in only seven resonances for $[\mathrm{Pb(THEC)}]^{2+}$. Unfortunately, crystals suitable for X-ray diffraction determination of the crystal structures of $[\mathrm{M(THEC)}](\mathrm{ClO_4})_2$ have not been obtained.

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Registry No. $[\mathrm{Hg(THEC)}]^{2+}$, 130063-16-0; $[\mathrm{Pb(THEC)}]^{2+}$, 130063-17-1; $^{13}\mathrm{C}$, 14762-74-4.

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Volumes of Activation for Electron Transfer between a Series of Cobalt Clathrochelates and Ferrocenes as a Function of Solvent and Added Electrolyte

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Electron-transfer rate constants for the reaction between a series of $\mathrm{Co(dioxime)_3(BX)_2}$ compounds and either ferrocene or 1,1′-dimethylferrocene have been measured as a function of pressure, electrolyte, and solvent. Eight reactions were studied in acetonitrile as a function of pressure. Volumes of activation for these reactions ranged from −4 cm³/mol for the reaction between $\mathrm{Co(dmg)_3(BC_6H_5)_2^+}$ (dmg is doubly deprotonated dimethylglyoxime) and $\mathrm{Fe(CpCH_3)_2}$ (Cp is cyclopentadienide), to −14 cm³/mol for the reaction between $\mathrm{Co(dpg)_3(BC_6H_5)_2^+}$ (dpg is doubly deprotonated diphenylglyoxime) and $\mathrm{Fe(CpCH_3)_2}$. Volumes of activation generally became more negative with increasing size of the reactants. The reaction between $\mathrm{Co(dmg)_3(BF)_2^+}$ and $\mathrm{FeCp_2}$ was studied in both the forward and reverse directions. From these reactions, a volume of reaction of +4 cm³/mol has been determined for the forward reaction. From the pressure derivative of the Marcus theory cross-reaction relation, a volume of activation for the electron self-exchange of $\mathrm{Co(dmg)_3(BF)_2^{0/+}}$ has been calculated to be $\Delta V^* = -15$ cm³/mol. The dependence of the volume of activation on added electrolyte was determined for the reactions of $\mathrm{Co(nox)_3(BF)_2^+}$ (nox is doubly deprotonated cyclohexanedione dioxime) and $\mathrm{Co(dmg)_3(BF)_2^+}$ with $\mathrm{FeCp_2}$. For both reactions the volumes of activation become more negative with the addition of the salt tetrabutylammonium tetrafluoroborate. This is taken as further evidence for two paths of electron transfer, one being the reaction of the free ion and the other of the ion pair. The reactions between $\mathrm{Co(dmg)_3(BC_6H_5)_2^+}$ with $\mathrm{Fe(CpCH_3)_2}$ (reaction VI) and $\mathrm{Co(dmg)_3(BF)_2^+}$ with $\mathrm{FeCp_2}$ (reaction II) were studied as a function of solvent. The four solvents used were acetonitrile, methylene chloride, acetone, and nitrobenzene. Volumes of activation ranged from −4 to −14 cm³/mol for reaction II and from −8 to −15 cm³/mol for reaction VI. Trends in the data are discussed within current theories for the volume of activation.

Introduction

The measurement of volumes of activation has been shown to be an important tool for the elucidation of reaction mechanisms.[1-5] Recently there has been an increased use of this technique for the study of electron-transfer reactions.[6] Within transition-state theory, the volume of activation is defined as the difference between the volume of the transition state and that of the reactants and includes contributions from solvation of the reactants and the transition state. It is determined from the pressure dependence of the rate constant.[7] For outer-sphere electron-transfer processes, such as the reactions studied here, large, negative volumes of activation are often observed.[1,5,6]

Volumes of activation studies are increasing, but the majority of the work on electron-transfer reactions has been performed on reactions in aqueous media and on self-exchange systems where the only difference in the two reacting species is the oxidation state.[4] Our laboratory is especially interested in studying the effects of structure, solvent, and added electrolyte on volumes of activation.

The most commonly tested theory for the prediction of electron-transfer rate constants and how the rates vary with the parameters mentioned above is that of Marcus, especially as presented by Sutin.[8] A generalized example of the outer-sphere electron-transfer reaction is described as follows:

$$\mathrm{Co(dioxime)_3(BX)_2^+ + FeCp_2 \xrightleftharpoons{K_{OS}} Co(dioxime)_3(BX)_2^+{,}FeCp_2} \quad (1)$$

$$\mathrm{Co(dioxime)_3(BX)_2^+{,}FeCp_2 \xrightarrow{k_{et}} Co(dioxime)_3(BX)_2{,}FeCp_2^+} \quad (2)$$

$$\mathrm{Co(dioxime)_3(BX)_2{,}FeCp_2^+ \rightarrow Co(dioxime)_3(BX)_2 + FeCp_2^+} \quad (3)$$

The first step is the formation of an encounter complex with a formation constant K_{OS}. The second step is electron transfer, which occurs with a rate constant k_{et}. The final step represents the formation of the products from the successor complex. The rate law for such a mechanism is

$$\mathrm{d[Co(dioxime)_3(BX)_2]}/\mathrm{d}t = k_{\mathrm{et}}K_{\mathrm{OS}}\mathrm{[Co(dioxime)_3(BX)_2^+][FeCp_2]} \quad (4)$$

It is the product $k_{\mathrm{et}}K_{\mathrm{OS}}$ that is measured as a function of pressure and is defined as the observed second-order rate constant. Thus the volume effects associated with the formation of the encounter complex, as well as the actual electron-transfer process, contribute to the observed value of ΔV^*.

The work presented here is a continuation of our study of electron transfer on a series of cobalt clathrochelates.[9-13] The reactions studied are as follows:

$$\mathrm{Co(nox)_3(BF)_2^+ + FeCp_2 \rightleftharpoons Co(nox)_3(BF)_2 + FeCp_2^+} \quad (\mathrm{I})$$

$$\mathrm{Co(dmg)_3(BF)_2^+ + FeCp_2 \rightleftharpoons Co(dmg)_3(BF)_2 + FeCp_2^+} \quad (\mathrm{II})$$

$$\mathrm{Co(dpg)_3(BC_6H_5)_2^+ + FeCp_2 \rightleftharpoons Co(dpg)_3(BC_6H_5)_2 + FeCp_2^+} \quad (\mathrm{III})$$

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(1) Stranks, D. R. *Pure Appl. Chem.* **1974**, *38*, 303.
(2) Lawrence, G. A.; Stranks, D. R. *Acc. Chem. Res.* **1979**, *12*, 403.
(3) Palmer, D. A.; Kelm, H. *Coord. Chem. Rev.* **1981**, *36*, 89.
(4) van Eldik, R.; Asano, T.; le Noble, W. J. *Chem. Rev.* **1989**, *89*, 549.
(5) van Eldik, R. *Inorganic High Pressure Chemistry*; Elsevier: New York, 1986; p 273.
(6) Swaddle, T. W. *Ibid.*; Chapter 5.
(7) Evans, M. G.; Polanyi, M. *Trans. Faraday Soc.* **1935**, *34*, 875.
(8) (a) Cannon, R. D. *Electron Transfer Reactions*; Butterworth: London, 1980. (b) Brown, G. M.; Sutin, N. J. *J. Am. Chem. Soc.* **1979**, *101*, 883. (c) Zuckerman, J. J., Ed. *Inorganic Reactions and Methods*; VCH Publishers: Deerfield Beach, FL, 1986; Vol. 15, Chapter 12. (d) Sutin, N. *Prog. Inorg. Chem.* **1983**, *30*, 441.
(9) Borchardt, D.; Pool, K.; Wherland, S. *Inorg. Chem.* **1982**, *21*, 93.
(10) Borchardt, D.; Wherland, S. *Inorg. Chem.* **1984**, *23*, 2537.
(11) Borchardt, D.; Wherland, S. *Inorg. Chem.* **1986**, *25*, 901.
(12) Borchardt, D. Ph.D. Thesis, Washington State University, 1985.
(13) Gribble, J. D.; Wherland, S. *Inorg. Chem.* **1989**, *28*, 2859.

0020-1669/91/1330-0139$02.50/0

$$\mathrm{Co(dmg)_3(BF)_2^+ + Fe(CH_3Cp)_2 \rightleftharpoons Co(dmg)_3(BC_6H_5)_2 + Fe(CH_3Cp)_2^+} \quad \mathrm{(IV)}$$

$$\mathrm{Co(dmg)_3(BC_4H_9)_2^+ + Fe(CH_3Cp)_2 \rightleftharpoons Co(dmg)_3(BC_4H_9)_2 + Fe(CH_3Cp)_2^+} \quad \mathrm{(V)}$$

$$\mathrm{Co(dmg)_3(BC_6H_5)_2^+ + Fe(CH_3Cp)_2 \rightleftharpoons Co(dmg)_3(BC_6H_5)_2 + Fe(CH_3Cp)_2^+} \quad \mathrm{(VI)}$$

$$\mathrm{Co(nox)_3(BC_6H_5)_2^+ + Fe(CH_3Cp)_2 \rightleftharpoons Co(nox)_3(BC_6H_5)_2 + Fe(CH_3Cp)_2^+} \quad \mathrm{(VII)}$$

$$\mathrm{Co(dpg)_3(BC_6H_5)_2^+ + Fe(CH_3Cp)_2 \rightleftharpoons Co(dpg)_3(BC_6H_5)_2 + Fe(CH_3Cp)_2^+} \quad \mathrm{(VIII)}$$

$$\mathrm{Co(dmg)_3(BF)_2 + FeCp_2^+ \rightleftharpoons Co(dmg)_3(BF)_2^+ + FeCp_2} \quad \mathrm{(IX)}$$

These systems possess several features that make them ideal for electron-transfer studies. Firstly, the reactants are substitution inert in both oxidation states, and thus the reactions are limited to an outer-sphere pathway. Secondly, one of the reactants is always neutral. This simplifies calculations for comparison to theory since the Coulombic work of bringing the two reactants together is zero. Thirdly, the ability to modify the structure allows for variation in the thermodynamic driving force and for aspects such as electrostatic interaction with the solvent and counterion, as well as the electron-transfer distance, to be studied. Fourthly, the ability to select between ferrocene and 1,1′-dimethylferrocene allows the reactions to be studied under conditions of low driving force and keeps the observed rates within the range measurable by the stopped-flow technique. Finally, reaction II can be studied in both the forward and reverse directions (reaction IX), thus allowing for the determination of the volume of reaction, ΔV°.

For reactions I, II, VI, and VII the electron-transfer reactivity was shown to be sensitive to the concentration of added electrolyte.[9,10] This sensitivity was interpreted as an ion-pairing effect. A free-ion path and an ion-paired path for electron transfer were suggested, and electron-transfer rate constants for the free-ion path and the ion-paired path, as well as an ion-pair association constant, were determined. Ion-pairing equilibria should be pressure dependent. Therefore, studies as a function of pressure may lead to a better understanding of rate inhibition by added electrolyte.

The rate constant for reaction II has been studied in various solvents at ambient pressure.[10] For this reaction there was poor agreement between the predictions of Marcus theory and the measured values. However, numerous assumptions and simplifications are made in the calculation of the predicted rate constant. Many of these errors may cancel out in taking the pressure derivative of the rate constant and may lead to accurate predictions of ΔV^*.[14] In addition, determination of the volumes of activation in different solvents may allow for the separation of the contribution of the inner-sphere reorganization of the complex and the outer-sphere reorganization of the solvent. Finally, along with the extensive thermodynamic, solvent, and electrolyte studies done on these systems, similar studies have also been done for the self-exchange of ferrocene.[15,16] This information, along with pressure studies conducted by Hunt and co-workers,[17] allows for a more complete Marcus theory evaluation of these results.

Experimental Section

Starting materials and solvents were purchased from Aldrich Chemical Co. and Baker Chemicals. Solvents were purified by the methods of Borchardt.[10] Tetrabutylammonium tetrafluoroborate and the cobalt clathrochelates were made by methods previously described.[11,13,18] Cyclic voltammetry measurements were made with a PAR 174A polarographic analyzer and a Model 303 cell using Pt-wire working and counter electrodes and a shielded Ag reference electrode. In all cases, 0.1 M $\mathrm{Bu_4NBF_4}$ was the supporting electrolyte and the temperature was 25 °C. Potentials are reported with respect to ferrocene. $E_{1/2}$ values were determined for $\mathrm{Co(dmg)_3(BF)_2BF_4}$ and $\mathrm{FeCp_2}$ in $\mathrm{CH_2Cl_2}$ and for $\mathrm{Co(dmg)_3(BC_6H_5)_2BF_4}$ and $\mathrm{Fe(CH_3Cp)_2}$ in $\mathrm{(CH_3)_2CO}$, $\mathrm{C_6H_5NO_2}$, and $\mathrm{CH_2Cl_2}$; other values were already available.[11] The electrochemical data were used to determine equilibrium constants for the reactions in their respective solvents.

Within transition-state theory, the volume of activation is defined by eq 5.[19] The data were thus analyzed by plotting ln k vs P. For a typical fit, 15–20 data points were collected over a range of 5–150 MPa. A linear model was adequate to describe the data, so more complex models were not required.[20] The errors in ΔV^* were determined from the scatter about the fit line.

$$[\partial(\ln k)/\partial P]_T = -\Delta V^*/RT \qquad (5)$$

Kinetic measurements were performed on a Hi-Tech high-pressure stopped-flow 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 Teflon tubing and valves. A Pressure Products Industries pump filled with Dow Corning 200 fluid (dimethylpolysiloxane) was used for pressurizing the vessel. The stopped-flow apparatus allows for a maximum of eight measurements for each filling of the syringes. Data were ususally collected in the following manner. The first one or two measurements were used to determine the proper settings on the transient recorder. With the remaining measurements, data were collected for pressure increments of not less than 10 MPa and not more than 30 MPa. With the second filling of the syringes, a different initial pressure was chosen and incremented in the same manner. Measurements were taken for a decrease in pressure as well. The pressure range over which data were collected was determined either by reaching the maximum recommended pressure of 150 MPa or by limitations imposed by the solvent (nitrobenzene freezes at 100 MPa and 25 °C). In all experiments a minimum of a 10-fold excess of ferrocene was used. A constant temperature of 25 ± 0.2 °C 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 syringes.

Transmittance data, 2048 points per shot with 10-bit precision, were collected at 470 or 490 nm, depending on the reaction, by a Physical Data Model 514A transient digitizer. The data were transferred to a personal computer for analysis and plotting. For the reactions that proceeded to more than 90% complete consumption of the limiting reactant at equilibrium, first-order analysis and linear least-squares fits were used. Reactions that were not more than 90% complex were fit to an approach to equilibrium rate law, pseudo first order in the forward direction and second order, with equal concentrations of the two reactants, in the reverse direction.[12] Analysis was performed with use of nonlinear least-squares routine CURFIT of Bevington,[21] converted to Microsoft QuickBasic.

Results

The spectrophotometric characteristics, electrochemical data, and equilibrium constants in acetonitrile of all the compounds have been described.[9-13] Equilibrium values for reactions II and VI in the various solvents are given in Table I.

The pseudo-first-order rate constant k_{obs} as a function of pressure for reactions I–IX in acetonitrile are given in Tables S-1–S-9 (supplementary material). Plots of ln k_{obs} vs pressure for these reactions are shown in Figure 1 for reactions I–V and in Figure 2 for reactions VI–IX. Volumes of activation from these plots are presented in Table II.

The pressure dependences of k_{obs} as a function of salt concentration for reactions I and II are given in Tables S-10–S-13

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(14) Doine, H.; Swaddle, T. W. *Can. J. Chem.* **1988**, *66*, 2763.

(15) Shih, E.; Man-Sheung, C.; Wahl, A. *J. Phys. Chem.* **1980**, *84*, 3094.

(16) Nielson, R. M.; McManis, G. E.; Safford, L. K.; Weaver, M. J. *J. Phys. Chem.* **1989**, *93*, 2152.

(17) Kirchner, K.; Dang, S.-Q.; Stebler, M.; Dodgen, H. W.; Wherland, S.; Hunt, J. P. *Inorg. Chem.* **1989**, *28*, 3605.

(18) Jackels, S. C.; Zektzer, J; Rose, N. *Inorg. Synth.* **1977**, *17*, 139.

(19) (a) Funahashi, S.; Yamaguchi, Y.; Ishihara, K.; Tanaka, K. *J. Chem. Soc., Chem. Commun.* **1982**, 976. (b) Hamann, S. D.; le Noble, W. J. *J. Chem. Educ.* **1984**, *61*, 658.

(20) Golinkin, H. S.; Laidlaw, W. G.; Hyne, J. B. *Can. J. Chem.* **1966**, *44*, 2193.

(21) Bevington, P. R. *Data Reduction and Error Analysis for the Physical Sciences*; McGraw-Hill: New York, 1969.

Table I. Summary of Electrochemical Data for Reactions II ($Co(dmg)_3(BF)_2^+/FeCp_2$) and VI ($Co(dmg)_3(BC_6H_5)_2^+/Fe(CH_3Cp)_2$)[a]

reaction	solvent	$\Delta E_{1/2}$,[b] mV	K_{eq}[c]
II	CH_3CN	-28	0.33
	$C_6H_5NO_2$	-47	0.16
	$(CH_3)_2CO$	-49	0.15
	CH_2Cl_2	-40	0.21
VI	CH_3CN	-95	0.024
	$C_6H_5NO_2$	-113	0.012
	$(CH_3)_2CO$	-115	0.011
	CH_2Cl_2	-105	0.017

[a] All values reported are in 0.1 M $(Bu_4N)BF_4$ at 20 °C. [b] All with errors of ±0.010 V. [c] All with errors of ±20%.

Table II. Volume of Activation in CH_3CN with No Added Salt for the Reactions of $Co(dioxime)_3(BX)_2^+ + Fe(RCp)_2$

reaction[a]	ΔV^*,[b] cm^3/mol	ΔV^*_{SV},[c] cm^3/mol	σ, Å *d*	 *e*
I (NF/C)	-6 ± 1	-16	9.6	3.8
II (MF/C)	-9 ± 1	-16	8.6	5.8
III (PP/C)	-10 ± 1	-15	12.0	8.4
IV (MF/M)	-11 ± 1	-15	9.1	7.0
V (MB/M)	-11 ± 1	-14	10.4	8.5
VI (MP/M)	-4 ± 1	-14	10.2	5.8
VII (NP/M)	-9 ± 1	-13	11.4	8.3
VIII (PP/M)	-14 ± 1	-13	12.5	13.3
IX (MF/C	-13 ± 2	-16	8.5	-

[a] Reactant abbreviations: (dioxime) M = dmg, N = nox, P = dpg; (cap) **F** = F, P = C_6H_5, B = C_4H_9; (ferrocene) C = $FeCp_2$, M = $Fe(CH_3Cp)_2$. [b] Measured results. [c] Calculated from eq 8 using the estimated radii. [d] Estimated radii. $r_a = (r_x r_y r_z)^{1/3}$ of cobalt complex: $Co(nox)_3(BF)_2^+$, 5.8; $Co(dmg)_3(BF)_2^+$, 4.8; $Co(dpg)_3(BC_6H_5)_2^+$, 8.2; $Co(dmg)_3(C_4H_9)_2^+$, 6.1; $Co(dmg)_3(BC_6H_5)_2^+$, 5.9; $Co(nox)_3(BC_6H_5)_2^+$, 7.1. r_b = radius of ferrocene, 3.8, or 1,1′-dimethylferrocene, 4.3. $\sigma = r_a + r_b$. All radii are in angstroms. [e] σ for which ΔV^*_{SR} equals the obsreved ΔV^*.

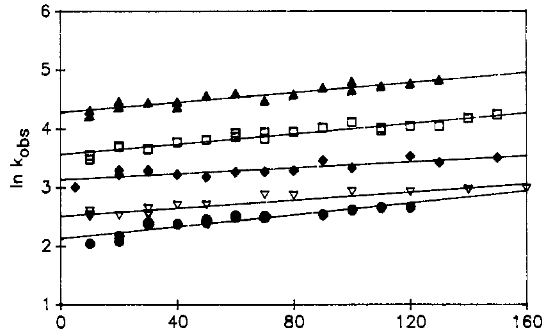

Figure 1. Logarithm of k_{obs} as a function of pressure for reactions I (◆), II (▽), III (□), IV (▲), and V (●).

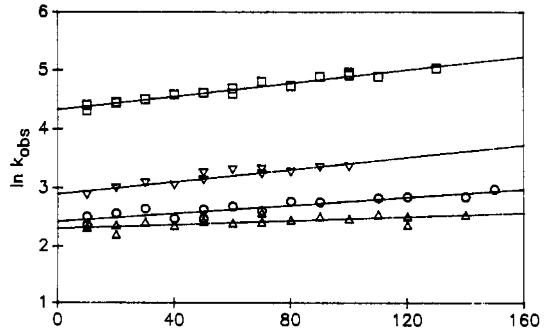

Figure 2. Logarithm of k_{obs} as a function of pressure for reactions VI (△), VII (○), VIII (□), and IX (▽).

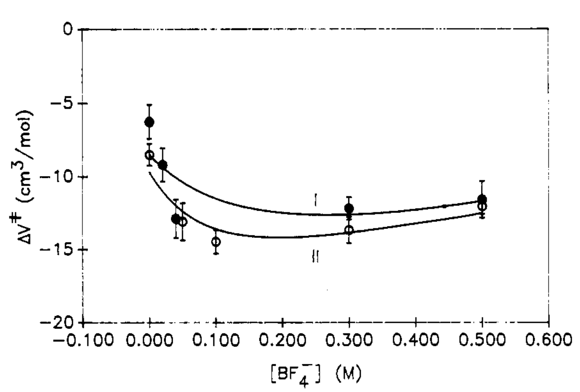

Figure 3. Volumes of activation for reactions I and II as a function of added $(Bu_4N)BF_4$.

Table III. Volume of Activation in CH_2Cl_2 with 0.1 M Salt for the Reaction $Co(dioxime)_3(BX)_2^+ + Fe(RCp)_2$

compound	reductant	ΔV^*, cm^3/mol
$Co(nox)_3(BF)_2^+$	$FeCp_2$	-14 ± 2
$Co(dmg)_3(BF)_2^+$	$FeCp_2$	-15 ± 1
$Co(dpg)_3(BC_6H_5)_2^+$	$Fe(CH_3Cp)_2$	-15 ± 2

Table IV. Volume of Activation (cm^3/mol) for Reactions II and VI as a Function of Solvent[a]

solvent	ε	$\partial(1/\epsilon)/\partial P$[b]	$\partial(n^{-2} - \epsilon^{-1})/\partial P$[c]	ΔV^*[d]	ΔV^*_{SR}[e]
CH_3CN	36.0	-3.2	-4.0	-4 ± 1	-14
				-9 ± 1	-17
$C_6H_5NO_2$	34.8	-4.9	-1.9	-5 ± 2	-7
				-9 ± 1	-8
$(CH_3)_2CO$	20.7	-16.9	-3.3	-12 ± 1	-12
				-12 ± 1	-14
CH_2Cl_2	8.9	-39.6	-0.3	-14 ± 1	-1

[a] The value listed in the same row as the solvent is for reaction VI; the value listed directly below is for reaction II. [b] (10^6 bar^{-1}) from ref 30. [c] (10^5 bar^{-1}) from ref 30 and assuming that $(1/\rho)((n^2 - 1)/(n^2 + 0.4))$ is constant. [d] Measured results. [e] Calculated results based on eq 8 and estimted σ as in Table II. [f] With 0.1 M $(Bu_4N)BF_4$. ε is taken from ref 30.

and Figure S-1 (supplementary material) for reaction I and in Tables S-14–S-17 and Figure S-2 (supplementary material) for reaction II. Volumes of activation from these plots are listed in Tables S-18 and S-19 (supplementary material) and plotted in Figure 3.

The pressure dependences of k_{obs} for reactions I, II, and VIII in methylene chloride and 0.1 M salt are given in Tables S-20–S-22 and Figure S-3 (supplementary material). Volumes of activation from these plots are listed in Table III. The k_{obs} values as a function of pressure for reactions II and VI in four different solvents are given in Tables S-23–S-27 and S-4 and S-5 (supplementary material). Volumes of activation from these plots are given in Table IV.

Discussion

From a Marcus theory[8] treatment for an adiabatic reaction in which the solvent is treated as a dielectric continuum and reactants are treated as spheres, the rate constant is defined as

$$k = (K_{OS}\kappa_{el}\nu_n)\exp(-\Delta G^*/RT) \qquad (6)$$

Here, K_{OS} is the precursor formation constant and is generally taken as $4000\pi N\sigma^3/3$. The formation of the precursor involves exponential contributions from Coulombic work (ΔG^*_{COUL}), and Debye–Hückel effects (ΔG^*_{DH}). Since one of the reactants is neutral, these terms are taken to be 0. The other terms are κ_{el}, the electronic transmission coefficient, and ν_n, the nuclear frequency factor, which may be set equal to k_BT/h.[22,23] Here, k_B is the Boltzmann, constant, and *h* is the Planck constant. The sum of the contributions from the inner-sphere (ΔG^*_{IR}), and the outer-sphere reorganizational free energy (ΔG^*_{SR}) is ΔG^*.

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(22) Spiccia, L.; Swaddle, T. W. *Inorg. Chem.* **1987**, *26*, 2265.

(23) Jolley, D. R.; Stranks, D. R.; Swaddle, T. W. *Inorg. Chem.* **1990**, *29*, 385.

Differentiation of ΔG^* with respect to pressure[5] gives an analogous expression for the volume of activation.

$$\Delta V^* = \Delta V^*_{\mathrm{IR}} + \Delta V^*_{\mathrm{SR}} \tag{7}$$

The contribution to the volume of activation that results from solvent rearrangement, ΔV^*_{SR}, is given by eq 8,

$$\Delta V^*_{\mathrm{SR}} = (Ne^2/16\pi\epsilon_0)(1/2r_a + 1/2r_b - 1/\sigma)[\partial(n^{-2} - \epsilon^{-1})/\partial P]_T \tag{8}$$

N is the Avogadro number, e is the charge of an electron, r_a and r_b are the effective radii of reactants, σ is the distance between the electron-transfer centers, n is the refractive index, ϵ is the static dielectric constant, and the remaining parameters have their usual meaning. In taking the pressure derivative, the pressure dependence of the electron-transfer distance has been ignored. Further work will be required to test this assumption.[5]

The magnitude of ΔV^*_{IR} has been assigned a range of values depending on the reaction.[24] In a study by Swaddle,[25] in which the volume of activation for the electron self-exchange of $\mathrm{Ru(hfac)_3}^{-/0}$ was measured, the contribution from ΔV^*_{IR} was estimated to be less than +1 cm^3/mol. Crystallographic data[26] show that the change in the cobalt–nitrogen bond length on reduction from Co(III) to Co(II) is less than 0.1 Å for $\mathrm{Co(dmg)_3(BF)_2}^{+/0}$. Bond distances are also known to be similar for the two oxidation states of ferrocene.[27] Thus, for these reactions the contribution of ΔV^*_{IR} to ΔV^* is expected to be negligible. Therefore, ΔV^*_{SR} will be compared to the measured volume of activation, ΔV^*.

The Marcus theory[8] also relates electron self-exchange rate constants (k_{11}, k_{22}) to the cross-reaction rate constant (k_{12}) and equilibrium constant (K_{12}) for outer-sphere electron transfer. If there is no work required to form the precursor or successor complex, eq 9 is used, and Z replaces the overall preexponential factor in eq 6, or is the collision frequency.

$$k_{12} = (k_{11}k_{22}K_{12}f_{12})^{1/2} \tag{9}$$

$$\ln f_{12} = (\ln K_{12})^2/[4 \ln (k_{11}k_{22}/Z^2)] \tag{10}$$

For the case when $f_{12} = 1$, the pressure derivative of eq 9 gives eq 11.

$$\Delta V^*_{12} = \tfrac{1}{2}(\Delta V^*_{11} + \Delta V^*_{22} + \Delta V^\circ) \tag{11}$$

Here, ΔV° is the volume of reaction. For $f \neq 1$ and Z still pressure independent, the pressure derivative of eq 9 is eq 12.

$$\Delta V^*_{12} = \tfrac{1}{2}(\Delta V^*_{11} + \Delta V^*_{22} + \Delta V^\circ + \mathrm{d}(\ln f)/\mathrm{d}P) \tag{12}$$

$$\frac{\partial \ln f}{\partial P} = \frac{2 \ln (k_{11}k_{22}/Z^2)\Delta V^\circ - (\ln K_{12})^2(\Delta V^*_{11} + \Delta V^*_{22})}{4(\ln (k_{11}k_{22}/Z^2))^2} \tag{13}$$

Considering first the series of reactions in CH_3CN, all gave negative volumes of activation. These varied by about 10 cm^3/mol, ranging from −4 cm^3/mol for reaction VI to −14 cm^3/mol for reaction VIII. By comparison of reactions II and IV the effect of changing the reductant from ferrocene to 1,1′-dimethylferrocene for $\mathrm{Co(dmg)_3(BF)_2}^+$ as the oxidant is demonstrated. The volume of activation becomes slightly, 2 cm^3/mol, more negative. From reactions III and VIII with $\mathrm{Co(dpg)_3(BC_6H_5)_2}^+$ as the oxidant and with the reductant again changed from ferrocene to 1,1′-dimethylferrocene, the volume of activation again becomes more negative, this time by approximately 4 cm^3/mol.

Reactions VI–VIII, for which the reducing agent is 1,1′-dimethylferrocene and the dioxime ligand is varied from dmg to nox to dpg, with BX always being BC_6H_5, have volumes of activation ranging from −4 to −14 cm^3/mol. The volume of activation becomes more negative with an increase in bulk of the reactants. This is the expected result if all compounds must reach a similar electron-transfer distance and the larger reactants interpenetrate to a greater extent. Reactions IV and V, in which the dioxime is dmg but BX is varied from BF to BC_4H_9, exhibit the same volume of activation. That the volume of activation is so similar for BF and BC_4H_9 may be an indication that the butyl groups are wrapping around so as to decrease the overall size of the caps. However, for reactions V and VI in which the dioxime is again dmg and BX is now varied from *n*-butyl to an even bulkier BC_6H_5, a dramatically more positive volume of activation, varying from −11 to −4 cm^3/mol, is observed. This may indicate that for the rigid BC_6H_5 cap approach of the reactants is forced along a direction that does not permit interpenetration.

Comparison of reactions VI and VII with reactions I and II in which the reductant is now $FeCp_2$ and the F-capped cages are reduced, shows that sensitivity to the dioxime is greatly reduced when the cap is small.

Attempts to calculate volumes of activation for outer-sphere electron-transfer reactions have met with mixed results (see references cited in Tables V and VI). Table II lists the calculated contribution of ΔV^*_{SR} to the volumes of activation based on eq 8 for comparison with the measured results. This ignores the contribution from ΔV° to the overall value. The reactants are assumed to be hard spheres with an electron-transfer distance (σ) that is the sum of the reactant radii.[28]

Table V. Volumes of Activation for Selected Outer-Sphere Electron-Transfer Reactions in H_2O and CH_3CN[a]

reaction	ΔV^*	ref
In H_2O		
$\mathrm{MnO_4}^{-/-2}$	−23	22
$\mathrm{Co(en)_3}^{2+/3+}$	−20	23
$\mathrm{Co_2(\mu\text{-}O_2^-, NH_2)(en)_4}^{4+} + \mathrm{TMPNO} \rightarrow \mathrm{CO_2(\mu\text{-}O_2^{2-}, NH_2)(en)_4}^{3+} + \mathrm{TMPNO}^+$	−1	
$\mathrm{Fe(phen)_3}^{2+/3+}$	−2	14
$\mathrm{Co(NH_3)_5py}^{3+} + \mathrm{Fe(CN)_6}^{4-} \rightarrow \mathrm{Co(NH_3)_5py}^{2+} + \mathrm{Fe(CN)_6}^{3-}$	+24–31	24, 34
In CH_3CN		
$\mathrm{Ru(hfac)_3}^{-/0}$	−6	25
$\mathrm{Mn(CNR)_6}^{+/2+}$		
R = CH_3	−2	29
R = CH_2CH_3	−5	
R = $C(CH_3)_3$	−10	
R = C_6H_{11}	−17	
R = $(CH_2)_3CH_3$	−20	
$\mathrm{Co(terpy)_2}^{2+} + \mathrm{Co(bpy)_3}^{3+} \rightarrow \mathrm{Co(terpy)_2}^{3+} + \mathrm{Co(bpy)_3}^{2+}$	−5	31
$\mathrm{Fe(phen)_3}^{2+/3+}$	−6	14
$\mathrm{FeCp_2}^{+/0}$	−7	32

[a] Ligand abbreviations: en, 1,2-ethanediamine; TMPNO, 2,2,6,6-tetrmethyl-1-piperidinyloxyl; pheny, 1,10-phenanthroline; py, pyridine; terpy, terpyridine; bpy, bipyridine.

Table VI. Volumes of Activation (cm^3/mol) for Selected Outer-Sphere Electron-Transfer Reactions in Various Solvents[a]

reaction	solvent	ΔV^*	ref
$\mathrm{Ru(hfac)_3}^{-/0}$	CH_3CN	−5.5	25
	CH_3OH	−5.8	
	$(CH_3)_2CO$	−6.0	
	$CHCl_3$	−8.1	
$\mathrm{Mn(CNC(CH_3)_3)_6}^{+/2+}$	CH_3CN	−12	29
	CH_3OH	−20	
	$(CH_3)_2CO$	−20	
	CH_2Cl_2	−18	
$\mathrm{Mn(CNC_6H_{11})_6}^{+/2+}$	CH_3CN	−17	29
	CH_3OH	−16	
	$(CH_3)_2CO$	−20	
	CH_2Cl_2	−21	
$\mathrm{Cu(dmp)_2}^{+/2+}$	CH_3CN	−3	35
	$(CH_3)_2CO$	−8	
$\mathrm{Co(terpy)_2}^{2+} + \mathrm{Co(bpy)_3}^{3+} \rightarrow \mathrm{Co(terpy)_2}^{2+} + \mathrm{Co(bpy)_3}^{3+}$	CH_3CN	−5	31
	H_2O	−9	
	$HCONH_2$	−14	

[a] Ligand abbreviations: hfac, hexafluoroacetylacetonate; dmp, dimethylphenanthroline; terpy, terpyridine; bpy, bipyridine.

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(24) Kanesato, M.; Ebihara, M.; Sasaki, Y.; Saito, K. *J. Am. Chem. Soc.* **1983**, *105*, 5711.

(25) Doine, D.; Swaddle, T. W. *Inorg. Chem.* **1988**, *27*, 665.

(26) Zakrzewski, G. A.; Ghilardi, C. A.; Lingafelter, E. C. *J. Am. Chem. Soc.* **1971**, *93*, 4411.

(27) (a) Rosenblum, M. *Chemistry of the Iron Group Metallocenes*; Interscience: New York, 1965; p 31.

The calculated volumes of activation exceed in magnitude the measured values, except for reaction VIII. The calculated volumes of activation predict only a 3 cm^3/mol variation in ΔV^*, whereas measured values exhibit a 10 cm^3/mol change. In addition, the trend in ΔV^*_{SR} with increasing size of the dioxime (reactions VI–VIII), BX (reactions IV–VI), and reductant (reactions II/IV and reactions III/VIII) show little agreement with measured values. Smaller values of σ, for example the use of the minimum radius of the clathrochelate, lead to estimates of ΔV^*_{SR} that are somewhat nearer to the measured values.

Table II lists the electron-transfer distances that would be required in order to exactly obtain the observed volumes of activation from only ΔV^*_{SR}. In general the electron-transfer distance required agrees better with the calculated distances for the larger reducing agent, 1,1′-dimethylferrocene but is physically unreasonable for some of the cases.

There have been relatively few measurements of the volume of activation for outer-sphere electron-transfer reactions (see Tables V and VI). Of the studies done, fewer yet are in nonaqueous media, most are self-exchange reactions, and only one looks at trends in reactant size. In aqueous solution, volumes of activation have been shown to span a large range from −20 cm^3/mol for the self-exchange of Co(1,2-ethanediamine)$_3^{3+/2+}$ [23] to +47 cm^3/mol for the cross-reaction of Co(NH$_3$)$_5$(pyridine)$^{3+}$ with the oppositely charged Fe(CN)$_6^{4-}$.[24,34] In acetonitrile a smaller range of values has been measured, with values ranging from near zero to −20 cm^3/mol.

Of the systems studied thus far, the Mn(CNR)$_6^{+/2+}$ system offers some basis for comparison.[29] In that system it was also difficult to predict ΔV^*. However, similar trends in the volume of activation with respect to reactant size and flexibility were observed. That is, more negative values of volumes of activation were also measured for the larger, more flexible ligands.

Reaction IX is the reverse of reaction II. From the difference in the volume of activation for these reactions, the volume of reaction for reaction II is +4 cm^3/mol. Application of eq 11 with ΔV^*_{11} = −7 cm^3/mol[17] ΔV^*_{12} = −9 cm^3/mol (reaction II), and ΔV° = +4 cm^3/mol, gives a volume of activation ΔV^*_{22} = −15 cm^3/mol for the electron self-exchange of Co(dmg)$_3$(BF)$_2^{+/0}$. This value is more negative than those obtained for the self-exchange reactions of FeCp$_2^{0/+}$ and Ru(hfac)$_3^{-/0}$, in which one reactant is also neutral. It is however similar to the values obtained for the Mn(CNR)$_6^{+/2+}$ systems.

The dependence of the electron-transfer rate on added salt for most of these reactions has been previously studied at ambient pressure.[11] The change in rate with added salt was found to correlate well with a mechanism that contained both free-ion and ion-paired electron-transfer paths, according to the following mechanism.

$$\mathrm{Co(nox)_3(BF)_2^+ + BF_4^- \underset{}{\overset{K_{IP}}{\rightleftharpoons}} Co(nox)_3(BF)_2BF_4} \quad (14)$$

$$\mathrm{Co(nox)_3(BF)_2^+ + FeCp_2 \xrightarrow{k_1} Co(nox)_2(BF)_2 + FeCp_2^+} \quad (15)$$

$$\mathrm{Co(nox)_3(BF)_2BF_4 + FeCp_2 \xrightarrow{k_2} Co(nox)_3(BF)_2 + FeCp_2^+ + BF_4^-} \quad (16)$$

Previously obtained data suggested that in acetonitrile the ion-paired path was not dominant until the salt concentration was in excess of 0.2 M. The rate constants k_1 and k_2 and the ion-pair formation equilibrium constant K_{IP} were determined to be 1.6 × 10^4 M^{-1} s^{-1}, 7.7 × 10^3 M^{-1} s^{-1}, and 9 M^{-1}, respectively, for reaction II and 3.4 × 10^4 M^{-1} s^{-1}, 9.3 × 10^3 M^{-1} s^{-1}, and 5 M^{-1}, respectively, for reaction I. Volume of activation studies (Figure 3) show a marked dependence of ΔV^* on the [BF$_4^-$]. Two interpretations of these data will be presented. If it is assumed that no ion pairs are formed under the experimental conditions of 1.7 × 10^{-4} M reactants or less, then volumes of activation for the free-ion path (ΔV^*_1) of −8 cm^3/mol for reaction II and −6 cm^3/mol for reaction VI can be assigned. If the volume of activation of the ion-paired path (ΔV^*_2) is assumed to be constant at high salt concentration, then ΔV^*_2 values of −13 and −12 cm^3/mol may also be assigned for these two reactions, respectively.

The more positive ΔV^* for the free-ion path can be accounted for by simple solvation arguments. In the formation of the precursor complex for the ion-paired path, solvation changes will be small, since two neutral species come together to form a larger neutral species. In the free-ion path, a charged species is reacting with a neutral one to form the precursor complex, and the charge density is reduced. This will release solvent and lead to a more positive ΔV^*. The above arguments require that in the ion-paired path the counterion serves only to neutralize charge and that it contributes the same volume to the reactants as to the transition state. In addition, we have ignored how the presence of the counterion will affect the way in which the reactants come together.

A second interpretation is derived from the model in eqs 14–16. ΔV^* for k_{obs} can be predicted based on k_1, k_2, and K_{IP} at ambient pressure[9–13] and ΔV^*_1, ΔV^*_2, and $\Delta V^\circ_{K_{IP}}$. The data for ΔV^* versus [BF$_4^-$] were fit by holding k_1, k_2, and K_{IP} constant and varying ΔV^*_1, ΔV^*_2, and $\Delta V^\circ_{K_{IP}}$. The results are shown by the solid lines in Figure 3. For reaction I ΔV^*_1 = −9 cm^3/mol, ΔV^*_2 = 60 cm^3/mol, and $\Delta V^\circ_{K_{IP}}$ = 26 cm^3/mol. For reaction II, the parameters are −10, 5, and 39 cm^3/mol, respectively. The value for ΔV^*_2 for either reaction is poorly defined as it depends primarily on the increase in ΔV^* at the highest salt concentrations, lowering it to 0 causes little change in the quality of the fit. The large, positive value for $\Delta V^\circ_{K_{IP}}$ is consistent with desolvation on ion-pair formation. The observed trend in Figure 3 is explained as follows. In those solutions that contain low [BF$_4^-$], increased pressure separates ion pairs,[30] forcing a larger fraction of the reaction to proceed by the faster free-ion path. This leads to a more negative ΔV^*. At high salt concentration the ion-paired path dominates despite the decrease in ion-pair formation that results from increased pressure. Therefore at high salt concentration the measured volume of activation is more reflective of ΔV^*_{IP}. Experimentally unattainable concentrations of salt are required to actually reach the ion-paired limiting value.

In Table III, the volumes of activation are given for reactions I, II, and VIII in CH$_2$Cl$_2$ in the presence of 0.1 M (Bu$_4$N)BF$_4$. In this solvent, given its low dielectric constant, and at the concentration of salt used, the ion-paired path should be the dominant mode of reaction. The volume of activation is similar for the three reactions studied with an average value of about −15 cm^3/mol. In acetonitrile, if ΔV^* at the highest salt concentration is taken as that of the ion-paired path, then volumes of activation of −12 cm^3/mol for reaction I and −13 cm^3/mol for reaction II can be compared to the methylene chloride values.

The dependence of volume of activation on solvent has been studied by several authors (Table VI), with the majority of the work having been done on self-exchange systems. The change in volume of activation with solvent is dependent on the system being studied. For Ru(hfac)$_3^{-/0}$, ΔV^* varies by 3 cm^3/mol and Mn(CNC$_6$H$_{11}$)$_6^{+/2+}$ shows a variation of 4 cm^3/mol, while Mn(CNC(CH$_3$)$_3$)$_6^{+/2+}$ exhibits a variation of 8 cm^3/mol for the same solvents. This study, which was done in three of the same solvents as the Mn(CNR)$_6^{+/2+}$ systems, shows a variation of 10 cm^3/mol for reaction II and 6 cm^3/mol for reaction VI (Table IV). For both of the reactions, agreement between the measured volume of activation and the calculated value of ΔV^*_{SR} based on eq 8,

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(28) Stranks, D. R. *Discuss. Faraday Soc.* **1960**, *29*, 73.

(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*, 2893.

(30) Isaacs, N. S. *Liquid Phase High Pressure Chemistry*; Wiley: New York, 1981.

(31) Braun, P.; van Eldik, R. *J. Chem. Soc., Chem. Commun.* **1985**, 1349.

(32) Kirchner, K.; Dang, S.-Q.; Stebler, M.; Dodgen, H. W.; Wherland, S.; Hunt, J. P. *Inorg. Chem.* **1989**, *28*, 3605.

(33) Ebihara, M.; Sasaki, Y.; Kubota, S. T.; Saito, K. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 391.

(34) Krack, I.; van Eldik, R. *Inorg. Chem.* **1986**, *25*, 1743.

(35) Doine, H.; Yano, Y.; Swaddle, T. W. *Inorg. Chem.* **1989**, *28*, 2319.

as given in Table IV, is quite good for nitrobenzene and acetone, but fails for acetonitrile and methylene chloride. Acetonitrile gives a less negative volume of activation than is predicted while the opposite is true for methylene chloride. At least part of the difference in the predicted and calculated values in methylene chloride may be the result of ion-pair formation (vide infra). For these experiments the concentration of the cobalt clathrochelates ranged from 0.06 to 0.1 mM. The last entry in Table IV gives the volume of activation for reaction VI in CH_2Cl_2, in the presence of 0.1 M added salt. These conditions were required for this reaction because in the absence of added salt the observed rate constant was beyond the limits of the instrument. Reaction II was slow enough not to necessitate added salt. The volume of activation here is quite similar to that of reaction VI.

From plots of k_{12} as a function of $[BF_4^-]$, ion-pair formation constants (K_{IP}) of 9, 27, 78, and 6.8×10^3 for acetonitrile, nitrobenzene, acetone, and methylene chloride, respectively, have been determined.[12] At the concentrations used in the current experiments and in the absence of $(Bu_4N)BF_4$, this leads to approximately 25% ion-pair formation in methylene chloride whereas in the other solvents ion pairs are essentially nonexistent. Assuming that the ion-paired path leads to volumes of activation that are more negative in methylene chloride as in acetonitrile, the volume of activation for the free-ion path is probably several cm^3/mol more positive than the measured value.

Correlation between ΔV^* and the Marcus solvent parameter $[d(1/n^2 - 1/\epsilon)/dP]_T$ as predicted by eq 8 has met with varying degrees of success. Swaddle and co-workers,[25] for example, found good agreement between measured and theoretical volumes of activation for their large rigid $Ru(hfac)_3^{-/0}$ species of low charge in solvents where ion-pair formation is not significant, whereas experiments in our laboratory on larger, less rigid, and more highly charged $Mn(CNR)_6^{+/2+}$ species did not show agreement.[29] In the present study the amount of rigidity as well as the size and charge are more similar to the ruthenium study. The results of this study show that a correlation between volume of activation and $[d(1/n^2 - 1/\epsilon)/dP]_T$ is evident for reaction II but less so for reaction VI, as can be seen from Table IV (Figure S-6, supplementary material). However this correlation is opposite in direction to what is predicted.

Correlation of ΔV^* with solvent dielectric constant as well as its pressure derivative does not exist as can be seen from Table IV (Figures S-7 and S-8, supplementary material). The trend is toward a more negative ΔV^* as ϵ decreases and the pressure derivative becomes more negative, as is expected from solvation arguments. Because the encounter complex will have a lower charge density than the reactants, the solvent sphere will expand on encounter complex formation. Since solvents of lower dielectric constant typically interact more weakly with solutes, the amount of solvent expansion should be less as the dielectric constant of the solvent decreases. This will lead to a more negative ΔV^* with decreasing solvent dielectric constant.

The problems of assuming pressure independence of K_{OS} and the electron-transfer distance and the exclusion of the possibility of nonadiabatic electron transfer ($\kappa \neq 1.0$) will now be considered as contributing factors in the discrepancies between measured and predicted values. Assuming that the assemblage of reactants compresses as does the surrounding medium, such that $-(\sigma^{-1})(d\sigma/dP)_T = \beta/3$ (β is the isothermal compressibility of the solvent), will allow for these contributions to be estimated.[22] This assumption should set an upper limit for the contribution from these terms. The pressure dependence of the precursor formation will thus contribute an additional amount of $RT\beta$ to the right side of eq 7. For the solvents studied, this term amounts to an additional contribution of between +1 and +3 cm^3/mol. Including the pressure dependence of σ will require that the term $-Ne^2/16\pi\epsilon_0(n^{-2} - \epsilon^{-1})\beta/3\sigma$ be added to the right side of eq 8. This yields calculated values of ΔV^*_{OS} that change by −2 to −8 cm^3/mol, depending on the reaction and the solvent. The pressure dependence of the transmission coefficient (nonadiabatic outer-sphere electron transfer) will require that a term $\Delta V^*_{NA} = -2RT\gamma\beta\sigma/3$ also be added to the right side of eq 11. Here, γ is the nonadiabatic distance scaling factor and has been taken as 1.5 Å^{-1}. This will also lead to a more negative calculated value of ΔV^* by as much as −32 cm^3/mol. Because including the pressure dependence of these terms will yield even more negative calculated volumes of activation, these contributions cannot be the sole source of the lack of agreement with the Marcus theory.

Conclusions

Volumes of activation have been determined for the electron-transfer cross-reactions for several cobalt clathrochelates with two different ferrocene reducing agents. A variation in ΔV^* of 10 cm^3/mol was observed. In general, ΔV^* became more negative with increased bulk of either dioxime, cap, or reducing agent. A notable exception occurs when the reductant is 1,1′-dimethylferrocene, the dioxime ligand is dmg, and the bulk of the cap is increased from the flexible BC_4H_9 to the rigid BC_6H_5. These results suggest that the mode of electron transfer is not exclusively at the dioxime ligand or BX cap and that the mode of approach of the reducing agent is sensitive to the bulk and the rigidity of both the capping agent and the dioxime ligand.

Marcus theory predicts values of ΔV^*_{SR} that are of greater magnitude than ΔV^*, but agreement is better for the larger reactants. The electron-transfer distances that would be required for exact agreement with the Marcus theory are not reasonable for several of the reactions. They do indicate that for the smaller less bulky reactants an electron-transfer distance smaller than the sum of r_a and r_b will lead to an improvement in the predictability of the volumes of activation.

In addition, ΔV° has been determined to be +4 cm^3/mol for reaction II, and from this, a self-exchange volume of activation, ΔV^*_{22}, of −15 cm^3/mol is calculated for $Co(dmg)_3(BF)_2^{0/+}$. This prediction can be tested in further experiments.

Volumes of activation for the outer-sphere electron-transfer reactions between $Co(nox)_3(BF)_2^+$ or $Co(dmg)_3(BF)_2^+$ and ferrocene were shown to be sensitive to the presence of added salt with a variation of about 6 cm^3/mol. The change in volume of activation has been attributed to an outer-sphere electron-transfer path involving ion-paired species. Fitting of the data to a standard two-path rate law has shown that the salt effect can be predicted if the formation of the ion pair is accompanied by a $\Delta V^\circ_{K_{IP}}$ of approximately +30 cm^3/mol. Simple solvation arguments can also account for the more positive volume of activation of the free-ion path as compared to the ion-paired path. Alternatively, the more negative volume of activation of the ion-paired species could result from the larger ion-paired $Co(dioxime_3)(BX)_2BF_4$ having to obtain the same electron-transfer distance as the smaller $Co(dioxime)_3(BF)_2^+$.

The value of ΔV^* for the outer-sphere electron-transfer reactions between $Co(nox)_3(BF)_2^+$ and $Co(dmg)_3(BF)_2^+$ with ferrocene has been shown to be solvent dependent and to vary by as much as 10 cm^3/mol between the solvents studied. No simple correlation between volume of activation and several solvent properties was found. A correlation with the Marcus theory solvent parameter $[d(1/n^2 - 1/\epsilon)/dP]_T$ showed the opposite of the predicted result, but correlations with either solvent dielectric constant or its pressure derivative were better. The Marcus theory was successful in predicting the volume of activation for two of the solvents but failed for methylene chloride. Ion-pair formation is believed to be significant in methylene chloride and contributes to the difficulty in making the correlations in this solvent.

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Supplementary Material Available: Listings (Tables S-1–S-27) and figures (Figures S-1–S-8) of kinetic data (34 pages). Ordering information is given on any current masthead page.