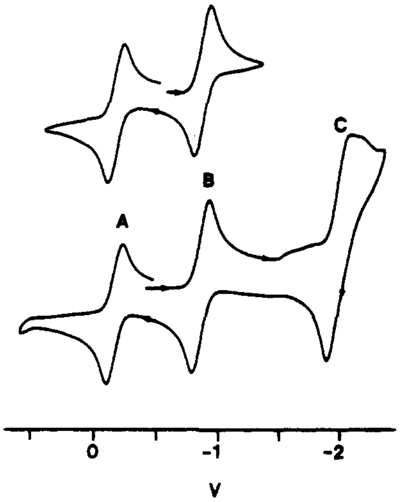

Figure 3. Cyclic voltammograms of $[CoCp_2][W(t\text{-}Bu_2cat)_3]$ in THF/TBAH scanned between −1.5 and +0.5 V or between −2.5 and +0.5 V beginning at −0.5 V in both cases. Peak A represents the couple $W(t\text{-}Bu_2cat)_3^- \rightleftarrows W(t\text{-}Bu_2cat)_3 + e^-$ while peak B represents the couple $CoCp_2^+ + e^- \rightleftarrows CoCp_2$. Wave C is a composite of the two couples $W(t\text{-}Bu_2cat)_3^- + e^- \rightleftarrows W(t\text{-}Bu_2cat)_3^{2-}$ and $CoCp_2 + e^- \rightleftarrows CoCp_2^-$. Scan rates are 50 mV/s.

sometimes oily products whose CV's are consistent with the above formulations (Figure 3). Unfortunately, these yellow cobaltocenium derivatives do not readily crystallize and are difficult to purify.

Experimental Section

Electrochemical Measurements. Cyclic voltammograms were obtained with a BioAnalytical Systems, Inc., Model CV-1A instrument. Potential control for coulometric experiments was performed with a potentiostat purchased from BioAnalytical Systems, Inc. A three-compartment (H) cell was used with a Pt-disk or -gauze working electrode, a Pt-wire auxiliary electrode and a Ag/AgCl pseudoreference electrode[4c] to which all potentials refer. Scan rates were 25 mV/s. Under these conditions the Cp_2Fe/Cp_2Fe^+ couple was measured at +0.47 V in THF/TBAH and +0.38 V in CH_2Cl_2/TBAH, consistent to ±10 mV with a separation between the anodic and cathodic waves of 90 mV.

Synthesis of Compounds. Because of the similarity of the methods used, a general procedure for synthesis of the two types of complexes in this study is given.

(a) Dichlorides. Tungsten hexachloride and the solid phenolic reagent (4 equiv for 4-methylphenol, 2 equiv for biphenol and catechols) were mixed in a round-bottom flask under nitrogen. Benzene was then added to the mixture to initiate reaction. Copious amounts of HCl were given off and vented to a fume hood. The black-purple solution was then stirred for 8–12 h before the solvent was removed under vacuum. The resulting glassy red-black solid was purified by heating under vacuum at 80–90 °C to remove any excess phenol or catechol. Anal. Calcd for $WCl_2O_4C_{28}H_{28}$ (**1a**): C, 49.22; H, 4.13; Cl, 10.38. Found: C, 48.19; H, 4.77; Cl, 10.92. Calcd for $WCl_2O_4C_{12}H_8$ (**3a**): C, 30.60; H, 1.72; Cl, 15.05. Found: C, 29.63; H, 1.76; Cl, 15.57. Calcd for $WCl_2O_4C_{14}H_{12}$ (**5a**): C, 33.83; H, 2.03; Cl, 14.27. Found: C, 34.35; H, 2.86; Cl, 14.92.

(b) Homoleptic Complexes. The dichlorides prepared in (a) were mixed with a slight excess of 4-methylphenol or catechol in benzene, and the mixture was refluxed for 12 h. Removal of solvent yielded a deep red impure product that was heated under vacuum at 80–90 °C to remove excess phenolic reagents. Anal. Calcd for $WO_6C_{36}H_{24}$ (**2b**): C, 58.72; H, 3.28. Found: C, 58.48; H, 3.92. Calcd for $WO_6C_{18}H_{12}$ (**3b**): C, 42.55; H, 2.39. Found: C, 42.43; H, 2.17. Calcd for $WO_6C_{42}H_{60}$ (**4b**): C, 59.71; H, 7.17. Found: C, 60.83; H, 7.62.

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Volumes of Activation for Electron Exchange by $Mn(CNR)_6^{+/2+}$ Complexes in Acetonitrile

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The volumes of activation for the electron-self-exchange reaction between manganese(I) and manganese(II) hexakis(alkyl isocyanide) complexes have been measured by ^{55}Mn NMR for acetonitrile solutions at ca. 0.1 M total reactant concentration and 5 °C. The values for ΔV^{*} in cm^3/mol, with a typical precision of ±1 cm^3/mol, as a function of the alkyl group, are as follows: methyl, −2.4; ethyl, −5.5; *tert*-butyl, −10.2; cyclohexyl, −17.4; *n*-butyl, −19.7. These results are discussed within two models for predicting ΔV^{*}, both of which are found to be inadequate, given the current knowledge of the relevant parameters. It is concluded that the flexibility of the ligands and not their size contributes most to the observed trends.

Introduction

The study of the kinetics of electron-transfer reactions of transition-metal complexes has long been a major field of research. In recent years, theory and experiment have developed rapidly and cooperatively, to the point that increasingly sophisticated theoretical treatments are being applied to what are superficially rather simple reactions.[1-3] It is our goal to provide experimental data to test these theories and better establish the detailed characteristics of electron-transfer kinetics. To this end, we have been investigating the electron-self-exchange reactivity of manganese(I) and manganese(II) hexakis(alkyl isocyanide) complexes. These complexes were chosen for several reasons. They are quite symmetric, the alkyl group can be varied over a wide range, and they are soluble in a variety of solvents. Both oxidation states of the complexes are substitution inert, thus they must react by an outer-sphere mechanism, and the electron-self-exchange process can be followed directly by ^{55}Mn NMR line broadening. Previous studies have concerned the physical properties of the complexes,[4-6] and the effect of changing the alkyl group, temperature, added electrolyte,[7] and the solvent[8] on the electron-transfer reactivity. Thus, this series of complexes is rapidly becoming one of the best characterized systems available.

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Table I. Activation Parameters for $Mn(CNR)_6^{+/2+}$ Electron Self-Exchange

R	$\Delta V^{\ddagger}$, cm³/mol	$\Delta\beta^{\ddagger}$, cm³/(mol Pa)	T, °C	$\Delta H^{\ddagger}$,[b] kcal/mol	$\Delta S^{\ddagger}$,[b] cal/(mol deg)
CH_3	−2.4 ± 0.8	[a]	0	1.79 ± 0.10	−20 ± 2
	−2.1 ± 0.8		9		
CH_2CH_3	−5.5 ± 0.5		6	3.61 ± 0.16	−18 ± 3
$C(CH_3)_3$	−10.2 ± 0.5		6	5.38 ± 0.10	−19 ± 1
	−13.3 ± 0.9	−0.045 ± 0.006	25		
C_6H_{11}	−17.4 ± 1.3		6	3.36 ± 0.10	−20 ± 1
	−20.2 ± 1.6	−0.082 ± 0.014	12		
$(CH_2)_3CH_3$	−19.7 ± 2.4	−0.081 ± 0.020	6	3.58 ± 0.39[c]	−21 ± 1[c]

[a] Data fit assuming that $\Delta\beta^{\ddagger}$ is zero. [b] From ref 7, except as noted. [c] This work.

This investigation extends the study of these complexes to the measurement of the volumes of activation in acetonitrile. A subsequent paper will discuss the effect of varying the solvent and added electrolyte. Studies of the volume of activation have long been used in organic chemistry and are becoming more common in the study of inorganic reaction mechanisms.[9] Most of the studies of inorganic systems have concerned ligand exchange and substitution reactions,[10] but several recent and a few older studies have been of electron-transfer processes.[11-17] By their nature, electron-transfer processes necessarily involve charged reactants or products and often involve bimolecular interaction between two charged complexes. The volumes of activation of such reactions are more difficult to interpret than are volumes of activation for reactions between neutral molecules.[18] However, if activation volumes are to be a generally useful tool to the inorganic kineticist, we must learn more about reactions between ions. Furthermore, the theory of electron-transfer kinetics has been quite successful at predicting relative and even absolute rate constants but is much less successful at interpreting activation parameters. The addition of the volume of activation as a measured parameter should help in the eventual understanding of the origin of these difficulties.

Experimental Section

The manganese complexes $Mn(CNR)_6(BF_4)$ and $Mn(CNR)_6(BF_4)_2$, where R is methyl, ethyl, *tert*-butyl, and cyclohexyl, were made, and acetonitrile was purified as previously described.[7,8] The complexes with *n*-butyl as the R group were made by a similar procedure. It is difficult to obtain solids of these complexes.[19] Crystals of $Mn(CN(CH_2)_3CH_3)_6(BF_4)$ were obtained by dissolving the product obtained from the usual procedure, an oil, in ethanol, and cooling it on solid CO_2 for 2 days. The resulting solid was rapidly filtered and washed with hexanes cooled on solid CO_2. This procedure was repeated until white crystals were obtained. A solid of the Mn(II) form of the complex could not be obtained. Solutions of known $Mn(CN(CH_2)CH_3)_6^{2+}$ concentration were made by dissolving the Mn(I) complex in acetonitrile and adding an equimolar amount of recrystallized and dried $NOBF_4$, all in a glovebag. Purity was established by ^1H, ^{13}C, and ^{55}Mn NMR spectroscopy and by infrared spectroscopy. The high-pressure NMR measurements were made on an instrument previously described.[20] The sample and the blank were contained in precision-bore glass cylinders with precision sliding glass plugs (Wilmad) in place of the previous polyethylene sample holder. The blank, a sample containing only the diamagnetic Mn(I) complex (ca. 0.1M), and the sample, which also contained some of the same complex in the paramagnetic Mn(II) form (ca. 0.001 M), were in the pressure vessel simultaneously, and their spectra were determined alternately. In all cases, the concentration of the Mn(I) complex was much greater than the concentration of the Mn(II) complex. Line widths of both the blank and the sample were determined by obtaining spectra at four different rf levels and extrapolating to zero rf level at each pressure. Temperature was maintained to ±0.1 °C by submersing the high-pressure vessel in a silicone oil thermostat and was measured by a copper–constantan thermocouple in the vessel. Temperatures of ca. 5 °C were standard to prevent thermal decomposition of the Mn(II) complexes. Measurements were made at a frequency of 22.29 MHz. The temperature-dependence data for the *n*-butyl isocyanide complexes were obtained on a Nicolet NT200 instrument by following the procedures used previously.[7,8] A slightly modified procedure was used to measure the temperature dependence of the volume of activation for the *tert*-butyl isocyanide complexes. For these experiments, a single-sample holder was used and the blank and paramagnetic solutions were studied separately.

Results and Data Treatment

The rate of the electron exchange process (eq 1) was obtained from the ^{55}Mn line widths by using eq 2, where $\Delta\nu_D$ is the width of the line for the diamagnetic complex and $\Delta\nu_P$ is the width of the line for the Mn(I) complex in the presence of added Mn(II).

$$Mn(CNR)_6^{+} + Mn(CNR)_6^{2+} \overset{k}{\rightleftharpoons} Mn(CNR)_6^{2+} + Mn(CNR)_6^{+} \quad (1)$$

$$k = \frac{2\pi(\Delta\nu_P - \Delta\nu_D)}{[Mn(CNR)_6^{2+}]} \quad (2)$$

Here $\Delta\nu$ is half of the width of the dispersion curve as measured between the maximum and minimum. This equation is applicable if the reaction is in the limiting slow-exchange regime, characterized by broadening but no shift of the ^{55}Mn $Mn(CNR)_6^{+}$ resonance with increasing concentration of $Mn(CNR)_6^{2+}$. Such was the case for all systems with the exception of $Mn(CNCH_3)_6^{+/2+}$, and $Mn(CNCH_2CH_3)_6^{+/2+}$. The methyl isocyanide complexes showed some shift of the ^{55}Mn resonance with the addition of the paramagnetic Mn(II) complex. In addition, there was a variation in the line widths between those obtained on the Nicolet (49.52 MHz) instrument and those obtained from the 22.29-MHz data collected in the current study. This variation was approximately proportional to the difference in the frequency. Thus, for this complex, the rate constants are a lower limit and the volume of activation contains a contribution from relaxation processes other than electron transfer. The ethyl isocyanide complexes showed similar behavior, but the effect was much smaller.

Within the transition-state theory of chemical kinetics, the volume of activation is defined by eq 3, and the compressibility of activation by eq 4.[9] The data are thus analyzed by plotting

$$\left(\frac{\partial(\ln k)}{\partial P}\right)_T = \frac{-\Delta V^{\ddagger}}{RT} \quad (3)$$

$$-\left(\frac{\partial(\Delta V^{\ddagger})}{\partial P}\right)_T = \Delta\beta^{\ddagger} \quad (4)$$

ln k vs. P. Such plots are typically curved, with the magnitude of the slope decreasing with increasing pressure. There is no single theoretical treatment that can be used to fit such data, but a

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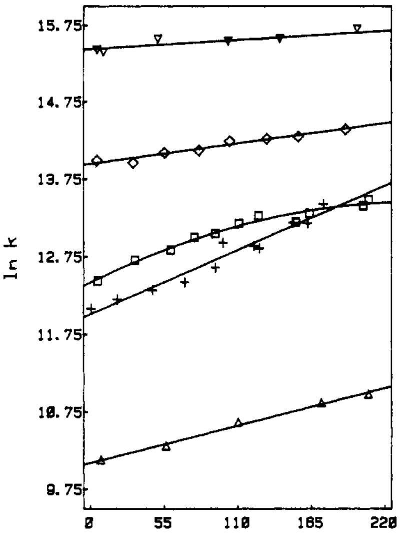

Figure 1. Activation volume data. Natural logarithm of the rate constant vs. pressure in MPa for methyl (▽), ethyl (◇), *n*-butyl (□), cyclohexyl (+), and *tert*-butyl (△).

common empirical equation that fits our data reasonably is eq 5. The data were fit to eq 5 by a least-squares method, giving

$$\ln k = a + bP + cP^2 = \ln k_{P=0} - \left(\frac{\Delta V^\ddagger}{RT}\right)_{P=0} P + \frac{\Delta\beta^\ddagger}{2RT}P^2 \quad (5)$$

the solid lines shown in Figure 1. In order to avoid some problems with the scatter in the data, the widths for the blank were fit to the above equation, and the values from the fit line were used for $\Delta\nu_D$ to analyze the data by eq 2. The parameters are given in Table I. The estimated errors in the parameters were determined from the variance of the points about the fit line. The quadratic term was significant only for *n*-butyl isocyanide complex. In the other cases, the data were fit to the linear function, and no $\Delta\beta^\ddagger$ is defined. The line width data as a function of pressure for each complex and the detailed experimental conditions are listed in the supplementary material.

Discussion

The methyl and ethyl complexes give the most positive $\Delta V^\ddagger$ values, but these results must be regarded with some caution. There is a modest shift of the $Mn(CNCH_3)_6^+$ ^{55}Mn resonance in the mixtures with $Mn(CNCH_3)_6^{2+}$. This may indicate some contribution from a fast-exchange mechanism, which would show a decrease in the line width for a negative $\Delta V^\ddagger$ instead of the increase that is observed in the slow-exchange region. The data are fit assuming the slow-exchange mechanism; thus the apparent $\Delta V^\ddagger$ will be more positive than the true value. This is consistent with the observation that $\Delta V^\ddagger$ is more positive at 9 °C than at 0 °C. There is a significant change in going from *tert*-butyl, −10 cm^3/mol, to cyclohexyl and *n*-butyl, −17 and −20 cm^3/mol respectively. In a study on the *tert*-butyl isocyanide complex, volumes of activation determined at −11 to +45 °C showed no regular variation with temperature, within the precision of these earlier experiments, ±5 cm^3/mol. Similarly, there is no significant variation of $\Delta V^\ddagger$ with temperature for the more limited temperature variation shown in Table I. Values of $\Delta\beta^\ddagger$ are not precisely defined, but there is a general trend that the magnitude of $\Delta\beta^\ddagger$ increases with the magnitude of $\Delta V^\ddagger$.

Before we discuss the possible origins of these results, they can be compared to other measurements of volumes of activation for electron-transfer reactions. Stranks[11] has found values for the $Co(1,2\text{-ethanediamine})_3^{2+/3+}$ and $Fe(H_2O)_6^{2+/3+}$ electron-self-exchange reactions of −20 and −12 cm^3/mol, respectively. Recently, Spiccia and Swaddle[14] have reported on the $MnO_4^{-/2-}$ reaction. This system shows a pronounced influence of the cation, but the cation-independent path gives a volume of activation of −21 cm^3/mol. Thus, it is common to obtain quite negative values of $\Delta V^\ddagger$ for reactions between ions that are both positive or both negative. These studies were done in aqueous solution, but our work shows a similar effect with acetonitrile as the solvent. However, ours is the only study in which the changes in the size of the complexes have been treated experimentally. Positive activation volumes have also been observed in several cases. Sasaki, Saito, and co-workers[15,17] have studied reactions between oppositely charged complexes. These reactions show quite positive values of $\Delta V^\ddagger$ up to 47 cm^3/mol. In some cases, the precursor formation step has been separated from the electron-transfer step, and both show positive values for their respective contributions. These reactions involve net electron-transfer processes and thus also involve net volume changes for the overall reactions. Another type of net electron-transfer reaction involves processes expected to proceed by an inner-sphere mechanism. Candlin and Halpern[12] and van Eldik[13] have reported data on the reduction of various Co(III) complexes by solvated Fe(II) in water and dimethyl sulfoxide. These reactions show generally positive volumes of activation, ranging up to 12 cm^3/mol. They are thus again quite distinct from our results.

Our data will be discussed by using two models. The first is based on the Marcus theory and current formulations of its various terms.[1] The measurement of volumes of activation is a test of the theory, but the theory is designed to account for a variety of factors that are not necessarily related to the concept of a volume of activation and thus is somewhat more complex than most treatments of volumes of activation. The second approach is to predict the volume of activation by using equations that predict the molal volume of ions in solvents and to apply these equations to the reactants and models of the transition state.

In the interpretation of electron-transfer rate constants within the Marcus theory, it has been found useful to consider the overall process in terms of several steps. These are not resolved in the kinetics, but are separated for the purposes of theoretical analysis.

The second-order rate constant, k, is expressed as the product of an equilibrium constant, K_a, for the formation of the precursor complex from the separated reactants and a first-order rate constant, k_{et}, for electron-transfer

$$k = K_a k_{et} \quad (6)$$

Within a semiclassical theory for electron transfer in the high-temperature limit

$$k_{et} = Ae^{-(\Delta G_{in} + \Delta G_{out})/RT} \quad (7)$$

where ΔG_{in} is the free energy required to distort the complexes to the common energy state appropriate for electron transfer. The analogous reorganization energy of the medium, which must occur prior to electron transfer, is ΔG_{out}. The preexponential frequency term, A, is further expressed by

$$A = \nu_{n,eff}\kappa_{el}\, S(r,\theta) \quad (8)$$

where $\nu_{n,eff}$ is an effective nuclear frequency, κ_{el} is the electronic transmission coefficient, and $S(r,\theta)$ is a steric factor, which has a value of 1 for spherical reactants.

For the purpose of interpreting data on volumes of activation, we will consider each step or process and its dependence on pressure. In doing so, we must consider changes in the dimensions of the complexes and the transition state, changes in the volume of the solvent near the reactants and the transition state, and changes in the physical properties of the medium with pressure.

The first step to treat is the formation of the precursor complex from the separated reactants. Considering only electrostatic interactions and encounter probabilities

$$K_a = Pe^{-w/RT} \quad (9a)$$

$$P = \frac{4\pi N r^2\,\partial r}{1000} \quad (9b)$$

$$w = \frac{Z_1 Z_2 e^2}{\epsilon r_\mu (1 + \beta r_\mu)} \quad (9c)$$

$$\beta = \left(\frac{8\pi N e^2 \rho}{1000\epsilon k_B T}\right)^{1/2} \mu^{1/2} \quad (9d)$$

Table II. Predictions of $\Delta V^{\ddagger}$

R	$\Delta V^{\ddagger}$, cm^3/mol	
	Marcus theory	Drude–Nernst eq
CH_3	−5.8	−13.8
CH_2CH_3	−5.2	−12.5
$C(CH_3)_3$	−5.2	−9.6
C_6H_{11}	−3.8	−10.2

Here P is a probability factor, r is the distance between metal centers, ∂r is the range of distances over which electron transfer is likely, r_μ is the distance of closest approach between cations and anions appropriate for the extended Debye–Hückel theory being used to estimate the electrostatic work (w), ϵ is the dielectric constant of the solvent, μ is the ionic strength, N is Avogadro's number, Z_1 and Z_2 are the charges on the reactants, ρ is the solvent density, e is the charge on the electron, and k_B is Boltzmann's constant. On the basis of previous measurements, we assume that the reactants are not ion paired.[4,7]

The parameters that change with pressure are the density of the solvent and the dielectric constant. The variation of the dielectric constant is especially significant. At 10 °C, the bulk dielectric constant of acetonitrile is 38.38 at 0.1 MPa, 41.29 at 100 MPa, and 43.30 at 200 MPa.[21]

The inner-sphere reorganization energy is the energy required to distort the complexes to a compromise geometry between the ground state of the Mn(I) and Mn(II) complexes. This is primarily a small change in the Mn–C bond lengths. The force constant and bond length change should be independent of pressure in the range considered,[11] and thus this term does not contribute to the pressure dependence of the rate constant.

The outer-sphere reorganization energy for an elliptical transition state with axes a and b can be calculated from the following equations due to Cannon:[22]

$$\Delta G_{\text{out}} = \left(\frac{e^2r^2}{2a^2b}\right)\left(\frac{1}{n^2} - \frac{1}{\epsilon}\right) T(\lambda) \tag{10a}$$

$$T(\lambda) = \sum_{l=1,3,5,\ldots}^{\infty} (2l + 1)(\lambda)(\lambda^2 - 1)\,\frac{Q_l(\lambda)}{P_l(\lambda)} \tag{10b}$$

$$\lambda = \frac{a^2}{a^2 - b^2} \tag{10c}$$

Here, n is the index of refraction, and P and Q are Legendre polynominals of the first and second kind. Again, the dielectric constant can contribute to a pressure dependence, as well as the change in the index of refraction.[23]

The preexponential A term is dependent on distances through the electronic transmission coefficient but otherwise is not pressure-dependent.

For all equations, changes in the radius terms with pressure should also be considered. The radii will change little due to compression of bonds since this does not occur at the moderate pressures involved. However, the more flexible ligands, such as cyclohexyl or n-butyl isocyanide, can change conformation and thus change the dimensions of the manganese complexes and the metal–metal distance in the transition state.

The above equations can be used to predict the variation of rate constant with pressure. Such a prediction is dependent on the estimates used for the radius terms. However, assuming that the radius terms are those estimated previously,[7] that they do not vary with pressure, and that density, dielectric constant, and index of refraction of the solution vary as they do for the solvent, a prediction can be made. This was done by calculating the variation in K_a and ΔG_{out} with the variation in the solvent parameters, then assuming that this is the only contribution to the variation in the rate, and fitting the rate variation in the same way the actual data were analyzed. The data fit a second-order polynomial well, with some curvature, and gave the predictions in Table II. The values of $\Delta V^{\ddagger}$ from the simulated pressure dependence show little correlation with the measured values. For the simulated case, there is some increase in $\Delta V^{\ddagger}$ (decrease in magnitude) with increasing molecular weight and radii. This is the expected trend since solvent interaction decreases as charge density decreases. This trend is not seen in the experimental data, indicating that the Marcus theory terms considered are not involved or that there are further contributions to $\Delta V^{\ddagger}$ that dominate the precursor formation constant and outer-sphere reorganization factors. Other possible contributions will be discussed below.

A second method of estimating $\Delta V^{\ddagger}$ is to estimate the difference between the molal volume of the transition state and that of the reactants. This can be done crudely as follows. If the molal volume of the ions is represented as separable into an intrinsic and an electrostatic contribution (eq 11) and the intrinsic volume

$$\bar{V} = \bar{V}_{\text{int}} + \bar{V}_{\text{el}} \tag{11}$$

contribution to the transition state (TS) is considered to be just the sum of the intrinsic volumes of the reactants, then $\Delta V^{\ddagger}$ can be expressed as in eq 12. An expression for the electrostatic

$$\Delta V^{\ddagger} = \bar{V}_{\text{el}}(\text{TS}) - \bar{V}_{\text{el}}(Mn(CNR)_6^{+}) - \bar{V}_{\text{el}}(Mn(CNR)_6^{2+}) \tag{12}$$

contribution to the molal volume at zero ionic strength is the Drude–Nernst equation (eq 13). Few measurements of molal

$$\bar{V}_{\text{el}}^{\circ} = -\frac{NZ^2e^2}{2\epsilon r_{\text{D}}}\,\frac{\partial(\ln \epsilon)}{\partial P} = -\frac{BZ^2}{r_{\text{D}}} \tag{13}$$

volumes in nonaqueous solvents are available. Equation 13 does work reasonably well for 1:1 salts in methanol,[24] but the general validity for acetonitrile is not established. Molal volumes increase with ionic strength. However this effect is probably not the largest error in using eq 13, since the effective B in sea water (0.725 m ionic strength) is only about 7% lower than in pure water.[25] In making these calculations, we have chosen the minimum radii previously estimated for the manganese complexes.[7] These allow for solvent penetration between the extended ligands, as has been concluded occurs for tetraalkylammonium ions in methanol.[26] The reactants and the transition state are assumed to be spheres. The transition state is assigned a volume that is the sum of the volumes of the reactants and a charge of +3. The resulting $\Delta V^{\ddagger}$ values are given in Table II. These values are expected to be overestimates of the magnitude of $\Delta V^{\ddagger}$ because the transition state cannot be a sphere, because the Drude–Nernst equation is probably an overestimate of the charge effect for +3 ions, and because it does not include any compensation for the ionic strength. Although the magnitude of $\Delta V^{\ddagger}$ estimated by this method is closer to that observed than is the Marcus theory estimate, the trend with variation of the ligand is again opposite to that observed.

The two models used for estimating the $\Delta V^{\ddagger}$ relied wholly or primarily on electrostatic interactions. Since they failed to predict even the trend in $\Delta V^{\ddagger}$ with ligand, it is reasonable to look next at differences in intrinsic volume of the complex and the transition state. It has previously been observed that electron-transfer rate constants should be quite sensitive to the distance between the donor and acceptor.[27] Such a dependence is apparently observed for rigid bimolecular systems and for frozen matrices.[28] However, with the possible exception of the series of manganese isocyanides being considered here, the trend of bimolecular reactions is typically for the rate to increase with increasing size of the complex.[29-32] This presumably is due to the decrease in outer-sphere

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reorganization energy and an increase in the probability of forming the precursor complex with increasing size.

The maximum variation in rate with pressure is about a factor of 2 for 100 MPa. On the basis of the variation of rate with the estimated radii previously observed at 1 atm for these complexes,[7] the variation with pressure could be explained by a change in electron-transfer distance of about 0.1 Å for a pressure change of 100 MPa. The trend in $\Delta V^{\ddagger}$ appears to be related to the flexibility of the ligands more than any other parameter. The more flexible ligands, those that can form a smaller complex by a change in conformation, give the more negative $\Delta V^{\ddagger}$ values. These changes in volume of the reactants through changes in ligand conformation are part of the intrinsic volume component and can be understood as follows. Assuming that electron transfer is especially sensitive to the Mn–Mn distance, the transition state will have the ligands between the Mn centers in their most compact conformations at a given pressure. The reactants must assume this more compact conformation before collision to form the precursor complex takes place. Thus there is formally a conformational preequilibrium between the ground state and the compact state, with a negative ΔV. The complexes with inflexible ligands will not show this effect and will give more positive values of $\Delta V^{\ddagger}$. The contribution from the electrostatic component is not zero, but is probably constant within ± 3 cm^3/mol as in the estimates made of it.

It has been previously observed that curvature of the ln k vs. P plots, apparent $\Delta\beta^{\ddagger}$ different from zero, is associated with changes in solvation.[33] This could be the case for the *n*-butyl isocyanide complexes, but it is not clear why only these ions should show this effect, when other ones, such as the ethyl isocyanide complexes, are at least as solvent accessible. Another interpretation, consistent with the proportionality between $\Delta V^{\ddagger}$ and $\Delta\beta^{\ddagger}$, is that the ligand flexibility decreases with pressure, and thus $\Delta\beta^{\ddagger}$ is negative and proportional to ligand flexibility and $\Delta V^{\ddagger}$. It is reasonable to expect ligand flexibility to decrease with pressure since as the ligand adopts a more compact conformation, its ability to compact further merely through conformational changes is decreased.

The other activation parameters can now be considered. These have been discussed previously in more detail.[7,8] To summarize, the observation is that the rate variation with ligand is entirely the result of a change in enthalpy. The simplest interpretation of this is that the larger complexes must distort to allow the manganese centers to approach to a comparable electron-transfer distance regardless of ligand. This is consistent with the negative volumes of activation arising from reaction through a compact form of the complex. It is also possible that the variation of electron-transfer rate with ligand at ambient pressure is due wholly or partly to a change in electron-transfer distance. It this is the case, the entropies of activation should have become less favorable with decreasing rate, and there should not have been a significant difference in intrinsic volume between the transition state and the reactants. It is likely that both electron-transfer distance and selective reactivity of intrinsically smaller ions is involved, along with solvent effects that cause compensation between the activation parameters. These questions are important ones if any understanding of the effect of the medium on electron-transfer reactivity is to be attained. Better models for the precursor association and solvent reorganization properties are needed, as are further results on rate constants and activation parameters as a function of solvent. Data on the molal volumes of large ions of different charges in organic solvents at concentrations typical for kinetic measurements would help greatly in the second method used to estimate $\Delta V^{\ddagger}$. The work presented here is being extended through a study of the volume of activation as a function of solvent and ionic strength.

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Supplementary Material Available: Tables of reactant concentrations, temperatures, and line widths (5 pages). Ordering information is given on any current masthead page.

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Stopped-Flow Study of Ligand-Exchange Kinetics between Terbium(III) Ion and Calcium(II) Ethylenediaminetetraacetate

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Exchange of EDTA between calcium(II) and terbium(III) in the pH range 4.4–6.0 was studied by using a stopped-flow spectrophotometer to monitor the increase in Tb^{3+} luminescence as it binds EDTA. The data suggest competing pathways for exchange of the ligand in the pH range 5.0–6.0, involving either a direct attack by Tb^{3+} followed by release of Ca^{2+} or a faster, H^+-catalyzed process involving the dissociation of $CaH(EDTA)^-$ followed by rapid binding of Tb^{3+}. Evidence for an additional pathway of dissociation of $Ca(EDTA)^{2-}$ at pH values less than 5.0 is also presented.

Introduction

The substitution of tripositive lanthanide ions, Ln^{3+}, for Ca^{2+} in biomolecular systems has been shown to be a useful technique for probing such systems.[1,2] A logical step toward understanding the binding of these ions to macromolecules is first to characterize the kinetics of binding to model systems such as polycarboxylate ligands, e.g. EDTA, which are potential models for the calcium-binding sites in proteins. We focus our attention on EDTA as the ligand in this study because the rate of exchange of EDTA between Ca^{2+} and Tb^{3+} occurs on a time scale which can be conveniently measured on a stopped-flow spectrophotometer.

A large volume of work exists concerning the kinetics of exchange between chelated and unchelated metal ions of various types including the lanthanides and actinides.[3-27] Most studies

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