1130 *Inorg. Chem.* **1990**, *29*, 1130–1132

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Electron Self-Exchange of the Dicyclopentadienylnickel(II,III) Couple in Dichloromethane

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Received August 3, 1989

Electron transfer has been observed between dicyclopentadienylnickel(II) (nickelocene) and dicyclopentadienylnickel(III) (nickelocenium) in dichloromethane by the nuclear magnetic resonance line broadening technique. The rate constant for this electron-self-exchange reaction is 2.1×10^8 M^{-1} s^{-1}, extrapolated to 25 °C from lower temperatures. The enthalpy of activation is low at 6.9 ± 0.5 kJ/mol, and the entropy of activation is -63 ± 2 J/(mol·K). Attempts to measure the electron exchange in other solvents gave ambiguous NMR signals. The rate constant for electron self-exchange in decamethylnickelocene and decamethylnickelocenium was also observed and is estimated to be approximately an order of magnitude larger than for the unsubstituted complex. These results support recent interpretations of trends for electron-transfer reactions between metallocenes based upon changes in metal character of the highest occupied molecular orbital of the reductant.

Introduction

Metallocenes and their derivatives have been the subject of extensive study since the original synthesis of dicyclopentadienyliron(II), or ferrocene ($\mathrm{FeCp_2}$), in 1951.[1] The nuclear magnetic resonance (NMR) shift of nickelocene ($\mathrm{NiCp_2}$) was reported in 1957 and was the first example of the phenomenon now known as a contact shift.[2] The electron-self-exchange rate constant (k_{11}) of the ferrocene–ferrocenium couple ($\mathrm{FeCp_2^{0/+}}$) was the first to be measured for any metallocene, and this was accomplished through the use of the NMR line broadening technique.[3] This approach has now been extended to include measurement of k_{11} values for cobaltocene ($\mathrm{CoCp_2}$), decamethylferrocene ($\mathrm{FeCp'_2}$), and decamethylcobaltocene ($\mathrm{CoCp'_2}$) as well. In contrast, while nickelocene has been used in other kinetic studies,[1i,4] its k_{11} value has not been reported.

Recent work has exposed a pattern in the reactivities of the iron and cobalt metallocenes and in their decamethyl derivatives.[5] It was observed that the $\mathrm{CoCp_2^{0/+}}$ couple consistently gives a k_{11} about 10-fold higher than the $\mathrm{FeCp_2^{0/+}}$ couple in various solvents and that the same pattern is present in their decamethyl counterparts. Furthermore, the decamethyl derivatives had k_{11} values 10-fold higher than the unsubstituted complexes of the same metal ions. The trend upon changing metal centers was attributed to the lessening of the metal character of the highest occupied molecular orbital (HOMO) and, thus, to the delocalization of the highest energy electron into a more spacially diffuse, ligand-centered, e_{1g} orbital. This investigation of the electron self-exchange in the nickelocene–nickelocenium couple ($\mathrm{NiCp_2^{0/+}}$) and in their decamethyl derivatives ($\mathrm{NiCp'^{0/+}_2}$) provides an opportunity to study the factors that influence self-exchange rates. New k_{11} values from this work can be used, through Marcus theory, to calculate apparent cross-reaction rate constants[6] or to predict other k_{11} values not experimentally observable.[7] This study also presents new data to assess the validity of the proposed cause for the trend in metallocene rate constants as the metal center is varied.

Experimental Section

Reactants and Solvents. Nickelocene was purchased from Aldrich Chemical Co. and sublimed once at 0.3 mmHg and 40 °C. It was characterized by visible spectroscopy performed under a constant pressure of argon. Maxima at 690 and 434 nm were confirmed.[8] The NMR signal of the compound also agreed with the known value.[9]

The nickelocenium salt $[\mathrm{NiCp_2}]\mathrm{BF_4}$ was synthesized in small batches under argon within 72 h of use by dissolving $\mathrm{NiCp_2}$ in a minimum of $\mathrm{CH_2Cl_2}$ and adding a 5% stoichiometric excess of ferrocenium as the tetrafluoroborate salt, $[\mathrm{FeCp_2}]\mathrm{BF_4}$. The brown solution of approximately 20 mL was filtered to remove excess oxidant, and its volume was reduced to approximately 3 mL by rotary evaporation. Small, shiny, black crystals were quickly filtered from solution, washed with cold $\mathrm{CH_2Cl_2}$ and then anhydrous ether, and placed under vacuum for several hours.

Decamethylnickelocenium was purchased from Strem Chemicals and used as received. Attempts to produce the tetrafluoroborate salt of the permethylated compound, $[\mathrm{NiCp'_2}]\mathrm{BF_4}$, by the method of Robbins[10] failed. After other routes to the pure compound were explored,[11] $[\mathrm{FeCp_2}]\mathrm{BF_4}$ was used as both the oxidant and the counterion source, as described above for $[\mathrm{NiCp_2}]\mathrm{BF_4}$, except that precipitation of the product was induced by addition of an equal volume of hexane to the $\mathrm{CH_2Cl_2}$ solution and subsequent removal of the lower boiling solvent under vacuum until a fine brown solid formed. The product was removed, washed with cold hexane, and dried under vacuum. The resulting solid showed four proton NMR peaks: a major peak at 106 ppm and three minor peaks at 111, 83, and 56 ppm versus tetramethylsilane, TMS. The relative sizes of the peaks varied slightly in each preparation, but all peaks persisted. A small-scale recrystallization from acetone as described by Robbins[10] produced no usable compound even after several attempts. The impure product was used. The peaks of the impurities were not observed in the spectra of the $\mathrm{NiCp'^{0/+}_2}$ mixtures. From this fact and their chemical shifts, the impurities were taken as Ni(III) species, which exchanged an electron with $\mathrm{NiCp'_2}$, thus "disappearing" into the noise in the NMR base line. A correction was applied to both reactant concentrations to account for the presence of impurities.

All nickel compounds were stored in sealed containers that were alternately evacuated to 0.3 mmHg and then filled to 1 atm with argon a minimum of three times. All syntheses and sample preparations for nickel compounds were performed in a glovebag carefully evacuated and then filled with argon a minimum of three times before exposure of reactants. A positive pressure was maintained in the bag during all operations. The only exposure of compounds to air was the weighing of the oxidized species for sample preparations. Conventional 5-mm NMR tubes were employed with septa to maintain gastight seals after removal

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from the glovebag. This procedure produced results comparable to those in a trial using a Dri-Lab glovebox from Vacuum Atmospheres.

Deuterated solvents of >99% purity were purchased in ampules from MSD Isotopes and were used as received. Solvent was degassed prior to use by three freeze-pump-thaw cycles.

Stability and Material Preparation. Preliminary work indicated that all reagents were sensitive to air in solution and as solids to varying degrees. The stability of all but the $NiCp'_2$ solid was great enough, however, to permit weighing at ambient conditions. Masses were obtained by using a Cahn gram electrobalances, and samples were immediately sealed in airtight containers as described above. The compounds were exposed to air at no other time. No difference in chemical shift or line width was observed for samples prepared by this method and trial samples prepared by weighing under argon.

Amounts of the very air-sensitive $NiCp'_2$ compound in mixtures of the two oxidation states were calculated from the NMR peak position (ν_{23}), the observed chemical shifts of the pure $NiCp'_2$ (ν_2) and $[NiCp'_2]BF_4$ (ν_3) compounds, and the weight of $[NiCp'_2]BF_4$ by using eq 1, where χ_i is the

$$\nu_{23} = \chi_2\nu_2 + \chi_3\nu_3 \qquad (1)$$

mole fraction of the Ni^{i+} complex.

Stability of the pure nickelocenes and their mixtures was observed in acetonitrile (CD_3CN), acetone ($(CD_3)_2CO$), nitromethane (CD_3NO), and methylene chloride (CD_2Cl_2). $NiCp_2$ was insoluble in carbon tetrachloride (CCl_4). Only in CD_2Cl_2 were the signals of pure and mixed compounds observed to be stable over the several hours required for a temperature dependence study.[11]

Nuclear Magnetic Resonance Data. NMR data were collected by using a Nicolet NT200WB instrument operating at 200 MHz. The unusual chemical shifts of the various compounds (+400 to −450 ppm vs TMS) required wide sweep widths. Peak positions were confirmed by varying sweep widths and reference frequencies to obtain consistent shifts. Low signal-to-noise ratios dictated the use of a wide variety of acquisition parameters; typical conditions are ±62 500-Hz sweep width, 8–15 000 acquisitions, 8K or 16K real data points, 65–130-ms acquisition time, and a 45° pulse angle.

The temperature control for the Nicolet instrument is of standard gas-flow type and has been described previously.[12] The chemical shifts of the pure compounds were determined between −90 and +30 °C. Mixtures of oxidation states were observed over the same temperature range. Temperature was calculated from the method of Van Geet[13] as modified by Raiford[14] and corrected to accommodate the 200-MHz instrument. In some cases, a sealed capillary of acidified CH_3OH in the sample tube was observed. In other trials, especially those involving the $NiCp'_2{}^{0/+}$ mixtures, a separate standard tube was used. Here, CH_3OH was observed just before or after each temperature trial of a mixture. Both methods gave accuracies of ±1 °C with precisions of ±0.5 °C. Shifts and widths of all pure compounds were independent of concentration over the range used for this work.

Data Analysis. Line widths and chemical shifts for all pure compounds were determined with a least-squares-fitting program available on the Nicolet instrument. Data were fit to a Lorentzian function to minimize χ^2. Typically, 100–200 points were fit at each temperature, and in all cases excellent fits were obtained. Line widths and chemical shifts as functions of temperature or its inverse were then fit to linear or quadratic equations, and again, excellent fits occurred for all compounds. These fit lines were then used to interpolate to the temperatures measured in the appropriate Ni(II)/Ni(III) mixtures. This process yielded chemical shifts and widths for the pure compounds at temperatures of interest.

The second-order rate constant for a simple, bimolecular electron-self-exchange mechanism was determined by using the line-fitting program previously described[12] with minor adaptations to accommodate the metallocene data. Supplementary Figures 1 and 2 show typical spectra and fit results. Error is taken as 5% for the nickelocene system. For the permethylated derivative, error is discussed below. Activation parameters and their errors were derived by linear least-squares methods.

Results

Values of the chemical shifts and widths for the single proton resonances of pure $NiCp_2$, $NiCp_2{}^+$, and $NiCp'_2$ and the major proton peak of $NiCp'_2{}^+$ as a function of temperature are given in Supplementary Tables 1 and 2. A large change was observed in both the shift and width of each compound.

Rate constants for the nickelocene–nickelocenium self-exchange are listed by temperature and reactant concentration in Supplementary Table 3 and shown in Figure 1. The best fit to these data yields a self-exchange rate constant of 2.1×10^8 M^{-1} s^{-1} at 25 °C, an enthalpy of activation (ΔH^*) of 6.9 ± 0.5 kJ/mol, and an entropy of activation (ΔS^*) of −63 ± 2 J/(mol·K). Results of the $NiCp'_2{}^{0/+}$ kinetic trials indicate an increase in k_{11} of approximately a factor of 5 over the $NiCp'_2{}^{0/+}$ value, or approximately 1×10^9 M^{-1} s^{-1} at 25 °C.[9]

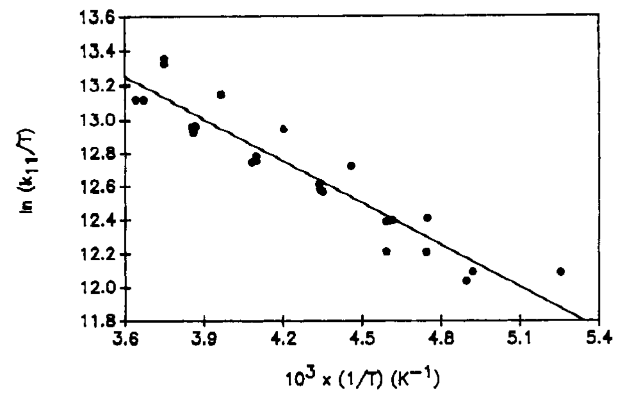

Figure 1. Dependence on temperature of the self-exchange rate constant for the nickelocene–nickelocenium couple in dichloromethane. The data represent three series, with $[NiCp_2]$ = 10.9, 7.96, and 12.0 mM and $[(NiCp_2)BF_4]$ = 9.01, 4.34, and 20.4 mM, respectively.

Table I. Solvent Dependence of Metallocene Self-Exchange Rate Constants

	$10^{-7}k_{11}$, M^{-1} s^{-1}				
solvent[a]	$FeCp_2$[b]	$CoCp_2$[c]	$NiCp_2$[d]	k_{Co}/k_{Fe}	k_{Ni}/k_{Co}
CD_3CN	0.53	4.2		7.9	
$(CD_3)_2CO$	0.46	2.1		4.6	
CD_2Cl_2	0.43	9.8	22	23	2.2
$(CD_2Cl)_2$	0.43	6.9		16	
DMSO	0.16	2.6		16	
CH_3OH	0.6	7.9		13	

[a] Solvents in order listed are the deuterated forms of acetonitrile, acetone, methylene chloride, ethylene dichloride, dimethyl sulfoxide, and methanol. [b] From ref 16. [c] From ref 17. Values taken from this work are corrected here as suggested in ref 5 to adjust to the condition of no added electrolyte. [d] From this work.

Discussion

The observed self-exchange rate constant for outer-sphere electron transfer in $NiCp_2{}^{0/+}$ is among the highest measured to date. The enthalpy of activation is low at 6.9 kJ/mol. The rate constant for intermolecular quenching of excited-state porphyrins by anthraquinone in CH_2Cl_2 has been measured[15] as 8.9×10^9 M^{-1} s^{-1}, and the value of ΔH^* measured in the present work is below that predicted for diffusion.[11] Therefore, the similarity of the rate constant measured here and previously[11] for substituted chromium isocyanide complexes is considered coincidental.

Recent work has uncovered a pattern in the electron-transfer rate on changing from the iron to the cobalt metallocenes.[5] As shown in Table I, the cobaltocene self-exchange is from 4 to 23 times faster than that of ferrocene in the same solvents. The same study found this rate increase also present in the permethylated forms of the two metallocenes.

After considerable experimental and theoretical investigation of the electronic structures of the metallocenes, a molecular orbital diagram as shown in Figure 2 has been developed for the energy levels surrounding the HOMO–LUMO orbitals of interest here.[18-20] While the orbital splitting in this figure is not a

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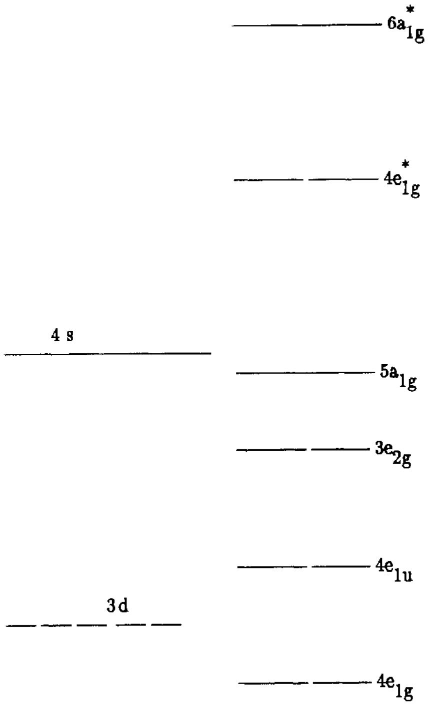

Figure 2. Molecular orbital diagram for orbitals at energies near those of the HOMO–LUMO pair in ferrocene, cobaltocene, and nickelocene. The data are taken from refs 18 and 20.

quantitative representation of the energies of the molecular orbitals (MO's), it gives a reasonable qualitative picture of the MO placements with respect to the valence metal orbitals. In the ground state of $FeCp_2$, all MO's are filled up to and including the $5a_{1g}$ HOMO with two spin-paired electrons. In $CoCp_2$, one additional electron is found in a $4e_{1g}^*$ orbital, and in $NiCp_2$, one unpaired electron is found in each of the $4e_{1g}^*$ orbitals. Some reordering of the energies occurs from electronic relaxation upon oxidation,[18,19] but this effect is only expected to modify the electronic interaction between the two oxidation states slightly.[5]

Detailed studies of the molecular orbitals in Figure 2 agree that the major metal–ring covalent bonding comes from interactions in the $4e_{1g}$ orbital with approximately equal contributions from metal and from ligand orbitals. The $4e_{1u}$ orbital is essentially a ligand-centered orbital of π symmetry. The $3e_{2g}$ and $5a_{1g}$ orbitals lie close in energy and are highly metal centered as described below. The $4e_{1g}^*$ orbital has considerable ligand contribution and is the antibonding partner to the strongly bonding $4e_{1g}$ orbital discussed earlier.[18] For $CoCp_2$ and $NiCp_2$, the electrons in this antibonding orbital are extensively delocalized onto the ligand rings.[19]

Attempts were made to investigate this pattern further. First, the $NiCp_2^{0/+}$ system was observed in CD_3CN, $(CD_3)_2CO$, and CD_3NO_2. Ambiguous signals were observed for the pure compounds in all of these solvents.[11] Next, on the basis of the same observed pattern for $FeCp'_2$ and $CoCp'_2$,[5] $NiCp'_2$ was observed in dichloromethane. Data from the earlier studies show that the ratio of the cobaltocene k_{11} to the ferrocene k_{11} is 11 in both acetonitrile and acetone.[16,17] The cobalt value has not been reported in CD_2Cl_2, but if the increase for the permethylated complex is similar to that observed in Table I for the unsubstituted compound, then the value of the $CoCp'_2{}^{0/+}$ rate constant is calculated to be 5×10^8 M^{-1} s^{-1}. On the basis of this value and the same rate of increase as observed for the $NiCp_2^{0/+}$ electron exchange in CD_2Cl_2, k_{11} for the electron transfer in $NiCp'_2{}^{0/+}$ is calculated to be 1×10^9 M^{-1} s^{-1}.

Studies of the $NiCp'_2{}^{0/+}$ couple were difficult both because of the problem of purity and because of oxidation of $NiCp'_2$. The data that gave the most consistent picture yielded a rate constant approximately 10-fold higher than the unsubstituted compound, or about 1×10^9 M^{-1} s^{-1}.[9] Although these data are not of the same quality as those for the $NiCp_2^{0/+}$ system, they can be taken as some support for continuation of the trend observed in $FeCp'_2{}^{0/+}$ and $CoCp'_2{}^{0/+}$.

Conclusion

Electron transfer has been observed between nickelocene and nickelocenium in CD_2Cl_2 by the NMR line broadening technique. The self-exchange rate constant has been measured as 2.1×10^8 M^{-1} s^{-1} at 25 °C. The reaction has a low ΔH^* of 6.9 ± 0.5 kJ/mol and a ΔS^* of -62 ± 2 J/(mol·K). An estimate of the observed k_{11} value for electron transfer in the decamethyl derivative is 1×10^9 M^{-1} s^{-1}. These results support a recent suggestion that the increase in electron-self-exchange rate constants on moving from iron metallocenes to cobalt metallocenes is attributable to an increase in orbital overlap resulting from a lessening of the metal contribution to the highest occupied molecular orbital.

Supplementary Material Available: Tables of temperature dependences of NMR chemical shifts and line widths and of k_{11} and figures showing NMR spectra for $NiCp_2/NiCp_2^+$ and $Ni(CpMe_5)_2/Ni(CpMe_5)_2^+$ self-exchange reactions (5 pages). Ordering information is given on any current masthead page.

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