

Figure 2. ^{39}K NMR spectra of polycrystalline $\text{K}^+(\text{15crown5})_2\text{K}^-$ at 180 K. (Top) Static spectrum; (middle) static, ^1H decoupled spectrum; (bottom) MAS spectrum with ^1H decoupling. All spectra were obtained with 3200 acquisitions and have 60-Hz exponential broadening.

Table I. ^{39}K MAS-NMR Chemical Shifts and Line Widths of Polycrystalline Potassides and Simple Potassium Salts

compound	δ , ppm from $\text{K}^+(\text{aq})^a$	$\Delta\nu_{1/2}$, Hz
KCl	+46.7 (5)	28
KBr	+54.5 (5)	20
$\text{K}^+(\text{15crown5})_2\text{K}^-$	-105 (1)	70
$\text{Rb}^+(\text{15crown5})_2\text{K}^-^b$	-105 (2)	120
$\text{Cs}^+(\text{15crown5})_2\text{K}^-$	-105 (5)	220
$\text{KRb}(\text{18crown6})_2^b$		no signal
$\text{Cs}^+(\text{18crown6})_2\text{K}^-$	-115 (10)	150

^aUncertainty of the last digit given in parentheses. ^bProbably contain both K^- and Rb^- as indicated by rubidium XANES.²³

chemical shift (-105 ppm, within experimental error) is the same as that calculated for gaseous K^- . The line widths increase with cation size in $\text{M}^+(\text{15-crown-5})_2\text{K}^-$, suggesting stronger cation-anion interactions.

Possibly the absence of a signal for $\text{KRb}(\text{18-crown-6})$ results from strong Rb^+-K^- interactions. The presence of K^- in samples of this composition is suggested from rubidium XANES studies²³ that show the presence of both $\text{Rb}^+(\text{18-crown-6})$ and Rb^- .

The ^{39}K NMR studies of K^- both in solution and in potasside crystals show that K^- is a "genuine" anion with two electrons in the 4s orbital that shield the 3p electrons from appreciable interaction with the surroundings. Thus, K^- , as Na^- , shows no chemical shift from the gaseous anion. Previous studies show, however, that Rb^- and Cs^- are shifted paramagnetically from the corresponding gaseous anion.^{4,11,13} This could be caused by less effective shielding of p and/or d electrons by the outer s electrons or by an admixture of p or d character with the ground-state s wave function.

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Note Added in Proof. K^- was recently observed by ^{39}K NMR in solutions of $\text{KCs}/\text{12-crown-4}$ in tetrahydrofuran.²⁴

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Gas-Phase Electron Transfer: Kinetics of Metallocene Self-Exchange Reactions

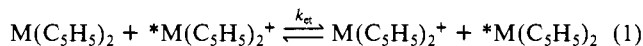
John R. Eyley* and David E. Richardson*

Department of Chemistry, University of Florida
Gainesville, Florida 32611

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Considerable insight into the kinetics and thermodynamics of chemical processes in solution can be provided by direct study of analogous processes in the gas phase. In this way, factors intrinsic to the molecular species involved can be separated from contributions of the solvent, which can markedly alter (or even reverse) trends observed in the gas phase. The vast majority of such comparisons made thus far involve organic systems,^{1,2} but we recently have begun to investigate reactions at metal centers for which direct solution/gas-phase comparisons should be possible. In this report, the kinetics of self-exchange electron-transfer reactions for four metallocenes are considered, and evidence for the observation of intrinsic kinetic barriers is presented.

The contribution of the solvent to activation barriers for electron transfer is known to be significant³⁻¹⁰ and is often the dominant term for reactions of charged complexes. The total free energy of activation is given theoretically by $\Delta G^*_{\text{tot}} = \Delta G^*_{\text{in}} + \Delta G^*_{\text{out}} + w_r$, where w_r is the work required to bring the reactants together forming the precursor complex, ΔG^*_{in} is the inner barrier presented by the necessary internal reorganization of the reactants, and ΔG^*_{out} is the outer barrier due to reorganization of the solvent.^{3,4,8,9} For self-exchange reactions of the metallocenes (1) where one



reactant is uncharged, the term w_r is negligible. We have initiated studies of gas-phase electron-transfer reactions involving metal centers to provide data necessary to evaluate ΔG^*_{in} directly and, in principle, allow more detailed evaluation of results for solution studies.

The self-exchange reactions of metallocenes are well suited for these initial studies, as they can be examined in solution by a variety of techniques such as NMR,^{11,12} EPR,¹³ isotopic tracers,¹⁴ electrochemistry,^{15,16} and pseudo-self-exchange.^{17,18} By far the best characterized is ferrocene/ferrocenium,^{19,20} for which a

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Table I. Results for Gas-Phase Self-Exchange Reactions of Metallocenes

reactants	$r_0, \text{\AA}^a$	$r_+, \text{\AA}^a$	$\Delta E_{in}^*, \text{ kcal/mol}^c$	k_L^f	k_{et}^g	efficiency ^h
MnCp ₂ ^{0/+}	2.04 ^b	1.80 ^c	8.7	1.05×10^{-9}	6.3×10^{-12}	0.006
FeCp ₂ ^{0/+}	1.666 ^b	1.706 ^b	0.34	1.05×10^{-9}	1.3×10^{-10}	0.12
CoCp ₂ ^{0/+}	1.733 ^b	1.622 ^d	2.5	1.04×10^{-9}	3.7×10^{-10}	0.36
RuCp ₂ ^{0/+}	1.827 ^f			9.0×10^{-10}	1.2×10^{-10}	0.13

^a Estimated distances from metal to center of Cp in neutrals (r_0) and ions (r_+). ^b Reference 19. ^c Estimated from chromocene structure.¹⁹ ^d Estimated from distances in [(C₅H₅)(C₅H₄COOH)Co]PF₆ (Riley, P. E.; Davis, R. E. *J. Organomet. Chem.* **1978**, *152*, 1978). ^e Estimated using $\Delta E_{in}^* = f_0 f_+ (\Delta r)^2 / (f_0 + f_+)$,^{6,7,24} where f_0 and f_+ are the estimated M-Cp force constants¹⁹ and $\Delta r = r_0 - r_+$. ^f Langevin collision frequency ($\text{cm}^3 \text{molecules}^{-1} \text{s}^{-1}$).²³ The polarizability of ferrocene was used in all cases. ^g From eq 2 in text ($\text{cm}^3 \text{molecules}^{-1} \text{s}^{-1}$). Rates determined at $\sim 375 \text{ K}$. ^h Efficiency = k_{obsd}/k_L . ⁱ Haaland, A.; Nilson, J. E. *Acta Chem. Scand.* **1968**, *22*, 2653.

self-exchange rate, (1), of $\sim 6 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ has been determined by NMR (in CD₃OD at 298 K)^{11,12} and pseudo-self-exchange methods.^{17,18} We have studied the gas-phase self-exchange rates for ferrocene, ruthenocene, cobaltocene, and manganocene with their corresponding cations using Fourier transform ion cyclotron resonance mass spectrometry. By use of the double resonance technique, one or more isotopes of the parent ion are ejected from the cell thereby leaving isotopically "enriched" cations to react with the neutrals present in their natural isotopic abundancies. Related ICR studies of metallocenes have been reported,²¹ but the self-exchange processes were not investigated.

The ratios of the parent ion peaks were established for various reaction times and second-order rate constants were derived from eq 2, where a_0 and a_0' are the fractional natural abundancies of

$$\ln \left[\frac{R_t - (a_0'/a_0)}{R_t + 1} \right] = -k_{et} P t \quad (2)$$

the ejected and nonejected isotopes, respectively ($a_0 = 1 - a_0'$), R_t is the value of a'/a detected at time t after ejection, and P is the total pressure of reactants during the reaction.²²

Results for the four metallocenes are summarized in Table I along with theoretically estimated values of the inner reorganization barrier ΔE_{in}^* and the Langevin collision rate k_L .²³ In three of the ion-neutral reactions studied here, the estimated efficiencies are somewhat lower than the maximum 0.5, but the manganocene-manganocenium reaction is substantially slower than the others.

A useful qualitative picture for the appropriate gas-phase potential energy surface for these reactions would be similar to the double-well potential used extensively by Brauman and others to interpret gas-phase nucleophilic displacement reactions² and proton transfers.^{1a,c} The central barrier would derive from ΔE_{in}^* and the potential minima result from stabilizing ion-molecule interactions.²⁴

It is possible that the much lower efficiency of the MnCp₂^{+/0} self-exchange results from the relatively higher reorganizational barrier (ΔE_{in}^*) for changing the M-C bond lengths in the neutral-ion interconversion (Table I). The dimensions of the neutral metallocenes are known from gas-phase electron-diffraction studies,¹⁹ and manganocene has unusually long M-C bonds due to its high-spin d⁵ electronic configuration. Unfortunately, no crystal structure or spectroscopic data for the manganocenium ion is available, but the predicted ground state is a low-spin d⁴ electronic configuration.²⁵

Another possible reason for the low efficiency of the Mn(Cp)₂^{+/0} self-exchange is the nature of spin multiplicities in the reactants. The direct exchange between the ⁶A ground state of manganocene

and the predicted ³E or ³A ground state^{25,26} of the manganocenium ion is forbidden. The coupling of these states must rely on spin-orbit mixing with higher lying states, as described for the [Co(NH₃)₆]^{3+/2+} exchange reaction²⁷ and spin-equilibrium processes.²⁸ At this point, the contribution of nonadiabaticity to the Mn(Cp)₂^{+/0} reaction cannot be assessed because of the absence of spectroscopic data for the reactants.

The present results are consistent with a relatively small barrier for ferrocene, cobaltocene, and ruthenocene self-exchange due to molecular reorganization and the predominance of ΔG_{out}^* in their solution self-exchange kinetics.^{15,16} For example, the rate for FeCp₂^{+/0} is a factor of $\geq 10^4$ faster in the absence of solvent. On the other hand, a significant contribution from ΔG_{in}^* in analogous manganocene reactions is expected. We are exploring other gas-phase redox reactions to define the proper theoretical basis for quantifying the values of ΔE_{in}^* .

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Direct Measurements of Rate Differences among Nuclear Spin Sublevels in Reactions of Biradicals¹

G. L. Closs* and O. D. Redwine

Department of Chemistry, The University of Chicago
Chicago, Illinois 60637
Chemistry Division, Argonne National Laboratory
Argonne, Illinois 60439
Received May 3, 1985

Ever since the formulation of the radical pair theory of CIDNP² it has been accepted that in radical pairs and certain biradicals different nuclear spin states may exhibit different reaction kinetics. However, direct measurements of the kinetics describing population differences of individual nuclear sublevels have never been reported, presumably because nuclear states are hard to resolve optically and NMR measurements are considered too slow to give the necessary temporal resolution. In this paper we wish to report the first such measurement employing our time-resolved CIDNP technique.³

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