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Pressure Dependence of the Rate of Electron Transfer between Tris(ethylenediamine)cobalt(II) and -(III) in Water

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The thermal self-exchange reaction of $Co(en)_3^{2+}$ and $Co(en)_3^{3+}$ in aqueous solution at 65 °C and ionic strength 0.5 mol L^{-1} proceeds by a homogeneous and a minor heterogeneous path, both of which are accelerated by applied pressure (0.1–207 MPa). For the homogeneous path, the logarithmic plot of the bimolecular rate constant k against pressure P is best described as nonlinear, as theory requires, with a volume of activation ΔV^* of -20 cm^3 mol^{-1} at 0.1 MPa and -13 cm^3 mol^{-1} at 200 MPa. The experimental data can be accounted for through a nonadiabatic version of the Stranks–Hush–Marcus theory with nonadiabaticity distance scaling factor $\alpha \simeq 19$ nm^{-1} (16 nm^{-1} if Fuoss anion–cation pairing is invoked) or, less satisfactorily, through an adiabatic mechanism in which electron transfer to ground-state $Co(en)_3^{3+}$ occurs from the ^2E excited state of $Co(en)_3^{2+}$ in equilibrium with its ^4T ground state. The results are not consistent with direct adiabatic electron transfer between the Co^{II} and Co^{III} ground states.

Introduction

The thermal self-exchange reaction of $Co(en)_3^{2+}$ and $Co(en)_3^{3+}$ (en = 1,2-diaminoethane, "ethylenediamine") in aqueous solution is an important example of its genre, and was among the first such reactions to be studied by kineticists.[5,6] Reliable rate constants k are much more readily obtainable for this reaction than for the otherwise closely related $Co(NH_3)_6^{3+/2+}$ exchange,[7,8] the rate of which was originally thought to be at least 10^6-fold slower than the $Co(en)_3^{3+/2+}$ self-exchange[7] but is now recognized to be less than 100-fold slower.[9] Thus, from the experimental standpoint, the recently renewed controversy[10] over the possibility that the large difference in spin multiplicity between the reactants may result in nonadiabaticity in the $Co(NH_3)_6^{3+/2+}$ reaction may be better addressed by consideration of the analogous $Co(en)_3^{3+/2+}$ self-exchange. In particular, the measured effect of pressure P on the $Co(en)_3^{3+/2+}$ exchange rate, described in this article, can, in principle, provide insights into the question of nonadiabaticity.[11]

A brief summary of the results of this study in an early review article[12] included an apparently successful attempt (Stranks–Hush–Marcus or "SHM" theory) to account for the observed zero-pressure volume of activation ΔV_0^* and mean compressibility coefficient of activation $\Delta\beta^*$

$$\ln k = \ln k_0 - (\Delta V_0^*/RT)P + (\Delta\beta^*/2RT)P^2 \qquad (1)$$

for the $Co(en)_3^{3+/2+}$ and other self-exchange reactions in terms of theoretical contributions ΔV_{IR}^* from reorganization of the first coordination spheres of the reactants, ΔV_{SR}^* from solvent reorganization, ΔV_{COUL}^* from the Coulombic work of bringing the reactant ions together, and ΔV_{DH}^* arising from ionic strength (Debye–Hückel) effects.

$$\Delta V_0^* = \Delta V_{IR}^* + \Delta V_{SR}^* + \Delta V_{COUL}^* + \Delta V_{DH}^* \qquad (2)$$

Wherland,[13] however, has pointed out that, because of an error in the sign of ΔV_{DH}^*, the apparent agreement between SHM theory and experiment was fortuitous and that, of the systems considered in ref 12, the $Co(en)_3^{3+/2+}$ case was the most seriously aberrant. It is therefore timely to report the experimental data for the $Co(en)_3^{3+/2+}$ exchange in full and to reconsider eq 2 in the light of more recent concepts.[11,14]

Experimental Section

Materials. Tris(ethylenediamine)cobalt(III) perchlorate was prepared by a standard method[15] and gave good elemental analyses. *Warning! Perchlorate salts of ethylenediaminecobalt complexes are explosive.*[16] Tris(ethylenediamine)cobalt(II) perchlorate was prepared in situ at the beginning of each kinetic run by mixing solutions containing respectively $Co(ClO_4)_2$ and a sufficient (≥16-fold) excess of ethylenediamine to ensure essentially complete complexation. Doubly distilled deionized water was used throughout. "High-purity oxygen-free nitrogen" was scrubbed in a $CrCl_2$ column immediately before it entered the reaction vessel described below. Cobalt-60 was obtained as the metal (Australian Atomic Energy Commission) and was dissolved in nitric acid; trace amounts were used as a label in the kinetic runs. All other materials were AR grade or were purified before use. The ionic strength I was maintained with $NaClO_4$ (G. F. Smith).

Kinetic Measurements. The $Co(en)_3^{3+}$/en and Co^{2+} solutions were initially kept apart in the two compartments of the all-glass vessel shown in Figure 1 and were thoroughly deoxygenated by purging with nitrogen. When the nitrogen flow was reversed, the two solutions were mixed, thus initiating the $Co(en)_3^{3+/2+}$ exchange reaction. Kinetic runs at atmospheric pressure were carried out with the reaction mixture still in this vessel immersed in a thermostat bath at 65.0 ± 0.1 °C; samples (2 mL) were withdrawn at selected intervals and quenched by mixing them with 3 mL of HCl (6 mol L^{-1}), thus converting the $Co(en)_3^{2+}$ to $Co(H_2O)_6^{2+}$, which did not undergo measurable ^{60}Co exchange with $Co(en)_3^{3+}$. The quenched sample was treated with NH_4NCS solution, and the cobalt(II) was extracted into a solution of pyridine in chloroform and assayed radiochemically with a scintillation counter.

For runs at elevated pressures, the solutions were again prepared in the vessel shown in Figure 1 but were then drawn into a Perspex (poly(methyl methacrylate)) syringe contained within a pressure assembly, described previously,[17] from which samples were withdrawn periodically for radiochemical assay as above. Thus, during the kinetic runs, the solutions were in contact only with inert surfaces—Perspex, Teflon, rubber O-rings, and the Pt–Ir sampling capillary.

Initially, reaction mixtures were analyzed spectrophotometrically for cobalt(II) (as $Co(NCS)_4^{2-}$ in acetone) at the beginning and end of each kinetic run to determine whether any oxidation had occurred; oxidative losses were never more than 1%.

Results

The $Co(en)_3^{3+/2+}$ electron exchange rates R were determined graphically from the McKay equation[18]

$$R = -[ab/t(a + b)] \ln (1 - F) \qquad (3)$$

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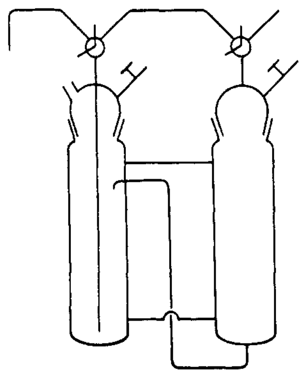

Figure 1. All-glass reaction vessel (schematic).

Table I. Rate Data for the $Co(en)_3^{3+/2+}$ Exchange Reaction at Pressures *P*, 65.0 °C, and Ionic Strength 0.5 mol L^{-1} [a]

P/ MPa	$[Co(en)_3^{2+}]$/ mmol L^{-1}	$[Co(en)_3^{3+}]$/ mmol L^{-1}	10^7R^b/ mol L^{-1} s^{-1}	10^7S^c/ mol L^{-1} s^{-1}	10^4k^c/L mol^{-1} s^{-1}
0.1	9.3	10.0	1.61	0.91 ± 0.10	7.9 ± 0.4
	9.3	20.0	2.44		
	18.6	16.9	3.33		
	18.6	20.0	3.78		
	18.6	20.0	3.94		
51.7	9.3	10.0	3.14	2.07 ± 0.42	11.3 ± 1.7
	9.3	20.0	3.94		
	18.6	15.0	5.61		
	18.6	20.0	6.08		
103.4	9.3	10.0	3.86	2.68 ± 0.40	14.9 ± 1.6
	9.3	20.0	5.83		
	18.6	15.0	6.67		
	18.6	20.0	8.19		
155.2	9.3	10.0	5.22	3.51 ± 0.27	20.0 ± 1.1
	9.3	20.0	7.50		
	18.6	15.0	9.03		
	18.6	20.0	10.92		
206.8	9.3	10.0	6.19	3.92 ± 0.16	24.7 ± 0.6
	9.3	20.0	8.44		
	18.6	15.0	11.03		
	18.6	20.0	13.06		
	18.6	20.0	13.06		

[a] Symbols as in eq 4. [b] Uncertainty ±5%. [c] Uncertainties are standard deviations.

where *a* and *b* are the concentrations[19] of the two exchanging species and *F* is the fraction of exchange at time *t*. The McKay plots were accurately linear, with a very small intercept (≤2%; cf. 20% reported by Lewis et al.[5]). The reaction rate was first order with respect to $Co(en)_3^{3+}$ and $Co(en)_3^{2+}$ individually and was independent of the concentrations of OH^- and free ethylenediamine. These results are summarized in Table I.

Plots of *R* vs $[Co(en)_3^{2+}][Co(en)_3^{3+}]$, though linear, showed an intercept *S* (see Table I)

$$R = k[Co(en)_3^{2+}][Co(en)_3^{3+}] + S \qquad (4)$$

which, as Hasany[20] has demonstrated, was due to a heterogeneous contribution to the overall exchange rate (an alternative interpretation, that *S* represents oxidative loss of Co^{II}, is ruled out by the observation noted above that such losses never amounted to more than 1%). Hasany[20] has shown that this contribution would be surface-dependent but independent of the reactant concentrations under our reaction conditions (i.e., surface coverage was complete; less than 1 μmol L^{-1} of a reactant would have been taken up in forming an adsorbed monolayer). The rate component *S* was not observed by Dwyer and Sargeson[6] because their reactant concentration products were an order of magnitude higher than ours, so that *S* would only have been 2–5% of the total exchange rate. If the ionic strength dependence[6] of *k* at 65 °C is proportional to that at 98 °C, the data of Dwyer and Sargeson[6] ($\Delta H^* = 57.6$ kJ mol^{-1} and $\Delta S^* = -130.1$ J K^{-1} mol^{-1} at $I = 0.98$ mol L^{-1}) give $k = 9.0 \times 10^{-4}$ L mol^{-1} s^{-1} at 65 °C, 0.1 MPa, and $I = 0.50$ mol L^{-1}, in good agreement with the present results. Table I indicates that both the homogeneous and heterogeneous reactions are accelerated by increased pressure; only the homogeneous component is considered further in this report.

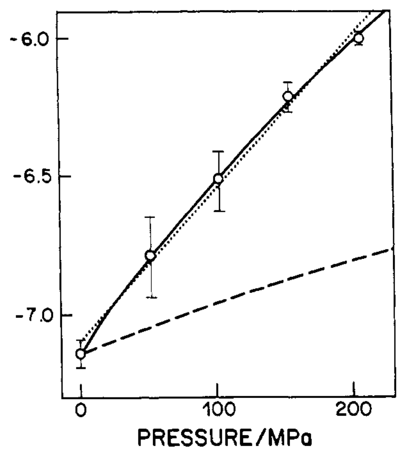

Figure 2. Experimental and theoretical pressure dependences of the rate constant for the $Co(en)_3^{3+/2+}$ self-exchange reaction in homogeneous aqueous solution at 65 °C, ionic strength 0.5 mol L^{-1}. Ion pairing was neglected. Solid curve: theoretical nonadiabatic electron transfer according to eq 12, 13 and 16–19, with $\alpha = 19$ nm^{-1}; corresponding activation parameters given in Table II. Broken curve: theoretical adiabatic electron transfer between ground states of reactants. Dotted line: empirical linear least-squares fit of the experimental data. Bars indicate standard error limits.

Figure 2 shows that ln *k* values from Table I could be adequately described as a linear function of pressure at the 95% confidence level (1.96 × standard error limits); i.e., $\Delta\beta^*$ may be set to zero and ΔV^* is -15.5 ± 0.8 cm^3 mol^{-1}. Theory predicts,[14,22] however, and the curved trend of the data points in Figure 2 seems to confirm that $\Delta\beta^*$ should be a significant negative quantity, in which case this linear least-squares value of ΔV^* is an average over the 0.1–206 MPa range. A least-squares fit of the data to the quadratic equation (1) gave $k_0 = (7.92 \pm 0.13) \times 10^{-4}$ L mol^{-1} s^{-1}, ΔV_0^* (at 0.1 MPa) $= -19.7 \pm 1.0$ cm^3 mol^{-1}, and $\Delta\beta^* = -(4.1 \pm 1.0) \times 10^{-2}$ cm^3 mol^{-1} MPa^{-1}.

As noted below, $\Delta\beta^*$ can be expected to be significantly pressure-dependent itself, so that this last value is effectively an average over the pressure range 0–207 MPa. A slightly different approach was suggested by Dubrawski[21] who defined a *compressibility of activation* $\Delta\kappa^*$

$$\Delta\kappa^* = -(1/\Delta V^*)(\partial \Delta V^*/\partial P)_T = -(\partial \ln \Delta V^*/\partial P)_T \qquad (5)$$

which can be expected to be somewhat less pressure dependent than $\Delta\beta^*$; a Maclaurin expansion of

$$\Delta V^* = \Delta V_0^* \exp(-P\Delta\kappa^*) \qquad (6)$$

then gives

$$\Delta V^* = \Delta V_0^* - \Delta\kappa^*\Delta V_0^*P + ((\Delta\kappa^*)^2\Delta V_0^*/2!)P^2 - ((\Delta\kappa^*)^3\Delta V_0^*/3!)P^3 + \ldots \qquad (7)$$

which leads after truncation to eq 8, a cubic alternative to eq 1 with the same number of parameters.

$$\ln k = \ln k_0 - (\Delta V_0^*/RT)P + (\Delta\kappa^*\Delta V_0^*/2RT)P_2 - ((\Delta\kappa^*)^2\Delta V_0^*/6RT)P^3 \qquad (8)$$

Least-squares fitting of the data of Table I to eq 8 gave $k_0 = (7.92 \pm 0.13) \times 10^{-4}$ L mol^{-1} s^{-1}, $\Delta V_0^* = -19.5 \pm 1.0$ cm^3 mol^{-1},

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(19) Concentrations are reported as if at 20 °C and 0.1 MPa, i.e., as pressure and temperature independent quantities. Thus, no "corrections" of measured parameters for thermal or compressional volume changes are necessary. See: Hepler, L. G. *Thermochim. Acta* **1981**, *50*, 69; Hamann, S. D.; le Noble, W. J. *J. Chem. Educ.* **1984**, *61*, 658.

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and $\Delta\kappa^* = (1.76 \pm 0.30) \times 10^{-3}$ MPa^{-1} (mean over the range of P), with the same correlation coefficient as with eq 1 ($r^2 = 0.99924$). Hence, the mean $\Delta\beta^* = \Delta\kappa^*\Delta V_0^* = -3.4 \times 10^{-2}$ cm^3 mol^{-1} MPa^{-1}, according to eq 8. Thus, eq 8 offers no major advantage over eq 1 but gives confidence in the empirical assignment of a ΔV_0^* value of about -20 cm^3 mol^{-1}. It will be shown below that analysis of the data of Table I according to a current theory of electron-transfer reactions yields the same value of ΔV_0^*, within the experimental uncertainty.

Discussion

Data Analysis through Calculation of Activation Parameters. As discussed elsewhere,[11,14,22] the earlier theory[12] of pressure effects on outer-sphere electron-transfer rates needs to be modified to take into account (inter alia) compression of the separation σ of the reactants; this appears not only in the expressions for ΔV_{SR}^* and ΔV_{COUL}^* but also in the preexponential part $(4000\pi N\sigma^3/3)$ of the work terms (which contributes an amount $+\beta RT$ to ΔV^*, where β is the isothermal compressibility of the solvent). Calculations previously presented[12] show that ΔV_{IR}^* for the $Co(en)_3^{3+/2+}$ exchange is small ($+0.60$ cm^3 mol^{-1}); the other components of eq 2 can be calculated as follows for a two-sphere, continuous-dielectric, adiabatic model of electron transfer.[22]

$$\Delta V_{SR}^* = (Ne^2/16\pi\epsilon_0)[((2r_1)^{-1} + (2r_2)^{-1} - \sigma^{-1}) \times (\partial(n^{-2} - D^{-1})/\partial P)_T - (n^{-2} - D^{-1})\beta/3\sigma] \quad (9)$$

$$\Delta V_{COUL}^* = (NZ_1Z_2e^2/4\pi\epsilon_0\sigma)[(\partial D^{-1}/\partial P)_T + \beta/3D] \quad (10)$$

$$\Delta V_{DH}^* = [RTZ_1Z_2CI^{1/2}/(1 + BaI^{1/2})^2] \times [(\partial \ln D/\partial P)_T(3 + 2BaI^{1/2}) - \beta] \quad (11)$$

Here, r_1 and r_2 are the radii of $Co(en)_3^{2+}$ and $Co(en)_3^{3+}$ (taken to be 413 and 398 pm) respectively, σ is the Co^{II}–Co^{III} separation when the electron is transferred (this was arbitrarily set to $(r_1 + r_2)$, as the result is not very sensitive to this choice), n is the refractive index of the solvent water (at 593 nm—see below),[23] D is its relative permittivity (dielectric constant),[24] Z_1 and Z_2 are the reactant charge numbers, and a, B, and C are the Debye–Hückel parameters for water (B and C were calculated for 65 °C and appropriate P from values of D and the solvent density ρ;[25] the anion–cation closest approach distance a was estimated to be 686 pm). From these data for 0.1 MPa, one can calculate from eq 9–11 $\Delta V_{SR}^* = -9.23$ cm^3 mol^{-1}, $\Delta V_{COUL}^* = -5.76$ cm^3 mol^{-1}, and $\Delta V_{DH}^* = +6.10$ cm^3 mol^{-1}, from which eq 2 gives $\Delta V_0^* = -7.01$ cm^3 mol^{-1} when $\Delta V_{IR}^* = +0.60$ cm^3 mol^{-1} and βRT (from the preexponential part of the work terms) $= +1.28$ cm^3 mol^{-1} are included. *This is about 13* cm^3 mol^{-1} *too positive*. For the midpoint (103 MPa) of the pressure range, the same calculation predicts $\Delta V_{103}^* = -5.34$ cm^3 mol^{-1}, which is still over 10 cm^3 mol^{-1} more positive than the experimental mean ΔV^* for the whole pressure range (from the linear ln k vs P fit). Even if ΔV_{103}^* is adjusted for the postulated ion pairing of the reactants with perchlorate (see below), a 9 cm^3 mol^{-1} gap remains. These discrepancies are well outside the experimental uncertainty.

Since the updated SHM theory appears to account fairly accurately for pressure effects on the rates of (apparently adiabatic) self-exchange in various solvents between pairs of relatively large cations such as $Fe(phen)_3^{3+/2+}$,[11] $Ru(hfac)_3^{-/0}$,[26] $Cu(dmp)_2^{2+/+}$,[27] and $Fe(H_2O)_6^{3+/2+}$,[12,28] it would appear that the $Co(en)_3^{3+/2+}$ exchange represents a special case. Only for the $MnO_4^{-/2-}$ self-exchange in water has a ΔV_0^* value (-23 cm^3 mol^{-1}) as strongly negative as that for $Co(en)_3^{3+/2+}$ been found, but in the $MnO_4^{-/2-}$ case its origin appears to lie in the failure of the two-sphere continuous-dielectric model for these very small anionic reactants,[14,22,29] and there is no reason to suppose that $Co(en)_3^{3+}$ and $Co(en)_3^{2+}$ are significantly different from the other relatively large cations listed above in this respect.

The most obvious special feature of the $Co(en)_3^{3+/2+}$ exchange reaction is the large change in spin multiplicity on going from the ^4T ground state of $Co(en)_3^{2+}$ to the ^1A ground state of $Co(en)_3^{3+}$ or vice versa. This might be expected to affect the internal reorganization terms, but ΔV_{IR}^* is determined by the change in the *compressibilities* of the reactant ions, which are inherently small and will inevitably give a small *positive* ΔV_{IR}^* regardless of spin states.[12] The most likely explanation for the anomalously negative value of ΔV_0^* for the $Co(en)_3^{3+/2+}$ exchange is (a) that it is nonadiabatic because of the large spin difference between the ground states or (b) that fully adiabatic electron transfer occurs through an excited doublet (^2E) state that is in pressure-sensitive equilibrium with the ground state.[10,30-33] The alternative suggested by Geselowitz,[10] that the direct $Co(NH_3)_6^{3+}(^1A)$–$Co(NH_3)_6^{2+}(^4T)$ exchange is fully spin-allowed and adiabatic, would not account for the -13 cm^3 mol^{-1} shortfall in the calculated ΔV_0^* value for the $Co(en)_3^{3+/2+}$ reaction.

Possibility of Nonadiabaticity. In simple terms, an electron-transfer reaction is customarily designated adiabatic if the electronic interaction between the reactant molecules is sufficiently strong to ensure electron transfer in every encounter in which the internal and solvent reorganizational restrictions are met, i.e., if the electronic transmission coefficient κ_{el} is unity. Departures of κ_{el} from unity can be expected when large multiplicity differences between the initial and final states exist (cf. spin-forbidden transitions in spectroscopy). Equation 12[14,22] accommodates such

$$k = (4000\pi N\sigma^3/3)[L_0^2 \exp(-2\alpha(\sigma - d))] \exp(-\Delta G^*/RT) \quad (12)$$

nonadiabaticity in a simple way, and shows that an important distance (σ) dependence of k is introduced. Here, α is a distance scaling factor, L_0 is the electronic matrix element, d is the farthest approach distance at which coupling is strong enough for the reaction to be adiabatic, and ΔG^* is the theoretical free energy of activation (corresponding to ΔV^* of eq 2).

$$\Delta G^* = \Delta G_{IR}^* + \Delta G_{SR}^* + \Delta G_{COUL}^* + \Delta G_{DH}^* \quad (13)$$

If the $Co(en)_3^{3+/2+}$ electron transfer is nonadiabatic, then an important additional term ΔV_{NA}^* involving α, σ, and the isothermal compressibility of the solvent β must be added to the right-hand side of eq 2.[14,22,29]

$$\Delta V_{NA}^* = -2RT\alpha\beta\sigma/3 \quad (14)$$

In order to account for the discrepancy of 13 cm^3 mol^{-1} between SHM theory and the experimental ΔV_0^*, one can treat α as an adjustable parameter in eq 9–11 and 14. A value of about 19 nm^{-1} for α is required; this falls well within the range of α values (6–25 nm^{-1}) reported for various electron-transfer reactions in the literature.[30] Thus, the anomalously strongly negative experimental ΔV_0^* value for the $Co(en)_3^{3+/2+}$ exchange is highly suggestive of nonadiabaticity. It is conceivable that the $Co(NH_3)_6^{3+/2+}$ exchange in water could still be adiabatic, since these smaller reactants might permit approach distances shorter than d, but its rate constant is *smaller* than k for $Co(en)_3^{3+/2+}$, which suggests that if the latter of these self-exchange reactions is nonadiabatic, then both are.

Possibility of Adiabatic Electron Transfer through an Excited State of $Co(en)_3^{2+}$. If, as has been suggested for the $Co(NH_3)_6^{3+/2+}$ self-exchange,[32] the $Co(en)_3^{3+/2+}$ reaction involves fully adiabatic[33] electron transfer from small concentrations of

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the doublet excited state of $Co(en)_3^{2+}$ in rapid[34] equilibrium with the quartet ground state

$$Co(en)_3^{2+}(^4T) \rightleftharpoons Co(en)_3^{2+}(^2E) \qquad (15)$$

to the ^1A ground state of $Co(en)_3^{3+}$, the thermodynamic volume change ΔV_{SPIN} for reaction 15 must be added to the right-hand side of eq 2. To account for the pressure dependence of the $Co(en)_3^{3+/2+}$ exchange rate, ΔV_{SPIN} for process 15 would have to be pressure dependent with a zero-pressure value of about −13 cm^3 mol^{-1}. This parameter is not presently accessible, either theoretically or experimentally, but Binstead and Beattie found ΔV_{SPIN} = −10.1 cm^3 mol^{-1} (0.1–140 MPa) for the bis(terpyridine)cobalt(II) spin-isomer equilibrium and similar values for some iron(III) cations,[35] and it may be anticipated that ΔV_{SPIN} for the more compact $Co(en)_3^{2+}$ ion will be numerically somewhat smaller (less negative) than this. Thus, although the spin-isomerism mechanism of electron transfer is qualitatively consistent with the results of this study, it cannot at present be used to make numerical predictions of the pressure effects on the rate of the $Co(en)_3^{3+/2+}$ exchange, whereas the nonadiabatic model can account for the value of ΔV_0^* and the curvature of the ln k vs P plot quantitatively, as follows.

Data Analysis through Direct Calculation of Relative Rate Constants. We have stressed elsewhere[11,12,14,22,29] that the SHM and related theories require that ΔV^* for outer-sphere electron-transfer reactions be pressure-dependent, since the pressure derivatives of n, D, and ρ themselves depend on pressure. Furthermore, since the pressure dependences of these derivatives are markedly nonlinear, it follows that $\Delta\beta^*$ and $\Delta\kappa^*$ will also be pressure dependent in ways that cannot easily be reduced to useful parameters and that very different values of $\Delta\beta^*$ and $\Delta\kappa^*$ will be obtained from measurements over different pressure ranges. It may therefore be more meaningful to ask not whether theory can predict ΔV^* and $\Delta\beta^*$ values that agree with experiment but whether it can reproduce the pressure dependence of k directly.

For this purpose, if one accepts that the $Co(en)_3^{3+/2+}$ exchange is nonadiabatic, one need only calculate k at selected pressures relative to its zero-pressure value k_0, through eq 12, 13, and 16–19;

$$\Delta G_{SR}^* = (Ne^2/16\pi\epsilon_0)[(2r_1)^{-1} + (2r_2)^{-1} - \sigma^{-1}](n^{-2} - D^{-1}) \qquad (16)$$

$$\Delta G_{COUL}^* = NZ_1Z_2e^2/4\pi\epsilon_0 D\sigma \qquad (17)$$

$$\Delta G_{DH}^* = -2RTZ_1Z_2CI^{1/2}/(1 + BaI^{1/2}) \qquad (18)$$

$$\sigma = \sigma_0(\rho_0/\rho)^{1/3} \qquad (19)$$

terms in L_0 and any pressure-independent terms omitted from eq 12 cancel, and the small pressure dependence of ΔG_{IR}^* can be set with the calculated ΔV_{IR}^* given above. The parameters r_1, r_2, a, and σ_0 (the reagent separation for most probable electron transfer at zero pressure, assumed to be approximately $r_1 + r_2$) are estimable from molecular dimensions. Thus, the nonadiabatic scaling factor α can be used as a single adjustable parameter to fit the experimental data (in principle, α can be obtained from theory but is sensitive to assumptions made in the calculation).[30] The pressure dependence of the relevant solvent properties are contained in the empirical equations of Grigull et al.[23,25] and Owen et al.,[24] which can readily be incorporated into a computer program to calculate k/k_0.

The best fit of the experimental ln (k/k_0) data from Table I was obtained with α = 19.0 nm^{-1} and is represented by the solid line in Figure 2, which lies well within the experimental uncertainties in k. As a refinement, the Fuoss equation[36] can be incorporated in an attempt to accommodate possible depletion of the reactant pool through ion pairing with perchlorate (which is counteracted by pressure); reiteration of the calculation to constant I implies that some 45% of the Co^{II} and 55% of the Co^{III} are paired with ClO_4^-, and the best-fit value of α becomes 16 nm^{-1}. The broken curve in Figure 2 represents the calculated behavior of ln (k/k_0) for the fully adiabatic reaction (without ion pairing, which makes little difference) and is clearly inconsistent with experiment.

Table II. Calculated Values of Activation Parameters at Selected Pressures[a]

model	P/ MPa	ΔV_0^*/ cm^3 mol^{-1}	$\Delta\beta^*$/ cm^3 mol^{-1} MPa^{-1}	av ΔV^{*b}/ cm^3 mol^{-1}	$10^3\sum\delta^{2c}$
nonadiabatic[d]	0	−20.2	−0.071	−15.9	1.03
	100	−15.5	−0.031		
	200	−13.2	−0.016		
quadratic	0	−19.7	−0.041	−15.6	0.65
	100	−15.6			
	200	−11.5			
linear	0–207	−15.5	0	(−15.5)	6.02

[a] 65.0 °C; r_1 = 398 pm; r_2 = 413; $\sigma_0 = r_1 + r_2$; a = 686 pm; I = 0.5 mol L^{-1}; ΔV_{IR}^* +0.60 cm^3 mol^{-1}; ion pairing neglected. [b] From 21 values at 10 MPa intervals. [c] Sums of squares of residuals in ln k vs P plot. [d] α = 19.0 nm^{-1}.

With this approach, it is easy to calculate ΔV^*, $\Delta\beta^*$, and $\Delta\kappa^*$ at any pressure P by computing ln (k/k_0) at $P \pm \delta P$, where δP is a very small increment of P; some typical results are collected in Table II and show clearly that ΔV^* and $\Delta\beta^*$ are markedly and nonlinearly pressure-dependent. This procedure represents the data more rationally than do eq 1 and 8, which have no sound theoretical basis, and the sums $\sum\delta^2$ of the squares of the residuals, given Table II, show that the two-parameter theoretical models fit the data almost as well as the three-parameter empirical quadratic and significantly better than the two-parameter linear equation. A value of ΔV_0^* = −20 ± 1 cm^3 mol^{-1} may be taken as definitive; the *average* value of ΔV^* has no unique meaning, as it will depend on both the pressure range chosen and the method of averaging, but with a working value of $-15._5$ cm^3 mol^{-1} (0–200 MPa) may be adopted.

As with all attempts to account quantitatively for reaction rates in solution, several tacit assumptions are involved, any one of which could prove to be poor enough to invalidate the procedure even if the theory itself were fully satisfactory. In particular, the pressure dependences of the activity coefficients of complex ions in solution are unknown, and the validity of eq 11 and 18 at ionic strengths on the order of 0.5 mol L^{-1} may be questioned; we note, however, that a Debye–Hückel-derived equation served adequately to describe the concentration dependences of the molar volumes of several transition-metal ions in aqueous solution in this regime of ionic strengths.[37] It should also be noted that the equations of Grigull et al.[23,25] and Owen et al.[24] describe the properties of water accurately to 100 MPa at least, but are not necessarily reliable at 200 MPa. Furthermore, the decision to use refractive index values for the conventional wavelength of 593 nm was arbitrary, but is acceptable because the key quantity $(\partial n^{-2}/\partial P)_T$ varies monotonically only from -1.51×10^{-10} Pa^{-1} at 200 nm to -1.35×10^{-10} Pa^{-1} at 2000 nm. The assumption that the solvent can be treated as a continuous dielectric is questionable, although probably acceptable for large ions, as the work of Hupp and Weaver suggests.[38] The expedient use of the high-pressure properties of pure water rather than of a perchlorate solution of $I \simeq 0.5$ mol L^{-1} is not a major source of error.[39] In any event, the cumulative effect of any such shortcomings will be much less than the discrepancy between the observed pressure effect on k and that predicted by simple SHM theory, as highlighted by Figure 2.

Conclusions. The rate of the $Co(en)_3^{3+/2+}$ self-exchange reaction is more strongly accelerated by pressure than would be expected from theory of the Hush or Marcus type or from comparison with other typical self-exchange reactions of transition-metal complexes in solution. The pressure dependence of the rate constants, in-

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cluding the curvature of the ln *k* vs *P* plot, can be accounted for to well within the experimental uncertainty on the basis of a two-sphere, continuous-dielectric, *nonadiabatic* model with a distance scaling factor α of about 19 nm^{-1}. The data are also qualitatively consistent with a mechanism in which electron transfer to Co^{III} occurs adiabatically through the doublet excited state of the Co^{II} complex, in equilibrium with its quartet ground state, but direct adiabatic self-exchange between $Co(en)_3^{3+}(^1A)$ and $Co(en)_3^{2+}(^4T)$ seems to be ruled out.

The extensive experimental work of Endicott and co-workers[40] implies various degrees of nonadiabaticity in the net electron-transfer reactions of a variety of cobalt(III) complexes, more particularly where the electronic structures of the reactant and product are very different; we suggest that it is also important in the symmetrical $Co(en)_3^{3+/2+}$ exchange reaction. For the oxidation of $Co(bpy)_3^{2+}$ by $Co(terpy)_2^{3+}$, which, as noted above, may well involve spin-isomer equilibria but which, because of electron delocalization through the ligand π systems, is also more likely than the $Co(en)_3^{3+/2+}$ exchange to be adiabatic in electron transfer between the ground states of the reactants, ΔV^* is -9.4 cm^3 mol^{-1},[41] quite close to that predicted from simple SHM theory for, e.g., the $Co(terpy)_2^{3+/2+}$ self-exchange reaction. Comparison of the $Co(bpy)_3^{2+}/Co(terpy)_2^{3+}$ *net* reaction with symmetrical *self-exchange* processes may not be quite legitimate, but it underscores the anomaly of the $Co(en)_3^{3+/2+}$ exchange and suggests that this originates in nonadiabatic electron transfer between the ground states.

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Electrochemical Polymerization of 4-Methyl-4′-vinyl-2,2′-bipyridine-Containing Metal Complexes: Polymer Structure and Mechanism of Formation

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The polymer structure and mechanism of formation of electroreductively polymerized 4-methyl-4′-vinyl-2,2′-bipyridine-containing metal complexes are described. Results from TLC and laser desorption Fourier transform mass spectrometry demonstrate that normal "polyvinyl-type" chains are formed through chain propagation. For electrochemically polymerized poly-$Fe(vbpy)_3^{2+}$ an average chain length of seven repeat monomer units is determined. Separate copolymerization studies of mono- and tris(vinyl)-substituted complexes provide additional information on the nature of the polymerization process.

Introduction

Electrode-bound polymer films formed by the reductive polymerization of metal complexes that contain either 4-methyl-4′-vinyl-2,2′-bipyridine (vbpy) or 4-vinylpyridine have remained a subject of much interest.[2-12] While there has been speculation, the structure and mechanism of formation and these polymers have remained experimentally undetermined. Herein we report studies on the electrochemical polymerization of iron and ruthenium complexes that contain vbpy. Laser desorption Fourier transform mass spectral studies of electrochemically polymerized demetalated poly-$Fe(vbpy)_3^{2+}$ demonstrate that these polymers contain normal "polyvinyl-type" chains. In the case of poly-$Fe(vbpy)^{2+}$, the average polymer chain length is seven repeat monomer units. Additionally, we have reexamined the data that originally led Murray and co-workers[2] to propose a "tail-to-tail" radical-pair coupling path for the formation of these polymers. New electrochemical data allow for a rationalization of these previous results in light of a normal chain propagation mechanism.

Experimental Section

Chemicals and Solvents. Acetonitrile (Burdick & Jackson) for electrochemical measurements was stored under nitrogen and used without further purification. Tetra-*n*-butylammonium hexafluorophosphate ((TBA)PF_6) was prepared as previously reported.[13] Electrochemical solutions were all 0.1 M (TBA)PF_6 in acetonitrile.

4-Methyl-4′-vinyl-2,2′-bipyridine (vbpy) was prepared from 4,4′-dimethyl-2,2′-bipyridine (Me_2bpy) (Strem) by using the method of Guarr and Anson.[14]

Tris(4-methyl-4′-vinyl-2,2′-bipyridine)iron(II), $[Fe(vbpy)_3]^{2+}$. A solution containing 27.7 mg of $FeSO_4 \cdot 7H_2O$ (1.0×10^4 mol) dissolved in 30 mL of H_2O was added to 59 mg (3.0×10^4 mol) of vbpy in 50 mL of

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