Contribution from the Department of Chemistry,
Washington State University, Pullman, Washington 99164-4630

Nonaqueous, Outer-Sphere Electron Transfer: $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, and $\Delta V^{\ddagger}$ for a 0/2+ Charge-Type Reaction

Kim A. Anderson and Scot Wherland*

Received July 3, 1990

The kinetics of the outer-sphere electron-transfer reaction between hexakis(2,6-diisopropylphenyl isocyanide)chromium(II) tetrafluoroborate, $Cr(CNdipp)_6(BF_4)_2$, and a series of cobalt(II) clathrochelates of the type $CoL_3(BX)_2$ (L = doubly deprotonated diphenylglyoxime (dpg) or 1,2-cyclohexanedione dioxime (nox) and X = C_4H_9 or C_6H_5) have been studied as a function of the cobalt(II) concentration, temperature, pressure, and added electrolyte (tetra-*n*-butylammonium tetrafluoroborate) in acetonitrile. Second-order rate constants for all reactions vary only a factor of 12 from 1.02×10^5 to 11.7×10^5 M^{-1} s^{-1} at 298 K and an ionic strength of ca. 10^{-5} M. With the exception of the slowest reaction, these rate constants agree with the Marcus theory predictions based on previously studied reactions between the cobalt clathrochelates and ferrocenes and the directly measured electron self-exchange of $Cr(CNdipp)_6^{+/2+}$. The enthalpies of activation vary from 8 to 4 kcal/mol, and the entropies of activation vary from −8 to −17 cal/(mol K). A pattern previously observed with the cobalt complexes of increasing rate constant with increasing size, due to lowering of the outer-sphere reorganization energy, is not observed here. Increasing the Bu_4NBF_4 concentration does not affect the rate constant, a result which is in contrast to other reactions studied. Activation volumes for these reactions varied from +2 to +11 cm^3/mol at 298 K and an ionic strength of ca. 10^{-5} M. This is the first time positive volumes of activation have been measured for outer-sphere reactions that do not involve reactants of opposite charge. Increasing the $[BF_4^-]$ had little effect on the volume of activation, although a trend of slightly less positive values with increasing salt concentration was observed for the reaction of $Co(dpg)_3(BPh)_2$ with $Cr(CNdipp)_6(BF_4)_2$. Although only three different reactions were measured, a direct linear correlation between the entropy and volume of activation was observed. The results are discussed within the Marcus model and on the basis of expectations of molar volumes from intrinsic volume and electrostriction considerations.

Introduction

Outer-sphere electron-transfer reactions are of considerable interest due to their fundamental role in chemical reactions such as catalytic processes, energy conversion, and photosynthesis.[1-5] As part of our ongoing effort to understand nonaqueous electron transfer by transition-metal complexes, we have chosen to study the reduction of chromium(II) hexakis(2,6-diisopropylphenyl isocyanide), $Cr(CNdipp)_6(BF_4)_2$, by a series of cobalt(II) clathrochelates in acetonitrile as a function of concentration, temperature, pressure, and added electrolyte. Cross-reactions have been studied with $Co(dpg)_3(BPh)_2$, $Co(nox)_3(BPh)_2$, and $Co(nox)_3(BBu)_2$ where the chelating dioximes are, respectively, diphenylglyoxime and 1,2-cyclohexanedione dioxime and the caps are phenyl- or *n*-butyl-substituted borates.

There is an extensive background of information on both the physical and reactivity properties of these complexes in both oxidation states being considered. They are substitution inert and are adequately stable and soluble in acetonitrile and other solvents.[6-9] Crystal structures are available for $Co(dmg)_3(BF)_2$, $Co(dmg)_3(BF)_2BF_4$, $Co(dpg)_3(BPh)_2$, $Cr(CNdipp)_6$, $Cr(CNPh)_6(CF_3SO_3)$, and $Cr(CNPh)_6(PF_6)_2$.[10-14]

In previous work from this laboratory, we have measured the large bimolecular electron self-exchange rate constants of the $Cr(CNdipp)_6$(0/I) and -(I/II) couples directly by ^1H NMR line broadening.[15,16] The relatively low inherent reactivity of the cobalt clathrochelates makes it possible to study reactions with highly reactive compounds, such as $Cr(CNdipp)_6^{2+}$, by the stopped-flow method. The rate constants for the reactions between the cobalt clathrochelate complexes and ferrocene or one of its derivatives in acetonitrile and other solvents as a function of temperature and added salt were previously measured.[6-9] By use of Wahl's directly measured electron self-exchange rate constant for ferrocene,[17] the apparent electron self-exchange rate constants of the cobalt clathrochelate complexes were calculated. The work with the cobalt cages was continued with the examination of reactions between $Co(dpg)_3(BPh)_2$ and other cobalt clathrochelates, also as a function of temperature, solvent, and added electrolyte.[9] Recently, we have extended the study of these reactions with the measurement of the volume of activation for some of the reactions between ferrocenes and cobalt clathrochelate complexes. The influence of solvent and added electrolyte were studied, and $\Delta V^{\ddagger}$ was found to be quite sensitive to the electrolyte concentration.[18] This analysis was extended by using the volume of activation for the ferrocene self-exchange to calculate the apparent $\Delta V^{\ddagger}$ for the clathrochelate self-exchange assuming Marcus theory.

The extensive and detailed comparison of reactivity of rather simple reactants is necessary in order to reliably identify trends in this reactivity. The various properties of the reactants, such as size, shape, charge, and electronic structure, must be controlled as much as possible to isolate the factors that might contribute to variation in the reactivity so that the origin of the trends can be identified. The change in reactivity in response to variation of the conditions of the reactions, such as temperature, pressure, solvent, and added electrolyte, add more dimensions to the description of the reactions, and these responses provide much more information and are often more characteristic than a simple rate constant.

A particular concern, especially for reactions in organic solvents, is the influence on reactivity of the electrostatic interaction between reactants and between reactants and counterions. Reactions between neutral and +1 reactants to give neutral and +1 products formally eliminate the Coulombic interaction. Such reactions have been found to still be affected by added salt, and this has been attributed to the formation of ion pairs which have lower reactivity than the free ions. Examples of such behavior include the reduction of the +1 Co(III) clathrochelates by ferrocene[6-8] or $Co(dpg)_3(BPh)_2$[9] and the ferrocene self-exchange.[17] A more

---

[1] Zuckerman, J. J. *Inorganic Reactions and Methods*; Deerfield Beach, FL, 1986; Vol. 15, Chapter 12.

[2] Marcus, R. A.; Sutin, N. *Biochim. Biophys. Acta* **1985**, *811*, 265.

[3] Newton, M. D.; Sutin, N. *Annu. Rev. Phys. Chem.* **1984**, *35*, 437.

[4] Cannon, R. D. *Electron Transfer Reactions*; Butterworth: London, 1980.

[5] Sutin, N. *Prog. Inorg. Chem.* **1983**, *30*, 441.

[6] Borchardt, D.; Wherland, S. *Inorg. Chem.* **1986**, *25*, 901.

[7] Borchardt, D.; Wherland, S. *Inorg. Chem.* **1984**, *23*, 2537.

[8] Borchardt, D.; Pool, K.; Wherland, S. *Inorg. Chem.* **1982**, *21*, 93.

[9] Gribble, J. D.; Wherland, S. *Inorg. Chem.* **1982**, *21*, 93.

[10] Zakrzewski, G. A.; Ghilardi, C. A.; Lingafelter, E. C. *J. Am. Chem. Soc.* **1971**, *93*, 4411.

[11] Gribble, J. D. Ph.D. Thesis, Washington State University, 1989.

[12] Bohling, D. A.; Mann, K. R. *Inorg. Chem.* **1984**, *23*, 1426.

[13] Ljungstrom, E. *Acta Chem. Scand. A* **1978**, *32*, 47.

[14] Anderson, K. A.; Scott, R.; Willett, R. D.; Wherland, S. Submitted to *Acta Crystallogr., Sec. C*.

[15] Anderson, K. A.; Wherland, S. *Inorg. Chem.* **1989**, *28*, 601.

[16] Anderson, K. A.; Wherland, S. *Inorg. Chem.*, in press.

[17] Yang, E. S.; Chau, M. S.; Wahl, A. C. *J. Phys. Chem.* **1980**, *84*, 3094.

[18] Murguia, M. A.; Wherland, S. Submitted to *Inorg. Chem.*

complex case is electron self-exchange by $Mn(CNC_6H_{11})_6^{+/2+}$.[19-21] In this reaction a range of effects, from increasing rate constant with added electrolyte in the higher dielectric constant solvents to constant or slightly decreasing rate constant with added electrolyte in the low dielectric constant solvents, is observed. This is the expected pattern if electrostatic work and ion pairing both inhibit the reaction.

The current study is an extension of this detailed analysis to the rare case of a neutral reducing agent reacting with a dication to form singly charged products in a nonaqueous solvent. Here ion pairing should be more extensive for +2 than for +1 reactants, but the Coulombic repulsion between the products adds a complication. Such repulsion has been used in an attempt to force a separation of the products of electron transfer by a photoexcited center. These reactions typically lead to extensive reverse electron transfer by the ground-state products and thus loss of the charge separation and energy storage in the immediate products.

The general cross-reaction can be represented by eq 1.

$$CoL_3(BX)_2 + Cr(CNdipp)_6^{2+} \rightarrow CoL_3(BX)_2^{+} + Cr(CNdipp)_6^{+} \quad (1)$$

There are no reactions of analogous charge type with which to compare, but the experimental results are compared to values calculated from the electron self-exchange constants measured for Cr(I/II) and calculated for the cobalt clathrochelates along with consideration of the electrostatic effects. Both ion pairing to the $Cr(CNdipp)_6^{2+}$ and Coulombic interaction between the products would be expected to be affected by salt. Surprisingly, increasing the Bu_4NBF_4 concentration does not affect the rate constant. The origin of this effect is discussed in terms of the highly delocalized nature of π-electron acceptor orbitals on the Cr complexes.

The pressure dependence of these rate constants provides the first reported case of positive volumes of activation for an outer-sphere reaction that does not involve oppositely charged reactants.[22-24] For outer-sphere reactions such as those studied here, negative volumes of activation are typically observed:[25-27] $Co(terpyridyl)_3^{2+}/Co(bipyridyl)_3^{3+}$, −5 cm^3/mol; $Mn(CNR)_6^{+/2+}$, −2 to −22 cm^3/mol depending on R and solvent; $FeCp_2^{0/+}$, −7 cm^3/mol; Cu(2,9-dimethyl-1,10-phenanthroline)$_2^{+/2+}$, −3 to −8 cm^3/mol depending on solvent; Ru(hexafluoroacetylacetonate)$_3^{0/-}$, −6 to −8 cm^3/mol depending on solvent; Co(1,2-ethanediamine)$_3^{2+/3+}$, −20 cm^3/mol; Fe(1,10-phenanthroline)$_3^{2+/3+}$, −2 to −6 cm^3/mol depending on the medium.[28-34] We have recently measured ΔV^* for the reduction of several cobalt(III) clathrochelates by ferrocene and 1,1′-dimethylferrocene in nonaqueous solvents and as a function of added salt and obtained values in the range −4 to −15 cm^3/mol.[18] Several reactions that involve the reduction of Co(III) complexes by oppositely charged Fe(II) cyanide complexes give positive volumes of activation for the first-order electron-transfer process when this is resolved from the bimolecular association step.[35,36] The extensive charge neutralization and the rate saturation observed in these systems make them distinctively different cases. The current results are discussed in terms of a simple solvent electrostriction model as well as the Marcus model. The added electrolyte dependence of ΔV^* has also been measured, and this is compared to analogous measurements previously made.

Experimental Section

Starting materials and solvents were purchased from Aldrich Chemical Co. and Baker Chemicals. Acetonitrile for kinetic measurements was distilled under argon from P_4O_{10} and stored under argon and over 4-Å molecular sieves. The ligand 2,6-diisopropylphenyl isocyanide was prepared by literature methods.[15,37,38] $Cr(CNdipp)_6(BF_4)_2$ was prepared as described previously;[16,38] it was characterized by ^1H NMR and infrared spectroscopy.[16] All cobalt(II) compounds were prepared as described previously.[17] The cobalt compounds were characterized by infrared and visible spectroscopy and elemental analysis.[9] Tetra-*n*-butylammonium tetrafluoroborate was prepared and purified as described previously.[39,40]

All kinetic measurements were performed with the concentration of the Co(II) reactant in pseudo-first-order excess. Typical concentrations for the Cr(II) complexes were 2×10^{-5} M and for the Co(II) complexes were 2×10^{-4} to 2×10^{-3} M. Concentrations are reported at 298 K and 0.1 MPa, pressure- and temperature-independent quantities.[41,42] All reactions were followed for a minimum of 4 half-lives. For reactions where there was no added salt, the ionic strength varied slightly during the reactions. For example, if the starting ionic strength was 3×10^{-5} M, the ending ionic strength would be 2×10^{-5} M.

Ambient-pressure stopped-flow kinetics were measured on a Dionex spectrophotometer (D-110). A dual-detector accessory (D-137) was used to follow the signal, log (I_{500}/I_{450}). The absorbance at 450 nm increases, corresponding primarily to the appearance of the intense metal-to-ligand, $d\pi$ to π^*, charge-transfer band in the Cr(I) complex at 445 nm with an ϵ of 39 000 M^{-1} cm^{-1}.[43] The absorbance at 500 nm decreases due to the disappearance of both the Co(II) and the Cr(II) complexes. The Cr(II) complex has a ligand-to-metal, σ(CNR) to $d\pi^*$, band at 476 nm with an ϵ of 9000 M^{-1} cm^{-1}, which disappears in the Cr(I) complex.[43] In the Co(II) complexes there is typically a charge-transfer band at 490 nm with an ϵ of about 7000 M^{-1} cm^{-1}, which is not present in the Co(III) complex.[9] A water bath was used to control the temperature to within 0.05 K. Rate constants for the stopped-flow trials were calculated from the 2048 points digitized and stored as previously described.[6] The data were fit to a pseudo-first-order rate law by using an iterative least-squares process that varied the absorbance at infinite time to minimize χ^2. The optimized infinite time absorbance values were within the 1% noise level of the measured value. A weighted least-squares program then gave second-order rate constants from a fit of k_{obs} to the concentration of the reactant in excess. Because the $Co(nox)_3(BBu)_2$ reaction is especially fast, the concentration dependence was studied at 279 K. All rate constants were measured in triplicate. Reproducibility was typically better than 5%, but a conservative estimate of the overall uncertainty in k_{obs} is 10%. Activation parameters and error estimates were obtained from weighted least-squares fits of second-order rate constants to the Eyring equation.

The visible spectra of the cobalt(II) complexes have been found to be unchanged for days in acetonitrile.[9] The $Cr(CNdipp)_6(BF_4)_2$ gave linear changes of 5–10%/h. From visible, ^1H NMR, and infrared spectral studies the decomposition occurring in the $Cr(CNdipp)_6(BF_4)_2$ samples was found to be reduction of the complex to $Cr(CNdipp)_6(BF_4)$.[16] To minimize this concentration change, the samples were prepared by weighing appropriate quantities into a volumetric flask. The flask was then evacuated, and the solvent was vacuum-transferred into the flask. The samples were kept under a positive argon pressure until they were put into the stopped-flow syringes. All samples were made individually and used within 1 h of dissolution. The $Cr(CNdipp)_6(BF_4)_2$ visible

---

(19) Nielson, R. M.; Wherland, S. *Inorg. Chem.* **1984**, *23*, 1338.
(20) Nielson, R. M.; Wherland, S. *Inorg. Chem.* **1986**, *25*, 2437.
(21) Nielson, R. M.; Wherland, S. *J. Am. Chem. Soc.* **1985**, *107*, 1505.
(22) (a) Stranks, D. R. *Pure Appl. Chem.* **1974**, *38*, 303. (b) Stranks, D. R. *Discuss. Faraday Soc.* **1960**, *29*, 73.
(23) (a) van Eldik, R. *Inorganic High Pressure Chemistry*; Elsevier: New York, 1986; p 273. (b) Isaacs, N. S. *Liquid Phase High Pressure Chemistry*; Wiley: New York, 1981.
(24) Swaddle, T. W. *Liquid Phase High Pressure Chemistry*; Wiley: New York, 1981; Chapter 5.
(25) Lawrence, G. A.; Stranks, D. R. *Acc. Chem. Res.* **1979**, *12*, 403.
(26) Palmer, D. A.; Kelm, H. *Coord. Chem. Rev.* **1981**, *36*, 89.
(27) van Eldik, R.; Asano, T.; le Noble, W. J. *J. Chem. Rev.* **1988**, *89*, 549.
(28) Braun, P.; van Eldik, R. *J. Chem. Soc., Chem. Commun.* **1985**, 1349.
(29) (a) Nielson, R. M.; Hunt, J. P.; Dodgen, H. W.; Wherland, S. *Inorg. Chem.* **1986**, *25*, 1964. (b) Stebler, M.; Nielson, R. M.; Siems, W. F.; Hunt, J. P.; Dodgen, H. W.; Wherland, S. *Inorg. Chem.* **1988**, *27*, 2895.
(30) Kirchner, K.; Dang, S.-Q.; Stebler, M.; Dodgen, H. W.; Wherland, S.; Hunt, J. P. *Inorg. Chem.* **1989**, *28*, 3605.
(31) Doine, H.; Yano, Y.; Swaddle, T. W. *Inorg. Chem.* **1986**, *25*, 1743.
(32) Doine, H.; Swaddle, T. W. *Inorg. Chem.* **1988**, *27*, 665.
(33) Doine, H.; Swaddle, T. W. *Can. J. Chem.* **1988**, *66*, 2763.
(34) Jolley, W. H.; Stranks, D. R.; Swaddle, T. W. *Inorg. Chem.* **1990**, *29*, 385.
(35) Sasaki, Y.; Endo, K.; Nagasawa, A.; Saito, K. *Inorg. Chem.* **1986**, *25*, 4843.
(36) Krack, I.; van Eldik, R. *Inorg. Chem.* **1989**, *28*, 851.
(37) Weber, W. P.; Gokel, G. W. *Tetrahedron Lett.* **1972**, 1637.
(38) Essenmacher, G. J.; Treichel, P. M. *Inorg. Chem.* **1977**, *16*, 800.
(39) Boyer, J. H.; Reinisch, R. F.; Dansiz, M. J.; Stoner, T.; Sahhar, F. *J. Am. Chem. Soc.* **1955**, *77*, 5688.
(40) House, H. O.; Feng, E.; Peet, N. P. *J. Org. Chem.* **1971**, *36*, 237.
(41) Hepler, L. G. *Thermochim. Acta* **1981**, *50*, 69.
(42) Hamann, S. D.; le Noble, W. J. *J. Chem. Educ.* **1984**, *61*, 658.
(43) Bullock, J. P.; Mann, K. R. *Inorg. Chem.* **1989**, *28*, 4006.

Table I. Second-Order Rate Constants[a] and Activation Parameters for the Cross-Reaction with $Cr(CNdipp)_6(BF_4)_2$[b] in Acetonitrile

complex[c]	$10^{-5}k_{12}$, $M^{-1}\,s^{-1}$	$\Delta H_{12}^{\ddagger}$,[d] kcal/mol	$\Delta S_{12}^{\ddagger}$,[e] cal/(mol K)	$10^{-5}k_{12}^{calc}$,[f] $M^{-1}\,s^{-1}$
$Co(dpg)_3(BPh)_2$	1.24	8.2 ± 1.3	−8 ± 4	3.73
$Co(nox)_3(BBu)_2$[g]	11.7	4.0 ± 0.9	−17 ± 3	55.8
$Co(nox)_3(BPh)_2$	1.02	6.3 ± 0.6	−14 ± 2	18.3

[a] 298 K; errors in k are ±10%. [b] Cr(II) concentration for all reactions ca. 10^{-5} M. [c] Co(II) concentration for all reactions 10^{-4}–10^{-3} M. [d] BF_4^- concentration ca. 10^{-5} M. [e] Temperature varied from 6 to 35 °C, except for $Co(nox)_3(BBu)_2$ where the temperature was varied from 6 to 18.8 °C because the reaction was especially fast. [f] Cr(I/II)k_{11} value used is $1.65 \times 10^7\ M^{-1}\,s^{-1}$, and $Co(dpg)_3(BPh)_2$, $Co(nox)_3(BBu)_2$, and $Co(nox)_3(BPh)_2$ k_{22} values used are 349, 272, and 132 $M^{-1}\,s^{-1}$, respectively; K_{eq} values for the reaction with $Co(dpg)_3(BPh)_2$, $Co(nox)_3(BPh)_2$, or $Co(nox)_3(BBu)_2$ are 7.0, 3.4×10^2, or 1.19×10^4, respectively, and W_{12} values used were ca. 1.9, 1.8, and 1.7 kcal/mol, respectively. [g] k_{12} was calculated for 298 K from the activation parameters; because the reaction was especially fast, the concentration dependence study was done at 279 K and k_{12} was $7.1 \times 10^5\ M^{-1}\,s^{-1}$.

spectrum does not change during the time that the cross-reactions with cobalt complexes occurred.

High-pressure stopped-flow kinetics were measured on a Hi-Tech instrument. It consists of a model HPS-2000 drive unit, a model SF-40C spectrophotometer control unit, and a high-pressure vessel. The spectrophotometer control unit is equipped with a MG-10 grating monochromator, a LS-10 quartz–halogen lamp, a PM-60 photomultiplier unit, and fiber optic cables. The stopped-flow system consists of a solenoid-powered ratcheted drive for the 2-mL glass-barreled syringes, a fused quartz cell, and a 5-mL waste syringe. The flow system components are connected by valves and Teflon tubing. A Pressure Products Industries pump filled with Dow Corning 200 fluid (dimethylpolysiloxane) was used for pressurizing the vessel.

The high-pressure stopped-flow apparatus gives a maximum of eight measurements for each filling of the syringes. Data were usually collected in the following manner. The first measurement was used to determine the proper settings on the transient recorder. With the remaining measurements data were collected for pressure changes of not less than 10 MPa and not more than 50 MPa. With the second filling of the syringes a different initial pressure was chosen and varied in a similar manner. Measurements were made for both increases and decreases in pressure. The pressure range over which data were collected was determined by the maximum recommended pressure of 160 MPa. A constant temperature of 298 K was maintained by surrounding the high-pressure vessel with a thermostated bath. Thermal equilibrium was determined from the reading of a Pt resistance thermometer placed inside the pressure vessel in close proximity to the optical cell.

Transmittance data were collected at 450 nm and digitized as above. The data were transferred to a personal computer for analysis and plotting. They were converted to relative absorbance and fit to a pseudo-first-order rate law by using an iterative least-squares process, which varied the absorbance at infinite time to minimize χ^2. The optimized infinite time absorbance values were within the 1% noise level of the measured value.

From transition-state theory, the volume of activation is defined by $[\partial(\ln k)/\partial P]_T = -\Delta V^{\ddagger}/RT$. The volumes of activation were determined from analysis of $\ln k_{12}$ versus pressure plots. For a typical fit 10–30 data points were collected over a range 5–160 MPa. A linear model was adequate to describe the data, so more complex models were not required.[44] The errors in the volumes of activation were determined from the scatter about the fit line.

Results

Table I presents the second-order rate constants and thermal activation parameters for each reaction with $Cr(CNdipp)_6(BF_4)_2$ in acetonitrile. Supplementary Tables 1–3 show the dependence of k_{obs} on the concentration of $Co(dpg)_3(BPh)_2$, $Co(nox)_3(BPh)_2$, or $Co(nox)_3(BBu)_2$ reacted with $Cr(CNdipp)_6(BF_4)_2$. All of these plots are linear with an intercept at or near zero. Table I presents the calculated second-order rate constants at 298 K. For the $Co(nox)_3(BBu)_2$ reaction the second-order rate constant at 298 K was calculated from the activation parameters. All Eyring plots were linear and the data are presented in Supplementary Tables 4–6. For the reaction between $Cr(CNdipp)_6(BF_4)_2$ and $Co(nox)_3(BBu)_2$ in acetonitrile, the dependence of k_{12} on the total $[BF_4^-]$ is presented in Supplementary Table 7. The value of k_{12} was constant to within ±10% for the seven concentrations studied over the range 4×10^{-5} to 0.4 M Bu_4NBF_4.

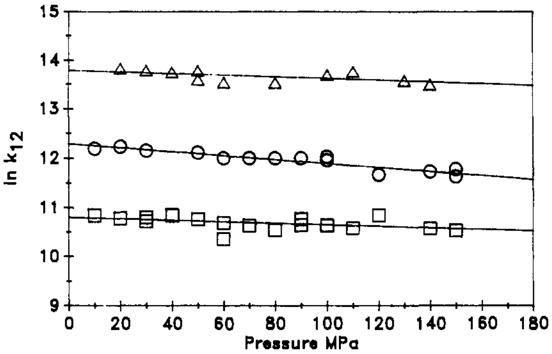

Figure 1. $\ln k_{12}$ vs pressure for the reduction of $Cr(CNdipp)_6(BF_4)_2$ by $Co(dpg)_3(BPh)_2$ (○), $Co(nox)_3(BBu)_2$ (▲), and $Co(nox)_3(BPh)_2$ (□) in acetonitrile at 298 K with no added electrolyte. Errors in k are ±10% and are approximately the size of the symbols.

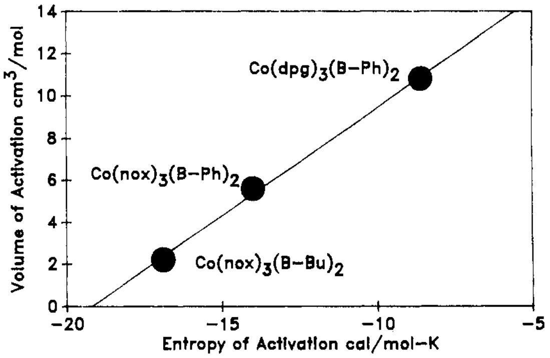

Figure 2. Volume vs entropy of activation for the reduction of $Cr(CNdipp)_6(BF_4)_2$ by a series of Co(II) clathrochelates. Errors are approximated by the size of the symbols.

Supplementary Tables 8–11 present the pseudo-first order rate constant, k_{obs}, as a function of pressure for each reaction with $Cr(CNdipp)_6(BF_4)_2$ in acetonitrile. Plots of $\ln k_{12}$ vs pressure for these reactions are shown in Figure 1. Volumes of activation derived from these plots are presented in Table II. The data are plotted as second-order rate constants calculated from the single concentration of the Co(II) clathrochelate used in each experiment. Any deviation between the intercept and the more precise atmospheric pressure rate constant obtained in the concentration dependence study is due to error in this single concentration. The most precise measurements of $\Delta V^{\ddagger}$ are made in this way from one set of reactant solutions.

The pressure dependence of the pseudo-first-order rate constant, k_{obs}, as a function of total $[BF_4^-]$ for the reaction of $Cr(CNdipp)_6(BF_4)_2$ and $Co(dpg)_3(BPh)_2$ in acetonitrile are presented in Supplementary Tables 12–17. Volumes of activation derived from these data are presented in Table III. A plot of the entropy of activation versus the volume of activation is shown in Figure 2.

Discussion

The second-order rate constants in Table I do not show a large variation. The cross-reactions between $Co(dpg)_3(BPh)_2$ and $Co(nox)_3(BPh)_2$ with $Cr(CNdipp)_6(BF_4)_2$ have essentially the same rate constants of $1 \times 10^5\ M^{-1}\,s^{-1}$ in spite of a 50-fold difference in K_{eq}. For the reaction with $Co(nox)_3(BBu)_2$ the rate constant is a factor of 12 larger and K_{eq} is much larger. Variation of the observed rate constants with driving force has been observed before for the $FeCp_2$ reduction of the Co(III) clathrochelates; however, once the contribution from K_{eq} is removed, there is little variation in the rate constants.[6-8] Theory must be used to separate the contributions from the various factors.

---

[44] Golinkin, H. S.; Laidlaw, W. G.; Hyne, J. B. *Can. J. Chem.* **1966**, *44*, 2193.

Table II. Volume of Activation for the Cross-Reaction[a] of Co(II) with $Cr(CNdipp)_6(BF_4)_2$[b] in Acetonitrile with No Added Salt

complex	$\Delta V^{\ddagger}$, cm^3/mol	no. of pts	$\Delta V_{el}^{\ddagger}$,[c] cm^3/mol	$\Delta V_W^{\ddagger}$,[d] cm^3/mol	r_a[e]	$\Delta V^{\ddagger}$[f,g] vs $FeCp_2^*$, cm^3/mol
$Co(nox)_3(BBu)_2$	2.2 ± 2	11	1.1	3.0	5.8	
$Co(nox)_3(BPh)_2$	5.6 ± 2	20	1.8	3.5	7.1	−9
$Co(dpg)_3(BPh)_2$	10.8 ± 1	16	2.0	3.9	8.2	−14
$Co(dpg)_3(BPh)_2$	11.0 ± 1	19				

[a] 298 K; no added salt. [b] Co(II) concentration ca. 10^{-4} M, Cr(II) concentration ca. 10^{-5} M; see text and supplementary material. [c] Calculated from the Drude–Nernst equation, by using eq 4 (see text). [d] $\Delta V_W^{\ddagger}$, as defined in eq 7, was calculated from the pressure derivative of eq 2c where each w_{ii} was calculated from eq 6. Values for W_{12} are given in footnote *f* of Table I. Cr(I/II) $\partial w_{22}/\partial P$ is −7.1, and $\partial w_{21}/\partial P$ values for $Co(nox)_3(BBu)_2$, $Co(nox)_3(BPh)_2$, and $Co(dpg)_3(BPh)_2$ are −3.7, −3.3, and −3.1, respectively. [e] Radius of Co(II) $(r_xr_yr_z)^{1/3}$ (see text); radius of $Cr(CNdipp)_6^{2+}$ 6.2 Å (see ref 48 and 49). [f] Volumes of activation for the reaction of Co(III) with 1,1′-dimethylferrocene, $FeCp^*_2$, in acetonitrile, from ref 18. [g] K_{eq} values for the reactions of $Co(nox)_3(BPh)_2$ and $Co(dpg)_3(BPh)_2$ with 1,1′-dimethylferrocene in acetonitrile are 0.03 and 1.5, respectively.

Table III. Volume of Activation for the Cross-Reaction[a] of $Co(dpg)_3(BPh)_2$[b] with $Cr(CNdipp)_6(BF_4)_2$[c] in Acetonitrile as a Function of Salt[d] Concentration

BF_4^- concn, M	$\Delta V^{\ddagger}$, cm^3/mol	BF_4^- concn, M	$\Delta V^{\ddagger}$, cm^3/mol
0.00004	10.8 ± 1	0.050	8.5 ± 2
0.005	9.7 ± 2	0.120	11.0 ± 2
0.010	7.3 ± 2	0.204	15.0 ± 3
0.025	8.2 ± 2		

[a] 298 K; errors in *k* are ±10%. [b] Co(II) concentration ca. 10^{-4} M. [c] Cr(II) concentration ca. 10^{-5} M. [d] Electrolyte was Bu_4NBF_4.

The extent to which these rate constants could have been predicted can be sought in the Marcus theory. The Marcus cross-reaction relationship, if the work terms are not neglected, is given by eq 2.[1-3] The definitions for the symbols are given in footnote 45. The work terms were calculated from eq 3.[5,15] The Coulombic work to bring the reactants or products together, corrected to finite ionic strength, is given by eq 3. Values used in the calculations are given in footnote 46 and references therein.

$$k_{12} = (k_{11}k_{22}K_{eq}f_{12})^{1/2}W_{12} \qquad (2a)$$

$$\ln f_{12} = \frac{[\ln K_{eq} + (w_{12} - w_{21})/RT]^2}{4[\ln (k_{11}k_{22}/Z_{11}Z_{22}) + (w_{11} + w_{22})/RT]} \qquad (2b)$$

$$W_{12} = \exp[-(w_{12} + w_{21} - w_{11} - w_{22})/2RT] \qquad (2c)$$

$$Z_{ii} = N[8\pi k_B T(m_1 + m_2)/m_1m_2]^{1/2}r^2/1000 \qquad (2d)$$

$$w = [z_1z_2e^2/D_sr][(\exp(\beta\sigma))/(1 + \beta\sigma)][\exp(-\beta r)] \qquad (3a)$$

$$\beta = [(8\pi N\mu e^2)/(1000D_sk_BT)]^{1/2} \qquad (3b)$$

It has generally been found that the cross-reaction rate constants for reactions of the cobalt clathrochelates with ferrocenes and with each other agree with the cross-reaction relationship. In the current study, the agreement between the observed and calculated rate constants, shown in Table I, is good, especially for the first two cross-reactions. This is important support for the high, directly measured electron self-exchange rate constant for the $Cr(CNdipp)_6(I/II)$ reaction.[16] The calculated cross-reaction rate constants are a factor of 3, 5, and 18 higher than the observed rate constants for $Co(dpg)_3(BPh)_2$, $Co(nox)_3(BBu)_2$, and $Co(nox)_3(BPh)_2$ oxidations, respectively. Other attempts to calculate cross-reaction rate constants from self-exchange rate constants have given agreement within a factor of 2–100,[5,9,50-53] typically the calculated values are larger than the observed values.

The relatively high predicted rate constant for $Co(nox)_3(BPh)_2$ indicates an inconsistency compared with the $Fe(CpCH_3)_2$ reduction of the Co(III) form, the reaction used to calculate the apparent self-exchange rate constant for the clathrochelate, and the present result. One possible explanation for this behavior is that an especially short-lived or unreactive encounter complex between $Cr(CNdipp)_6(BF_4)_2$ and $Co(nox)_3(BPh)_2$ is formed. A complementary explanation is that the encounter complex formed between $Fe(CpCH_3)_2$ and $Co(nox)_3(BPh)_2$ is especially long-lived or reactive. Since the same pattern of reactivity, a 14 times lower observed than predicted cross-reaction rate constant, was observed[9] for the $Co(dpg)_3(BPh)_2$ reduction of $Co(nox)_3(BPh)_2$, the latter explanation appears likely.

An unexpected result is that there is no effect of $[BF_4^-]$ on the rate constant for the reaction between $Co(nox)_3(BBu)_2$ and $Cr(CNdipp)_6(BF_4)_2$. Two types of influence are expected. As discussed in the Introduction, previous studies lead us to expect ion pairing to exist and decrease the rate constants. For example, the rate constant for the reduction of $Co(nox)_3(BBu)_2^+$ by $Co(dpg)_3(BPh)_2$ decreases by a factor of 2 as the concentration of Bu_4NBF_4 is increased from 0.01 to 0.4 M.[9] The second influence is predicted by the nonzero W_{12} term in eq 2a. Based on calculations using eqs 2 and 3 and assuming no ion pairing, this effect should decrease the rate constants by about a factor of 1.7. A similar lack of a salt effect was seen in earlier work on the $Cr(CNdipp)_6^{0/+}$ electron self-exchange.[15] Further, in the solvent dependence study on the $Cr(CNdipp)_6^{+/2+}$ electron self-exchange reaction,[16] the calculated rate constant from a Marcus theory treatment was found to be in excellent agreement if the full charges were used in all solvents, even solvents with low dielectric constants in which ion pairing is expected to be extensive. Such a +1/+2 system should be influenced by added salt both through changes in the electrostatic work to bring the reactants together and by changes in inherent reactivity brought about by ion pairing. These lead to compensating effects, as has been observed for the $Mn(CNC_6H_{11})_6^{+/2+}$ electron self-exchange reaction.[19-21] We suggest that the pattern of insensitivity of the $Cr(CNdipp)_6^{0/+/2+}$ reactions to added electrolyte is due to extensive delocalization of the acceptor π orbitals from the metal center onto the phenyl ligand. This then leads to especially extensive orbital overlap between

---

(45) k_{ii} is the self-exchange rate constant, K_{eq} is the equilibrium constant for the cross-reaction, Z_{ii} is the collision frequency, w_{12} is the work term for the cross-reaction, w_{21} is the work term for the reverse reaction, w_{ii} is the work term for the self-exchange reaction, m_1 and m_2 are the masses of the two reactants, *r* is the separation of the metal centers at the time of electron transfer, *N* is Avogadro's number, σ is equal to the hard sphere radius of the reactant plus the radius of the ion of opposite charge, μ is the ionic strength, and β is the ion interaction parameter.

(46) In the calculated work term the anion BF_4^- radius of 2.2 Å was taken from tabulated values;[47] the $Cr(CNdipp)_6(BF_4)_2$ radius of 6.2 Å was taken from the Cr–Cr distance in the crystal structure of $Cr(CNdipp)_6$.[12,13] The $Co(dpg)_3(BPh)_2$, $Co(nox)_3(BPh)_2$, and $Co(nox)_3(B\text{-}n\text{-}Bu)_2$ radii of 8.2, 7.1, and 6.1 Å were taken from known crystal structures and tabulated values for bond lengths and angles.[48] Since the cobalt complexes are not spherical, the radius was taken as the cube root of the product of the three perpendicular axes, r_x, r_y, and r_z.[49] The collision frequencies are calculated to be ca. 5 × 10^{11} s^{-1} for Z_{11} and ca. 3 × 10^{11} s^{-1} for Z_{22}. Work terms w_{21} and w_{11} are zero since each reaction involves a neutral reactant; however, w_{12} and w_{22} are not zero. Typical values for w_{11} are ca. 0.6 kcal/mol and for w_{22} are ca. 1.3 kcal/mol. An ionic strength, μ, of 2 × 10^{-5} M was used in all the calculations for reactions in which there was no added electrolyte.

(47) Huheey, J. E. *Inorganic Chemistry*, 3rd ed.; Harper & Row: Cambridge, U.K., 1983.

(48) Murguia, M. A. Ph.D. Thesis, Washington State University, 1989.

(49) *r* values: $Co(dpg)_3(BPh)_2^+$ r_x = 8.0 Å, r_y = 8.0 Å, r_z = 8.5 Å; $Co(nox)_3(BPh)_2^+$ r_x = 6.5 Å, r_y = 6.5 Å, r_z = 8.5 Å; $Co(nox)_3(BBu)_2^+$ r_x = 6.5 Å, r_z = 6.5 Å, r_y = 4.7 Å.

(50) Hoddenbagh, J. M. A.; Macartney, D. H. *Inorg. Chem.* **1990**, *29*, 245.

(51) Howes, K. R.; Pippin, L. G.; Sullivan, J. C.; Meisel, D.; Espenson, J. H.; Bakac, A. *Inorg. Chem.* **1988**, *27*, 2932.

(52) McAuley, A.; Xu, C. *Inorg. Chem.* **1988**, *27*, 1204.

(53) Aquino, M. A. S.; Foucher, D. A.; Macartney, D. H. *Inorg. Chem.* **1989**, *28*, 3357.

donor and acceptor, which then leads to reactions which are adiabatic (with a transmission coefficient of 1) even if the approach of the reactants is partially blocked by the anion. A corollary of this interpretation is that reactions that do show inhibition by counterions must be nonadiabatic. This interpretation does not predict the lack of the small added electrolyte effect which should come from the work terms. However this term would only cause a factor of 1.7 difference in the rate constant and, if ion pairs were considered, this work term contribution would be even smaller.

The observed enthalpy and entropy of activation for the three reactions in acetonitrile here differ from the activation parameters for the reactions of these same cobalt clathrochelates and ferrocene or one of its derivatives.[6-8] In both studies the enthalpy of activation varied from 4 to 8 kcal/mol; however the order was different. In contrast to the ferrocene study where the entropy of activation was constant at −15 cal/(mol K), here the entropy of activation varied a great deal from −8 to −17 cal/(mol K). The large negative entropies accompany the small enthalpies such that a plot of $\Delta H^{\ddagger}$ vs $\Delta S^{\ddagger}$ is linear for the reactions studied here. This compensating effect has been observed before in the solvent dependence of the $Cr(CNdipp)_6^{+/2+}$ self-exchange[16] and other types of reactions.[54-58] A more complete analysis, using Marcus theory to factor out the self-exchange and cross-reaction driving force terms, is not possible with the available data.

The volumes of activation obtained in this study are positive and vary from 2.2 to 10.8 cm^3/mol. As described in the Introduction, volumes of activation for outer-sphere electron-transfer reactions between like-charged reactants or a neutral and a charged reactant are typically negative. This is the first-reported case of a positive volume of activation for an outer-sphere reaction, except for reactions between ions of opposite charge.[24-27] A possible second case is the $Fe(CN)_6^{3-/4-}$ electron self-charge exchange.[59] This reaction is highly electrolyte dependent, and the volume of activation study involved only three pressure points, so further investigation is warranted.

The value of $\Delta V^{\ddagger}$ measured increases with the size of the clathrochelate and with decreasing equilibrium constant. These results can be compared with those for the reduction of $Co(nox)_3(BPh)_2^+$ and $Co(dpg)_3(BPh)_2^+$ by $Fe(CpCH_3)_2$ which, as shown in Table II, give the opposite trend with size.[18] Further investigation will be required to establish the precise contributions of size and shape, as well as driving force.

Although only three reactions were studied here, a linear relationship between $\Delta V^{\ddagger}$ and $\Delta S^{\ddagger}$ is observed, as displayed in Figure 2. Examples of a linear correlation between $\Delta S^{\ddagger}$ and $\Delta V^{\ddagger}$ have been observed before for aqueous reactions.[60,61] The data do not fall on the same line with other reactions displaying this same behavior; however, the slopes are nearly exactly the same.[60] For the aqueous reactions the slope was found to be 1.04 ± 0.1 and the slope here was found to be 0.94. Phillips suggests a composite solvation shell model to explain this interesting correlation.[61] However this explanation is specific to aqueous reactions and includes the ionization of water; therefore, this interpretation would not be valid for acetonitrile.[61]

The data obtained can be further discussed by considering two models for $\Delta V^{\ddagger}$. In the first model, the volume of activation is considered as the sum of an intrinsic change due to bond length changes, ΔV_{int}, and the change in solvation due to electrostatic interaction, ΔV_{el}. The intrinsic term is estimated as the volume occupied by the complex in a crystal.[62] By considering the crystal structures of $Co(dmg)_3(BF)_2$, $Co(dmg)_3(BF)_2BF_4$, $Cr(CNdipp)_6$, $Cr(CNC_6H_5)_6$, and $Cr(CNC_6H_5)_6(PF_6)_2$,[10-14] it was found that the volume of the unit cell was 1.4–1.5 times the volume within a van der Waals surface, calculated by using Sybyl and the volume feature of MacroModel.[63] Thus the volume of an ion was taken as 1.5 times the van der Waals volume. It was further assumed that the substituents on the clathrochelates or the isocyanides did not greatly affect the difference in volume between two oxidation states. The result of this analysis was that the volume of the Cr complexes decreased about 6 cm^3/mol on reduction and the volume of the Co clathrochelates decreased in volume by about 3 cm^3/mol on oxidation. Thus the overall volume change is on the order of −9 cm^3/mol. The precision of this method is no better than ±10 cm^3/mol; thus all we can predict is that ΔV^0 is near zero. If the intrinsic volume change on going to the transition state is a linear combination of the intrinsic volumes of the complexes and these are between the volumes of the products and reactants then the intrinsic volume change is also near zero. The solvation change is considered to be the change in the electrostriction of the solvent around the charged reacting species. A commonly used expression for the solvent electrostriction is the Drude–Nernst equation, given by eq 4. The definitions for the symbols used are given in ref 64.

$$\Delta V_{el} = (Nz^2e^2/2Dr)(\partial \ln D/\partial P)_T \qquad (4)$$

$\Delta V_{el}^{\ddagger}$ is just the ΔV_{el} for the transition state minus the ΔV_{el} for the dicationic Cr(II) complex. The transition-state radius is that of the sphere with the same volume as the sum of the reactant volumes. The results and values used in eq 4 are given in Table II. The calculated values are positive, and increase slightly from 1 to 2 cm^3/mol with increasing size of the clathrochelate. The sign of $\Delta V_{el}^{\ddagger}$ and its trend are thus the same as the experimentally observed values. However the magnitude of the changes between the three reactions is much smaller from the Drude–Nernst calculations than the observed values. There are several simplifying assumptions used in the electrostatic calculations, including that the complexes and the transition state are spheres, that the charge is at the center, that the solvent is a dielectric continuum, and that only simple electrostatic interactions are involved. It appears that the electrostatic term alone makes a reasonable prediction of the overall $\Delta V^{\ddagger}$. The radii used in the calculation are reasonable for predicting the Co/Cr separation in the transition state but are probably overestimates of the distance between the centers of charge and the solvent. The predicted values of ΔV_{el} would be larger if smaller radii were used.

The second method that will be used for predicting the volume of activation is based on the Marcus cross-reaction relationship. The pressure derivative of eq 2a, assuming that *f* is independent of pressure, is given by eq 5, where the pressure dependence of

$$\Delta V_{12}^{\ddagger} = 0.5[(-RT\,\partial \ln k_{11}/\partial P)_T - RT(\partial \ln k_{22}/\partial P)_T - RT(\partial \ln K_{12}/\partial P)_T] - RT(\partial W_{12}/\partial P)_T \qquad (5)$$

W_{12}, eqs 2c and 3, was calculated by assuming the ionic strength was zero; the pressure dependence of each w_{ii} is given by eq 6.

$$(\partial w_{ii}/\partial P)_T = Nz_1z_2e^2/4\pi\epsilon_0 r[\partial(1/D)/\partial P]_T \qquad (6)$$

The actual ionic strength of ca. 10^{-5} M is small, and it was determined that the pressure dependence of this term was insensitive to the actual number. The parameters used in the calculations are given in a footnote in Table II. Using the definition of the volume of activation from transition-state theory, eq 5 can be expressed as eq 7. The values for $\Delta V_W^{\ddagger}$ for the reactions studied are given in Table II. The other three terms

$$\Delta V_{12}^{\ddagger} = \tfrac{1}{2}(\Delta V_{11}^{\ddagger} + \Delta V_{22}^{\ddagger} + \Delta V^{\circ}) + \Delta V_W^{\ddagger} \qquad (7)$$

---

(54) Yang, E. S.; Chan, M.; Wahl, A. C. *J. Phys. Chem.* **1980**, *84*, 3094.

(55) Li, T. T.; Weaver, M. J.; Brubaker, C. H. *J. Am. Chem. Soc.* **1982**, *104*, 238.

(56) Banett, J. F. *Tech. Chem. Ser.* **1972**, *6*, 367.

(57) Conner, W. C. *J. Catal.* **1982**, *78*, 238.

(58) Linert, W.; Kudrjawtsev, A. B.; Schmid, R. *Aust. J. Chem.* **1983**, *J6*, 1903.

(59) Sato, M.; Uamada, T. *High Pressure Science and Technology*; Vodar, B., Marteau, Ph., Eds.; Pergamon Press: Oxford, U.K., 1980; Vol. 2, p 812.

(60) Phillips, J. C. *J. Phys. Chem.* **1985**, *89*, 3060.

(61) Phillips, J. C. *J. Chem. Phys.* **1984**, *81*, 478.

(62) Conway, B. E. *Annu. Rev. Phys. Chem.* **1966**, *17*, 481.

(63) Still, W. C.; Mohamadi, F.; Richards, N. G. J.; Guida, W. C.; Lipton, M.; Liscamp, R.; Chang, G.; Hendrickson, T.; DeGunst, F.; Hasel, W. MacroModel, Version 3.0. Department of Chemistry, Columbia University, New York. Sybyl, Molecular Modeling System, Tripos Assoc., St. Louis, MO.

(64) Symbols are as defined in refs 45 and 46, *z* is the charge of an ion, *D* is the static dielectric constant, and *P* is the pressure.

in eq 7 are not as easily calculated. A value of -14 cm^3/mol, ΔV_{11}^*, has been calculated for $Co(dmg)_3(BF)_2^{+/0}$ from the study of the pressure dependence of the Co(III) clathrochelate reduction by $FeCp_2$.[18] The value of ΔV_{22}^* is not available but is constant for the series of reactions. The reaction volume, ΔV^0, is estimated above at 0 to ± 10 cm^3/mol. All of the calculated values for ΔV_W^* are positive and increase with the size of the clathrochelate. The agreement between just this term and the observed ΔV_{12}^* for the $Co(nox)_3(BBu)_2$ reaction is good, but the progressively larger complexes have larger volumes of activation than are predicted from ΔV_W^*. The ΔV_{11}^* is negative, and ΔV^0 is small; thus a constant, positive value for ΔV_{22}^* could be consistent with the observed pattern.

The volume of activation shows a small dependence on $[BF_4^-]$, with a decrease in ΔV^* up to ca. 0.05 M added electrolyte. A similar pattern but a larger change is observed for the reactions between the positive Co(III) clathrochelates and ferrocenes.[18] The smaller effect observed here is consistent with the smaller sensitivity of the $Cr(CNdipp)_6^{+/2+}$ reactions to added electrolyte. The remaining effect is not inconsistent with a lack of influence of electrolyte on the rate constant, since an ion-paired path could give the same rate constant and still have a different volume of activation than a free-ion path.

Conclusion

In summary, the experimental cross-reaction rate constants are in good agreement with the predictions from the Marcus cross-reaction relationship. This further supports the values used for the electron self-exchange rate constants. The rate constant is not affected by the presence of added salt. The volumes of activation are positive, ranging from 2.2 to 10.8 cm^3/mol, a result in contrast to all other outer-sphere electron-transfer reactions between reactants that are not oppositely charged.

The unexpected results reported here, the lack of salt dependence at ambient pressure, and the positive volumes of activation, we believe, are related. We suggested that the lack of salt effect was due to the Cr(II) complex. The spherical Cr(II) complex has conjugated ligands which extend the π symmetry orbitals involved in the electron-transfer process, thus giving excellent orbital overlap with the electron acceptor. The presence of an anion does not significantly disturb this overlap. The rate constant decreases with pressure. Although we cannot provide a model with adequate precision to predict this, we believe that it is primarily the solvent release on forming the precursor complex and the reorganized complexes that produces this effect. Since the reactants already have such good orbital overlap, any improvement in the orbital overlap, brought on by a decreased electron-transfer distance accompanying increased pressure, has no effect. This makes us conclude further that the negative volumes of activation and inhibition by ion pairing previously observed occur because these other reactions have inadequate orbital overlap, and this is improved by pressure or further weakened by ion pairing. A similar conclusion about the sensitivity of ΔV^* to the pressure dependence of the electron-transfer distance has been reached by Swaddle and co-workers from the study of the $MnO_4^{-/2-}$ electron exchange.[31-34,65]

Further work on these problems will be pursued through the study of other reactions of 0/2+ or 0/3+ charge types, and through the study of reactants like the $Cr(CNdipp)_6^{+/2+}$ complexes, but which lack the extensive conjugation. Molar volume studies of the complexes are also being pursued in order to better understand whether the equations being used to estimate molar volumes are adequate and in order to obtain volumes of reaction to use in the calculations.

Acknowledgment. We are pleased to acknowledge helpful discussions with Susan Johns (computer graphics) and Drs. Mark Murguia (data analysis program), Jacqueline Gribble (cobalt synthesis), and Karl Kirchner and Prof. John P. Hunt. This work was supported by the National Science Foundation.

Supplementary Material Available: Tables of second-order rate constant dependence on added electrolyte, concentration, and temperature (15 pages). Ordering information is given on any current masthead page.

---

(65) (a) Spiccia, L.; Swaddle, T. W. *Inorg. Chem.* **1987**, *26*, 2265. (b) Jolley, W. H.; Stranks, D. R.; Swaddle, T. W. *Inorg. Chem.* **1990**, *29*, 1948.

Contribution from the Department of Chemistry,
The University of North Carolina, Chapel Hill, North Carolina 27599-3290

Electrocatalytic Reduction of Nitrite Ion by edta Complexes of Iron(II) and Ruthenium(II)

Matthew R. Rhodes, Mark H. Barley, and Thomas J. Meyer*

Received June 12, 1989

The reductive electrochemistries of both $[Ru^{II}(Hedta)(NO^+)]^0$ and $[Fe^{II}(Hedta)(NO^\bullet)]^-$ have been investigated as a function of pH. The nitrosyl complexes are effective electrocatalysts for the reduction of NO_2^- or HONO to give the reduced products N_2O, N_2, NH_3OH^+, or NH_4^+. An element of product selectivity is available by making appropriate choices in pH, applied potential, or catalyst. The mechanisms by which nitrite is reduced appear to be similar to those identified earlier for polypyridyl complexes of Ru and Os and for water-soluble porphine complexes of Fe.

Introduction

One of the themes in our current research is an attempt to uncover pathways for the redox transformations of small inorganic molecules or ions such as CO_2/HCO_2H,[1] H_2O/O_2,[2] SO_2/H_2S,[3] or NO_2^-/NH_3.[4-6] The approach that has been taken has been (1) to identify the individual steps by which these multiple electron

---

(1) (a) Bolinger, C. M.; Story, N.; Sullivan, B. P.; Meyer, T. J. *Inorg. Chem.* **1988**, *27*, 4582. (b) O'Toole, T. R.; Sullivan, B. P.; Bruce, M. R.; Margerum, L. D.; Murray, R. W.; Meyer, T. J. *J. Electroanal. Chem. Interfacial Electrochem.* **1989**, *259*, 217. (c) Bruce, M. R.; Megehee, E.; Sullivan, B. P.; Thorp, H.; O'Toole, T. R.; Downard, A.; Meyer, T. J. *Organometallics* **1988**, *7*, 238. (d) Sullivan, B. P.; Bruce, M. R.; O'Toole, T. R.; Bolinger, C. M.; Megehee, E.; Thorp, H.; Meyer, T. J. In *Catalytic Activation of Carbon Dioxide*; Ayers, W. M., Ed., ACS Symposium Series 363; American Chemical Society: Washington, DC, 1988; Chapter 6, p 52.

(2) (a) Gersten, S. W.; Samuels, G. J.; Meyer, T. J. *J. Am. Chem. Soc.* **1982**, *104*, 4029. (b) Gilbert, J. A.; Eggleston, D. S.; Murphy, W. R.; Geselowitz, D. A.; Gersten, S. W.; Hodgson, D. J.; Meyer, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 3855. (c) Raven, S. R.; Meyer, T. J. *Inorg. Chem.* **1988**, *27*, 4478.

(3) Kline, M. A.; Barley, M. H.; Meyer, T. J. *Inorg. Chem.* **1987**, *25*, 2197.

(4) (a) Murphy, W. R., Jr.; Takeuchi, K. J.; Barley, M. H.; Meyer, T. J. *Inorg. Chem.* **1986**, *25*, 1041. (b) Thompson, M. S.; Meyer, T. J. *J. Am. Chem. Soc.* **1981**, *103*, 5577. (c) Rhodes, M. R.; Barley, M. H.; Meyer, T. J. Manuscript in preparation.

(5) Ogura, K.; Ishikaw, H. *J. Chem. Soc., Faraday Trans.* **1984**, *80*, 2243-53.

0020-1669/91/1330-0629$02.50/0