$$[\mathrm{RuCl(OH)(py)_4}]^+ \rightarrow [\mathrm{RuCl(O)(py)_4}]^+ + \mathrm{e}^- \qquad (10)$$

oxidation of $Ru^{II}—OH_2$ species to the corresponding $Ru^{IV}=O$ species has been known to be a common preparative route for high-valent ruthenium complexes with an oxygen ligand,[5-13] and in fact, eq 10 has been demonstrated.[27]

In contrast, the analogous *trans*-$[Ru(NO_2)(H_2O)(py)_4]^+$ changed to *trans*-$[Ru(ONO)(O)(py)_4]^+$ with retention of the nitro nitrogen, as was indicated by a ^{15}N labeling experiment (Table I). Although both *trans*-$[RuCl(O)(py)_4]^+$ and *trans*-$[Ru(ONO)(O)(py)_4]^+$ have identical oxo ligands, the origin of the ligand in each product is clearly different. The oxygen-transfer process expressed by Scheme III is not necessary for the explanation. One possible oxidation process of *trans*-$[Ru(NO_2)(H_2O)(py)_4]^+$ is expressed by Scheme IV (eqs 11-13). Equation 13 will proceed rapidly before $[HO-Ru^{III}-ONO]^+$ dimerizes with $[HO-Ru^{III}-NO_2]^+$ to give a transient intermediate because $[HO-Ru^{III}-ONO]^+$ is less reactive toward the dimerization reaction, as is suggested by electrochemical observations.

Scheme IV

$$[\mathrm{H_2O—Ru^{II}—NO_2}]^+ \rightarrow [\mathrm{HO—Ru^{III}—NO_2}]^+ + \mathrm{e}^- + \mathrm{H}^+ \qquad (11)$$

$$[\mathrm{HO—Ru^{III}—NO_2}]^+ \rightarrow [\mathrm{HO—Ru^{III}—ONO}]^+ \qquad (12)$$

$$[\mathrm{HO—Ru^{III}—ONO}]^+ \rightarrow [\mathrm{O{=}Ru^{IV}—ONO}]^+ + \mathrm{e}^- + \mathrm{H}^+ \qquad (13)$$

The source of the oxygen atom in *trans*-$[RuCl(O)(py)_4]^+$ can be the one oxygen atom of the nitro ligand in *trans*-$[RuCl(NO_2)(py)_4]$, while that in *trans*-$[Ru(ONO)(O)(py)_4]^+$ can be ascribed to the aqua ligand, which existed originally in *trans*-$[Ru(NO_2)(H_2O)(py)_4]^+$. The selectivity observed in the formation reaction of the high-valent ruthenium complexes with a monooxygen ligand can reasonably be explained by a consideration of the reactivity of *trans*-$[RuX(NO_2)(py)_4]^n$ where a strong dependence of the X ligand trans to NO_2^- is seen. One reason that gives rise to the selectivity appears to be that while the nitro-nitrito isomerization occurs rapidly at 25 °C in both nitro complexes, a concomitant oxygen transfer to give a monooxygen moiety (Scheme I, compound e to A or B), via the formation of transient intermediate (Scheme I, compound c to compound e), is relatively slow in *trans*-$[Ru(NO_2)(H_2O)(py)_4]^+$. How OH_2 (or OH) ligand deaccelerates the oxygen transfer reaction is a problem for future study.

Conclusion

A chemical oxidation reaction of *trans*-$[RuX(NO_2)(py)_4]^n$ depends on the X ligand, which exists trans to NO_2^-. For X = Cl, *trans*-$[RuCl(O)(py)_4]^+$ is formed as the sole product (95% yield is usual), while *trans*-$[Ru(ONO)(O)(py)_4]^+$ is produced when X = H_2O, with retention of the original nitro nitrogen. The conversion processes were revealed through electrochemical investigations at various temperatures (−25 to −40 °C). Both chemical and electrochemical oxidation of *trans*-$[RuCl(NO_2)(py)_4]$ proceed by an oxygen transfer from one nitro group to another, via an intermediate consisting of *trans*-$[RuCl(NO_2)(py)_4]^+$ and its isomer, *trans*-$[RuCl(ONO)(py)_4]^+$. The key to the occurrence of the rare reaction is a decomposition mode of the intermediate existing transiently.

Such an intermediate process is not required for the oxidation of *trans*-$[Ru(NO_2)(H_2O)(py)_4]^+$ to give *trans*-$[Ru(ONO)(O)(py)_4]^+$. It can reasonably be assumed that a one-electron oxidation of *trans*-$[Ru(NO_2)(H_2O)(py)_4]^+$ gives first predominantly *trans*-$[Ru(ONO)(OH)(py)_4]^+$, which then changes directly to *trans*-$[Ru(ONO)(O)(py)_4]^+$ by a further one-electron oxidation.

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Temperature and Pressure Effects on the Outer-Sphere Electron-Transfer Reaction between Hexacyanoferrate(II) and Pentaamminecobalt(III) Complexes in Aqueous Solution. Comparison of Experimental and Theoretical Volumes of Activation

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The kinetics of a series of outer-sphere electron-transfer reactions of the type $Co(NH_3)_4(NH_2R)X^{(3-n)+} + Fe(CN)_6^{4-} \rightarrow Co^{2+} + 4NH_3 + NH_2R + X^{n-} + Fe(CN)_6^{3-}$ ($X = N_3^-$, R = H; $X = Cl^-$, R = H, CH_3, $i\text{-}C_4H_9$) were studied as a function of temperature and pressure. It was possible to separate the ion-pair formation constant and the electron-transfer rate constant in a kinetic way, and the corresponding thermodynamic and activation parameters were determined. For the electron-transfer process, the rate and activation parameters lie in the ranges $0.06 \le k \times 10^2 \le 20\ \mathrm{s^{-1}}$, $84 \le \Delta H^\ddagger \le 118\ \mathrm{kJ\ mol^{-1}}$, $+11 \le \Delta S^\ddagger \le 113\ \mathrm{J\ K^{-1}\ mol^{-1}}$, and $+19 \le \Delta V^\ddagger \le +34\ \mathrm{cm^3\ mol^{-1}}$. The experimentally observed activation volumes are in good agreement with those predicted theoretically on the basis of an average $\lambda^\ddagger$ value of 0.48 ± 0.07. The results are discussed in reference to related studies reported in the literature.

Introduction

In recent years significant advances have been achieved in the application of pressure as a kinetic parameter in mechanistic studies of transition-metal complexes.[1-3] This has in many cases added a further dimension to our mechanistic insight, since such studies enable us to visualize the chemical process in terms of volume changes along the reaction coordinate. We have in the past systematically studied the pressure dependence of a wide range of typical reactions of inorganic and organometallic systems[1-3] and are convinced of the mechanistic discrimination ability of pressure when employed as a kinetic parameter. In this respect, we and others have studied the effect of pressure on some typical outer-sphere electron-transfer reactions.[4-12] Theoretical calcu-

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lations based on the classical Hush–Marcus theory have been employed to account for the observed pressure effects.[7,9-14] However, the rather limited experimental data available restrict the general validity of such theoretical calculations and the understanding of such processes.

We have now completed a systematic study[15] of a series of typical outer-sphere electron-transfer reactions between $Fe(CN)_6^{4-}$ and four different pentaamminecobalt(III) complexes in which we have varied one of the ammine ligands as well as the ligand in the sixth coordination site. These data along with the three complexes studied previously[4,5] give us a total of seven complete systems for which all the activation parameters ($\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, and $\Delta V^{\ddagger}$) are now available. In addition, we report results for the theoretical calculation of the activation volumes for the rate-determining electron-transfer reactions.

Outer-sphere electron-transfer reactions usually proceed according to a multistep process, involving the formation of an encounter (ion-pair) complex followed by rate-determining electron transfer. For the reactions under investigation this can be formulated as in (1). Under pseudo-first-order conditions, i.e. in

$$Co(NH_3)_4(NH_2R)X^{(3-n)} + Fe(CN)_6^{4-} \overset{K}{\rightleftharpoons} \{Co(NH_3)_4(NH_2R)X^{(3-n)+},Fe(CN)_6^{4-}\}$$

$$\{Co(NH_3)_4(NH_2R)X^{(3-n)+},Fe(CN)_6^{4-}\} \xrightarrow{k} Co^{2+} + 4NH_3 + NH_2R + X^{n-} + Fe(CN)_6^{3-} \quad (1)$$

the presence of excess $Fe(CN)_6^{4-}$, the observed rate constant is a composite quantity as shown in (2). It is therefore essential

$$k_{obs} = kK[Fe(CN)_6^{4-}]/\{1 + K[Fe(CN)_6^{4-}]\} \quad (2)$$

to analyze the $[Fe(CN)_6^{4-}]$ dependence of k_{obs} in detail in order to be able to resolve the values of k and K as a function of temperature and pressure. The systems studied in this investigation are as follows: $X = N_3^-$, $R = H$; $X = Cl^-$, $R = H$, CH_3, $i\text{-}C_4H_9$.

Experimental Section

The following complexes were prepared according to published procedures: $[Co(NH_3)_5N_3](ClO_4)_2$,[16] $[Co(NH_3)_5Cl](ClO_4)_2$,[17,18] *trans*-$[Co(NH_3)_4(CH_3NH_2)Cl](ClO_4)_2$,[19,20] and *trans*-$[Co(NH_3)_4(i\text{-}C_4H_9NH_2)Cl](ClO_4)_2$.[19,20] Cemical analyses[21] and UV-visible spectral data were in good agreement with the theoretically expected values and those reported before,[19,22,23] respectively. All chemicals used were of analytical reagent grade, and doubly distilled water was used as solvent throughout this study. The ionic strength of the medium was maintained constant at 1.0 M with the aid of $NaClO_4$. The redox reactions were followed via the formation of $Fe(CN)_6^{3-}$, and H_2EDTA^{2-} was added to prevent the formation of $Co_3[Fe(CN)_6]_2$ by binding the produced Co^{2+} as Co(EDTA).

UV-visible absorption spectra were recorded on Shimadzu UV 250 and Perkin-Elmer Lambda 5 spectrophotometers. pH measurements were performed on a WTW instrument equipped with a reference electrode filled with 3 M NaCl in order to prevent the precipitation of $KClO_4$ when KCl was used as electrolyte. Kinetic measurements were performed with a modified Aminco stopped-flow instrument at ambient pressure and with a homemade high-pressure stopped-flow unit at elevated pressure.[24] The slower reactions were followed in the thermostated cell compartment of the mentioned spectrophotometers at ambient pressure and in a Zeiss spectrophotometer equipped with a thermostated high-pressure cell[25] at elevated pressure. The temperature control on all the kinetic instruments was within ±0.1 °C. All kinetic measurements were performed under pseudo-first-order conditions, and the rate constants were observed in the usual way using an on-line data acquisition system[26] in the case of the

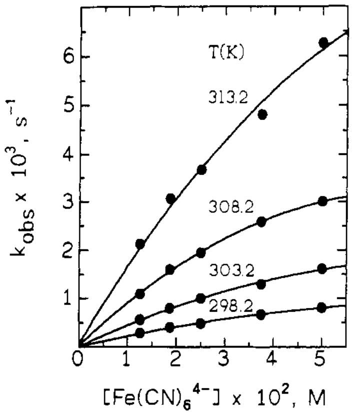

Figure 1. Plots of k_{obs} versus $[Fe(CN)_6^{4-}]$ for the reduction of *trans*-$Co(NH_3)_4(i\text{-}C_4H_9NH_2)Cl^{2+}$ as a function of temperature. Solid lines represent nonlinear best fits of the data points.

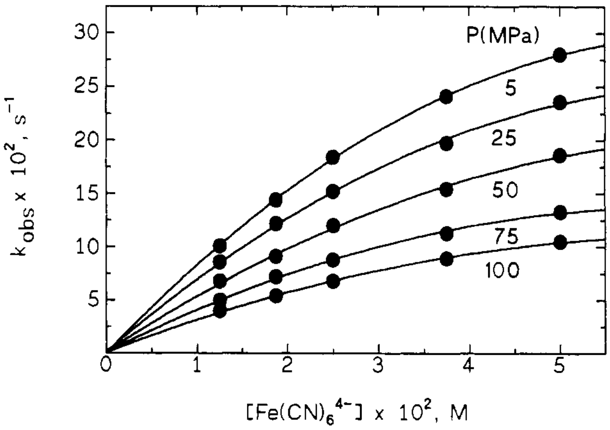

Figure 2. Plots of k_{obs} versus $[Fe(CN)_6^{4-}]$ for the reduction of *trans*-$Co(NH_3)_4(i\text{-}C_4H_9NH_2)Cl^{2+}$ as a function of pressure at 308.2 K. Solid lines represent nonlinear best fits of the data points.

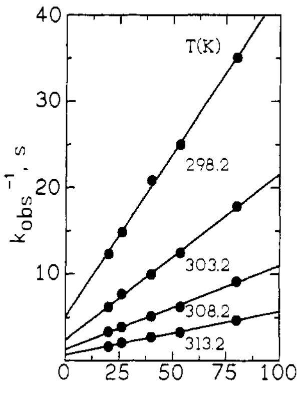

Figure 3. Plots of k_{obs}^{-1} versus $[Fe(CN)_6^{4-}]^{-1}$ for the data in Figure 1.

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Table I. Values of *K* and *k* as a Function of Pressure for the Reaction[a]

$$\mathrm{Co(NH_3)_4(NH_2R)X^{(3-n)+} + Fe(CN)_6^{4-} \rightarrow Co^{2+} + 4NH_3 + NH_2R + X^{n-} + Fe(CN)_6^{3-}}$$

R	X^{n-}	*T*, K	*P*, MPa	*K*,[b] M^{-1}	thermodynamic parameters	*k*,[b] s^{-1}	activation params
H	N_3^-	290.2	0.1	66 ± 1	$\Delta H° = 2 \pm 14$ kJ mol^{-1}	$(1.73) \pm 0.07) \times 10^{-4}$	$\Delta H^\ddagger = 104 \pm 6$ kJ mol^{-1}
		298.2		49 ± 1	$\Delta S° = -204 \pm 46$ J K^{-1} mol^{-1}	$(6.2 \pm 0.4) \times 10^{-4}$	$\Delta S^\ddagger = +44 \pm 20$ J K^{-1} mol^{-1}
		300.7		45 ± 1		$(9.9 \pm 0.6) \times 10^{-4}$	
		303.2		71.6 ± 0.4		$(1.12 \pm 0.06) \times 10^{-3}$	
		308.2		70.5 ± 0.1		$(2.36 \pm 0.06) \times 10^{-3}$	
			5	61.7 ± 0.3	$\Delta \bar{V} = -16.5 \pm 2.2$ cm^3 mol^{-1}	$(2.46 \pm 0.05) \times 10^{-3}$	$\Delta V^\ddagger = +18.8 \pm 1.1$ cm^3 mol^{-1}
			25	69.9 ± 0.2		$(2.07 \pm 0.04) \times 10^{-3}$	
			50	90.4 ± 0.2		$(1.65 \pm 0.04) \times 10^{-3}$	
			75	105.0 ± 0.3		$(1.42 \pm 0.02) \times 10^{-3}$	
			100	110 ± 1		(1.22 [illegible] 0.03) × 10^{-3}	
H	Cl^-	298.2	0.1	37.9 ± 0.3	$\Delta H° = 28 \pm 8$ kJ mol^{-1}	$(2.7 \pm 0.2) \times 10^{-2}$	$\Delta H^\ddagger = 85 \pm 3$ kJ mol^{-1}
		303.2		51.8 ± 0.3	$\Delta S° = -120 \pm 27$ J K mol^{-1}	$(4.6 \pm 0.2) \times 10^{-2}$	$\Delta S^\ddagger = +11 \pm 8$ J K^{-1} mol^{-1}
		308.2		50.6 ± 1.0		$(8.7 \pm 0.6) \times 10^{-2}$	
		313.2		74 ± 2		$(14.5 \pm 0.7) \times 10^{-2}$	
		308.2	5	56.5 ± 0.8	$\Delta \bar{V} = -3 \pm 8$ cm^3 mol^{-1}	$(8.5 \pm 0.6) \times 10^{-2}$	$\Delta V^\ddagger = +25.9 \pm 3.1$ cm^3 mol^{-1}
			25	63.6 ± 1.6		$(6.8 \pm 0.5) \times 10^{-2}$	
			50	47.9 ± 0.3		$(5.9 \pm 0.5) \times 10^{-2}$	
			75	43.9 ± 0.2		$(4.7 \pm 0.3) \times 10^{-2}$	
			100	76.5 ± 1.9		$(3.0 \pm 0.1) \times 10^{-2}$	
CH_2	Cl^-	293.2	0.1	48.5 ± 0.1	$\Delta H° = -20 \pm 9$ kJ mol^{-1}	$(2.1 \pm 0.2) \times 10^{-2}$	$\Delta H^\ddagger = 114 \pm 4$ kJ mol^{-1}
		298.2		37.2 ± 0.3	$\Delta S° = -280 \pm 29$ J K^{-1} mol^{-1}	$(5.0 \pm 0.2) \times 10^{-2}$	$\Delta S^\ddagger = +112 \pm 14$ J K^{-1} mol^{-1}
		303.2		31.6 ± 0.5		$(11.0 \pm 0.1) \times 10^{-2}$	
		308.2		35.2 ± 0.4		$(21.0 \pm 0.8) \times 10^{-2}$	
			5	35.3 ± 0.3	$\Delta \bar{V} = +3 \pm 2$ cm^3 mol^{-1}	$(19.0 \pm 0.5) \times 10^{-2}$	$\Delta V^\ddagger = +25.1 \pm 1.5$ cm^3 mol^{-1}
			25	30.9 ± 1.2		$(17.9 \pm 1.8) \times 10^{-2}$	
			50	36.9 ± 1.1		$(12.6 \pm 1.5) \times 10^{-2}$	
			75	32.7 ± 0.2		$(10.2 \pm 0.7) \times 10^{-2}$	
			100	30.1 ± 0.9		$(7.8 \pm 0.6) \times 10^{-2}$	
$i\text{-}C_4H_9$	Cl^-	298.2	0.1	13.2 ± 0.8	$\Delta H° = -4 \pm 3$ kJ mol^{-1}	$(20 \pm 2) \times 10^{-2}$	$\Delta H^\ddagger = 103 \pm 2$ kJ mol^{-1}
		303.2		12.2 ± 0.7	$\Delta S° = -240 \pm 9$ J K^{-1} mol^{-1}	$(42 \pm 3) \times 10^{-2}$	$\Delta S^\ddagger = +87 \pm 8$ J K^{-1} mol^{-1}
		308.2		12.9 ± 1.3		$(78 \pm 8) \times 10^{-2}$	
		313.2		12.9 ± 1.1		$(156 \pm 16) \times 10^{-2}$	
		308.2	5	12.4 ± 0.9	$\Delta \bar{V} = -6 \pm 1$ cm^3 mol^{-1}	$(76 \pm 6) \times 10^{-2}$	$\Delta V^\ddagger = +31.3 \pm 0.9$ cm^3 mol^{-1}
			25	14.5 ± 0.3		$(56 \pm 2) \times 10^{-2}$	
			50	14.6 ± 1.2		$(44 \pm 5) \times 10^{-2}$	
			75	16.1 ± 0.9		$(30 \pm 2) \times 10^{-2}$	
			100	16.0 ± 0.5		$(24 \pm 1) \times 10^{-2}$	

[a] Rate data are reported in Table SI (supplementary material): [Co(III)] = 1×10^{-3} M; $[H_2EDTA^{2-}] = 2 \times 10^{-3}$ M; ionic strength = 1.0 M; [Fe(II)] = $(0.6\text{–}7.5) \times 10^{-2}$ M. [b] Estimated from plots of k_{obs}^{-1} versus $[Fe(CN)_6^{4-}]^{-1}$ according to eq 3.

Table II. Summary of the Equilibrium Constants and Associated Thermodynamic Parameters for Ion-Pair Formation According to

$$\mathrm{Co(NH_3)_4(NH_2R)X^{(3-n)+} + Fe(CN)_6^{4-} \overset{K}{\rightleftharpoons} \{Co(NH_3)_4(NH_2R)X^{(3-n)+}, Fe(CN)_6^{4-}\}}$$

R	X^{n-}	*K*(25 °C), M^{-1}	$\Delta H°$, kJ mol^{-1}	$\Delta S°$, J K^{-1} mol^{-1}	$\Delta \bar{V}$, cm^3 mol^{-1}	ref
H	H_2O	480 ± 110			−15 ± 8	5
H	C_5H_5N	168 ± 7				5
H	DMSO	34 ± 4	−8 ± 21	−240 ± 67	−11 ± 3	5
H	N_3^-	49 ± 1	+2 ± 14	−204 ± 46	−16 ± 2	this work
H	Cl^-	37.9 ± 0.3	+28 ± 8	−120 ± 27	−3 ± 8	this work
CH_3	Cl^-	37.2 ± 0.3	−20 ± 9	−280 ± 29	+3 ± 2	this work
$i\text{-}C_4H_9$	Cl^-	13 ± 1	−4 ± 3	−240 ± 9	−6 ± 1	this work

stopped-flow instrumentation. The corresponding first-order plots were linear for at least 3 half-lives of the reaction under all experimental conditions.

Results and Discussion

The observed pseudo-first-order rate constant, k_{obs}, was measured as a function of $[Fe(CN)_6^{4-}]$ at different temperatures and pressures, and the results for the four investigated systems are summarized in Table SI (supplementary material). A typical example of the results for one system is presented in Figures 1 and 2, at various temperatures and pressures, respectively. For all the investigated systems, plots of k_{obs} versus $[Fe(CN)_6^{4-}]$ are strongly curved and the double-reciprocal-plot procedure according to (3) can be adopted to resolve the values of *k* and *K* as a function

$$k_{obs}^{-1} = k^{-1} + \{kK[Fe(CN)_6^{4-}]\}^{-1} \qquad (3)$$

of temperature and pressure (see Figures 3 and 4, respectively). The resulting values of *K* and *k* for all the investigated systems

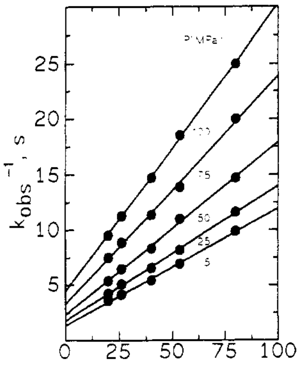

Figure 4. Plots of k_{obs}^{-1} versus $[Fe(CN)_6^{4-}]^{-1}$ for the data in Figure 2.

Table III. Summary of Rate and Activation Parameters for Electron Transfer According to the Reaction

$$\{Co(NH_3)_4(NH_2R)X^{(3-n)+},Fe(CN)_6^{4-}\} \rightarrow Co^{2+} + 4NH_3 + NH_2R + X^{n-} + Fe(CN)_6^{3-}$$

R	X^{n-}	10^2k(25 °C), s^{-1}	$\Delta H^\ddagger$, kJ mol^{-1}	$\Delta S^\ddagger$, J K^{-1} mol^{-1}	$\Delta V^\ddagger$, cm^3 mol^{-1}	ref
H	H_2O	12.7 ± 1.0	102 ± 5	+79 ± 15	+26.5 ± 2.4	5
H	C_5H_5N	0.89 ± 0.03	118 ± 8	+113 ± 29	+29.8 ± 1.4	5
H	DMSO	20 ± 1	84 ± 2	+25 ± 8	+34.4 ± 1.1	5
H	N_3^-	0.062 ± 0.004	104 ± 6	+44 ± 20	+18.8 ± 1.1	this work
H	Cl^-	2.7 ± 0.2	85 ± 3	+11 ± 8	+25.9 ± 3.1	this work
CH_3	Cl^-	5.0 ± 0.2	114 ± 4	+112 ± 14	+25.1 ± 1.5	this work
i-C_4H_9	Cl^-	20 ± 2	103 ± 2	+87 ± 8	+31.3 ± 0.9	this work

Table IV. Summary of Theoretically Calculated Activation Volume Data for the Reduction of Various Co(III) Complexes by $Fe(CN)_6^{4-}$ [a]

Co(III) complex	$\Delta V^\ddagger_{SR}$	$\Delta V^\ddagger_{COUL}$	$\Delta V^\ddagger_{DH}$	$\Delta V^\ddagger_{NA}$	$\Delta V^\ddagger_{LS/HS}$	$\Delta\bar{V}^b$	$\Delta V^\ddagger_{exp}$	$\lambda^\ddagger$
$Co(NH_3)_5H_2O^{3+}$	−7.4	+13.1	−11.1	−5.0	+10	54.9	+26.5	0.49
$Co(NH_3)_5py^{3+}$	−5.4	+9.9	−9.3	−6.6	+10	62.6	+29.8	0.50
$Co(NH_3)_5DMSO^{3+}$	−5.5	+10.1	−9.4	−6.5	+10	60.9	+34.4	0.59
$Co(NH_3)_5N_3^{2+}$	−5.0	+6.1	−5.9	−7.2	+10	56.0	+18.8	0.37
$Co(NH_3)_5Cl^{2+}$	−5.9	+7.2	−6.6	−6.1	+10	57.7	+25.9	0.47
$Co(NH_3)_4(NH_2CH_3)Cl^{2+}$	−6.6	+8.1	−7.1	−5.4	+10	58.9	+25.1	0.44
$Co(NH_3)_4(NH_2\text{-}i\text{-}C_4H_9)Cl^{2+}$	−6.1	+7.5	−6.7	−5.8	+10	61.1	+31.3	0.53

[a] Data taken from ref 15 and quoted in cm^3 mol^{-1}. [b] Calculated from the partial molar volume data in Table V: $\Delta\bar{V} = \bar{V}_{Fe(III)} + \bar{V}_{Co(II)} - \bar{V}_{Fe(II)} - \bar{V}_{Co(III)}$.

are summarized in Table I as a function of temperature and pressure, along with the associated thermodynamic and kinetic parameters, respectively. A comparison of the results of this investigation with those published previously on closely related systems is presented in Tables II and III for K and k, respectively.

The values for the ion-pair formation constants K vary between 13 and 480 M^{-1} with no specific trend that can be correlated with the charge on the Co(III) complex. This indicates that the interaction is not purely electrostatic and that other effects such as hydrogen bonding may be very important and account for the observed formation constants. This deviation from the expected trends is also clearly seen in the values of $\Delta\bar{V}$. On the basis of ion-pair formation that is accompanied by charge neutralization and a decrease in electrostriction, $\Delta\bar{V}$ is expected to be positive. Although our values are subjected to large errors due to the errors in K and the indirect way in which the latter is determined, it is clear from Table II that our values are all slightly negative or at most close to zero. Sasaki and co-workers[27] reported a very significantly positive $\Delta\bar{V}$ for ion-pair formation between $Co(NH_3)_5py^{3+}$ and $Fe(CN)_6^{4-}$, viz. +23.4 ± 3.3 cm^3 mol^{-1}, compared to an almost zero value of +3.5 ± 0.6 cm^3 mol^{-1} for the $Co(NH_3)_5H_2O^{3+}/Fe(CN)_6^{4-}$ system.[8] The majority of our data indicate that no significant volume increase occurs during ion-pair formation; i.e. no significant charge neutralization occurs. Thus we tend to support our earlier conclusion[5] that charge neutralization effects are probably smaller than intrinsic volume decreases due to the overlap of the molecular spheres, suggesting that the ionic nature of the species within the ion pairs is retained and they can act on the surrounding solvent molecules almost as if they are separated individual ions. This means that no significant desolvation occurs during the formation of the precursor (ion-pair) species and that the reactants are separated by solvent molecules.

According to the data on the electron-transfer process in Table III, there is no specific correlation between the value of k and the size of the NH_2R or X^{n-} ligands that may determine the distance of closest approach between the redox centers. It has been reported by Haim et al.[28] that the optimal interaction between the redox centers occurs under preservation of the orbital symmetry, i.e. only when the reductant contacts the cobalt center via an amine ligand. Under such conditions, steric hindrance or other effects on NH_2R or X^{n-} cannot affect the electron-transfer rate constant significantly. Some specific ligand effects, such as a unique coordination geometry in Co–N_3 or π-back-bonding effects in Co–py, may partially account for some of the variations observed in k. In a similar way the values of $\Delta H^\ddagger$ vary in the range 84–114 kJ mol^{-1}, and $\Delta S^\ddagger$ and $\Delta V^\ddagger$ are significantly positive throughout the series of complexes. In this respect, it is appropriate to note that $\Delta V^\ddagger$ values reported in the literature, viz. +37.6 ± 1.2 cm^2 mol^{-1} for the reduction of $Co(NH_3)_5H_2O^{3+}$ [8] and +23.9 ± 1.0 cm^3 mol^{-1} for the reduction of $Co(NH_3)_5py^{3+}$ [27], also fall within the range of values reported for this parameter in Table III. Very significant is the fact that $\Delta V^\ddagger$ does not show any apparent correlation with the overall charge on the Co(III) complex.

There are basically two ways in which $\Delta V^\ddagger$ for the electron-transfer step can be interpreted, a more qualitative and a more quantitative one. We have argued previously[5] that during electron transfer within the precursor (ion-pair) species, major volume changes occur due to intrinsic and solvational changes. It was predicted[5] that an overall volume increase of ca. 22 cm^3 mol^{-1} occurs during the reduction of Co(III) to Co(II) and an increase of ca. 43 cm^3 mol^{-1} during the oxidation of $Fe(CN)_6^{4-}$ to $Fe(CN)_6^{3-}$.[29] In this way the redox reaction will result in an overall volume increase of ca. 65 cm^3 mol^{-1}, if we consider the reaction partners to exist as separated ions in the ion-pair precursor and successor species (see earlier discussion). It follows that the values of $\Delta V^\ddagger$ in Table III are approximately 50% of the overall $\Delta\bar{V}$; i.e. the transition state for the electron-transfer process is ca. halfway between the reactant and product states on a volume basis. This result is also in line with the general principle that a rearrangement of the reactant molecules must occur prior to electron transfer such that the energy of the electron is the same at either redox sites and will fit both states equally well.[30] This must, according to our results, represent the halfway position on a volume basis. This would mean that both the Co(III) and Fe(II) centers reach a half-reduced/half-oxidized geometry in the transition state.

A more quantitative interpretation of the data is possible if one calculates $\Delta V^\ddagger$ theoretically on the basis of the Marcus–Hush theories of electron-transfer reactions[31,32] as applied by Swaddle and co-workers.[9,10] These theoretical treatments have been developed for outer-sphere electron-transfer reactions and take into account volume changes resulting from the internal rearrangement of the two reacting molecules ($\Delta V^\ddagger_{IR}$), the rearrangement of the surrounding solvent molecules ($\Delta V^\ddagger_{SR}$), the Coulombic work required to bring the reactants together ($\Delta V^\ddagger_{COUL}$), and Debye–Hückel or other electrolyte effects ($\Delta V^\ddagger_{DH}$). It follows that for

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Table V. Summary of Partial Volume Data for the Different Co(II/III) and Fe(II/III) Complexes in Aqueous Solution at 25 °C

complex	partial molar vol, $cm^3\ mol^{-1}$ M(II)[a]	partial molar vol, $cm^3\ mol^{-1}$ M(III)[b]
$Co(NH_3)_5H_2O^{2+/3+}$	72.3	60.3
$Co(NH_3)_5py^{2+/3+}$	148.9	129.2
$Co(NH_3)_5DMSO^{2+/3+}$	130.2	112.2
$Co(NH_3)_5N_3^{+/2+}$	82.0	68.9
$Co(NH_3)_5Cl^{+/2+}$	98.3	83.5
trans-$Co(NH_3)_4(NH_2CH_3)Cl^{+/2+}$	109.8	93.8
trans-$Co(NH_3)_4(NH_2\text{-}i\text{-}C_4H_9)Cl^{+/2+}$	165.0	143.8
$Fe(CN)_6^{4-/3-}$	89.7[c]	132.6[c]

[a] Calculated on the basis of the closest packing of spheres involving a dead volume between the spheres of 30% and an increase in radius of 0.16 Å on going from Co(III) to Co(II). [b] Calculated from the partial molar volume data for the corresponding perchlorate complexes on the basis that $\bar{V}(ClO_4^-) = 48.6\ cm^3\ mol^{-1}$ since $\bar{V}(H^+) = -4.5\ cm^3\ mol^{-1}$. [c] Calculated from the partial molar volume data given in ref 29 as indicated in ref 5.

a symmetrical ET reaction, such as self-exchange, $\Delta V^\ddagger$ can be expressed as in (4). This equation must be modified in the case

$$\Delta V^\ddagger = \Delta V^\ddagger_{IR} + \Delta V^\ddagger_{SR} + \Delta V^\ddagger_{COUL} + \Delta V^\ddagger_{DH} \qquad (4)$$

of a nonsymmetrical reaction to include the term $\lambda^\ddagger\Delta\bar{V}$,[13] where $\lambda^\ddagger$ is a reaction parameter between 0 and 1 depending on the location of the transition state along the reaction coordinate. In addition, it was shown that more accurate predictions of $\Delta V^\ddagger$ are reached if a term $\Delta V^\ddagger_{NA}$ for the nonadiabaticity of the process is included.[9,10] Finally, it is known that electron transfer is accompanied by a low-spin to high-spin change on the Co center, which requires a further correction term. Equation 4 is therefore modified to eq 5, and a detailed account of the equations adopted

$$\Delta V^\ddagger = \Delta V^\ddagger_{IR} + \Delta V^\ddagger_{SR} + \Delta V^\ddagger_{COUL} + \Delta V^\ddagger_{DH} + \Delta V^\ddagger_{NA} + \Delta V^\ddagger_{LS/HS} + \lambda^\ddagger\Delta\bar{V} \qquad (5)$$

to calculate the various contributions and the assumptions made along the lines indicated in the literature[9,10] is reported elsewhere.[15]

For the outer-sphere electron-transfer process under investigation, a summary of the different contributions of each term in (5) is reported in Table IV. It is important to note that we are dealing with an electron-transfer process within the precursor complex to produce a successor complex as indicated in (6), which

$$\{Co(NH_3)_4(NH_2R)X^{(3-n)+},Fe(CN)_6^{4-}\} \xrightarrow{k} \{Co(NH_3)_4(NH_2R)X^{(2-n)+},Fe(CN)_6^{3-}\} \qquad (6)$$

is followed by a rapid decomposition to the final reaction products as indicated in (1). Such an electron-transfer process is accompanied by significant desolvation due to a decrease in electrostriction as a result of the reduction of the Co(III) and the oxidation of the Fe(II) complexes. In these calculations it was accepted that $\Delta V^\ddagger_{IR}$ is close to zero,[13] and a maximum value of $+10\ cm^3\ mol^{-1}$ was assumed for the contribution of $\Delta V^\ddagger_{LS/HS}$.[33] The reaction volume, $\Delta\bar{V}$, for the process outlined in (6) could not be measured experimentally due to the subsequent decomposition reactions. It was calculated on the basis of the partial molar volumes of the complex ions (determined from density measurements[1,29]) quoted in Table V. The ion-pair species (precursor and successor) were treated as separated ions on the basis of the observed $\Delta\bar{V}$ for ion-pair formation reported above.

The sum of the first six terms in (5) is close to zero and varies between −0.4 and $-2.0\ cm^3\ mol^{-1}$. We therefore calculated a value of $\lambda^\ddagger$ that would lead to the experimentally observed $\Delta V^\ddagger$ value reported in Table III. It is seen from Table IV that (5) satisfactorily describes the experimental $\Delta V^\ddagger$ value when $\lambda^\ddagger$ has values between 0.37 and 0.59 with an average of 0.48 ± 0.07. It must be emphasized that the calculations include many assumptions and that the quoted volume contributions in Table IV are subjected to large error limits. Nevertheless, the average value of $\lambda^\ddagger$ is close to the qualitative assumption made earlier that the transition state is approximately halfway between the reactant and product states on a volume basis along the reaction coordinate. The deviations in $\lambda^\ddagger$ may reflect the early or late nature of the transition state in terms of the reaction coordinate, in order to align the experimental and theoretical data.

The above outlined analysis of the $\Delta V^\ddagger$ data underlines the importance of solvational changes that accompany the electron-transfer reaction within the precursor ion-pair species. This is also reflected by the positive (in some cases even large positive) $\Delta S^\ddagger$ values reported in Table III. The $\Delta V^\ddagger$ values, ranging between +19 and $+34\ cm^3\ mol^{-1}$, seem to be more consistent than the $\Delta S^\ddagger$ values that range between +11 and $+113\ J\ K^{-1}\ mol^{-1}$. Both these parameters do not exhibit a specific trend with the nature of the Co(III) complex, indicating that the observed effects are mainly controlled by solvational changes associated with the oxidation of $Fe(CN)_6^{4-}$ to $Fe(CN)_6^{3-}$, the common redox partner in all investigated reactions. We are presently extending these studies to reactions in which the reducing agent does not undergo such extreme changes in order to obtain more information on the intrinsic volume changes associated with outer-sphere electron-transfer processes.

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Supplementary Material Available: Tables of k_{obs} as a function of $[Fe(CN)_6^{4-}]$ at various temperatures and pressures for $Co(NH_3)_4(NH_2R)X^{(3-n)+}$ ($R = H$, $X = N_3^-, Cl^-$; $R = CH_3, i\text{-}C_4H_9$, $X = Cl^-$) (2 pages). Ordering information is given on any current masthead page.

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