Kinetics of the Tris(1,10-phenanthroline)cobalt(III/II) Self-Exchange Reaction in Aqueous Solution at Variable Pressure

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The marked dependence of the rate constant k_2 for the $Co(phen)_3^{3+/2+}$ self-exchange reaction in water on the nature and concentration of the anion X^- can be accommodated in terms of the full Debye–Hückel equation taking ion size parameter $\mathring{a}$ as adjustable (520 pm for X = Cl, 360 pm for X = NO$_3$). A small additional contribution to the exchange rate, most evident at low electrolyte concentrations, appears to come from a heterogeneous pathway. At infinite dilution, k_2 is estimated to be 0.35 L mol^{-1} s^{-1} at 25 °C; cf. 6.7 and 10.7 L mol^{-1} s^{-1} for X = Cl and NO$_3$, respectively, at ionic strength I = 0.107 mol L^{-1}. By contrast, the corresponding volume of activation ΔV^* shows only a small dependence on I (−20.1 ± 0.4 cm^3 mol^{-1} as $I \rightarrow 0$; cf. −17.6 ± 0.7 and −16.0 ± 0.7 cm^3 mol^{-1} for X = Cl and NO$_3$, respectively at I = 0.107 mol L^{-1}), and this is accurately calculable from Debye–Hückel-based theory (*Inorg. Chem.* 1990, *29*, 5017). Within the limits of detection, $Co(phen)_3^{2+}$ is entirely high-spin in aqueous solution (μ_{eff} = 4.79 μ_B with Θ = 20 K, 13–85 °C). For $Co(phen)_3^{3+/2+}$, ΔV^* is much more negative (by some 15 cm^3 mol^{-1}) than adiabatic electron-transfer theory can accommodate, and this appears to be typical of low-spin/high-spin $Co^{III/II}$ self-exchange reactions such as $Co(en)_3^{3+/2+}$, except for $Co(sep)^{3+/2+}$, for which ΔV^* conforms well to predictions for adiabatic electron transfer. The behavior of $Co(phen)_3^{3+/2+}$ and $Co(en)_3^{3+/2+}$ is attributed to either adiabatic electron transfer from a low-spin isomer of the Co^{II} complex in highly unfavorable equilibrium with the high-spin form or, more likely, nonadiabatic electron transfer involving the Co^{II} and Co^{III} ground states.

Introduction

It is commonly stated[1] that the effects of pressure P on the rate constants k of inorganic reactions in solution (usually expressed as a volume of activation $\Delta V^* = -RT(\partial \ln k/\partial P)_T$) can provide insights into the reaction mechanisms. Implicit in this contention, however, is the assumption that these effects can indeed be accounted for quantitatively in cases representing the archetypal mechanisms. For redox processes, adiabatic outer-sphere electron-transfer processes provide such archetypes for which ΔV^* is, in principle, calculable from adaptations[2–4] of the theories of Hush[5] and Marcus.[6] A major thrust of the work of our laboratory is to determine the extent to which this theoretical approach is reliable. Experience to date suggests that the theory is quite accurate for self-exchange reactions in water[4,7] but is less reliable for nonaqueous media, particularly where the dielectric constant of the medium is low.[4,8]

The chief concern of this article is the problem of major deviations from theoretical expectations in the pressure response of the kinetics of certain $Co^{III/II}$ self-exchange reactions in water. The $Co([9]aneS_3)_2^{3+/2+}$ couple,[9] in which both the Co^{III} and Co^{II} ground states are low spin (electronic singlet and doublet, respectively), is "well-behaved" in terms of the theory inasmuch as the self-exchange reaction is as fast as predicted (k^{298} = 9.5 × 10^4 L mol^{-1} s^{-1} at ionic strength I = 0.1 mol L^{-1}) and the experimental ΔV^* (−4.8 cm^3 mol^{-1}) is essentially identical with the theoretical value.[7] In contrast, self-exchange for the $Co(en)_3^{3+/2+}$ couple[9] is unusually slow ($k^{298} \approx 8 \times 10^{-5}$ L mol^{-1}

s^{-1} at I = 0.98 mol L^{-1}) and ΔV^* is some 13 cm^3 mol^{-1} more negative at 0.1 MPa than predicted for adiabatic reactions of the complexes in their ground states.[10] The respective ground states of $Co(en)_3^{3+}$ and $Co(en)_3^{2+}$ are a singlet and a quartet, and one can account for both the strongly negative, pressure-dependent volume of activation and the very slow rate of self-exchange in terms of nonadiabaticity originating in the large spin change involved.[10] Alternatively, one can argue that electron transfer to Co^{III} occurs adiabatically via a low-spin $Co(en)_3^{2+}$ excited state formed in an unfavorable preequilibrium step with a volume change of ≈−10 cm^3 mol^{-1}, but this seems less likely on energetic grounds.[10] For the $Co(sep)^{3+/2+}$ self-exchange,[7,9] however, we again have singlet and quartet ground states, yet k^{298} (5 L mol^{-1} s^{-1} at I = 0.2 mol L^{-1}) and ΔV^* (−6.4 cm^3 mol^{-1}) have the "normal" adiabatic values predicted by the Marcus–Hush-based theory. The questions therefore arise as to whether the $Co(en)_3^{3+/2+}$ self-exchange is an isolated aberrant case and whether large changes in spin in electron transfer have as much influence on kinetic parameters as is usually supposed.

We have therefore examined the self-exchange kinetics of the $Co(phen)_3^{3+/2+}$ couple[9] in water at variable pressure, building upon published ambient-pressure kinetic studies of this system.[11,12] Although $Co(phen)_3^{2+}$ is apparently exclusively in the high-spin (quartet) state in its solid perchlorate salt,[13] analogy with Fe(phen)$_3^{2+}$, which is diamagnetic, and $Co(terpy)_2^{2+}$, which exhibits quartet–doublet spin isomerism in solution,[9,14,15] suggests that a doublet state of $Co(phen)_3^{2+}$ should be much more accessible thermally than that of $Co(en)_3^{2+}$ and may even be present as an experimentally detectable fraction of the $Co(phen)_3^{2+}$ in water at near-ambient temperatures, so providing an important pathway for adiabatic electron transfer. We have therefore also measured the apparent magnetic moment of $Co(phen)_3^{2+}$ in aqueous solution

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over the temperature range 286–360 K. Finally, we have sought to quantify the marked effects of anions[11,12] on the kinetics of the $Co(phen)_3^{3+/2+}$ self-exchange in water.

Experimental Section

Materials. [Λ-(+)$_{589}$-Co(phen)$_3$](ClO$_4$)$_3$·xH$_2$O was prepared by the method of Lee et al.[16] and recrystallized from the minimum of ice-cold water that had been presaturated with chlorine gas. The solid was precipitated by the addition of saturated aqueous NaClO$_4$; yield 86% (x = 4). [**Warning!** Perchlorate salts of Co complexes containing organic ligands are potentially explosive.] Elemental (C, H, N) analyses, perchlorate content determinations by anion-exchange chromatography on Dowex 1-X4, and water content determinations by ^{1}H-NMR in acetone-d_6 all confirmed that the product was the tetrahydrate (x = 4, with specific rotation [α]$_{588}$ = +691° cm^3 g^{-1} dm^{-1}; cf. x = 2, [α] = +796° cm^3 g^{-1} dm^{-1} reported by Lee et al.[16]).

[Co(phen)$_3$](ClO$_4$)$_2$·H$_2$O was prepared by mixing hot (>80 °C) aqueous solutions of [Co(H$_2$O)$_6$](ClO$_4$)$_2$ and 1,10-phenanthroline in a 1:4 molar ratio. Dropwise addition of aqueous NaClO$_4$ gave a yellow precipitate which was recrystallized from hot water containing a small amount of phen. Microanalyses for C, H, and N were in good accordance with [Co(phen)$_3$](ClO$_4$)$_2$·H$_2$O.

Susceptibility Measurements. The magnetic susceptibility of a solution of Co(phen)$_3^{2+}$ (0.019 28 mol L^{-1} Co^{II} by Ce^{IV} titration, after conversion of the perchlorate to the chloride salt with Dowex 1-X4 anion-exchange resin) in D$_2$O (99.9% isotopic purity, Cambridge Isotope Laboratories) containing 2% v/v *tert*-butyl alcohol and 0.0026 mol L^{-1} phen was determined by Evans' NMR method[17] on a Bruker AM-400 spectrometer over the temperature range 285–360 K. The Co^{II} solution was placed in the inner tube, and a solution of 2% *tert*-butyl alcohol in D$_2$O, in the outer compartment of a coaxial NMR tube. Signal lock was provided by the D$_2$O in the outer tube. The temperature sensor was calibrated using pure 1,2-ethanediol as a standard.

Spontaneous Racemization of Co(phen)$_3^{3+}$. The spontaneous racemization rate of [Λ-(+)$_{589}$-Co(phen)$_3$](ClO$_4$) in water at 25 °C was obtained from the decay of the optical rotatory dispersion (ORD) signal at 589 nm measured with a Rudolph Autopol III polarimeter. Yamamoto and Yamamoto[18] noted that the rate of spontaneous racemization is enhanced by UV light and by sodium halides; accordingly, the thermostated flask containing the solution from which samples were periodically withdrawn was darkened with aluminum foil, and the only anion present in the solution was perchlorate.

Co(phen)$_3^{3+/2+}$ Self-Exchange Rate Measurements. Since the perchlorate salts of the complexes were of limited solubility, solutions of optically active [Co(phen)$_3$]X$_3$ with X$^-$ = Cl$^-$ or NO$_3^-$ were prepared by passing aqueous [Λ-(+)$_{589}$-Co(phen)$_3$](ClO$_4$)$_3$ through a column of Dowex 1-X4 anion-exchange resin in the X$^-$ form. The ionic strength I was adjusted with NaCl (BDH Assured) or NaNO$_3$ (Fisher Certified). Refrigeration of the solutions in storage limited the spontaneous loss of optical activity to less than 10% over the typical 2-week duration of a set of experiments. The Co(phen)$_3^{3+}$ concentration was determined spectrophotometrically at 350 nm (molar absorbance ϵ = 3.60 × 10^3 L mol^{-1} cm^{-1}).

The Co(phen)$_3^{2+}$ solutions were prepared by mixing the desired [Co(H$_2$O)$_6$]X$_2$ (X = Cl$^-$ or NO$_3^-$) in solution with phen in a 4:1 molar ratio and were used immediately, since a decrease in [Co(phen)$_3^{2+}$] was apparent over a few days even with refrigeration. The Co^{II} concentration was determined spectrophotometrically (ϵ = 4.84 L mol^{-1} cm^{-1})[19] prior to mixing with the phen.

The progress of the self-exchange reaction was monitored by following the disappearance of the circular dichroism of Λ-(+)$_{589}$-Co(phen)$_3^{3+}$ as a function of [Co^{III}], [Co^{II}], [X$^-$], and pressure (1–160 MPa), using a Hi-Tech HPSF56 high-pressure stopped-flow apparatus in conjunction with a Jasco J-500A spectropolarimeter as described elsewhere.[7] At least three (more usually four) transients were recorded for each reaction set, and all reactions were followed for at least 3 half-lives.

Table I. Temperature Dependence of the Molar Magnetic Susceptibility χ_M and Magnetic Moment μ_{eff} for [Co(phen)$_3$]Cl$_2$ in D$_2$O[a]

T/K	$\Delta\nu^{HDO}$/Hz	χ_M/10^{-7} m^3 mol^{-1}	μ_{eff}^b/μ_B	μ_{eff}^c/μ_B
286	320.91	1.1737	4.622	4.784
300	307.68	1.1256	4.636	4.791
314	294.44	1.0795	4.644	4.793
329	280.98	1.0342	4.653	4.795
344	267.11	0.9879	4.651	4.786
358	255.69	0.9516	4.656	4.787

[a] D$_2$O containing 2% *tert*-butyl alcohol, 0.019 28 mol L^{-1} [Co(phen)$_3$]Cl$_2$, 0.10 mol L^{-1} HDO, and 0.0026 mol L^{-1} phen. [b] Equation 2. [c] Equation 3, with Θ = 20.$_4$ K.

Results

Magnetic Susceptibility of Co(phen)$_3^{2+}$ Solutions. For a superconducting magnet, as in the Bruker AM-400 spectrometer, the mass susceptibility χ in SI units of a paramagnetic solute can be obtained[17] from the frequency shift $\Delta\nu$ (in hertz) of solvent proton resonances relative to the paramagnetics-free solvent by the relation

$$\chi = \chi_0 + (3\Delta\nu/m\nu_0) \tag{1}$$

where χ_0 is the mass susceptibility of the solvent in m^3 kg^{-1}, ν_0 is the proton resonance frequency (here, 400 MHz), and m is the mass of paramagnetic solute in kg m^{-3} of solution. The molar susceptibility χ_M of the paramagnetic solute of molar mass M is then given in m^3 mol^{-1} by $M\chi/1000$. Values of χ_0 for our D$_2$O solutions at the selected temperatures T were obtained by interpolation from the measurements of Ergin and Kostrova.[20] For [Co(phen)$_3$](ClO$_4$)$_2$ in D$_2$O containing 2% *tert*-butyl alcohol and excess phen, shifts of the resonance of residual HDO gave the χ_M values listed in Table I, after correction of the concentration for thermal expansion. The magnetic moment μ_{eff} of the complex cation in Bohr magnetons from the Curie equation

$$\mu_{eff} = 797.74(\chi_M T)^{0.5} \tag{2}$$

is also given for various temperatures in Table I and shows only a marginal tendency to rise with temperature. This slight temperature dependence disappears (Table I) if the data are fitted to the Curie–Weiss equation

$$\mu_{eff} = 797.74[\chi_M(T + \Theta)]^{0.5} \tag{3}$$

giving Θ = +20.4 ± 3.7 K and an average μ_{eff} of 4.789 ± 0.025 μ_B, which may be compared with Figgis and Nyholm's μ_{eff} = 4.70 μ_B for the solid salt.[21] Thus, there is no evidence for a spin equilibrium in aqueous solutions of Co(phen)$_3^{2+}$; i.e., this ion exists exclusively in the high-spin (quartet) state within the limits of detectability.

Parallel determinations of the methyl proton shifts of the dissolved *tert*-butyl alcohol (the traditional NMR measure of χ for paramagnetic solutes) showed a slight decline in μ_{eff} as calculated using eq 2 from 4.76 μ_B at 286 K to 4.66 μ_B at 358 K. These data are generally consistent with those obtained from the HDO shifts but are less reliable in the present context in view of the hydrophobic ion–dipole interactions with *tert*-butyl alcohol that are characteristic of transition-metal phen complexes.[22]

Spontaneous Racemization of Co(phen)$_3^{3+}$. The first-order decay in the optical activity of pure aqueous Co(phen)$_3^{3+}$ is given by

$$kt = \ln[A_{tot}/(2A_t - A_{tot})] \tag{4}$$

where A_t and A_{tot} are the concentrations of Λ-Co(phen)$_3^{3+}$ at

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time t and total Co(phen)₃³⁺, respectively. The ORD signal ϕ_t is

$$\phi_t = \Omega(2A_t - A_{tot}) \qquad (5)$$

where the proportionality constant $\Omega = \phi_0/A_{tot}$; thus,

$$A_t = (\phi_t/2\Omega) + (A_{tot}/2) \qquad (6)$$

At 25 °C, eq 4 is followed for about the first 10 days with $k = (2.1 \pm 0.2) \times 10^{-7}$ s⁻¹ (corresponding to a half-life of 38 days), but over longer periods the rate of racemization becomes faster than expected (see supplementary material, Figure S1). This is probably due to a very slow reduction of Co(phen)₃³⁺ to Co-(phen)₃²⁺, traces of which would then catalyze the racemization as explained below. Yamamoto and Yamamoto[18] also remarked on the deviation of the racemization rate of Co(phen)₃³⁺ from first order in the longer term and found that halide ions (especially iodide) and light accelerated the process; in our experiments, light and halide ions were excluded. The essential points to note are that the rate of spontaneous racemization of Co(phen)₃³⁺ is negligible on the time scale of the electron-transfer-induced racemization described below and that the solutions could be kept for 1 week or more without significant loss of optical activity or buildup of Co^II.

Co(phen)₃³⁺/²⁺ Self-Exchange Kinetics. In all cases, the decay in the Co(phen)₃³⁺ circular dichroism signal X_t at time t followed the simple exponential equation[12]

$$X_t = X_0 + (X_\infty - X_0) \exp(-k_{obsd}t) \qquad (7)$$

Weighted average values of the rate constant k_{obsd} for a 160-MPa range of the pressure P (at 40-MPa intervals, three or four measurements at each pressure) are listed in the supplementary material. As noted by Warren et al.,[12] k_{obsd} values depended in complicated ways upon the concentration of the anion, being larger in nitrate media than in chloride, and upon the concentration of Co(phen)₃²⁺. We found that the dependence of [Co(phen)₃²⁺] was linear, within the experimental uncertainty but that, at constant [Co^III], there was a small but significant intercept k_1 at zero [Co(phen)₃²⁺] except at the highest total electrolyte concentrations (0.1 mol L⁻¹)[23] (Table II).

$$k_{obsd} = k_1 + k_2[\text{Co(phen)}_3^{2+}] \qquad (8)$$

This phenomenon is strongly reminiscent of the behavior of the analogous couple Co(en)₃³⁺/²⁺, in which the observed electron-exchange *rate* comprised a component first-order in each of [Co^II] and [Co^III] and a minor [Co^II]- and [Co^III]-independent contribution that has been shown to arise from a heterogeneous (surface dependent) pathway.[10,24,25] Because the present rate measurements were made using a rapid-mixing system of fixed geometry, it was not possible to verify that $k_1/[\text{Co}^{III}]$ represented the rate of a surface-dependent pathway, but its disappearance at high supporting electrolyte concentrations and lack of correlation with the nature of the anion would be consistent with the saturation of the exposed surfaces of the stopped-flow apparatus with redox-inactive cations at the expense of active ones. We have therefore treated the relatively small and poorly reproducible k_1 simply as a correction to be applied when calculating k_2.

At a given pressure P, k_2 can be represented within the experimental uncertainty as a linear function of the anion concentration, with different slopes for chloride and for nitrate. This, however, should not be interpreted as evidence for competing

Table II. Rate Constants for the Co(phen)₃³⁺/²⁺ Self-Exchange Reaction According to Eq 8[a]

I/mol L⁻¹	P/MPa	$k_1/10^{-4}$ s⁻¹	k_2/L mol⁻¹ s⁻¹
		X⁻ = Cl⁻	
0.1072	1.1	1.0 ± 1.0	6.72 ± 0.47
	40.8	1.8 ± 0.7	8.15 ± 0.28
	80.6	1.7 ± 1.3	10.70 ± 0.51
	120.4	−0.7 ± 1.0	14.90 ± 0.71
	160.3	−3.7 ± 1.3	20.40 ± 0.69
0.0565	1.3	3.0 ± 0.8	3.71 ± 0.23
	40.7	5.9 ± 0.9	4.43 ± 0.22
	80.4	6.0 ± 1.1	5.81 ± 0.39
	120.5	4.2 ± 1.1	8.20 ± 0.30
	160.5	2.2 ± 1.8	11.20 ± 0.54
0.0154	1.3	5.1 ± 0.5	1.45 ± 0.08
	40.6	5.5 ± 1.6	1.91 ± 0.22
	80.3	6.8 ± 0.5	2.43 ± 0.08
	120.7	5.4 ± 0.5	3.60 ± 0.11
	160.3	4.3 ± 0.4	4.82 ± 0.10
		X⁻ = NO₃⁻	
0.1065	1.5	0.0 ± 0.3	10.66 ± 0.27
	40.5	1.6 ± 0.6	13.40 ± 0.53
	80.8	−0.2 ± 0.6	18.83 ± 0.35
	120.5	1.9 ± 0.8	23.14 ± 0.45
	160.4	4.3 ± 1.5	29.3 ± 1.1
0.0567	1.3	2.0 ± 0.5	6.11 ± 0.32
	40.7	4.1 ± 0.7	7.46 ± 0.28
	80.6	1.7 ± 0.3	10.87 ± 0.14
	120.6	0.4 ± 0.7	14.73 ± 0.29
	160.4	5.4 ± 1.4	17.01 ± 0.50
0.0156	1.5	4.5 ± 1.3	1.64 ± 0.26
	40.9	2.7 ± 1.7	2.63 ± 0.29
	80.7	5.8 ± 1.0	3.15 ± 0.15
	120.3	6.0 ± 0.6	4.12 ± 0.10
	160.3	5.7 ± 1.3	5.70 ± 0.25

[a] 25 °C, [Co^III] = 1.6–2.1 mmol L⁻¹, [Co^II] = 0.10–0.89 mmol L⁻¹ (chloride media) or 0.084–0.76 mol L⁻¹ (nitrate media).

anion-dependent and -independent pathways because electrolyte effects of the Debye–Hückel type must also be taken into account, and it was not experimentally possible to eliminate these by varying the anion concentrations and keeping the ionic strength constant. In fact, the Brønsted–Bjerrum–Christiansen adaptation[26] of the Debye–Hückel equation[27,28]

$$\ln(k_2^I/k_2^{I=0}) = 2Cz_1z_2I^{1/2}/(1 + B\dot{a}I^{1/2}) \qquad (9)$$

where z_1 and z_2 are the charge numbers of the reactant ions, B and C are the Debye–Hückel parameters, and $\dot{a}$ is the anion–cation closest approach distance, leads to a roughly linear dependence of k_2 on the ionic strength I in the range of I covered by our experiments, the difference between various anions being accounted for by the magnitude of $\dot{a}$ (treated here as a semiempirical parameter).

As a comprehensive test of the validity of eq 9, the k_2 values of Table II (chloride and nitrate separately) were fitted by nonlinear-least-squares regression to the equation

$$\ln(k_2^{P,I}/k_2^{P=0,I=0}) = [2Cz_1z_2I^{1/2}/(1 + B\dot{a}I^{1/2})] -$$
$$P\Delta V_0^*/RT \qquad (10)$$

in which ΔV_0^*, the volume of activation for the electron-transfer process at zero ionic strength, and the ion size parameter $\dot{a}$ are assumed to be independent of pressure. For this computation, values of B and C were calculated for each pressure, as described elsewhere.[4] The results are given in Table III. The agreement in $k_2^{P=0,I=0}$ values for the chloride and nitrate systems (0.35 ±

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(25) A reviewer has suggested that the anomalous intercepts might have originated in the incomplete conversion of Co(phen)₂(OH₂)₂²⁺ to Co-(phen)₃²⁺, for which $K_3^{298} = 2.4 \times 10^6$ L mol⁻¹ (Irving, H.; Miller, D. H. *J. Chem. Soc.* **1962**, 5222). On this basis, however, over 99.5% of the Co^II was present as Co(phen)₃²⁺ in the worst case (8.4 × 10⁻⁵ mol L⁻¹ excess phen).

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Table III. Ion Size Parameters and Rate Constants and Volumes of Activation at Infinite Dilution for the $Co(phen)_3{}^{3+/2+}$ Self-Exchange Reaction According to Eq 10[a]

anion	$\mathring{a}/pm$	$k_2{}^{P=0,I=0}/L\ mol^{-1}\ s^{-1}$	$\Delta V_0{}^{*}/cm^3\ mol^{-1}$
Cl⁻	520 ± 20	0.327 ± 0.011	−20.4 ± 0.5
NO₃⁻	355 ± 30	0.396 ± 0.026	−19.7 ± 1.1

[a] 25 °C.

Table IV. Volumes of Activation at Each Ionic Strength[a]

anion	$I/mol\ L^{-1}$	$\Delta V_{obsd}{}^{*\ b}/$ $cm^3\ mol^{-1}$	$\Delta V_{DH}{}^{*\ b}/$ $cm^3\ mol^{-1}$	$\Delta V_0{}^{*}(calcd)/$ $cm^3\ mol^{-1}$
Cl⁻	0.015	−18.9 ± 0.8	1.5	−20.4
	0.056	−17.6 ± 1.1	2.4	−20.0
	0.107	−17.6 ± 0.7	3.0	−20.6
NO₃⁻	0.016	−18.3 ± 1.5	1.6	−19.9
	0.057	−17.0 ± 1.4	2.8	−19.8
	0.107	−16.0 ± 0.7	3.6	−19.6

[a] 25 °C. [b] At the mean pressure 80 MPa.

0.04 L mol⁻¹ s⁻¹) is satisfactory in view of the large change in k_2 on going to infinite dilution, while that in $\Delta V_0{}^{*}$ is excellent (−20.1 ± 0.4 cm³ mol⁻¹). A satisfactory fit of *all* the data of Table II (chloride and nitrate simultaneously) to eq 10 may be obtained with these values of $k_2{}^{P=0,I=0}$ and $\Delta V_0{}^{*}$ fixed, giving $\mathring{a}$ = 560 pm for Cl⁻ and 300 nm for NO₃⁻ (supplementary material, Figure S2). The assumption that ΔV^{*} is independent of pressure is questionable on theoretical grounds;[4] however, at each ionic strength, the ln(k_2) vs. P plot is linear within the experimental uncertainty for both chloride and nitrate systems, and the corresponding values of ΔV^{*} (Table IV) can be adjusted theoretically[4] for the rather small Debye–Hückel contribution $\Delta V_{DH}{}^{*}$ to give $\Delta V_0{}^{*}$ values (=$\Delta V_{obsd}{}^{*}$ − $\Delta V_{DH}{}^{*}$) in excellent agreement with those obtained directly from eq 10 (average: −20.1 ± 0.4 cm³ mol⁻¹).

Discussion

Anion Effects. Significant results to emerge from the analysis of the effects of added electrolytes on k_2 include the following.

(a) ΔV^{*} for the $Co(phen)_3{}^{3+/2+}$ self-exchange reaction in solution is rather insensitive to ionic strength in the practical range (Table IV), even though k_2 is markedly affected by the nature and concentration of the anion (Table II). In a future publication, we will show that the same is true for an unrelated cross-reaction ($Fe(H_2O)_6{}^{3+}$ + $Co([9]aneS_3)_2{}^{2+}$ in water) over a wide range of I and so is probably valid for all outer-sphere redox processes in the absence of extensive ion association.[4,29]

(b) The contribution $\Delta V_{DH}{}^{*}$ of ionic strength effects to ΔV^{*} can be calculated quite accurately from existing theory[4,30] and is small (Table IV). This, together with observation a, means that experimental ΔV^{*} data from different reactions can be compared or combined directly if the difference in ionic strength is not large; otherwise, a simple theoretical correction $\Delta V_{DH}{}^{*}$ will suffice.

(c) It appears that specific anion effects on cation–cation electron-transfer kinetics can be accommodated through use of the extended Brønsted–Bjerrum–Christiansen equation (10) with $\mathring{a}$ as an adjustable parameter, at least up to $I \approx 0.2$ mol L⁻¹. The approach of Rampi Scandola et al.,[31] in which $B\mathring{a}$ is tacitly set equal to unity, fails to explain the different ionic strength effects associated with various anions, as this difference residues in $\mathring{a}$ (at least at moderate ionic strengths). At higher electrolyte concentrations, addition of a term linear in I to the right-hand side of eqs 9 and 10 may be necessary,[32] and factors such as ion

pairing[4,27–29] and the availability of water to hydrate the ions[27,28,33] come into play.

The value of $\mathring{a}$ should not be interpreted quantitatively in terms of actual "ion sizes",[28,32] particularly since the derivation of eqs 9 and 10 involves the questionable assumption that the anion–cation contact distance is the same for each reactant and for the transition-state assemblage too. Nevertheless, cations such as phen complexes that have open structures allowing deep interligand penetration of the counterions can be expected to have relatively small $\mathring{a}$ values and so show marked anion effects in their redox kinetics, despite the large overall size of the complex ion. Similarly, the thin, flat nitrate ion can be expected to penetrate more deeply than chloride, and so on. The relative magnitudes of anion kinetic effects noted by Warren et al.[12] can be rationalized qualitatively in this way, bearing in mind that *hydrated* ion radii are more relevant than the crystallographic values.[28]

Endicott and co-workers[34–36] noted the marked effect of anions X⁻ on the rates of cross-reactions involving $Co(phen)_3{}^{3+}$ and attributed this to involvement of ion pairs {$Co(phen)_3{}^{3+}$,X⁻}, which could facilitate otherwise markedly nonadiabatic electron transfer reactions through provision of a superexchange-like mechanism. While ion pairing undoubtedly occurs in $Co(phen)_3{}^{3+}$ solutions, its inclusion in eq 10 would introduce too many additional parameters. In any event, the effect of increased pressure is invariably to break up anion–cation pairs, primarily through increasing the dielectric constant of the medium, which, in this model, would lead to reaction rates slower (ΔV^{*} more positive) than predicted,[4] whereas our problem is to explain precisely the opposite effect.

Magnetic Properties of $Co(phen)_3{}^{2+}$ in Solution. Table I shows clearly that μ_{eff} for aqueous $Co(phen)_3{}^{2+}$ (4.79 μ_B) is temperature independent over a wide range, and furthermore it is almost identical with that for the solid perchlorate (4.70 μ_B at 300 K).[13] These values are as expected for a high-spin d⁷ ($^4T_{1g}$) Co^{II} ion, and the temperature independence indicates that there can be no significant ($\ll$1%) amount of low-spin (^2E_g) Co^{II} complex present in solutions of $Co(phen)_3{}^{2+}$ over the temperature range 286–358 K.

Volume of Activation for the $Co(phen)_3{}^{3+/2+}$ Exchange. If we take the radii of the reactants to be about 700 pm,[37] the Co–Co separation σ at which electron transfer is most probable to be the sum of these, the contribution of internal reorganization $\Delta V_{IR}{}^{*}$ in the complexes to be 0.6 cm³ mol⁻¹ (a typical value[2]), and $\mathring{a}$ from Table III, the average theoretical values of ΔV^{*} for simple adiabatic electron transfer between $Co(phen)_3{}^{2+}$ and $Co(phen)_3{}^{3+}$ over the 0–160 MPa range can be calculated[4] to be −2.2 ± 0.4 cm³ mol⁻¹ for chloride and −1.7 ± 0.4 cm³ mol⁻¹ for nitrate media at $I = 0.107$ mol L⁻¹ or −5.2 ± 0.9 cm³ mol⁻¹ at infinite dilution. Experience with the similar $Fe(phen)_3{}^{3+/2+}$ system[38] confirms that these values are realistic. Inclusion of a Fuoss correction for the formation of *inactive* anion–$Co(phen)_3{}^{3+}$ pairs[4] would make the first two numbers some 2–3 cm³ mol⁻¹ more negative; conversely, the involvement of *active* ion pairs as suggested by Endicott et al.[34–36] would make ΔV^{*} less negative by a similar margin.

In fact, the experimental ΔV^{*} data for the aqueous $Co(phen)_3{}^{3+/2+}$ couple are some 15 cm³ mol⁻¹ more negative than

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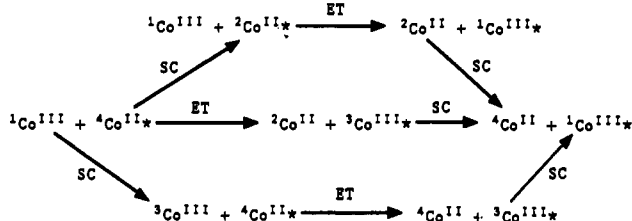(30) Swaddle, T. W. In ref 1, Chapter 5.
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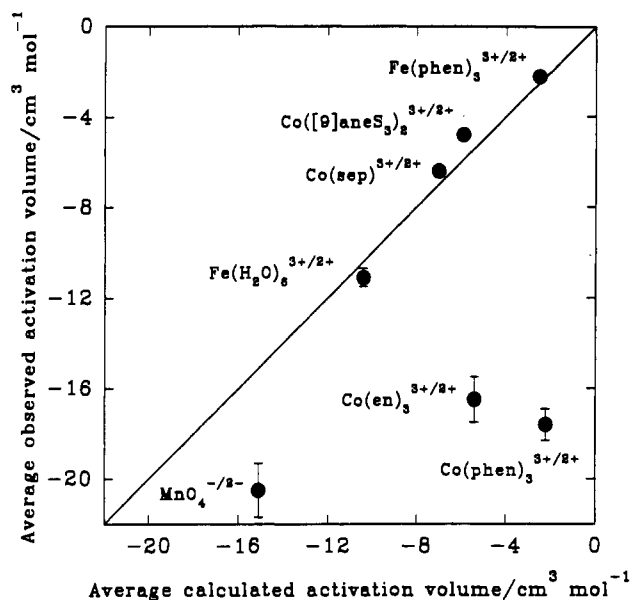
Figure 1. Comparison of observed ΔV^* values for self-exchange in water with theoretical values for adiabatic electron transfer (values averaged over the experimental pressure range). The diagonal line represents exact agreement. Data are from refs 4, 7, 10, 24, and 38 and this work.

the corresponding calculated values (Tables III and IV). Thus, this case is very similar to the Co(en)$_3$$^{3+/2+}$ self-exchange[10] but contrasts sharply with Co(sep)$^{3+/2+}$ and Co([9]aneS$_3$)$_2$$^{3+/2+}$, both of which have ΔV^* very close to the theoretical values for *adiabatic* electron transfer.[9] These anomalies are illustrated in Figure 1. The Co([9]aneS$_3$)$_2$$^{3+/2+}$ exchange involves low-spin Co^{II} as well as Co^{III} and so is expected to be adiabatic; thus, leaving the low-spin/high-spin Co(sep)$^{3+/2+}$ case aside for the moment, the strongly negative ΔV^* for self-exchange in the low-spin/high-spin Co(phen)$_3$$^{3+/2+}$ and Co(en)$_3$$^{3+/2+}$ couples can be attributed either to direct *nonadiabatic* electron transfer or to the involvement of intermediates in excited spin states, as in Scheme I (in which

Scheme I

the preceding superscripts indicate the electronic spin multiplicity, ET indicates *adiabatic* electron transfer, and SC denotes a change of spin). Of the three paths in this scheme, only the top one, involving low-spin Co^{II} and Co^{III} simultaneously, could generate a large negative volume change,[40] since low-spin complexes are generally more compact than their high-spin isomers (because the latter have more antibonding electrons) and, as we have seen, adiabatic ET can account for nothing more negative than about –5 cm^3 mol^{-1} in the Co(phen)$_3$$^{3+/2+}$ case. Furthermore, whereas several examples of Co^{II} complexes with low-spin ground states are known, high-spin Co^{III} ground states occur only in weak-field (O or F) environments.

A mechanism involving a fast[41] but unfavorable preequilibrium forming low-spin Co^{II}, followed by adiabatic electron transfer to low-spin Co^{III}, can therefore accommodate the ΔV^* data for both Co(phen)$_3$$^{3+/2+}$ and Co(en)$_3$$^{3+/2+}$ if the molar volume changes associated with the spin pairing are about –10 to –15 cm^3 mol^{-1}, which is feasible[40] (but not measurable, since no detectable concentrations of the low-spin Co^{II} complexes exist in solution in either case). It is less clear, however, how this could explain the fact that the Co(phen)$_3$$^{3+/2+}$ and Co(sep)$^{3+/2+}$ exchanges proceed at almost exactly the same rate but are 10^5-fold faster than Co(en)$_3$$^{3+/2+}$,[42] since the equilibrium constant for the spin preequilibrium should be much more favorable (i.e., the adiabatic low-spin/low-spin ET step should be much more accessible) for the phen complex than for the other two on the grounds of the greater ligand field strength of phen. The larger effective radius of the Co(phen)$_3$$^{2+}$ complexes ($\approx$700 pm) relative to the other two ($\approx$400 pm) acts through the solvent reorganization term in Marcus' theory to favor a faster Co(phen)$_3$$^{3+/2+}$ exchange by a factor of about 4 × 10^3. The Co–N bond length increase Δd on going from Co^{III} to Co^{II} is 19 pm for both Co(phen)$_3$$^{3+/2+}$ [43,44] and Co(sep)$^{3+/2+}$ [42] and 21 pm for Co(en)$_3$$^{3+/2+}$,[42] so the effect of these changes on the rate (a factor of perhaps 10 slower for each pm in Δd, acting through the internal reorganizational contribution to the Marcus free energy of activation) does not account fully for the observations. Taken together, these factors suggest a rate sequence Co(phen)$_3$$^{3+/2+}$ $\gg$ Co(sep)$^{3+/2+}$ > Co(en)$_3$$^{3+/2+}$, which is not the case.

Alternatively, electron transfer may be considered to occur nonadiabatically between the reactants in their ground states. The application of this model[45,46] to pressure effects in the kinetics of outer-sphere electron-transfer processes has been discussed elsewhere.[4] The square of the electronic coupling matrix element H_{AB}^2 is a measure of the electronic transmission coefficient κ_{el} and can be approximated by $(H_{AB}^0)^2 \exp[-2\alpha(\sigma - \sigma_a)]$ where σ_a is the separation beyond which electron transfer can no longer be regarded as adiabatic (i.e., where κ_{el} ceases to be effectively 1.0). Since H_{AB}^0, σ_a, and the distance scaling factor α can be taken to be independent of pressure, only α need be determined to characterize the contribution of nonadiabaticity to the overall pressure effect, resulting in a contribution of $-2RT\alpha\sigma\beta/3$ (where β is the isothermal compressibility of the medium) to ΔV^*. The data for the Co(phen)$_3$$^{3+/2+}$ exchange are well fitted by $\alpha = 18 \pm 1$ nm^{-1}, which is essentially the same value as was obtained from the pressure dependence of the Co(en)$_3$$^{3+/2+}$ kinetics[10] and is well within the range (6–25 nm^{-1}) typically found for various self-exchange reactions by other methods.[45]

Nonadiabaticity in Co$^{III/II}$ electron transfers has been considered in detail by Endicott et al.,[34–36] Newton,[47] and Larsson et al.[48] Endicott's experimentally-based work[34–36] indicates that nonadiabaticity is widespread in Co$^{III/II}$ chemistry, particarly in cross-reactions and in cases where large Δd effects combine with poor donor–acceptor overlap, but may be mitigated by mixing of low-energy charge-transfer states with the ground states. Newton[47] and Larsson et al.[48] consider the Co(NH$_3$)$_6$$^{3+/2+}$ self-exchange theoretically. The semiempirical INDO calculations of Larsson et al.[48] indicate that the ^2E_g state of Co(NH$_3$)$_6$$^{2+}$ is lower in energy than is generally supposed and could provide a thermally-accessible, essentially adiabatic pathway for electron transfer. In contrast, Newton[47] concluded that a thermally-excited ^2E_g pathway is unlikely to compete with ground-state

(40) Binstead, R. A.; Beattie, J. K. *Inorg. Chem.* **1986**, *25*, 1481. These authors found that an apparent contraction of –10.1 ± 0.4 cm^3 mol^{-1} accompanies the quartet-to-doublet spin change in aqueous Co(terpy)$_2$$^{2+}$, and this value is probably typical of such processes. However, H. Takagi and R. D. Shalders, in our laboratories, have found that some secondary process—probably a dechelation equilibrium involving the Co^{II} complex—complicates the spin isomerization in this case.

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processes at room temperature but that spin–orbit coupling could bring the $Co(NH_3)_6{}^{3+/2+}$ self-exchange rate reasonably close to the predictions of Marcus' theory. Unfortunately, the $Co(NH_3)_6{}^{3+/2+}$ self-exchange reaction rate is notoriously difficult to measure accurately,[49,50] and no high-pressure studies can be contemplated.

Interestingly, Endicott et al.[34,35,51] conclude that reductions by $Co(sep)^{2+}$ are relatively adiabatic, by $Co^{III/II}$ standards, with adiabaticity improving as the standard free energy change (zero, for self-exchange) diminishes, and this is in accordance with our observation that the effect of pressure on the $Co(sep)^{3+/2+}$ self-exchange reaction rate is accurately predicted by the adiabatic theory despite the large change in spin multiplicity.[4,7] If the $Co(sep)^{3+/2+}$ exchange is indeed adiabatic but $Co(en)_3{}^{3+/2+}$ and $Co(phen)_3{}^{3+/2+}$ are nonadiabatic to the extent of $\kappa_{el} \approx 10^{-4}$ (as was calculated by Newton[47] for $Co(NH_3)_6{}^{3+/2+})$, then the rate sequence $Co(phen)_3{}^{3+/2+} \approx Co(sep)^{3+/2+} \gg Co(en)_3{}^{3+/2+}$ can be explained. The reasons for the $Co(sep)^{3+/2+}$ anomaly are unclear (Hendry and Lüdi[42] point out that the detailed analysis by Endicott et al.[51] loses some of its force in that it takes $\Delta d = 16$ rather than the presently accepted 19 pm) but may originate in the *rigidity* of the sepulchrate cage rather than Co–N bond length effects or

static distortions, since Δd is not greatly different from that for other $Co^{III/II}$ complexes[41–43] and the CoN_6 skeleton is only slightly twisted (3.3°) away from O_h toward D_{3h} local symmetry.[52] In terms of Scheme I, twisting distortions of ligand systems may accompany the formation of spin isomers in nonrigid complexes and cause Franck–Condon retardation of the exchange reaction. In the alternative (nonadiabatic) model, adiabaticity might be more substantially improved by the enhanced mixing of excited states with the reactant ground states through spin–orbit coupling when the tendency of the excited states to undergo twisting distortion is suppressed by the rigidity of the ligand system. Such speculation notwithstanding, a key result of this variable-pressure study is that the $Co(sep)^{3+/2+}$ exchange, through its "normal" behavior in terms of adiabatic Marcus–Hush theory, acts "abnormally" in the context of other low-spin/high-spin $Co^{III/II}$ couples.

Supplementary Material Available: Tables S1 and S2 (rate constants for the $Co(phen)_3{}^{3+/2+}$ self-exchange reaction in chloride and nitrate media, respectively), Figure S1 (spontaneous racemization rate of [Δ-Co-(phen)_3](ClO_4)_3, and Figure S2 (goodness of fit to eq 10) (4 pages). Ordering information is given on any current masthead page.

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