

Mechanistic Information from the Effect of Pressure on Outer-Sphere Electron-Transfer Reactions Involving the Reduction of Cobalt(III) by Iron(II) Complexes in Aqueous Solution

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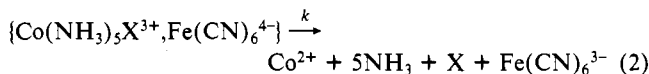
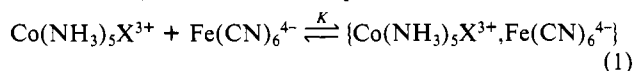
The outer-sphere electron-transfer reactions between $\text{Co}(\text{NH}_3)_5\text{X}^{3+}$ ($\text{X} = \text{H}_2\text{O}$, py, Me_2SO) and $\text{Fe}(\text{CN})_6^{4-}$ were studied at temperatures between 288 and 313 K and pressures up to 125 MPa. The activation parameters (ΔH^\ddagger , ΔS^\ddagger , ΔV^\ddagger) for the electron-transfer step itself are as follows (kcal mol^{-1} , $\text{cal K}^{-1} \text{mol}^{-1}$, $\text{cm}^3 \text{mol}^{-1}$): 21.4 ± 0.7 , $+9 \pm 2$, $+27 \pm 2$ ($\text{X} = \text{H}_2\text{O}$); 28.3 ± 2.0 , $+27 \pm 7$, $+30 \pm 1$ ($\text{X} = \text{py}$); 20.2 ± 0.5 , $+6 \pm 2$, $+34 \pm 1$ ($\text{X} = \text{Me}_2\text{SO}$). The volume of activation data can largely be accounted for on the basis of solvational changes during the oxidation of $\text{Fe}(\text{CN})_6^{4-}$ to $\text{Fe}(\text{CN})_6^{3-}$ within the ion-pair precursor. This conclusion contradicts an earlier report and is discussed in detail.

Introduction

A recent compilation of volume of activation data for inorganic and organometallic systems revealed the significant activity and advances in this area during the past few years.¹ The determination of volumes of activation from high-pressure kinetic measurements is becoming a powerful tool for the elucidation of the intimate nature of the involved reaction mechanism. In contrast to ligand substitution and isomerization reactions of transition-metal complexes,²⁻⁵ only a few studies reported volume of activation data for electron-transfer reactions of such complexes.⁶⁻¹⁵ Furthermore, the complexity of these reactions often did not allow a detailed interpretation of the data. The results, however, demonstrate that the pressure dependence of the electron-transfer reactions of transition-metal complexes cannot be explained on the basis of the simple theoretical considerations as outlined by Stranks.⁶

We have extended our earlier studies⁸⁻¹¹ on the pressure dependence of some typical inner-sphere and intramolecular electron-transfer reactions to include now some typical outer-sphere reactions.¹² In this study we investigated the reduction of $\text{Co}(\text{NH}_3)_5\text{py}^{3+}$ (py = pyridine) and $\text{Co}(\text{NH}_3)_5\text{Me}_2\text{SO}^{3+}$ (Me = methyl) by $\text{Fe}(\text{CN})_6^{4-}$ in aqueous medium. After completion of this work,¹⁶ Saito and co-workers¹⁵ reported data for the effect of pressure on the reduction of $\text{Co}(\text{NH}_3)_5\text{py}^{3+}$ by $\text{Fe}(\text{CN})_6^{4-}$. They¹⁵ stress the importance of intrinsic volume changes during outer-sphere and intramolecular electron-transfer processes. On the contrary, the results of this investigation show that solvational effects largely account for the observed pressure effects, as outlined in the Discussion.

Outer-sphere redox reactions are multistep processes in which an encounter complex (usually an ion pair) is formed within a rapid preequilibrium, followed by rate-determining electron transfer. For the reactions under investigation this can be formulated as in (1) and (2). Under pseudo-first-order conditions,



i.e. excess $\text{Fe}(\text{CN})_6^{4-}$, the observed rate constant is a composite quantity as shown in (3). It follows that the pressure dependence

$$k_{\text{obsd}} = kK[\text{Fe}(\text{CN})_6^{4-}] / \{1 + K[\text{Fe}(\text{CN})_6^{4-}]\} \quad (3)$$

of k_{obsd} will depend on the magnitude of the reaction volume, $\Delta V(K)$, and the volume of activation, $\Delta V^\ddagger(k)$, for reactions 1 and 2, respectively. Detailed kinetic measurements and appropriate analyses are therefore required to resolve the pressure dependencies of K and k . Intrinsic and solvational effects will both influence

the magnitude of these parameters.

Experimental Section

Materials. The complex $[\text{Co}(\text{NH}_3)_5\text{py}](\text{ClO}_4)_3$ was prepared from the corresponding aquo or Me_2SO complex according to the methods described in the literature.¹⁷⁻¹⁹ Chemical analysis²⁰ and ^1H NMR spectra recorded in $\text{Me}_2\text{SO}-d_6$ on a 270-MHz instrument¹⁶ confirmed the purity of the isolated complex. UV-visible spectral data (throughout λ_{max} in nm (ϵ in $\text{M}^{-1} \text{cm}^{-1}$)), 474 (70.8) and 338 (56.4), compare favorably with those reported in the literature: 474 (63.8), 340 (54.4);¹⁷ 475 (64), 338 (52);²¹ 474 (46), 340 (39);²² 479 (80.3), 340.5 (77.5).¹⁹ The corresponding Me_2SO complex was prepared from the aquo complex by heating it for several hours at 60 °C in Me_2SO .¹⁹ The ^1H NMR spectrum of a recrystallized sample¹⁶ indicated the presence of one molecule of Me_2SO as crystal solvent. Chemical analyses²⁰ also confirmed the complex to be $[\text{Co}(\text{NH}_3)_5\text{Me}_2\text{SO}](\text{ClO}_4)_3 \cdot \text{Me}_2\text{SO}$. UV-visible spectral data, 516 (63.7) and 349 (63.3), are in close agreement with those reported elsewhere: 517 (65.5), 357 (34.8);²³ 516 (63.9);²⁴ 515 (48.3), 352 (44.7);¹⁹ 515 (61.3), 351 (63.7);²⁵ 518 (60.2), 351 (60.8).²⁶ The cor-

- (1) van Eldik, R. *Mechanisms of Inorganic and Organometallic Reactions*; Twigg, M., Ed.; Plenum: New York, 1985; Vol. 3, p 399.
- (2) van Eldik, R.; Kelm, H. *Rev. Phys. Chem. Jpn.* **1980**, *50*, 185.
- (3) Palmer, D. A.; Kelm, H. *Coord. Chem. Rev.* **1981**, *36*, 89.
- (4) Merbach, A. E. *Pure Appl. Chem.* **1982**, *54*, 1479.
- (5) Swaddle, T. W. *Adv. Inorg. Bioinorg. Mech.* **1983**, *2*, 95.
- (6) Stranks, D. R. *Pure Appl. Chem.* **1974**, *38*, 303.
- (7) Candlin, J. P.; Halpern, J. *Inorg. Chem.* **1965**, *4*, 1086.
- (8) van Eldik, R.; Palmer, D. A.; Kelm, H. *Inorg. Chim. Acta* **1978**, *29*, 253.
- (9) van Eldik, R.; Kelm, H. *Inorg. Chim. Acta* **1982**, *60*, 177.
- (10) van Eldik, R. *Inorg. Chem.* **1982**, *21*, 2501.
- (11) van Eldik, R. *Inorg. Chem.* **1983**, *22*, 353.
- (12) van Eldik, R.; Kelm, H. *Inorg. Chim. Acta* **1983**, *73*, 91.
- (13) Sasaki, Y.; Ueno, F. B.; Saito, K. *J. Chem. Soc., Chem. Commun.* **1981**, 1135.
- (14) Ueno, F. B.; Sasaki, Y.; Ito, T.; Saito, K. *J. Chem. Soc., Chem. Commun.* **1982**, 328.
- (15) Kanetsato, M.; Ebihara, M.; Sasaki, Y.; Saito, K. *J. Am. Chem. Soc.* **1983**, *105*, 5711.
- (16) Krack, I. Diplomarbeit, University of Frankfurt, 1983.
- (17) Nordmeyer, F.; Taube, H. *J. Am. Chem. Soc.* **1968**, *90*, 1162.
- (18) Wang, Y.; Gould, E. J. *J. Am. Chem. Soc.* **1969**, *91*, 4998.
- (19) Mac-Coll, P.; Beyer, L. *Inorg. Chem.* **1973**, *12*, 8.
- (20) Analytical Laboratory, Hoechst AG, Frankfurt, FRG.
- (21) Gould, E. S. *J. Am. Chem. Soc.* **1965**, *87*, 4730.
- (22) Jordan, R. B.; Sargeson, A. M.; Taube, H. *Inorg. Chem.* **1966**, *5*, 1091.
- (23) Po, L. L.; Jordan, R. B. *Inorg. Chem.* **1968**, *7*, 526.
- (24) Jackson, W. G.; Hookey, C. N. *Inorg. Chem.* **1984**, *23*, 668.
- (25) Dixon, N. E.; Jackson, W. G.; Marty, W.; Sargeson, A. M. *Inorg. Chem.* **1982**, *21*, 688.
- (26) Dixon, N. E.; Jackson, W. G.; Sargeson, A. M. *Inorg. Chem.* **1981**, *20*, 470.

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Table I. Temperature Dependence of k for the Reduction of $\text{Co}(\text{NH}_3)_5\text{OH}_2^{3+}$ by $\text{Fe}(\text{CN})_6^{4-}$ ^a

temp, K	$10^2 k, ^b \text{s}^{-1}$	temp, K	$10^2 k, ^b \text{s}^{-1}$
289.0	3.5 ± 0.1	303.0	20.6 ± 0.4
293.0	5.4 ± 0.2	307.6	34 ± 2
298.0	10.0 ± 0.2		
$\Delta H^\ddagger, \text{kcal mol}^{-1}$		21.4 ± 0.7	
$\Delta S^\ddagger, \text{cal K}^{-1} \text{mol}^{-1}$		9.0 ± 2.0	

^a $[\text{Co}(\text{III})] = 5 \times 10^{-4} \text{ M}$; $[\text{Fe}(\text{II})] = 2 \times 10^{-2} \text{ M}$; $[\text{H}_2\text{EDTA}^{2-}] = 1 \times 10^{-3} \text{ M}$; $[\text{CH}_3\text{COOH}] = [\text{CH}_3\text{COONa}] = 2.5 \times 10^{-2} \text{ M}$; pH 4.7; ionic strength 0.5 M; wavelength 420 nm. ^b Mean value of six to eight kinetic runs.

responding aquo complex was prepared according to well-established procedures,^{27,28} and the sample used showed UV-visible spectra and analytical data identical with those found previously.²⁷

All chemicals used were of analytical reagent grade, and argon-saturated doubly distilled water was used throughout this study as solvent. NaClO_4 was used to adjust the ionic strength of the test solutions. The redox reactions were followed via the formation of $\text{Fe}(\text{CN})_6^{3-}$, and $\text{H}_2\text{EDTA}^{2-}$ was added to prevent the formation of $\text{Co}_3[\text{Fe}(\text{CN})_6]_2$.^{29,30} In the case of the aquo complex an acetate buffer was required²⁹ to control the pH of the solution during the redox reaction; this was not necessary for the other investigated complexes.

Instrumentation. UV-visible absorption spectra were recorded on a Perkin-Elmer 555 spectrophotometer. pH measurements were performed on a Radiometer PHM 64 instrument equipped with a reference electrode filled with 3 M NaCl. The slow redox reactions were followed in the thermostated (± 0.1 °C) cell compartment of the spectrophotometer at ambient pressure and on a Zeiss PMQ II spectrophotometer equipped with a thermostated (± 0.1 °C) high-pressure cell³¹ at elevated pressures. Kinetic measurements for the faster reactions were performed with an Aminco stopped-flow instrument at ambient pressure and a self-constructed³² high-pressure stopped-flow unit at elevated pressures. All kinetic measurements were performed under pseudo-first-order conditions, and the rate constants were calculated in the usual way.⁶ The corresponding first-order plots were found to be linear for at least 3 half-lives of the reaction. Data fitting was in general accomplished by using standard least-squares analysis.

Results and Discussion

Reduction of $\text{Co}(\text{NH}_3)_5\text{OH}_2^{3+}$. Detailed reports on the reduction of $\text{Co}(\text{NH}_3)_5\text{OH}_2^{3+}$ by $\text{Fe}(\text{CN})_6^{4-}$ at ambient and elevated pressures have appeared in the literature.^{12,29} However, different experimental conditions were selected in these studies to facilitate the measurements at elevated pressures, thus complicating a comparison. In addition, the activation parameters (ΔH^\ddagger and ΔS^\ddagger) for the electron-transfer step are needed in order to allow for a meaningful comparison with the other investigated systems. The temperature dependence of k was measured at 0.5 M ionic strength under conditions where eq 3 simplifies to $k_{\text{obsd}} = k$, i.e. in the presence of a high concentration of $\text{Fe}(\text{CN})_6^{4-}$. The results are summarized in Table I.

Reduction of $\text{Co}(\text{NH}_3)_5\text{py}^{3+}$. Haim et al.³³ studied the outer-sphere reduction of $\text{Co}(\text{NH}_3)_5\text{py}^{3+}$ by $\text{Fe}(\text{CN})_6^{4-}$ at ambient pressure and an ionic strength of 0.1 M. This reaction was monitored by following the production of $\text{Fe}(\text{CN})_6^{3-}$ at 420 nm. Unfortunately, the optical density changes are relatively small, which forced the investigators to use 10-cm optical cells. Similar measurements at elevated pressures are usually restricted to cell paths of up to 2 cm. We therefore had to select higher $\text{Co}(\text{III})$ concentrations and an ionic strength of 1.0 M to allow a variation in $[\text{Fe}(\text{CN})_6^{4-}]$ over the range $(0.3\text{--}7.5) \times 10^{-2} \text{ M}$. The iron(II)

Table II. Rate Data for the Reduction of $\text{Co}(\text{NH}_3)_5\text{py}^{3+}$ by $\text{Fe}(\text{CN})_6^{4-}$ as a Function of $[\text{Fe}(\text{II})]$, Temperature, and Pressure^a

$10^2 [\text{Fe}(\text{II})], \text{ M}$	temp, K	press., MPa	$10^3 k_{\text{obsd}}, ^b \text{ s}^{-1}$
0.31	298	0.1	3.09 ± 0.02
0.50			3.93 ± 0.16
0.625			4.50 ± 0.29
0.80			5.37 ± 0.27
1.0			5.43 ± 0.15
1.2			6.13 ± 0.01
1.25			6.34 ± 0.14
2.0			7.36 ± 0.03
2.5			7.49 ± 0.01
4.0			7.34 ± 0.09
7.5			7.70 ± 0.05
$k, \text{ s}^{-1}$			$(8.94 \pm 0.30) \times 10^{-3}$
$K, \text{ M}^{-1}$			168 ± 7
4.0	293	0.1	3.48 ± 0.23
	298		7.51 ± 0.18^c
	308		30.7 ± 0.9
	313		92.6 ± 5.7
$\Delta H^\ddagger, \text{ kcal mol}^{-1}$			28.3 ± 2.0
$\Delta S^\ddagger, \text{ cal K}^{-1} \text{ mol}^{-1}$			27.0 ± 6.8
4.0	288	2	1.15 ± 0.04
		5	1.07 ± 0.01
		25	0.77 ± 0.01
		50	0.65 ± 0.01
		75	0.44 ± 0.03
		95	0.36 ± 0.01
		125	0.22 ± 0.01
7.5		5	1.09 ± 0.04
		25	0.78 ± 0.07
		50	0.62 ± 0.06
		75	0.44 ± 0.02
		100	0.34 ± 0.03
$\Delta V^\ddagger, \text{ cm}^3 \text{ mol}^{-1}$			$+30.7 \pm 1.3^d$
			$+28.9 \pm 1.4^e$

^a Ionic strength 1.0 M; wavelength 420 nm. $[\text{Co}(\text{III})] = 5 \times 10^{-4} \text{ M}$; $[\text{H}_2\text{EDTA}^{2-}] = 1 \times 10^{-3} \text{ M}$ —for $[\text{Fe}(\text{II})]$ - and temperature-dependence study. $[\text{Co}(\text{III})] = 1 \times 10^{-3} \text{ M}$; $[\text{H}_2\text{EDTA}^{2-}] = 2 \times 10^{-3} \text{ M}$ —for pressure-dependence study. ^b Mean value of at least three kinetic runs. ^c Mean value of data at 298 K for $[\text{Fe}(\text{II})] = (2.5\text{--}7.5) \times 10^{-2} \text{ M}$. ^d $[\text{Fe}(\text{II})] = 4 \times 10^{-2} \text{ M}$. ^e $[\text{Fe}(\text{II})] = 7.5 \times 10^{-2} \text{ M}$.

concentration dependence of k_{obsd} at ambient pressure is given in Table II, from which it follows that the limiting rate constant (k) is reached at $[\text{Fe}(\text{II})] > 2 \times 10^{-2} \text{ M}$. The double-reciprocal-plot procedure was used to estimate k and K with the aid of eq 3. The corresponding values reported by Haim et al.³³ at 0.1 M ionic strength and 25 °C are $k = 1.5 \times 10^{-2} \text{ s}^{-1}$ and $K = 2.4 \times 10^3 \text{ M}^{-1}$. The data in Table II indicate that the electron-transfer rate constant does not depend strongly on ionic strength, whereas the ion-pair formation constant, as expected, decreases significantly with increasing ionic strength.

The temperature and pressure dependencies of k were studied at high $[\text{Fe}(\text{II})]$, and the results are also included in Table II. To ensure that the limiting rate constant (k) is reached under all conditions, the pressure dependence study was performed at 4×10^{-2} and $7.5 \times 10^{-2} \text{ M Fe}(\text{II})$. This rate constant exhibits a remarkable pressure dependence, which results in a very large positive volume of activation. The mechanistic interpretation of these activation parameters will be given in an overall discussion of the investigated systems. It is, however, important to note that the plot of $\ln k$ vs. pressure is linear over the studied pressure range.

Reduction of $\text{Co}(\text{NH}_3)_5\text{Me}_2\text{SO}^{3+}$. The reduction of this complex by $\text{Fe}(\text{CN})_6^{4-}$ has not been previously reported in the literature. Plots of k_{obsd} vs. $[\text{Fe}(\text{II})]$ are strongly curved but do not reach a limiting value at high $[\text{Fe}(\text{II})]$. The iron(II) concentration dependence of k_{obsd} was therefore measured as a function of temperature and pressure, and the results are summarized in Table III. Double-reciprocal plots of k_{obsd}^{-1} vs. $[\text{Fe}(\text{II})]^{-1}$ were used

- (27) van Eldik, R.; Harris, G. M. *Inorg. Chem.* **1980**, *19*, 880.
 (28) Basolo, F.; Murmann, R. K. *Inorg. Synth.* **1953**, *4*, 172.
 (29) Gaswick, D.; Haim, A. *J. Am. Chem. Soc.* **1971**, *93*, 7347.
 (30) Kremer, E.; Cha, G.; Morkevicius, M.; Seaman, M.; Haim, A. *Inorg. Chem.* **1984**, *23*, 3028.
 (31) Fleischmann, F. K.; Conze, E. G.; Stranks, D. R.; Kelm, H. *Rev. Sci. Instrum.* **1974**, *45*, 1427.
 (32) van Eldik, R.; Palmer, D. A.; Schmidt, R.; Kelm, H. *Inorg. Chim. Acta* **1981**, *50*, 131.
 (33) Miralles, A. J.; Armstrong, R. E.; Haim, A. *J. Am. Chem. Soc.* **1977**, *99*, 1416.

to determine k and K as functions of temperature and pressure. It is seen from the data in Table III that K shows no distinct temperature dependence, which is in agreement with that reported by Haim et al.³³ for the corresponding pyridine system. However, K does show a distinct pressure dependence, whereas k exhibits both temperature and pressure dependencies. Plots of $\ln K$ and $\ln k$ vs. pressure are linear within the experimental error limits.

Thermodynamic and Kinetic Parameters. A summary of the thermodynamic and kinetic parameters obtained in this study and those reported in the literature is given in Table IV. The outer-sphere complex (ion-pair) formation constants K exhibits a strong ionic strength dependence in agreement with the generally expected tendency, viz. an increase in K with decreasing ionic strength. Although all the investigated Co(III) complexes are of similar charge, K decreases significantly along the series of complexes at comparable ionic strengths. This less understandable trend was also observed in typical substitution reactions that proceed via the formation of ion pairs³⁴⁻³⁶ and indicates that electrostatic interactions alone cannot account for the value of K . It follows that other effects such as hydrogen bonding, dipole interactions, and charge distribution may account for the variation in K .

The pressure dependence of K results in negative values for $\Delta\bar{V}$ in the case of the aquo and dimethyl sulfoxide complexes. Saito et al.¹⁵ reported a positive value for the corresponding pyridine complex. However, some uncertainty exists concerning the latter value,³⁷ and we will therefore not discuss this discrepancy any further. The pressure dependence of K for the pyridine complex was not measured in this study since it was possible to measure the pressure dependence of the electron-transfer rate constant, this being our main interest, in a direct way, i.e. by measuring k_{obsd} at high $[\text{Fe(II)}]$. We could not present a plausible explanation for the rather puzzling negative $\Delta\bar{V}$ value in our earlier study.¹² On the basis of simple electrostatic considerations the formation of an ion pair between oppositely charged species should be accompanied by an increase in volume due to the release of solvent molecules following the charge neutralization process. The result for the Me_2SO complex parallels that for the corresponding aquo complex, which suggests to us that the observed effect must be real. Thus we can conclude that in the present cases charge neutralization effects are probably smaller than the intrinsic decrease in volume due to the overlap of the molecular spheres, suggesting that the ions within the ion pair act on the surrounding solvent molecules as if they are separated individual ions and that no meaningful charge neutralization has occurred. Theoretical calculations³⁸ always predict a positive $\Delta\bar{V}$ value for such ion-pair formation equilibria, although the value approaches zero at high ionic strength. It follows that the results in Table III reveal interesting information on the nature of the precursor complex and motivate further investigations along these lines.³⁹

The electron-transfer rate constants do not exhibit a distinct ionic strength dependence and decrease in the order $\text{Me}_2\text{SO} > \text{OH}_2 > \text{py}$ as sixth ligand attached to the Co(III) center. This trend parallels the activation enthalpies, demonstrating that the py complex has the highest activation barrier. However, it is important to note that ΔH^\ddagger and ΔS^\ddagger for the py system are significantly higher than those reported by Haim et al.³³ and those found for the other complexes listed in Table IV. These values were thoroughly checked to exclude the possibility of a systematic error, and the discrepancy can only be ascribed to the different experimental conditions adopted. The insensitivity of the reduction rate to the nature of the substituent on the pyridine ring led to the suggestion³³ that electron transfer does not occur via the pyridine ring and that the reactive ion pair involves approach of the iron center to the ammonia side of the cobalt(III) complex.

Table III. Rate Data for the Reduction of $\text{Co}(\text{NH}_3)_5\text{Me}_2\text{SO}^{3+}$ as a Function of $[\text{Fe(II)}]$, Temperature, and Pressure^a

temp, K	press., MPa	$10^2 k_{\text{obsd}}^b$, s ⁻¹								K , M ⁻¹	$10k$, s ⁻¹
		0.5 ^c	1.0 ^c	2.0 ^c	3.0 ^c	4.0 ^c	5.0 ^c	10 ^c	20 ^c		
289	0.1		1.67 ± 0.08	2.72 ± 0.02	3.49 ± 0.01	4.09 ± 0.01	4.48 ± 0.06	27.3 ± 0.2	0.79 ± 0.03		
293			4.20 ± 0.10	6.29 ± 0.03		8.40 ± 0.10	8.92 ± 0.05	44 ± 2	1.30 ± 0.01		
298		3.1 ± 0.2	5.5 ± 0.2	8.6 ± 0.1	11.2 ± 0.1	11.8 ± 0.2	12.6 ± 0.4	34 ± 4	2.00 ± 0.10		
303		6.0 ± 1.0	10.3 ± 0.3	16.0 ± 0.2	19.6 ± 0.1	22.2 ± 0.6	26.5 ± 0.8	27 ± 2	3.90 ± 0.30		
									20.2 ± 0.5		
									+6 ± 2		
298	2.5	3.1 ± 0.2	5.1 ± 0.2	7.0 ± 0.5	9.8 ± 0.1		12.6 ± 0.4	49 ± 3	1.57 ± 0.01		
	4.0	3.2 ± 0.4	5.3 ± 0.5		9.3 ± 0.2		12.3 ± 0.2	48 ± 4	1.64 ± 0.12		
	25	2.7 ± 0.2	5.9 ± 0.2	5.9 ± 0.3	7.8 ± 0.3		10.2 ± 0.6	56 ± 6	1.23 ± 0.10		
	50	2.3 ± 0.1	3.3 ± 0.2	4.63 ± 0.01	5.9 ± 0.1		7.4 ± 0.3	74 ± 4	0.83 ± 0.01		
	75	1.48 ± 0.01	2.5 ± 0.1	2.95 ± 0.01	4.7 ± 0.3			63 ± 3	0.62 ± 0.03		
	100	1.12 ± 0.01	1.84 ± 0.03	2.07 ± 0.01	3.3 ± 0.2			77 ± 5	0.40 ± 0.02		
								-11 ± 3 ^d	+34.4 ± 1.1 ^d		

ΔH^\ddagger , kcal mol⁻¹
 ΔS^\ddagger , cal K⁻¹ mol⁻¹

$\Delta\bar{V}^\ddagger(k)$, $\Delta\bar{V}^\ddagger(k)$, cm³ mol⁻¹

^a Ionic strength 1.0 M; wavelength 420 nm. $[\text{Co(III)}] = 5 \times 10^{-4}$ M; $[\text{H}_2\text{EDTA}^{2-}] = 1 \times 10^{-3}$ M— for temperature-dependence study. $[\text{Co(III)}] = 1 \times 10^{-3}$ M; $[\text{H}_2\text{EDTA}^{2-}] = 2 \times 10^{-3}$ M— for pressure-dependence study. ^b Mean value of at least three kinetic runs. ^c $10^2[\text{Fe(II)}]$, M. ^d Calculated for the data obtained at 2.5–100 MPa.

(34) Joubert, P. R.; van Eldik, R. *Int. J. Chem. Kinet.* **1976**, *8*, 411.

(35) van Eldik, R. *Z. Anorg. Allg. Chem.* **1975**, *416*, 88.

(36) van Eldik, R.; Palmer, D. A.; Kelm, H. *Inorg. Chem.* **1979**, *18*, 1520.

(37) The authors¹⁵ are at present remeasuring their data: Saito, K., private communication, 1984.

(38) Martinez, P.; Krack, I.; van Eldik, R., unpublished results.

(39) Krack, I.; van Eldik, R., work in progress.

Table IV. Rate and Activation Parameters for the Reduction of $\text{Co}(\text{NH}_3)_5\text{X}^{3+}$ by $\text{Fe}(\text{CN})_6^{4-}$

complex ion	$K(25^\circ\text{C}),$ M^{-1}	$\Delta\bar{V},$ $\text{cm}^3 \text{mol}^{-1}$	$k(25^\circ\text{C}),$ s^{-1}	$\Delta H^\ddagger,$ kcal mol^{-1}	$\Delta S^\ddagger, \text{cal}$ $\text{K}^{-1} \text{mol}^{-1}$	$\Delta V^\ddagger,$ $\text{cm}^3 \text{mol}^{-1}$	ref
$\text{Co}(\text{NH}_3)_5\text{OH}_2^{3+}$	483 ± 112	-15 ± 8	$(11.2 \pm 0.7) \times 10^{-2}$			$+26.5 \pm 2.4$	$12^{a,b}$
	393 ± 72	-15.5 ± 0.4	$(11.9 \pm 0.7) \times 10^{-2}$			$+26.4 \pm 0.1$	$12^{a,c}$
	1000 ± 100		$(10.0 \pm 0.2) \times 10^{-2}$	21.4 ± 0.7	$+9 \pm 2$		this work ^a
$\text{Co}(\text{NH}_3)_5\text{py}^{3+}$	168 ± 7		$(1.9 \pm 0.1) \times 10^{-1}$				29^d
	2.4×10^3		$(8.9 \pm 0.3) \times 10^{-3}$	28.3 ± 2.0	$+27 \pm 7$	$+29.8 \pm 1.4$	this work ^c
		$+23 \pm 3$	1.5×10^{-2}	21.7 ± 2.2	$+6 \pm 7$		33^d
$\text{Co}(\text{NH}_3)_5\text{Me}_2\text{SO}^{3+}$	34 ± 4	-11 ± 3	$(2.0 \pm 0.1) \times 10^{-1}$	20.2 ± 0.5	$+6 \pm 2$	$+23.9 \pm 1.0$ $+34.4 \pm 1.1$	15^f this work ^e

^a Ionic strength 0.5 M. ^b Calculated by using experimental data points.¹² ^c Calculated from fitted data points.¹² ^d Ionic strength 0.1 M. ^e Ionic strength 1.0 M. ^f No experimental data are given in this reference.

Haim et al.³³ employed orbital symmetry considerations to account for this behavior. The higher activation parameter found for this process in the present study, may further underline the mechanistic difference in the case of the py complex. The low values of ΔS^\ddagger found for the reduction of the aquo and dimethyl sulfoxide complexes can be accommodated on the basis of a decrease in solvation due to charge redistribution in going from the precursor ion pair (+3, -4) to the successor ion pair (+2, -3). This implies that the electron transfer itself is adiabatic in such cases.³³ In most conventional kinetic investigations ΔS^\ddagger is considered as a strong mechanistic discriminator, such that the different ΔS^\ddagger value for the py system could be considered as evidence for a different mechanism as agreed above. However, we are aware of the difficulties encountered when ΔS^\ddagger is used as a discriminator¹⁰ and therefore prefer the application of ΔV^\ddagger instead.

The data in Table IV indicate that all the available volumes of activation are large and positive. Our value for the py system is higher than that reported by Saito et al.¹³ but could be due to the uncertainty regarding the latter data.³⁷ It is important to note that our values for ΔV^\ddagger do not reflect the apparent difference in the values of ΔS^\ddagger . On the basis of the sign and order of magnitude of the ΔV^\ddagger values, no mechanistic difference is expected for the three complexes investigated. The slightly less positive value for ΔV^\ddagger in the case of the aquo complex could be due to the lower ionic strength employed, viz. 0.5 M compared to 1.0 M for the py and Me_2SO complexes. The magnitude of ΔV^\ddagger is of significant importance and calls for a more detailed analysis.

During the electron transfer reaction within the ion pair, $\{\text{Co}(\text{NH}_3)_5\text{X}^{3+}, \text{Fe}(\text{CN})_6^{4-}\}$, the Co(III) center is reduced to Co(II), whereas Fe(II) is oxidized to Fe(III). The overall volume change for this step can be presented by the expression in (4), which should

$$\Delta\bar{V}_{\text{ET}} = \bar{V}(\text{Co(II)}) + \bar{V}(\text{Fe(III)}) - \bar{V}(\text{Co(III)}) - \bar{V}(\text{Fe(II)}) \quad (4)$$

reflect the maximum possible value of ΔV^\ddagger since the transition state lies between the reactant and product states. In this treatment we assume that the reactant ion-pair species behaves like the separated ions, as concluded from the $\Delta\bar{V}$ data for the ion-pair-formation step. In addition, the product ion pair should exhibit similar properties, such that the expression for $\Delta\bar{V}_{\text{ET}}$ in (4) presents the difference in partial molar volumes of the reactant and product species within their ion-pair environment. Saito et al.¹⁵ assume that the reductant, $\text{Fe}(\text{CN})_6^{4-}$, requires only a small change in volume on oxidation to $\text{Fe}(\text{CN})_6^{3-}$ and ascribe the observed ΔV^\ddagger to intrinsic volume increases on the cobalt center. They predict a volume increase of $19.7 \text{ cm}^3 \text{ mol}^{-1}$ on the basis of Co-N distances of 1.96 and 2.16 Å for $\text{Co}(\text{NH}_3)_6^{3+}$ and $\text{Co}(\text{NH}_3)_6^{2+}$, respectively.^{40,41} Their argument is based on very similar Fe-C distances reported for salts of $\text{Fe}(\text{CN})_6^{4-}$ and $\text{Fe}(\text{CN})_6^{3-}$ in the literature.^{42,43} From these considerations the authors¹⁵ conclude that the observed ΔV^\ddagger of $+23.9 \pm 1.0 \text{ cm}^3 \text{ mol}^{-1}$

for the py complex is mainly due to the change in volume of the cobalt complex.

We cannot agree with this interpretation. The partial molar volume of an ion in solution is determined not only by its intrinsic component but also by a solvational contribution.⁴⁴ It follows that the partial molar volumes of $\text{Fe}(\text{CN})_6^{4-}$ and $\text{Fe}(\text{CN})_6^{3-}$ could be quite different even if the intrinsic components are assumed to be very similar. This is indeed the case if one compares the experimentally determined molar volumes of these species,⁴⁵ according to which the Fe(III) species is $43 \text{ cm}^3 \text{ mol}^{-1}$ larger at infinite dilution. From recent partial molar volume measurements on bipyridine and terpyridine complexes of Co(II) and Co(III)⁴⁷ and the existing linear correlation between the partial molar volumes of $\text{Co}(\text{NH}_3)_5\text{X}^{3+}$ and X,⁴⁸ it is possible to extrapolate a volume increase of ca. $22 \text{ cm}^3 \text{ mol}^{-1}$ for the reduction of $\text{Co}(\text{NH}_3)_5\text{py}^{3+}$ to $\text{Co}(\text{NH}_3)_5\text{py}^{2+}$. This is in close agreement with the predicted value of Saito et al.¹⁵ However, it follows that the volume increase due to solvational changes on the iron center is significantly larger than the volume increase on the cobalt center and the former should account for ca. 70% of the observed ΔV^\ddagger . This conclusion also applies for the other complexes investigated, since their partial molar volumes⁴⁸ are smaller than that of the py complex. The fact that ΔV^\ddagger is almost constant for the three systems further underlines our conclusion that the volume increase mainly originates from changes on the iron center.

Substitution of the above partial molar volume differences into eq 4 results in a $\Delta\bar{V}_{\text{ET}}$ value of ca. $65 \text{ cm}^3 \text{ mol}^{-1}$ at infinite dilution. This is significantly larger than what one can extrapolate from $\Delta\bar{V}$ values for the neutralization of a series of differently charged octahedral complex ions.⁴⁹ For this series of complexes $\Delta\bar{V}$ was measured for the neutralization of aquo or ammine ligands and a good correlation between $\Delta\bar{V}$ and the overall charge on the complex was observed.⁴⁹ Application of this correlation to the neutralization of charges in the electron-transfer step⁵⁰ results in a $\Delta\bar{E}_{\text{ET}}$ value of $30 \text{ cm}^3 \text{ mol}^{-1}$, which is significantly smaller than the above estimated value. However, neutralizations of ligands attached to a metal center are bound to be accompanied by significantly smaller increases in the partial molar volume than neutralization of the central metal atom itself. From this we conclude that the predicted value of $65 \text{ cm}^3 \text{ mol}^{-1}$ for $\Delta\bar{V}_{\text{ET}}$ is quite reasonable. This value reduces to ca. $55 \text{ cm}^3 \text{ mol}^{-1}$ at 1 M ionic strength if we apply simple ionic strength corrections.⁴⁹ From

- (44) Drude, P.; Nernst, W. *Z. Phys. Chem.* **1894**, *15*, 79.
 (45) $\bar{V}(\text{K}_3\text{Fe}(\text{CN})_6) = 147.8$ and $\bar{V}(\text{K}_4\text{Fe}(\text{CN})_6) = 110 \text{ cm}^3 \text{ mol}^{-1}$ at 25°C .⁴⁶ If we assume $\bar{V}(\text{H}^+) = -4.5 \text{ cm}^3 \text{ mol}^{-1}$,⁴⁶ then it follows that $\bar{V}(\text{Fe}(\text{CN})_6^{3-}) = 132.6$ and $\bar{V}(\text{Fe}(\text{CN})_6^{4-}) = 89.7 \text{ cm}^3 \text{ mol}^{-1}$.
 (46) Millero, F. J. *Water and Aqueous Solutions: Structure, Thermodynamics and Transport Processes*; Horne, R. A., Ed.; Wiley-Interscience: London, 1972; Chapter 13.
 (47) Braun, P.; van Eldik, R., unpublished results.
 (48) Lawrance, G. A. *Inorg. Chem.* **1982**, *21*, 3687.
 (49) Kitamura, Y.; van Eldik, R. *Ber. Bunsen-Ges. Phys. Chem.* **1984**, *88*, 418.
 (50) For the reaction $\text{MA}^z + \text{OH}^- \rightarrow \text{MB}^{z-1} + \text{H}_2\text{O}$ it was found⁴⁹ that $\Delta\bar{V}_0 = 14.5 + 2.5(2z - 1) \text{ cm}^3 \text{ mol}^{-1}$, such that $\bar{V}(\text{MA}^z) - \bar{V}(\text{MB}^{z-1}) = 17.6 - \Delta\bar{V}_0 = 3.1 - 2.5(2z - 1) \text{ cm}^3 \text{ mol}^{-1}$. It follows that the volume increases for the processes $\text{Fe}(\text{CN})_6^{4-} \rightarrow \text{Fe}(\text{CN})_6^{3-}$ and $\text{Co}(\text{NH}_3)_5\text{py}^{3+} \rightarrow \text{Co}(\text{NH}_3)_5\text{py}^{2+}$ are 20.6 and $9.4 \text{ cm}^3 \text{ mol}^{-1}$, respectively, i.e. an overall volume increase of $30 \text{ cm}^3 \text{ mol}^{-1}$.

(40) Herlinger, A. W.; Brown, J. N.; Dwyer, M. A.; Pavkovic, S. F. *Inorg. Chem.* **1981**, *20*, 2366.

(41) Geselowitz, D. A.; Taube, H. *Adv. Inorg. Bioinorg. Mech.* **1982**, *1*, 391.

(42) Mullica, D. F.; Milligan, W. O.; Oliver, J. D. *Inorg. Nucl. Chem. Lett.* **1979**, *15*, 1.

(43) Fletcher, S. R.; Gibb, T. C. *J. Chem. Soc., Dalton Trans.* **1977**, 309.

a comparison of the latter value with the experimentally observed ΔV^\ddagger values in Table IV, one can conclude that the transition state for the electron-transfer process is approximately halfway along the reaction coordinate on a volume basis. This means that both the Co(III) and Fe(II) centers have approached a half-reduced/half-oxidized geometry in the transition state.

In summarizing we conclude that the ΔV^\ddagger data for the electron-transfer step within the ion pair can be explained on the basis of volume changes on the individual ions, of which the largest effect

originates from the iron center. No evidence for any significant mechanistic difference between the investigated systems can be observed on the basis of these data.

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Registry No. Co(NH₃)₅H₂O³⁺, 14403-82-8; Co(NH₃)₅py³⁺, 31011-67-3; Co(NH₃)₅Me₂SO³⁺, 44915-85-7; Fe(CN)₆⁴⁻, 13408-63-4.

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Competitive NMR Study of the Complexation of Several Cations with 18-Crown-6, 1,10-Diaza-18-crown-6, and Cryptand-2,2,2 in Nonaqueous Solutions

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Previously reported competitive NMR studies of formation constants of macrocyclic complexes have been extended to several new systems. The technique was found to be applicable to solutions containing two cations and a common ligand where the analysis of the NMR data makes it possible to determine simultaneously both formation constants. It also was used in systems where the exchange of the probe cation between the free and the complexed sites is slow and two resonances of the probe nucleus are observed. It is possible, therefore, to use the competitive technique to study the stabilities of metal complexes of diaza polyoxa macrobicyclic ligands (cryptands) where slow exchange at room temperature is often observed. Formation constants for several 18C6 and DA18C6 complexes are reported in acetonitrile, acetone, and propylene carbonate solutions. These results are discussed with respect to the size and charge of the cation, the solvating ability of the solvent, and the nature of the ligand binding groups.

Introduction

In a previous publication¹ we described a competitive NMR technique for the determination of stability constants of metal ion complexes with macrocyclic ligands. This method is essentially independent of the solvent (solubilities permitting), it can be used for the determination of stability constants that are higher than 10⁵ (upper limit for the direct NMR technique), and it allows NMR studies of complexes of cations with unsuitable NMR properties such as low receptivity, high quadrupole moments, etc.

In this paper we describe the application of this technique to several new solvents, to systems with very high stability constants, and to systems where the cation exchange between the free and complexed site is slow at the temperature of measurement so that two cationic resonances are observed.

Experimental Part

Cesium, rubidium, and potassium tetraphenylborates were prepared and purified by following the procedure of Mei et al.² Barium tetraphenylborate was prepared by the procedure described by Khol'kin et al.³ followed by drying at 40 °C for 2 days under vacuum in the dark. Thallium(I) perchlorate (K&K) and acetone (Baker) were purified by the procedure described by Lee et al.⁴ Sodium tetraphenylborate (Aldrich), barium perchlorate (Alfa), and lithium perchlorate (Alfa) were dried for several days under vacuum at 45 and 70 °C, respectively. Acetonitrile (Baker) was purified as described previously.¹ Propylene carbonate (Aldrich) was refluxed under reduced pressure over calcium hydride at 90–100 °C and then fractionally distilled under the same pressure. The middle fraction (~60%) was retained.

The ligand 18-crown-6 (18C6) (Aldrich) was purified and dried as previously described.¹ The ligands Kryptofix-2,2 (1,10-diaza-18-crown-6, DA18C6) and Kryptofix-2,2,2 (C222) were obtained from MCB and used as obtained except for being dried under vacuum at room temperature for 2 days.

All instrumentation, solution preparation, data treatment, and calculations for rapidly exchanging systems were carried out as previously described.¹ For those systems that were exchanging sufficiently slowly so that two separate resonance bands for the free and complexed species were observed at room temperature, a different procedure had to be used.

When separate bands were present, a solution was prepared that had both salts and the ligand at equal concentrations (mole ratios 1:1:1). The observed resonance bands were manually fitted to Lorentzian profiles. The parameters obtained from this fit (intensity, position, and width) were then corrected for the effect due to the delay between the end of the excitation pulse and the beginning of acquisition and for the effect due to the exponential multiplication (which is done to increase signal-to-noise). The equations for a resonance band thus collected and processed, as opposed to the true Lorentzian profile desired, is given by Strasser and others.⁵ The Lorentzian bands defined by corrected parameters are then directly integrated. The properly corrected band areas were then used to calculate the concentrations of the free and complexed species. These concentrations are then used to calculate all other concentrations. Once all concentrations are known, it is a trivial process to calculate the unknown formation constant.

Results and Discussion

A. Determination of High Stability Constants of Crown Complexes. In the previous publication we reported the determination of the formation constant of Ba²⁺ macrocyclic complexes is not possible (at this time at least) by the direct measurements of the ¹³⁵Ba or ¹³⁷Ba resonances because of low receptivities and high quadrupole moments of these nuclei.⁶ We therefore used the competitive technique (with the Na⁺ ion as the competing ion and as the observed nucleus), to obtain the formation constant of log K_f = 4.21 ± 0.19 for the Ba²⁺-18C6 complex in dimethylformamide solution.

The stability of the above complex should be considerably higher in acetone, acetonitrile, or propylene carbonate solution since the latter solvents have much lower solvating ability than DMF⁷ and would compete less with the ligand for the cationic coordination sites. As previously mentioned, however, one of the limitations of the competitive NMR technique¹ results from occasionally limited solubilities of salts and/or complexes in the solvents of interest.

(1) Boss, R. D.; Popov, A. I. *Inorg. Chem.* **1985**, *24*, 3660.
(2) Mei, E.; Popov, A. I.; Dye, J. L. *J. Phys. Chem.* **1977**, *81*, 1677.
(3) Khol'kin, A. I.; Kotzitskii, V. P.; Gindin, L. M.; Ovechkina, L. G. *Izv. Sib. Otd. Akad. Nauk Sssr, Ser. Khim. Nauk* **1976**, *66*.
(4) Lee, Y. C.; Allison, J.; Popov, A. I. *Polyhedron* **1985**, *4*, 441.

(5) (a) Strasser, B. O.; Hallenga, K.; Popov, A. I. *J. Am. Chem. Soc.* **1985**, *107*, 789. (b) Strasser, B. O. Ph.D. Thesis, Michigan State University, East Lansing, MI 48824, **1984**. (c) Szczygiel, P. M.S. Thesis, Michigan State University, East Lansing, MI 48824, **1984**.
(6) Harris, R. K.; Mann, B. E. *NMR and the Periodic Table*; Academic: New York, **1978**; p 7.
(7) Gutmann, V.; Wychera, E. *Inorg. Nucl. Chem. Lett.* **1966**, *2*, 257.
(8) Lin, J. D.; Popov, A. I. *J. Am. Chem. Soc.* **1981**, *103*, 3773.