-exchange" region; the relationships described by Wahl et al.[6] were used to extract the desired rate constants for homogeneous self-exchange, k^{h}_{ex}, by employing the measured chemical shifts and line widths of solutions of the oxidized/reduced mixture and of the separate redox states.[7]

Results and Discussion

Table I summarizes rate constants for homogeneous self-exchange, k^{h}_{ex}, as determined here for the cobaltocene redox couples $Cp_2Co^{+/0}$ and $(Cp\text{-}Me_5)_2Co^{+/0}$ in acetonitrile and dimethyl sulfoxide at 25 (±0.5) °C. These values were obtained for solutions containing 0.1 M tetraethylammonium tetrafluoroborate; k^{h}_{ex} values only about 10% larger were obtained in the absence of this added electrolyte. (Pertinent information regarding the NMR data are summarized in footnote 7.) Table I also includes corresponding k^{h}_{ex} values for $Cp_2Fe^{+/0}$, $(Cp\text{-}Me_5)_2Fe^{+/0}$, and $(C_6H_6)_2Cr^{+/0}$, taken from ref 3 and 4, which were obtained by using proton NMR and ESR line-broadening techniques, respectively. The former values were also replicated in our laboratory.[2]

Comparison of these rate constants in a given solvent reveals that the cobaltocenium–cobaltocene couple exhibits substantially (ca. tenfold) higher k^{h}_{ex} values than the ferrocenium–ferrocene couple. Comparable (ca. tenfold) rate increases are also seen upon methylating the cyclopentadienyl rings for both the cobalt and iron systems. The $(Cp\text{-}Me_5)_2Co^{+/0}$ couple exhibits k^{h}_{ex} values that are about 100-fold larger than for $Cp_2Fe^{+/0}$, with both $Cp_2Co^{+/0}$ and $(Cp\text{-}Me_5)_2Fe^{+/0}$ yielding similarly intermediate k^{h}_{ex} values in a given solvent (Table I). Roughly comparable rate ratios for these four reactions are also observed in a number of other solvents;[2] acetonitrile and dimethyl sulfoxide are chosen here chiefly for illustrative purposes. The value of k^{h}_{ex} for $(C_6H_6)_2Cr^{+/0}$ in dimethyl sulfoxide, 6 × 10^{7} $M^{-1}\ s^{-1}$, is relatively high, being intermediate between that for $Cp_2Co^{+/0}$ and $(Cp\text{-}Me_5)_2Co^{+/0}$.

In order to elucidate the origin of these surprising rate differences, it is useful to express the rate constant as[1,8]

$$k^{h}_{ex} = K_p \kappa_{el} \nu_n \exp[-(\Delta G^*_{os} + \Delta G^*_{is})/RT] \qquad (1)$$

where K_p is an equilibrium constant for forming the precursor state from the separated reactants, ν_n is the nuclear frequency factor, and κ_{el} is the electronic transmission coefficient (i.e., the probability that electron tunneling will occur upon formation of the nuclear transition state). The form of eq 1 applies to both homogeneous-phase and electrochemical outer-sphere processes.[1b]

As stated above, the inner-shell barriers, ΔG^*_{is}, for the present reactants are small. These values can readily be estimated from bond distance and vibrational spectroscopic data, using[8]

$$\Delta G^*_{is} = 0.5 n f^{r}_{is} (\Delta a/2)^2 \qquad (2)$$

where n is the number of bonds undergoing distortion, Δa is the change in bond distance between the oxidized and reduced forms, and f^{r}_{is} is the "reduced" force constant for each bond obtained from the individual force constants for the oxidized and reduced species using $f^{r}_{is} = 2 f^{ox}_{is} f^{red}_{is} / (f^{ox}_{is} + f^{red}_{is})$. The last can be obtained from

$$f_{is} = 4\pi^2 \nu_{is}^2 \mu \qquad (2a)$$

where ν_{is} is the observed vibrational frequency (s^{-1}) and μ is the reduced mass.

Fortunately, accurate bond distance data are available for the present redox couples, which indicate that the only significant structural difference between the oxidized and reduced forms is a small increase (or decrease) of the metal–ring distance. These Δa values are as follows:[9] $(Cp\text{-}Me_5)_2Co^{+/0}$, 0.045 Å; $Cp_2Co^{+/0}$, ≈0.05 Å; $(Cp\text{-}Me_5)_2Fe^{+/0}$, −0.035 Å; $Cp_2Fe^{+/0}$, ca. −0.035 Å;[10] $(C_6H_6)_2Cr^{+/0}$, ≈0.045 Å. Since the inner-shell distortion for these couples involves a symmetric metal–ring vibration, the appropriate ν_{is} values required are those for the Raman-active stretching mode. Such data are available for $Cp_2Co^{+/0}$,[12,13] $Cp_2Fe^{+/0}$,[13] and $(C_6H_6)_2Cr^{+/0}$.[14] The resulting force constants[15] together with

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(7) Typical experimental parameters obtained from NMR spectra used to obtain rate constants for $Cp_2Co^{+/0}$ and $(Cp\text{-}Me_5)_2Co^{+/0}$ self-exchange in Table I, using the analysis procedure in ref 6, are as follows (using nomenclature of Wahl et al.,[6] as noted below). $Cp_2Co^{+/0}$ in acetonitrile: w_{DP}, 193 Hz; w_P, 119 Hz; w_D, 1 Hz; $\delta\nu$, −11 228 Hz) c, 41.0 mM; f_D, 0.785. $Cp_2Co^{+/0}$ in DMSO: w_{DP}, 240 Hz; w_P, 152 Hz; w_D, 1 Hz; $\delta\nu$, −11 154 Hz; c, 44.8 mM; f_D, 0.842. $(Cp\text{-}Me_5)_2Co^{+/0}$ in acetonitrile: w_{DP}, 176 Hz; w_P, 45 Hz; w_D, 1 Hz; $\delta\nu$, 19 981 Hz; c, 14.3 mM; f_D, 0.720. $(Cp\text{-}Me_5)_2Co^{+/0}$ in DMSO: w_{DP}, 201 Hz; w_P, 59 Hz; w_D, 1 Hz; $\delta\nu$, 20 577 Hz; c, 13.8 mM; f_D, 0.884. Parameters are defined as follows: w_{DP}, w_P, and w_D are the peak widths of the diamagnetic–paramagnetic mixture, the pure paramagnetic species, and the diamagnetic species, respectively, $\delta\nu$ is the "contact shift", c is the total concentration (diamagnetic + paramagnetic species), and f_D is the mole fraction of the diamagnetic species. The measured parameters for $Cp_2Co^{+/0}$ and $(Cp\text{-}Me_5)_2Co^{+/0}$ refer to fields of 200.07 and 469.58 MHz, respectively.

(8) For a recent review, see: Sutin, N. *Prog. Inorg. Chem.* **1983**, *30*, 441.

(9) See Table I of ref 1b for detailed bond distances and literature sources.

(10) Although the difference in metal–ring bond lengths, Δa, between Cp_2Fe and Cp_2Fe^+ has not been evaluated since the latter crystal structure is apparently unavailable, the Δa value for $Cp_2Fe^{+/0}$ is almost certainly similar to that for $(Cp\text{-}Me_5)_2Fe^{+/0}$ in view of the identical metal–ring distance for Cp_2Fe and $(Cp\text{-}Me_5)_2Fe$.[11]

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(15) The ν^{ox}_{is} and ν^{red}_{is} values for these redox couples are taken as follows: $Cp_2Co^{+/0}$, 325,[12] 320 cm^{-1};[13] $Cp_2Fe^{+/0}$, 310, 315 cm^{-1};[13] $(C_6H_6)_2Cr^{+/0}$, 280, 270 cm^{-1}.[14] Since the central metal atom remains stationary during the symmetric vibration, the effective force constant for both metal–ring vibrations can be obtained by inserting these values into eq 2a with μ taken as the mass of a single ring; this yields f^{r}_{is} values of 4.0 × 10^{5}, 3.75 × 10^{5}, and 3.5 × 10^{5} dyn cm^{-1}, respectively.

the above Δa values inserted into eq 2, with $n = 4$ (i.e., two vibrating bonds for each reactant), yield ΔG^*_{is} values for these self-exchange reactions of ca. 0.7, 0.35, and 0.5 kcal mol^{-1}, respectively. While these estimates of ΔG^*_{is} cannot be regarded as precise, they are likely correct to about 20–30%, i.e., within ca. 0.2 kcal mol^{-1}. Although the force constants for the $(Cp\text{-}Me_5)_2Co^{+/0}$ and $(Cp\text{-}Me_5)_2Fe^{+/0}$ couples are known with less certainty,[17,18] it is likely that similar or slightly smaller ΔG^*_{is} values apply to these systems.

These small differences in ΔG^*_{is} between the self-exchange processes considered here eliminate this factor as a plausible explanation for the observed rate differences. In particular, the tenfold greater rate constants for $Cp_2Co^{+/0}$ with respect to $Cp_2Fe^{+/0}$ cannot be accounted for by differences in ΔG^*_{is} since this term is slightly (0.2–0.3 kcal mol^{-1}) larger for the former couple. (Note that to account for the observed tenfold difference in k^{h}_{ex} on this basis would require that ΔG^*_{is} is about 1.4 kcal mol^{-1} *smaller* for $Cp_2Co^{+/0}$.)

In view of their almost identical size and structure, the outer-shell reorganization energy, ΔG^*_{os}, for $Cp_2Co^{+/0}$ and $Cp_2Fe^{+/0}$ should be virtually identical, although ΔG^*_{os} may be slightly smaller for the decamethyl derivatives and $(C_6H_6)_2Cr^{+/0}$ due to their larger effective radius. It therefore might be argued that the rate increases seen upon methylation are due at least in part to a decrease in the outer-shell barrier, as well as to slightly smaller ΔG^*_{is} values. This possibility, however, appears unlikely since the rate constants for $Cp_2Co^{+/0}$, $(Cp\text{-}Me_5)_2Co^{+/0}$, and $(C_6H_6)_2Cr^{+/0}$ electrochemical exchange in a given solvent are almost identical, even though the ΔG^*_{os} values should be comparable to those for the corresponding homogeneous reactions.[1b]

Consequently, the primary origin of the sizable differences in k^{h}_{ex} for these five redox couples lies almost undoubtedly in corresponding variations in the preexponential factor $K_p\kappa_{el}\nu_n$. The nuclear frequency factor ν_n is expected to be dominated largely by solvent reorganization dynamics rather than by reactant inner-shell vibrations in view of the predominant contribution of ΔG^*_{os} to the electron-transfer barrier.[1b,c,2] (On the basis of recent numerical calculations,[21b] the residual contribution of inner-shell vibrations to ν_n for the systems encountered here is small and essentially the same for all the reactions in a given solvent.[1b,2])

We have recently been utilizing such metallocene systems to test experimentally the theoretical prediction[21] that ν_n is determined by "overdamped" solvent motion in most solvents. Although interesting deviations from this prediction have come to light,[1c,2] it suffices to note here that the solvent dependence of the rate constants for homogeneous self-exchange as well as electrochemical exchange for the present metallocene couples is roughly consistent with such theoretical expectations.[1,2] Irrespective of the detailed molecular factors that can influence the nuclear frequency factor, therefore, ν_n should be very similar in a given solvent for all the present reactions.

This leaves variations in K_p and/or κ_{el} as constituting the only tenable explanation for the observed variations in k^{h}_{ex} with reactant structure. For such homogeneous-phase outer-sphere processes, K_p will be determined by electrostatic interactions between the reactant pair ("work terms") together with the statistical probability of forming such a pair from the (presumed spherical) reactants. The former component should be absent here since one reactant is uncharged. In this case a suitable expression for K_p is[8,22]

$$K_p = 4\pi N r^2 \delta r \tag{3}$$

where N is Avogadro's number, r is the average separation of the reacting centers in the transition state, and δr is the effective "reaction zone thickness", i.e., the range of internuclear separations larger than that corresponding to molecular "contact" which contribute substantially to the overall reaction rate. The last term should be sensitive to the effective distance over which efficient electron tunneling between the donor and acceptor orbitals can occur and therefore is closely linked to the corresponding value of κ_{el} in eq 1.

It is useful here to identify two distinct limiting cases. First (case 1), the electronic coupling between the reaction centers may be sufficient so that efficient electron tunneling occurs (i.e., reaction adiabaticity is achieved) not only upon reactant contact but also for significantly larger internuclear separations. In this case $\kappa_{el} \sim 1$ and the magnitude of δr reflects the range of larger internuclear separations over which reaction adiabaticity is maintained. Alternatively (case 2), the reaction may be substantially nonadiabatic even at the reactant contact distance; here effectively $\kappa_{el} \ll 1$ and δr will be small, ca. 0.5 Å.[8,22,23] Additionally, κ_{el} may be sensitive to the reactant pair geometry, so that only certain specific internuclear configurations will correspond to sufficient electronic coupling so as to yield viable reaction channels (vide infra). In this case, therefore, the form of the K_p expression, and hence the magnitude of K_p as well as κ_{el}, can be very sensitive to the donor–acceptor electronic coupling.

There is ample evidence from ab initio electronic structural and other calculations that outer-sphere electron transfer even between small molecules tends to border on case 2 rather than case 1 behavior.[24] Some indirect experimental evidence based on absolute theory–experiment comparisons of rate parameters[8,25] and from analyses of ligand effects upon the rates of some related reactions[26] is also in harmony with this assertion. It is therefore of interest to compare the electronic structures of the metallocenes considered here to ascertain if the observed rate differences can be accounted for on this basis.

The primary factor influencing the degree of electronic coupling and hence $K_p\kappa_{el}$ is the extent of spatial overlap between the acceptor and donor orbitals, as this determines the magnitude of the electronic matrix coupling element, H_{12}.[24] This overlap for the present systems will tend to be greater for orbitals having a greater delocalization over the Cp rings.

Information on this question can be extracted from a number of ab initio, Xα, and semiempirical theoretical studies of ferrocene[27] and cobaltocene.[28] The effective donor orbital will be the HOMO for the reduced form of the couple. This orbital for ferrocene appears to be extremely metal centered. Thus INDO-SCF calculations identify it as having $4e_2$ symmetry with 86% metal character, with an $8a_{1g}$ orbital having 90% metal character lying immediately below it in energy;[27a] Xα calculations identify the HOMO as the latter orbital.[27c] This predicted metal-centered electron distribution is consistent with ESR observations for

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(16) These ΔG^*_{is} values for the homogeneous self-exchange reactions obtained here are roughly twice those calculated for the corresponding electrochemical exchange processes examined in ref 1b. Besides the use of slightly different force constants here, this arises since a pair of reactants are involved in the former rather than the single reactant species as in the latter process.

(17) For the $(Cp\text{-}Me_5)_2Fe^{+/0}$ couple, ν^{ox}_{is} and ν^{red}_{is} apparently occur at about 170 cm^{-1}.[18] Assuming, as for the $Cp_2Fe^{+/0}$ couple, that the ring can be treated as a single vibrating unit leads to a force constant $f_r \approx 2.3 \times 10^5$ dyn cm^{-1}. These somewhat smaller force constants derived for the decamethyl derivative are surprising, however, since almost identical values are anticipated from some theoretical considerations.[19] Attempts to evaluate ν^{ox}_{is} and ν^{red}_{is} for $(Cp\text{-}Me_5)_2Co^+$ and $(Cp\text{-}Me_5)_2Co$ were thwarted by fluorescence and compound air instability, respectively.[20]

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Cp_2Fe^+.[29] The highly metal-localized nature of the HOMO for ferrocene is strikingly apparent when viewed in pictorial form.[30] For cobaltocene, by comparison, the HOMO is distinctly more ligand centered and therefore delocalized; $X\alpha$[28a] and LCAO–HFS[28b] calculations identify this as the singly-occupied $4e_{1g}$ orbital with only around 50–55% metal character, in harmony with ESR observations for cobaltocene.[31]

Since the lowest *unfilled* molecular orbital (LUMO) on the oxidized reactants, ferrocenium and cobaltocenium, corresponds to the same orbital assignment as on the corresponding reduced species,[27a,b,28] we deduce that the extent of donor–acceptor orbital overlap for the Cp_2Co^+–Cp_2Co reaction will be greater than for the Cp_2Fe^+–Cp_2Fe exchange within a given internuclear geometry. A complication, however, arises from the relaxation in electron distribution which occurs for these systems upon removal of an electron from the HOMO; this reflects the multielectron screening of the formal metal charge and leads to relatively small and similar increases in the net metal charge upon the oxidation of both Cp_2Fe and Cp_2Co.[27a,28a] The implications of this "charge relaxation effect" upon the degree of electronic coupling have recently been addressed.[24a] However, this effect is expected only to modify rather than to eliminate the enhancement of H_{12} and hence $K_p\kappa_{el}$ that is predicted for Cp_2Co^+–Cp_2Co relative to Cp_2Fe^+–Cp_2Fe self-exchange. The substantially larger k_{ex}^h values for the former reaction can therefore be understood at least qualitatively on this basis.

The effect of methylation of the Cp rings upon k_{ex}^h for these reactions is also consistent with such electronic considerations, even though such comparisons between reactant systems having different geometric as well as electronic structures suffer from greater ambiguity than where $Cp_2Co^{+/0}$ and $Cp_2Fe^{+/0}$ [or $(Cp\text{-}Me_5)_2Co^{+/0}$ and $(Cp\text{-}Me)_2Fe^{+/0}$] are compared. Although detailed theoretical presentations involving individual orbitals are unavailable, LCAO–SCF calculations predict that the net electron density on the Cp ring is increased markedly by methylation.[32] A similar deduction has been made on the basis of NMR data for cobaltocenium[33a] and ferrocene,[33b] and also from photoelectron spectra.[34] Although it is difficult to infer from such information the desired effect upon the orbital involved in electron transfer, it nonetheless seems reasonable to anticipate a larger donor–acceptor orbital overlap, and hence larger κ_{el}, resulting from ring methylation.

The relative k_{ex}^h values for the four metallocene self-exchange reactions considered here are therefore nicely consistent with electronic overlap considerations, especially for $Cp_2Co^{+/0}$ versus $Cp_2Fe^{+/0}$, for which detailed electronic structures are available. Given the metal-centered nature of the redox orbitals for $Cp_2Fe^{+/0}$, one can envisage that the internuclear geometries leading to reaction would be restricted to those with the reactants approaching along a common fivefold axis, where some direct metal-metal orbital overlap is most likely to be achieved. As noted above, such a "geometric" limitation on the electron-transfer rate via the extent of orbital overlap and hence upon κ_{el} can be viewed as arising from correspondingly smaller *effective* K_p values than expected from the spherical reactant model (i.e., from eq 3). Thus instead of employing a radial distribution function, an orientation-dependent K_p, $K_p(\theta)$, is envisaged whereby only certain zones, θ, on the reactant surfaces provide sufficient orbital overlap to contribute significantly to the overall reaction rate. This interpretation is indeed consistent with the detailed solvent-dependent kinetics of these reactions.[2] Such a sensitivity of the orbital overlap to the reactant orientation has been considered occasionally in theoretical treatments.[8,35] Compared to $Cp_2Co^{+/0}$, therefore, the tenfold smaller k_{ex}^h value for $Cp_2Fe^{+/0}$ can be viewed as arising from the smaller probability of forming internuclear reactant configurations with sufficient donor–acceptor orbital overlap to contribute importantly to electron transfer.

The comparison of k_{ex}^h for these two reactions with that for $(C_6H_6)_2Cr^{+/0}$ is also of interest. Semiempirical and $X\alpha$ calculations[36] indicate that the HOMO of $(C_6H_6)_2Cr$ is a metal-localized $8a_{1g}$ orbital, although a substantially delocalized $4e_{2g}$ orbital lies close in energy and has been assigned as the HOMO on the basis of CNDO and SCF calculations.[37] However, given the relatively rapid self-exchange of $(C_6H_6)_2Cr^{+/0}$, the k_{ex}^h being intermediate between $Cp_2Co^{+/0}$ and $(Cp\text{-}Me_5)_2Co^{+/0}$ (Table I), one would expect that substantial donor–acceptor orbital overlap is nevertheless achieved. Indeed, on the basis of INDO–SCF calculations, $4e_{2g}$ orbitals are predicted to be only slightly lower in energy than the $8a_{1g}$ for $(C_6H_6)_2Cr^+$; moreover, these orbitals are increasingly degenerate for the larger Cr–ring bond distances[38] that would be appropriate for the Cr(I)/(0) transition state. The likely involvement of the ligand-delocalized $4e_{2g}$ orbital in the electron transfer may therefore account for the facile kinetics observed for this reaction.

In addition to examining the variations in k_{ex}^h with metallocene structure in comparison with the theoretical expectations, it is also informative to explore experiment–theory comparisons for the individual rate constants themselves.[8,25] Table I contains such theoretical estimates of k_{ex}^h, labeled k_{ex}^{th}, for each of the metallocene couples and $(C_6H_6)_2Cr^{+/0}$ in acetonitrile and dimethyl sulfoxide. These estimates were calculated essentially as described in ref 1b, using eq 1. (See the table footnotes and Table V of ref 1b for details.) Thus the ν_n values were obtained from the "overdamped" solvent relaxation model using eq 9 of ref 1b. (Note that the numerical value of ν_n should be relatively insensitive to the extent of donor–acceptor electronic coupling.[39]) The reactant radius is taken as 3.8 Å in each case, and K_p is calculated from eq 2 with $r = 7.6$ Å (i.e., twice the reactant radius) and $\delta r = 0.6$ Å, yielding $K_p = 0.26$ M^{-1}. The small difference between the k_{ex}^{th} values in Table I for the different systems in a given solvent arises from the slightly different estimates of ΔG^*_{is} (vide supra).

Comparison between the corresponding values of k_{ex}^h and k_{ex}^{th} in Table I shows that the experimental values are significantly smaller than the theoretical estimates only for $Cp_2Fe^{+/0}$. This finding that $k_{ex}^h < k_{ex}^{th}$ is suggestive of nonadiabatic (i.e., case 2) behavior for this system since the latter values are derived by presuming that $\kappa_{el} = 1$ (i.e., that adiabaticity is achieved, albeit with a small "reaction zone thickness", $\delta r = 0.6$ Å). The comparable or larger values of k_{ex}^h relative to k_{ex}^{th} observed for the other metallocene reactions (Table I) might be inferred as signaling the onset of reaction adiabaticity for these systems. If this is so, this would not be consistent with the above assertion that the observed rate variations are due primarily to electronic coupling factors. However, the observation that $k_{ex}^h > k_{ex}^{th}$ for $(Cp\text{-}Me_5)_2Co^{+/0}$ is more likely to be due to systematic uncertainties in the theoretical estimates of ν_n, ΔG^*_{os}, and/or K_p. (This issue is addressed in detail elsewhere.[2])

As noted above, in contrast to these homogeneous self-exchange processes the rate constants for the corresponding electrochemical exchange reactions at mercury electrodes display virtually no sensitivity to the metallocene structure.[1b,40] The simplest in-

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terpretation of this disparate behavior is that the electrochemical reactions involve sufficiently strong electronic coupling so that adiabaticity is achieved in each case; i.e., case 1 behavior is obtained. There are some indications from other measurements that electrochemical reactions can be markedly nonadiabatic, at least for surface–reaction site distances greater than ca. 6–8 Å.[23,41] On the other hand, there is evidence that simple outer-sphere electrochemical processes involving small metal complexes in aqueous media are more adiabatic than for the corresponding homogeneous-phase reactions.[25] Although the precursor-state geometries for such outer-sphere electrochemical processes are not known precisely, it is not unreasonable to envisage the reactant to lie suitably close to the surface so that adiabaticity is achieved. This would especially be the case if the reactant is able to at least partly penetrate the "inner layer" of solvent molecules adjacent to the metal surface.

Despite such uncertainties, the present results provide unusually direct evidence for the importance of orbital-overlap factors in outer-sphere redox reactivity. The differences in k^{h}_{ex} between the $Cp_2Fe^{+/0}$ and $Cp_2Co^{+/0}$, and the $(Cp\text{-}Me_5)_2Fe^{+/0}$ and $(Cp\text{-}Me_5)_2Co^{+/0}$, self-exchange reactions are of particular significance since these pairs of redox couples have structural properties that are otherwise virtually identical. Although such effects may well be prevalent in many other systems, they usually would remain masked by the presence of other obfuscating factors, such as large unknown variations in inner-shell barriers, work terms, and so on when the kinetics of related reactions are compared. It would be worthwhile to evaluate k^{h}_{ex} for other metallocene or arene couples featuring substituents that exert large electronic perturbations on the aromatic rings. The quantitative calculation of electronic matrix coupling elements for these systems using ab initio methods[24] would also be of considerable interest.

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Registry No. $[(Cp\text{-}Me_5)_2Co]BF_4$, 112840-73-0; $[Cp_2CO]BF_4$, 52314-53-1; $[(CpMe_5)_2Fe]BF_4$, 100021-51-0; $(Cp_2Fe)BF_4$, 1282-37-7; $[(C_6H_6)_2Cr]BF_4$, 11077-48-8; $(Cp\text{-}Me_5)_2Co$, 74507-62-3; Cp_2Co, 1277-43-6; $(Cp\text{-}Me_5)_2Fe$, 12126-50-0; Cp_2Fe, 102-54-5; $(C_6H_6)_2Cr$, 1271-54-1.

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(40) Admittedly, the electrochemical kinetics of $Cp_2Fe^{+/0}$ exchange at mercury can only be examined in a few solvents, such as acetonitrile, since the formal potential for this couple is close to, or positive of that for, mercury dissolution in most media. However, measurement of the exchange rate constant for this couple in acetonitrile under conditions as described in ref 1c yielded a value, ca. 5 cm s^{-1}, similar to that obtained for $Cp_2Co^{+/0}$.[1c]

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Infrared Vibrational Circular Dichroism in the Amide III Spectral Region of Peptides

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Abstract: The sensitivity of infrared vibrational circular dichroism (VCD) toward peptide secondary structure has been investigated previously in the amide I, II, and A spectral regions. Here, the first observation of VCD in the amide III vibration is reported in alanyl dipeptides in aqueous solution. Amide I′ and II′ spectral data for the same molecules are presented as well. Since the frequency of the amide III vibration is known to exhibit qualitative conformational sensitivity in infrared and Raman spectra, its VCD is expected to be a probe toward secondary structure as well. The VCD results observed for diastereomeric alanyl dipeptides in the 1200–1500-cm^{-1} region suggest that such a conformational sensitivity of the amide III vibration exists.

Infrared vibrational circular dichroism (VCD) has been observed in the amide I, II, and A vibrations of peptide linkages in a number of poly(amino acids) and various peptides.[1-8] In all but two[7,8] of these reports, the peptides were studied in nonaqueous media. These VCD results, particularly in the amide I region, have demonstrated the conformational sensitivity of VCD and have shown that conformational information derived from VCD is complementary to that obtained from electronic CD for certain small peptides.[5] Consequently, a new view of peptide solution conformation has started to emerge, based on VCD structural information. The structural sensitivity of VCD may be thought of as originating from the coupling of vibrational motions that are a few bonds apart and that are sampled at a very rapid time scale, since VCD is a form of vibrational spectroscopy.

In the following publication, the first observation of amide III VCD of peptides in aqueous solution is reported. The significance of this observation lies in the fact that the frequency shift of the amide III vibration (1250–1350 cm^{-1}) exhibits qualitative peptide conformational sensitivity[9] and consequently has been used to complement crystallographic and electronic CD structural information. Thus, it is likely that the amide III VCD may exhibit sensitivity toward peptide secondary structure. The problem with the amide III vibration is that it is by far less defined in terms of the atomic displacements than other vibrations of the peptide linkage, such as the amide I, II, or A modes. Furthermore, deuteriation of the amide moiety changes the composition of the

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