Inorg. Chem. **1995**, *34*, 4815−4820 **4815**

The Ligand Cage Effect in Volumes of Activation for Electron Transfer Reactions of Cobalt(III/II) Complexes in Aqueous Solution

Richard D. Shalders and Thomas W. Swaddle*

Department of Chemistry, The University of Calgary, Calgary, Alberta, Canada T2N 1N4

Received April 21, 1995[⊗]

The electrode reaction Co(diamsar)$^{3+/2+}$ in water at 25 °C, ionic strength $I = 0.14$ mol L^{-1}, is characterized by $E^{\circ\prime} = -0.24_5$ V and $\Delta V = +17.4 \pm 0.5$ cm^3 mol^{-1} vs Ag/AgCl/4 mol L^{-1} KCl, and the kinetics of the corresponding self-exchange reaction in homogeneous solution by $k_{ex} = 0.48 \pm 0.01$ L mol^{-1} s^{-1}, $\Delta H_{ex}^{\ddagger} = 50.7 \pm 0.6$ kJ mol^{-1}, $\Delta S_{ex}^{\ddagger} = -81 \pm 2$ J K^{-1} mol^{-1}, and $\Delta V_{ex}^{\ddagger} = -10.4 \pm 0.5$ cm^3 mol^{-1}. For the couple Co(diamsarH$_2$)$^{5+/4+}$ at 25 °C, the corresponding parameters are $E^{\circ\prime} = +0.03_2$ V and $\Delta V = +19.5 \pm 0.8$ cm^3 mol^{-1} ($I = 0.20$ mol L^{-1}) vs Ag/AgCl/4 mol L^{-1} KCl, $k_{ex} = 0.0149 \pm 0.0005$ L mol^{-1} s^{-1}, and $\Delta V_{ex}^{\ddagger} = -9.6 \pm 0.8$ cm^3 mol^{-1} ($I = 0.39$ mol L^{-1}). The rate constants and volumes of activation are as expected for these electron transfer reactions on the basis of an adaptation of Marcus−Hush theory. Comparison with data for other cation−cation self-exchange reactions shows that low-spin/high-spin Co$^{III/II}$ cage complexes behave normally in the Marcus−Hush context, despite the large change in spin multiplicity accompanying electron transfer, whereas nonencapsulated Co$^{III/II}$ chelate couples deviate strongly from the norm, especially in $\Delta V_{ex}^{\ddagger}$ values which are anomalously strongly negative. This is attributed to structural changes associated with a Co^{II} spin equilibrium preceding electron transfer in the nonencapsulated chelates—changes which are suppressed in the cage environment. The alternative view, that the anomalous behavior of the Co chelates stems from nonadiabaticity, now seems untenable. Thus, spin multiplicity change *per se* does not inhibit electron transfer, i.e., such reactions are not "spin forbidden", but distortions that may accompany it in electron transfer between flexible complexes may retard the reaction and make a substantial negative contribution to $\Delta V_{ex}^{\ddagger}$.

Introduction

An adaptation[1,2] of the Marcus−Hush theory of adiabatic outer-sphere electron transfer kinetics in solution[3] enables the volume of activation $\Delta V_{ex}^{\ddagger}$ ($= -RT(\partial \ln k_{ex}/\partial P)_T$, where k_{ex} is the rate constant) for self-exchange reactions of the type $A^+ + A \rightarrow A + A^+$ to be calculated reliably within the following limitations: (a) The calculations become numerically unstable in solvents of high compressibility β and low dielectric constant D, so that the theory is less successful for nonaqueous media.[4] (b) The theory predicts that $\Delta V_{ex}^{\ddagger}$ should itself be dependent upon pressure, particularly for solvents with high β and low D, but for aqueous systems this pressure dependence should be small and indeed is usually not observable over the customary experimental pressure range (0.1−200 MPa). (c) In cation−cation[4] and ion−molecule[5] electron transfer, interactions with the counterions appear to reduce k_{ex} and hence (since pressure tends to break up ion pairs) make $\Delta V_{ex}^{\ddagger}$ more negative, but these are significant only in solvents of low D. For anion−anion electron transfer, however, important cation-catalyzed paths can exist even in aqueous solution, and these are associated with anomalously positive values of $\Delta V_{ex}^{\ddagger}$.[4,6,7] (d) The incursion of inner-sphere pathways leads to $\Delta V_{ex}^{\ddagger}$ values more positive than predicted.[8] (e) Cobalt(III/II) *chelate* couples in which Co^{II} is in a high-spin (quartet) and Co^{III} in a low-spin (singlet) state (Co(en)$_3^{3+/2+}$,[9] Co(phen)$_3^{3+/2+}$,[10] and "Co(edta)$^{2-/-}$"[11]) have $\Delta V_{ex}^{\ddagger}$ values that are much more negative than the theory predicts; however, the $\Delta V_{ex}^{\ddagger}$ value for the low-spin/high-spin *cage complex* couple Co(sep)$^{3+/2+}$ fits the theory well.[12,13]

In this article, we address this last anomaly. It has long been thought[14] that electron transfer reactions that involve a large spin multiplicity change, such as those of low-spin/high-spin Co$^{III/II}$ couples, should be slower than predicted by Marcus−Hush theory. This could result from nonadiabaticity of electron transfer[15−19] (although Hupp and Weaver[20] and Geselowitz[21] offer dissenting views) or from adiabatic electron transfer

---

[⊗] Abstract published in *Advance ACS Abstracts*, August 1, 1995.

(1) Stranks, D. R. *Pure Appl. Chem.* **1974**, *38*, 303.

(2) Swaddle, T. W. *Inorg. Chem.* **1990**, *29*, 5017.

(3) Marcus, R. A. *J. Chem. Phys.* **1956**, *24*, 966, 979; **1957**, *26*, 867. Marcus, R. A. *Discuss. Faraday Soc.* **1960**, *29*, 21; *Faraday Discuss. Chem. Soc.* **1982**, *74*, 7. Hush, N. S. *Trans. Faraday Soc.* **1961**, *57*, 557.

(4) Swaddle, T. W. *J. Mol. Liquids*, in press.

(5) (a) Borchardt, D.; Wherland, S. *Inorg. Chem.* **1986**, *25*, 901. (b) Gribble, J.; Wherland, S. *Inorg. Chem.* **1989**, *28*, 2859. (c) Murguia, M. A.; Wherland, S. *Inorg. Chem.* **1991**, *30*, 139.

(6) Takagi, H.; Swaddle, T. W. *Inorg. Chem.* **1992**, *31*, 4669.

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

(8) Jolley, W. H.; Stranks, D. R.; Swaddle, T. W. *Inorg. Chem.* **1990**, *29*, 1948.

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

(10) Grace, M. R.; Swaddle, T. W. *Inorg. Chem.* **1993**, *32*, 5597.

(11) Jolley, W. H.; Stranks, D. R.; Swaddle, T. W. *Inorg. Chem.* **1992**, *31*, 507.

(12) Doine, H.; Swaddle, T. W. *Inorg. Chem.* **1991**, *30*, 1858.

(13) en = 1,2-diaminoethane; phen = 1,10-phenanthroline; sep = sepulchrate = 1,3,6,8,10,13,16,19-octaazabicyclo[6.6.6]eicosane; [9]aneS$_3$ = 1,4,7-trithiacyclononane; diamsar = diaminosarcophagine = 1,8-diamino-3,6,10,13,16,19-hexaazabicyclo[6.6.6]eicosane; edta = 1,2-ethanedinitrilotetraacetate.

(14) Basolo, F.; Pearson, R. G. *Mechanisms of Inorganic Reactions*, 2nd ed.; John Wiley and Sons: New York, 1967; pp 459, 480.

(15) Buhks, E.; Bixon, M.; Jortner, J.; Navon, G. *Inorg. Chem.* **1979**, *18*, 2014.

(16) Sutin, N. *Prog. Inorg. Chem.* **1983**, *30*, 441.

(17) Ramasami, T.; Endicott, J. F. *Inorg. Chem.* **1984**, *23*, 3324; *J. Am. Chem. Soc.* **1985**, *107*, 389; *J. Phys. Chem.* **1986**, *90*, 3740.

(18) Newton, M. D. *J. Phys. Chem.* **1991**, *95*, 30 and references cited.

(19) Although most theoretical discourse has centered upon the Co(NH$_3$)$_6^{3+/2+}$ exchange, similar considerations apply to the Co(en)$_3^{3+/2+}$ case at least, for which k_{ex} is only about 100-fold larger: Hammershøi, A.; Geselowitz, D.; Taube, H. *Inorg. Chem.* **1984**, *23*, 979.

(20) Hupp, J. T.; Weaver, M. J. *J. Phys. Chem.* **1985**, *89*, 2795.

(21) Geselowitz, D. A. *Inorg. Chim. Acta* **1988**, *154*, 225.

0020-1669/95/1334-4815$09.00/0

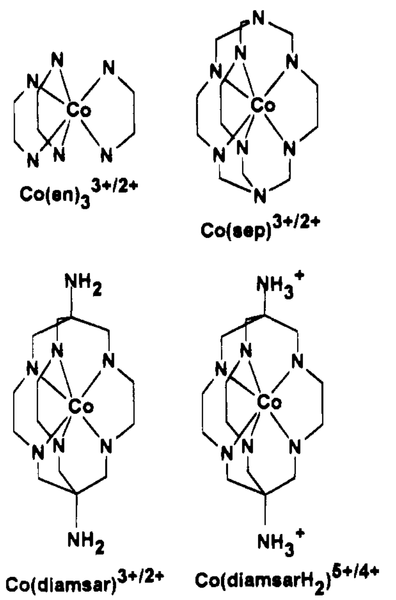

Figure 1. Relation of cobalt cage complexes to Co(en)$_3$$^{3+}$ (schematic).

following a fast, endergonic spin pre-equilibrium.[22] In either case, k_{ex} is expected to be a few orders of magnitude smaller, and $\Delta V_{ex}^\ddagger$ substantially more negative, than the simple adiabatic theory predicts, and this is observed for Co$^{III/II}$ chelates.[2, 9-12] Heretofore, we have tended to favor the nonadiabaticity explanation,[2,9-12] partly because it accommodates the $\Delta V_{ex}^\ddagger$ data with reasonable values of the distance scaling factor α but mainly because low-spin Co^{II} amine species in general appear to be energetically inaccessible—certainly, with the exception of the complicated case of Co(terpy)$_2$$^{2+}$,[23] the purported spin pre-equilibria have eluded detection even in the most favorable of CoN$_6$$^{2+}$ complexes studied to date (Co(phen)$_3$$^{2+}$ [10]) and so their quantitative contributions to k_{ex} and $\Delta V_{ex}^\ddagger$ are unknown. However, the close conformity of $\Delta V_{ex}^\ddagger$ for low-spin/high-spin Co(sep)$^{3+/2+}$ to the prediction of the adiabatic theory is hard to reconcile with the nonadiabaticity explanation, as the gross structures of Co(en)$_3$$^{3+}$ (from which the sepulchrate complex is made by capping on the 3-fold axis) and Co(sep)$^{3+}$ differ only slightly (Figure 1), and in a way that should make the latter a little larger and hence *less* likely than the former to transfer an electron adiabatically.

We have therefore studied the kinetics of self-exchange in the cage-complex couple Co(diamsar)$^{3+/2+}$ and its protonated form Co(diamsarH$_2$)$^{5+/4+}$ (Figure 1[13]) to determine whether the Co(sep)$^{3+/2+}$ case is an isolated anomaly or is typical of cage complexes generally. The diamsar couples also provide an opportunity to test the theory of pressure effects for a charge-type other than 3+/2+, which has dominated aqueous cation–cation high-pressure electron transfer studies to date. Related questions are whether the cage or the chelate couples represent "normal" behavior for Co$^{III/II}$ electron transfer kinetics and whether spin multiplicity changes *in themselves* are of direct importance in limiting redox rates—Geselowitz[21] has argued that they are not. We also report high-pressure electrochemical measurements on the relevant couples and attempts to test further the "cross relation" in volumes of activation reported previously.[5c,24]

Experimental Section

Materials. Optical isomers of [Co(en)$_3$]I$_3$ were prepared by the method of Broomhead et al.[25] and converted to the chloride salts by cation exchange using Dowex 50W-X2 resin. From these, the optical isomers of [Co(diamsarH$_2$)]Cl$_5$·4H$_2$O were prepared as described by Geue et al.[26] via the corresponding dinitro(sarcophagine)cobalt(III) chloride isomers, which were made by the following method, recommended by Harrowfield.[27] To a solution of [Co(en)$_3$]Cl$_3$·3H$_2$O (9.0 g), CH$_3$NO$_2$ (5.4 g), and aqueous formaldehyde (37%, 21.1g) in water (22.5 mL) at 5°C was added rapidly a solution of NaOH (3.6 g) in water (22.5 mL), also at 5 °C, and the mixture was stirred thoroughly with continuous cooling in an ice bath (failure to cool the mixture adequately resulted in violent effervescence and formation of a brown tar). After 15 min of continuous stirring, the resulting violet solution was treated with concentrated HCl (30 mL) and cooled in ice for 1 h. The orange precipitate of [Co(NO$_2$)$_2$sar]Cl$_3$·2H$_2$O (8.9 g, 69%) was then collected.

The integrity and degrees of hydration of [Co(NO$_2$)$_2$sar]Cl$_3$·2H$_2$O and [Co(diamsarH$_2$)]Cl$_5$·4H$_2$O were confirmed by CHN microanalysis and (for the diamsar complex) by dehydration. Optical rotatory dispersion measurements with a Rudolph Autopol III polarimeter gave the specific rotations $[\alpha]_{589}$ of -252 cm^3 g^{-1} dm^{-1} for [Λ-(−)$_{589}$-Co(diamsarH$_2$)]Cl$_5$·4H$_2$O and $+299$ cm^3 g^{-1} dm^{-1} for the Δ-(+)$_{589}$-isomer in aqueous solution. The sense of the optical rotation of the diamsar complex was opposite to that of its en precursor, i.e., Λ-(+)$_{589}$-Co(en)$_3$$^{3+}$ gives Λ-(−)$_{589}$-Co(diamsarH$_2$)$^{3+}$.

Potassium trifluoromethanesulfonate (potassium triflate) was prepared by neutralization of freshly distilled triflic acid (Eastman, 98%) with KOH (BDH, GPR) and was recrystallized twice from water. Morpholine (Fisher ACS Reagent), NaClO$_4$ (BDH, GPR), and HClO$_4$ (Baker Analyzed, 70%) were used as received.

Self-Exchange Kinetics. For study of self-exchange in the unprotonated Co(diamsar)$^{3+/2+}$ couple, solutions were prepared from [Co(diamsarH$_2$)]Cl$_5$·4H$_2$O with a morpholine/CF$_3$SO$_3$H buffer (pH 8.3, [triflate] = 0.025 mol L^{-1} [28]) and the ionic strength I was set with CF$_3$SO$_3$K. The measured pH of these solutions was 8.1, because of the acidity of Co(diamsarH$_2$)$^{5+}$ (pK_a = 3.2).[29] The Co^{III} concentration was determined spectrophotometrically at 473 nm (molar absorbance ϵ = 145.6 L mol^{-1} cm^{-1}). Solutions of both optical isomers were handled in a glovebox under nitrogen. The Δ-isomer was reduced to Δ-Co^{II}(diamsar)$^{2+}$ with mossy zinc, complete reduction requiring about 1 h.[30] The Co^{III} partner in the exchange reaction was the Λ isomer. All solutions were thoroughly deoxygenated with N$_2$ before loading into a Hi-Tech HPSF-56 high pressure stopped-flow unit, which was mounted in a Jasco J-500A spectropolarimeter as described previously.[12] The self-exchange kinetics at 25.0 ± 0.1 °C were monitored by observing the disappearance of the circular dichroism (CD) signal intensity X at 480 nm as a function of time t over at least 4 half-periods. The data were collected and processed digitally (1500 to 2000 data points) with a Macintosh IIsi computer. Two to three kinetic runs were made at each pressure (0.1−160 MPa).

---

(22) Larsson, S.; Ståhl, K.; Zerner, M. C. *Inorg. Chem.* **1986**, *25*, 3033.

(23) For bis(terpyridyl)cobalt(II) chloride in water, a fast quartet → doublet spin equilibrium is observed with an apparent molar volume change of −10.1 cm^3 mol^{-1}, 0.1−140 MPa (Binstead, R. A.; Beattie, J. K. *Inorg. Chem.* **1986**, *25*, 1481), and this is very close to the deviation of $\Delta V_{ex}^\ddagger$ from the theoretical values seen in self-exchange of Co$^{III/II}$ chelates. Detailed investigations in our laboratories by H. Takagi and R.D.S., however, have shown that dechelation equilibria complicate the Co(terpy)$_2$$^{2+}$ picture and that the spin equilibria are sensitive to the nature of the anion and the solvent. For this reason, we have not attempted the measurement of k_{ex} or $\Delta V_{ex}^\ddagger$ for the Co(terpy)$_2$$^{3+/2+}$ exchange reaction.

(24) Grace, M. R.; Takagi, H.; Swaddle, T. W. *Inorg. Chem.* **1994**, *33*, 1915.

(25) Broomhead, J. A.; Dwyer, F. P.; Hogarth, J. W. *Inorg. Synth.* **1960**, *6*, 183.

(26) Geue, R. J.; Hambley, T. W.; Harrowfield, J. M.; Sargeson, A. M.; Snow, M. R. *J. Am. Chem. Soc.* **1984**, *106*, 5478.

(27) Harrowfield, J. M. Personal communication.

(28) In this article, molar concentrations refer to 21 °C and 0.1 MPa; adjustment for other temperatures and pressures is neither necessary nor desirable (see: Hamann, S.; le Noble, W. J. *J. Chem. Educ.* **1984**, *61*, 658).

(29) Bond, A. M.; Lawrance, G. A.; Lay, P. A.; Sargeson, A. M. *Inorg. Chem.* **1983**, *22*, 2010.

(30) Creaser, I. I.; Sargeson, A. M.; Zanella, A. W. *Inorg. Chem.* **1983**, *22*, 4022.

Table 1. Temperature and Pressure Dependence of Self-Exchange Rate Constants k_{ex} for Co(diamsar)$^{3+/2+}$ Self-Exchange Reaction[a]

temp/°C	[Λ-Co^{III}]/ mmol L^{-1}	[Δ-Co^{II}]/ mmol L^{-1}	I^b/mol L^{-1}	P/MPa	$k_{ex}{}^c$/L mol^{-1} s^{-1}
12.2	1.54	1.48	0.144	0.1	0.188 ± 0.002
20.9					0.354 ± 0.004
30.3					0.705 ± 0.004
39.3					1.308 ± 0.020
25.0	1.53	1.51	0.094	1.5	0.395 ± 0.012
				41.3	0.460 ± 0.006
				81.0	0.549 ± 0.010
				120.8	0.681 ± 0.016
				160.8	0.753 ± 0.014
	1.52	1.50	0.144	1.9	0.431 ± 0.018
				41.3	0.507 ± 0.014
				80.5	0.616 ± 0.012
				120.0	0.752 ± 0.014
				160.0	0.841 ± 0.014
25.0	1.53	1.50	0.244	2.1	0.528 ± 0.016
				41.3	0.617 ± 0.036
				80.9	0.759 ± 0.016
				120.3	0.894 ± 0.016
				161.5	1.040 ± 0.018
	2.00	2.01	0.150	2.4	0.397 ± 0.010
				40.8	0.479 ± 0.012
				80.9	0.549 ± 0.010
				119.9	0.648 ± 0.010
				159.9	0.738 ± 0.014
	2.03	1.98	0.250	1.7	0.546 ± 0.010
				42.1	0.721 ± 0.002
				81.8	0.828 ± 0.008
				121.3	0.890 ± 0.020
				161.0	1.087 ± 0.006

[a] In morpholine/CF_3SO_3H buffer ([triflate] = 0.025 mol L^{-1}) at 25 °C. [b] Adjusted with CF_3SO_3K. [c] Average of 2–3 measurements.

Table 2. Volumes of Activation for Self-Exchange Reactions in Aqueous Solution at 25.0 °C

reacn	I/mol L^{-1}	k_{ex}/L mol^{-1} s^{-1}	$\Delta V_{ex}^{\ddagger}$/cm^3 mol^{-1}
Co(diamsar)$^{3+/2+}$	0.094	0.392 ± 0.010	−10.5 ± 0.6
	0.144	0.429 ± 0.010	−10.9 ± 0.6
	0.150	0.400 ± 0.006	−9.8 ± 0.4
	0.244	0.524 ± 0.008	−10.8 ± 0.4
	0.250	0.572 ± 0.026	−9.9 ± 1.1
Co(diamsarH$_2$)$^{5+/4+}$	0.390	0.0149 ± 0.0005	−9.6 ± 0.8

Table 3. Pressure Dependence of Rate Constants k_{ex} for the Co(diamsarH$_2$)$^{5+/4+}$ Self-Exchange Reaction in Aqueous Solution[a]

P/MPa	$k_{ex}{}^b$/10^{-2} L mol^{-1} s^{-1}	P/MPa	$k_{ex}{}^b$/10^{-2} L mol^{-1} s^{-1}
2.3	1.46 ± 0.09	122.0	2.40 ± 0.07
42.7	1.75 ± 0.07	162.3	2.70 ± 0.02
81.4	2.15 ± 0.08		

[a] 25.0 °C, [CF_3SO_3H] = 0.100 mol L^{-1}, [CF_3SO_3K] = 0.025 mol L^{-1}, [Λ-Co^{III}] = 0.0101–0.0102 mol L^{-1}, [Δ-Co^{II}] = 0.0098–0.0099 mol L^{-1}, I = 0.390–0.392 mol L^{-1}. [b] Mean of two runs at each pressure.

For the study of the Co(diamsarH$_2$)$^{5+/4+}$ exchange, solutions were prepared with 0.1 mol L^{-1} CF_3SO_3H, and the ionic strength was adjusted with CF_3SO_3K. The procedure was as for the Co(diamsar)$^{3+/2+}$ exchange, except that zinc amalgam was used in place of mossy zinc and Co^{III} concentrations were determined spectrophotometrically with ϵ = 147.6 L mol^{-1} cm^{-1} at 476 nm. Duplicate kinetic runs were made over not less than 4 half-periods.

Electrochemical Measurements. The high-pressure electrochemical system was as described elsewhere,[31,32] except that the sample cell was rebuilt with smaller (4.5 cm^3) internal volume. The three-electrode cell configuration consisted of either a gold or gold amalgam wire working electrode, a Pt wire auxiliary electrode, and a AgCl/Ag/4.0 mol L^{-1} KCl reference cell. Cyclic voltammograms (CV) were recorded for solutions at 25.0 ± 0.1 °C using a PAR 174A polarographic analyzer and a RE 0074 X-Y recorder with scan rate 20 mV s^{-1}. Solutions were prepared from racemic Co(diamsarH$_2$)Cl$_5$·1.5H$_2$O in perchlorate media ($HClO_4$/$NaClO_4$ for the 5+/4+ couple or $NaClO_4$ with pH adjustment with NaOH for the 3+/2+) rather than as for the kinetic studies because the CV peaks were poorly resolved in CF_3SO_3H/CF_3SO_3K solutions while reduction was almost irreversible in morpholine/CF_3SO_3H buffer. Formal potentials E were obtained by averaging the oxidation and reduction peak potentials.

Results

Co(diamsar)$^{3+/2+}$ Self-Exchange. From pseudo-first-order rate constants k_{obsd} calculated from eq 1,

$$X_t = X_\infty + (X_0 - X_\infty)\exp(-k_{obsd}t) \qquad (1)$$

the self-exchange rate constants k_{ex} = k_{obsd}/[Co]$_{total}$ given in Table 1 were obtained; values of k_{ex} at atmospheric pressure agreed well with that obtained by Sargeson et al.[30] at a comparable ionic strength I = 0.2 mol L^{-1} ($LiClO_4$). The dependence of k_{ex} on I at 0.1 MPa was investigated over the rather limited experimentally accessible range of I at constant reactant concentration and fitted to the Brønsted–Bjerrum–Christiansen equation

$$\ln k_{ex} = \ln k_{ex}{}^0 + 2z_1z_2CI^{1/2}/(1 + B\mathring{a}I^{1/2}) \qquad (2)$$

where z_1 and z_2 are the reactant charge numbers, B and C are the Debye–Hückel parameters for water at 25 °C (3.286 × 10^9 L$^{1/2}$ mol$^{1/2}$ m^{-1} and 1.175 L$^{1/2}$ mol$^{1/2}$, respectively), giving $k_{ex}{}^0$ = 0.057 ± 0.018 L mol^{-1} s^{-1} and $\mathring{a}$ = 1.31 ± 0.27 nm. Since I is quite high and limited in range, we regard $\mathring{a}$ as an empirical parameter with no physical significance.

Notwithstanding the theoretical expectations noted above,[2] the dependence of ln k_{ex} on pressure at each ionic strength was linear within the experimental uncertainty, so the corresponding values of $\Delta V_{ex}^{\ddagger}$ collected in Table 2 are, in effect, averages over the pressure range 0.1–160 MPa. No systematic dependence of $\Delta V_{ex}^{\ddagger}$ on I is discernible, and the average value $\Delta V_{ex}^{\ddagger}$ = −10.4 ± 0.5 cm^3 mol^{-1} may be assigned to the Co(diamsar)$^{3+/2+}$ exchange for this range of experimental conditions.

The temperature dependence of k_{ex} at 0.1 MPa and I = 0.14 mol L^{-1} (Table 1) is represented by an Eyring plot (ln k_{ex}/T vs $1/T$) of excellent linearity, giving $\Delta H_{ex}^{\ddagger}$ = 50.7 ± 0.6 kJ mol^{-1} and $\Delta S_{ex}^{\ddagger}$ = −80.9 ± 2.0 J K^{-1} mol^{-1}, whence $k_{ex}{}^{298}$ = 0.48 L mol^{-1} s^{-1} (cf. 0.50 ± 0.01 L mol^{-1} s^{-1}, reported for a $LiClO_4$ medium with I = 0.2 mol L^{-1} [30]).

Co(diamsarH$_2$)$^{5+/4+}$ Self-Exchange. A linear regression of ln k_{ex} for Co(diamsarH$_2$)$^{5+/4+}$ on P (Table 3) gives k_{ex} = 0.0149 ± 0.0005 L mol^{-1} s^{-1} and $\Delta V_{ex}^{\ddagger}$ = −9.6 ± 0.8 cm^3 mol^{-1} at 25.0 °C, 0.1 MPa, and I = 0.39 mol L^{-1} (H/K triflate). Sargeson et al.[30] report k_{ex} = 0.024 ± 0.003 L mol^{-1} s^{-1} at 25.0 °C and 0.1 MPa for a different medium (I = 0.2 mol L^{-1}, H/Li perchlorate); the agreement is reasonable, but since the expectation is that k_{ex} should *increase* with increasing I, there is a hint of minor specific anion effects involving these highly-charged cations.

Pressure Dependence of Electrode Potentials. In $NaClO_4$ media with pH adjustment with NaOH to 8.1 (cf. the Co(diamsar)$^{3+/2+}$ exchange kinetics using a morpholine buffer), the Co(diamsar)$^{3+/2+}$ voltammogram was obscured by a shift in the potential window imposed by the solvent, but CV peak resolution was greatly improved at pH 5.4, which shifted the window sufficiently yet was still high enough to ensure

---

(31) Doine, H.; Whitcombe, T. W.; Swaddle, T. W. *Can. J. Chem.* **1992**, *70*, 81.

(32) Sun, J.; Wishart, J. F.; van Eldik, R.; Shalders, R. D.; Swaddle, T. W. *J. Am. Chem. Soc.* **1995**, *117*, 2600.

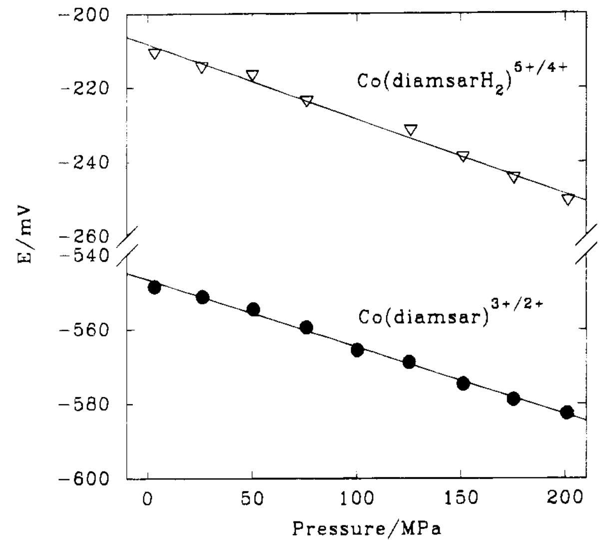

Figure 2. Pressure dependence of the formal potentials E of (diamsar)cobalt(III/II) couples vs a Ag/AgCl/4.0 mol L^{-1} KCl electrode. See text for conditions of measurements.

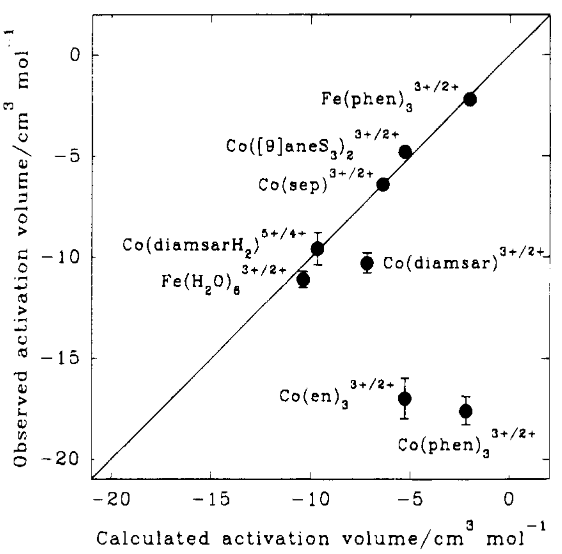

Figure 3. Calculated and observed mean volumes of activation, 0.1–200 MPa, for self-exchange reactions in aqueous solution. Data are from refs 2, 4, 6, 8–10, and 12 and this work. The diagonal line represents perfect agreement between theory and experiment.

substantially complete deprotonation of the diamsar complexes. The measured formal potential E at 0.1 MPa and 25.0 °C for reaction 3 (0.100 mol L^{-1} NaClO$_4$, pH 5.36, [Co] = 5.10 × 10^{-3} mol L^{-1}, 0.5 mm diameter gold wire working electrode, scan rate 20 mV s^{-1}) was −0.547 V, which is consistent with measurements reported for other media.[29,30,33]

$$\mathrm{Co(diamsar)^{3+}(aq) + Ag(s) + Cl^- \ (4\ mol\ L^{-1}\ KCl) \rightarrow Co(diamsar)^{2+}(aq) + AgCl(s)} \quad (3)$$

The pressure dependence of E, 0.1–200 MPa, was linear (Figure 2) and gave the volume of reaction $\Delta V = +17.4 \pm 0.5$ cm^3 mol^{-1} for reaction 3 under these same conditions ($I = 0.136$ mol L^{-1}). This may be compared to $\Delta V = +18.8 \pm 0.6$ cm^3 mol^{-1} previously obtained[33] for the Co(diamsar)$^{3+/2+}$ couple in nitrate media (pH 5.39) relative to a Ag$^+$(aq)/Ag(s) electrode; we have shown elsewhere[32] that the contributions of the AgCl/Ag and Ag$^+$/Ag electrodes to measured volumes of reaction are not very different, and thus it may be inferred that ΔV for reaction 3 is not sensitive to medium effects. For the cell

$$\mathrm{Co(diamsarH_2)^{5+}(aq) + Ag(s) + Cl^- \ (4\ mol\ L^{-1}\ KCl) \rightarrow Co(diamsarH_2)^{4+}(aq) + AgCl(s)} \quad (4)$$

at 25.0 °C and $I = 0.204$ mol L^{-1} (0.1005 mol L^{-1} HClO$_4$/0.0276 mol L^{-1} NaClO$_4$, [Co] = 5.10 × 10^{-3} mol L^{-1}, 0.5 mm gold wire working electrode, scan rate 20 mV s^{-1}), E at 0.1 MPa = −0.208 V, in good agreement with values obtained with other reference electrodes,[29,30,33] and $\Delta V = +19.5 \pm 0.8$ cm^3 mol^{-1} (cf. +23.7 ± 0.5 cm^3 mol^{-1}, measured in a nitrate medium vs Ag$^+$/Ag at pH 1.6;[33] as with the self-exchange kinetics, there is a suggestion of specific anion interactions with these highly-charged cations).

Cross Reactions Involving the Co(diamsar)$^{3+/2+}$ or Co(diamsarH$_2$)$^{5+/4+}$ Couples. We have previously proposed a cross relation in volumes of activation for outer-sphere net redox reactions.[24] Attempts to use the Co diamsar complexes to test this relation by high-pressure stopped-flow spectrophotometry[24] for reactions other than those involving the possibly anomalous[8,16,34] Fe(H$_2$O)$_6$$^{3+/2+}$ couple were unsuccessful because of a convergence of limitations. The cross reaction rate must fall in the stopped-flow region, which implies the choice of participating couples with relatively slow self-exchange rates and a driving force (ΔE) for the cross reaction that is not large—in any event, the theory of cross reaction rates and volumes of activation appears to break down at high ΔE.[24] In addition, $\Delta V_{ex}^{\ddagger}$ for self-exchange of the selected couples and ΔV for the overall reaction must be available. The solubilities and stabilities of reactant and product species in the reaction medium (which may contain traces of extraneous oxidants or reductants) impose further restrictions; for example, decomposition of the labile Co(phen)$_3$$^{2+}$ product obscured the redox process in the reaction of excess Co(diamsar)$^{2+}$ or Co(diamsarH$_2$)$^{4+}$ with Co(phen)$_3$$^{3+}$,[35] while unidentified parasitic reactions complicated the absorbance changes in the reaction of Co([9]aneS$_3$)$_2$$^{3+}$ with Co(sep)$^{2+}$. Finally, the change in optical absorbance accompanying the cross reaction must be large enough to be accurately measurable in the high-pressure stopped-flow system, and this prevented study of the Co(diamsar)$^{3+}$–Co(sep)$^{2+}$ reaction in the visible region.[36] To date, no cross reactions have been found, other than those previously described,[24] that meet all these requirements.

Discussion

Figure 3 illustrates the key result of this study, namely, that our adaptation of Marcus–Hush theory[1,2] is quantitatively successful in aqueous systems for a variety of self-exchanging cationic couples *including low-spin/high-spin Co$^{III/II}$ cage cations, regardless of charge,* as well as low-spin/low-spin Co([9]aneS$_3$)$_2$$^{3+/2+}$. For Co(diamsar)$^{3+/2+}$, $\Delta V_{ex}^{\ddagger}$ is some 3 cm^3 mol^{-1} more negative than calculated but is acceptably close. In

---

(33) Shalders, R. D. Ph.D. Thesis, The University of Melbourne, Parkville, Victoria, Australia, 1992. Lincoln, S. F.; Shalders, R. D.; Tregloan, P. A. Forthcoming publication.

(34) Hupp, J. T.; Weaver, M. J. *Inorg. Chem.* **1983**, *22*, 2557.

(35) We found that Co(phen)$_3$$^{2+}$ decomposes in 0.1 mol L^{-1} CF$_3$SO$_3$H at 25.0 °C with a first-order rate constant of 0.14 s^{-1}. At pH ≈ 8, the decomposition reactions were slower but no longer first-order. At neither pH could any clear-cut measure of the rate of the Co(diamsarH$_2$)$^{4+}$– or Co(diamsar)$^{2+}$–Co(phen)$_3$$^{3+}$ redox processes be extracted from absorbance changes in the stopped-flow timeframe (10 ms–100 s).

(36) Absorbance changes in the ultraviolet are adequate[29] but necessitate the use of concentrations of the reductant so low that oxidative losses over a series of high-pressure stopped-flow measurements become excessive.

Table 4. Electrochemical Parameters for $Co^{III/II}$ Cage and Chelate Complexes in Water[a]

	$Co(en)_3^{3+/2+}$	$Co(phen)_3^{3+/2+}$	$Co(sep)^{3+/2+}$	$Co(diamsar)^{3+/2+}$	$Co(diamsarH_2)^{5+/4+}$	$Co([9]aneS_3)_2^{3+/2+}$
$E^{\circ\prime}$/V (vs NHE)	−0.147[b]	+0.386[c]	−0.270[d,e]	−0.245[f,g]	+0.032[f,h]	+0.436[i,j]
k_{ex}/L mol^{-1} s^{-1}	8.1×10^{-5}[k]	6.7[j,l]	5.0[d,h]	0.48[f,g]	0.015[f,m]	9.5×10^{4}[d,j]
ΔV^{n}/cm^3 mol^{-1}	26.6[b]	28.2[c]	13.9[e,o]	17.4[f,g]	19.5[f,h]	20.6[e,i]
Δd_{Co-L}/pm	21[p]	19[q]	19[p]	(19)[r]	(19)[r]	7[q]
$\Delta V_{ex}^{\ddagger}$/cm^3 mol^{-1}	−15.5[s]	−17.6[j,t]	−6.4[d,h]	−10.4[e,f,j]	−9.6[f,u]	−4.8[d,j]
$\Delta V_{calc}^{\ddagger}$ [v]/cm^3 mol^{-1}	−5.3	−2.0	−6.4	−7.2	−9.7	−5.3
$\Delta H_{ex}^{\ddagger}$/kJ mol^{-1}	57.6[k]	35.3,[j,l] 20.6[j,w,x]	41.4[d,h]	50.7[f,g]		25.4[d,j]
$\Delta S_{ex}^{\ddagger}$/J K^{-1} mol^{-1}	−130[k]	−113,[j,l] −156[j,w,x]	−93[d,h]	−81[f,g]		−64[d,j]

[a] 25 °C. [b] Reference 33; $I = 0.10$ mol L^{-1}. [c] Reference 32; $I = 1.0$ mol L^{-1} (KCl). [d] Reference 12. [e] $I = 0.25$ mol L^{-1}. [f] This work. [g] $I = 0.14$ mol L^{-1}. [h] $I = 0.20$ mol L^{-1}. [i] Reference 24. [j] $I = 0.10$ mol L^{-1}. [k] $I = 0.98$ mol L^{-1} (Dwyer, F. P.; Sargeson, A. M. *J. Phys. Chem.* **1961**, *65*, 1892). [l] Cl^- medium. [m] $I = 0.39$ mol L^{-1}. [n] Relative to AgCl/Ag/4 mol L^{-1} KCl. [o] Reference 31. [p] Hendry, P.; Lüdi, A. *Adv. Inorg. Chem.* **1990**, *35*, 117. [q] Setzer, W. N.; Ogle, C. A.; Wilson, G. S.; Glass, R. S. *Inorg. Chem.* **1983**, *22*, 266. Küppers, H.-J.; Neves, A.; Pomp, C.; Ventur, D.; Wieghardt, K.; Nuber, B.; Weiss, J. *Inorg. Chem.* **1986**, *25*, 2400. [r] Estimated on basis that Co−N distances in sarcophagine complexes are close to those in sepulchrate: ref 37. [s] Reference 9; $I = 0.5$ mol L^{-1}. [t] Reference 10. [u] $I = 0.39$ mol L^{-1}. [v] Includes estimated inner-sphere reorganizational contribution $\Delta V_{IR}^{\ddagger} = +0.6$ cm^3 mol^{-1}. [w] NO_3^- medium. [x] Warren, R. M. L.; Lappin, A. G.; Mehta, B. D.; Neumann, H. M. *Inorg. Chem.* **1990**, *29*, 4185.

contrast, observed and calculated $\Delta V_{ex}^{\ddagger}$ are irreconcilable for the "open" (nonencapsulated) low-spin/high-spin $Co^{III/II}$ chelates $Co(en)_3^{3+/2+}$, $Co(phen)_3^{3+/2+}$, and "$Co(edta)^{-/2-}$"—this last couple is not included in Figure 3 because, in the reduced species at the working p*H*, edta is protonated and quinquedentate and there is a coordinated water molecule, but $\Delta V_{ex}^{\ddagger}$ is nevertheless more negative than expected after these complications are allowed for.[11]

Table 4 juxtaposes the kinetic and electrochemical results for $Co^{III/II}$ couples. Despite difficulties in making direct comparisons because of differences in the media, some generalities emerge. The conditional electrode potentials $E^{\circ\prime}$, which are reliable to ±10 mV, set the low-spin/low-spin $Co([9]aneS_3)_2^{3+/2+}$ apart from the low-spin/high-spin cases in general, although $E^{\circ\prime}$ for $Co(phen)_3^{3+/2+}$ appears to be more typical of a low-spin/low-spin couple. A careful search[10] for evidence of spin-pairing in $Co(phen)_3^{2+}$ detected none (<1%); the unusually positive $E^{\circ\prime}$ value, however, is quite consistent with the general pattern for phen complexes.[38] The volume change ΔV associated with $E^{\circ\prime}$ (relative, however, to Ag/AgCl rather than NHE) divides the $Co^{III/II}$ couples into the same two groups that are evident in Figure 3: the cage and low-spin/low-spin complexes (ΔV = 14−21 cm^3 mol^{-1}), for which $\Delta V_{ex}^{\ddagger}$ is predictable from Marcus−Hush-based theory, and the low-spin/high-spin chelates (ΔV = 27−28 cm^3 mol^{-1}), for which $\Delta V_{ex}^{\ddagger}$ is anomalously strongly negative. This implies that whatever causes the kinetic deviance of the low-spin/high-spin $Co^{III/II}$ chelates also has consequences for their equilibrium properties. Finally, the aberrance of $\Delta V_{ex}^{\ddagger}$ values for $Co(en)_3^{3+/2+}$ and $Co(phen)_3^{3+/2+}$ has a clear parallel in unusually strongly negative $\Delta S_{ex}^{\ddagger}$ values.

Franck−Condon effects due to increases Δd_{Co-L} in the cobalt−ligand bond distances on reduction (Table 4) clearly do not explain the trend in k_{ex} except in the case of the fast, low-spin/low-spin $Co([9]aneS_3)_2^{3+/2+}$ exchange. Neither is it satisfactory to attribute the strikingly low k_{ex} for $Co(en)_3^{3+/2+}$ to nonadiabaticity, as the sep and diamsar cage complexes are structurally related to this couple but are somewhat bulkier (so that donor−acceptor interactions may be diminished) and yet, on the evidence of Figure 3, they undergo self-exchange adiabatically. Although the configuration and conformation of Co cage complexes can have a significant influence on their redox reactivity both kinetically[39,40] and thermodynamically,[41] in general these complexes undergo self-exchange up to 10^5 times faster than the parent $Co(en)_3^{3+/2+}$ couple. According to molecular mechanics calculations,[39−44] this is because molecular strain within the cages is relieved on going to the transition state for electron transfer. Thus, self-exchange in *all* these complexes could well be fully adiabatic, but the Franck−Condon energy barrier associated with large Jahn−Teller-type distortions as $Co(en)_3^{3+/2+}$ goes to the transition state would be substantially reduced in the already strained cage couples. Such distortions will presumably include those of a twisting kind, as well as changes in the Co−ligand bond lengths Δd_{Co-L}, and many cage complexes are known to be twisted away from quasi-octahedral toward trigonal prismatic coordination in the ground state.[37]

In the case of $Co(phen)_3^{3+/2+}$, k_{ex} is 10^5-fold larger and $E^{\circ\prime}$ over 0.5 V more positive than for $Co(en)_3^{3+/2+}$, probably because of the high ligand field strength of phen relative to en.[38] Presumably, $Co(phen)_3^{2+}$ lies much closer in energy to a spin-paired excited state that can carry the electron transfer reaction efficiently (cf. $Co([9]aneS_3)_2^{3+/2+}$) than does $Co(en)_3^{2+}$. We noted above that less than 1% of $Co(phen)_3^{2+}$ is low-spin in aqueous solution[10] but only 0.001−0.01% would be required in a fast[45] spin pre-equilibrium to give the measured k_{ex}, if the $Co([9]aneS_3)_2^{3+/2+}$ exchange rate is typical of low-spin/low-spin Co couples. For $Co(en)_3^{3+/2+}$, the fraction of the Co^{II} as low-spin $Co(en)_3^{2+}$ needed to explain the observed k_{ex} on the basis of a quartet/doublet spin equilibrium preceding electron transfer would be about 1 in 10^9. These fractions seem reasonable. In either case, a contribution ΔV_{spin} of −10 to −16 cm^3 mol^{-1} from the spin equilibria is required to bring the observed $\Delta V_{ex}^{\ddagger}$ values in line with our Marcus−Hush-based predictions, and the measurements of Binstead and Beattie[23] on $Co(terpy)_2^{2+}$ indicate that ΔV_{spin} is indeed likely to be of this magnitude.

We conclude, then, that self-exchange between low-spin/high-spin $Co^{III/II}$ "open" chelates in water is essentially adiabatic and follows a fast[45] spin pre-equilibrium step involving the Co^{II} partner; the alternative view that we previously favored, that the overall exchange reaction is nonadiabatic, now seems untenable. Furthermore, as Geselowitz anticipated,[21] large spin-multiplicity changes do not *in themselves* inhibit electron

---

(37) Comba, P.; Sargeson, A. M.; Engelhardt, L. M.; Harrowfield, J. M.; White, A. H.; Horn, E.; Snow, M. R. *Inorg. Chem.* **1985**, *24*, 2325.

(38) Lappin, A. G. *Redox Mechanisms in Inorganic Chemistry*; Ellis Horwood: New York, 1994; p 21.

(39) Bernhardt, P. V.; Bygott, A. M. T.; Geue, R. J.; Hendry, A. J.; Korybut-Daszkiewicz, B. R.; Lay, P. A.; Pladziewicz, J. R.; Sargeson, A. M.; Willis, A. C. *Inorg. Chem.* **1994**, *33*, 4553.

(40) Geue, R. J.; Hendry, A. J.; Sargeson, A. M. *J. Chem. Soc. Chem. Commun.* **1989**, 1646.

(41) Hambley, T. W. *Inorg. Chem.* **1988**, *27*, 2494.

(42) Geselowitz, D. *Inorg. Chem.* **1981**, *20*, 4457.

(43) Geue, R. J.; Pizer, R.; Sargeson, A. M. *Abstracts of Papers*, 183rd National Meeting of the American Chemical Society, Las Vegas, NV, Apr 1982; American Chemical Society: Washington, DC, 1982; INOR 62.

(44) Sargeson, A. M. Personal communication.

(45) Beattie, J. K. *Adv. Inorg. Chem.* **1988**, *32*, 2.

transfer, since low-spin/high-spin $Co^{III/II}$ cage complexes conform well to expectations for simple adiabatic electron transfer (Figure 3) even though "open" Co chelates do not. In other words, the concept of "spin forbiddenness" of bimolecular electron transfer reactions is redundant. Large spin-state changes can, however, influence k_{ex} , $\Delta V_{ex}^{\ddagger}$, and $\Delta S_{ex}^{\ddagger}$ in open chelate complexes through Jahn–Teller and other distortions as the reactants proceed to the transition state, to a degree consistent with a fast Co^{II} spin equilibrium preceding electron transfer. For cage complexes, these distortions are suppressed by the rigidity of the cage, so that $\Delta V_{ex}^{\ddagger}$ reflects mainly the outer-sphere (solvent) reorganization in accordance with the Marcus–Hush-based theory,[2] while the activation energetics reflect destabilization of the ground state relative to the transition state by molecular strain, regardless of spin multiplicity changes. Finally, the fact that the thermodynamic ΔV values associated with *net* reduction of Co^{III} to Co^{II} in the cage complexes are significantly less positive than for the analogous open chelates confirms that changes in the volumes of the cage complexes and their solvation sheaths are suppressed by the rigidity of the cages.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada for financial support and Prof. A. M. Sargeson for discussions.

IC950489A