mechanism for energy transfer, the resonance process is favored by the overlap between the emission spectrum of D* and the absorption spectrum of A. Two basic criteria have been identified to differentiate between the two mechanisms and these are that (1) the "trivial" mechanism may occur over extremely large distances, whereas the resonance interaction is effective only over limited distances, and (2) the resonance energy-transfer process occurs before D* emits.

Since energy transfer is only observed in the copolymers but not in the monomer solutions, the "trivial" radiative energy-transfer mechanism can be ruled out.

Schmehl et al.[10] have reported that in $[(dmbpy)_2Ru(b\text{-}b)Ru(dmbpy)(CN)_2]^{2+}$ (dmbpy is 4,4′-dimethyl-2,2′-bipyridine; b-b is 1,4-bis[2-(4′-methyl-2,2′-bipyridyl-4-yl)ethyl]benzene) the emission from the $[(dmbpy)_2Ru(b\text{-}b)]$ center is quenched by the $[(b\text{-}b)Ru(dmbpy)(CN)_2]$ chromophore. The temperature dependence (between 200 and 300 K) indicated the existence of more than one energy-transfer path in this bimetallic complex. They postulated that both coulombic and energy-exchange mechanisms were responsible for the overall energy transfer. From emission-quenching studies as a function of temperature, it was apparent that both thermally activated and temperature-independent terms were contributing to the overall energy-transfer process. The observed temperature dependence could be the result of a combination of the energy-exchange and the coulombic energy-transfer paths, with the latter being temperature independent. At high temperature, energy transfer is dominated by energy exchange. As the solution temperature is lowered, the energy-transfer rate constant decreases until it reaches a constant value, attributed to coulombic energy transfer. Energy transfer for other similar binuclear complexes has also been reported by these authors.[11]

For the 1:1 and 1:5 Ru/Os copolymers (Figure 8C,D), energy transfer decreases at low temperature as evidenced by the relative decrease in the emission intensity from the osmium centers. (Since emission quenching data are not available at this time, the relative differences in energy transfer are based on the relative intensities of the ruthenium and osmium emission bands.) However, energy transfer is still evident at low temperature. Assuming that the osmium and ruthenium monomers are incorporated randomly in the polymer, the copolymers can be envisioned to be composed of Ru–Os "dimeric" units $([-Hvbpy)_2Ru(vbpyH-vbpyH)Os(vbpyH-)_2])$. These would be analogues of the dinuclear complexes studied by Schmehl and co-workers.[9,10] On the basis of the energy-transfer behavior at room and low temperatures, and in light of the results obtained by them, we believe that energy transfer in these copolymers is taking place by a simliar mechanism.

For the 5:1 Ru/Os copolymer (Figure 8B), the ratio of the emission intensities of the ruthenium and osmium chromophores does not change significantly with temperature. In this case, the probability of having a ruthenium chromophore next to an osmium center is much higher than for the 1:1 and 1:5 Ru/Os copolymers. Thus, diffusion of the polymer strands to bring osmium and ruthenium chromophores closer together (in order to allow for energy exchange) will play a relatively minor role. Thus the relative emission intensities would be expected to be insensitive to temperature differences as was indeed observed.

Conclusions

Copolymers of $M(vbpy)_3^{2+}$ (M = Ru, Os) in varying ratios (1:1, 1:5, 5:1) have been prepared by solution polymerization and purified by SEC. The visible spectra of the copolymers resemble the superposition of the individual components of the polymers mixed in the appropriate ratio. Cyclic voltammograms for the 1:1 Ru/Os copolymer deposited on a Pt electrode show similar currents for the $Os^{2+/3+}$ and the $Ru^{2+/3+}$ couples, indicating that the monomers were incorporated in the polymer in the same ratio in which they were mixed. Similar results were obtained by UV–vis spectrophotometry for films deposited onto transparent electrodes. However, cyclic voltammograms for the 5:1 and 1:5 (Ru/Os) copolymers similarly deposited only show the $Ru^{2+/3+}$ and $Os^{2+/3+}$ couples, respectively. However, spectrophotometry of films deposited onto transparent electrodes clearly indicated the presence of both metal centers.

In copolymers prepared by electroreductive polymerization of a 1:1 mixture of the monomers, the ratio of Ru/Os in the film was about 2:1, regardless of the electropolymerization conditions.

Finally, on the basis of the emission spectra of the copolymers prepared in solution, there appears to be effective energy transfer from ruthenium to osmium states in the polymer at both room and liquid-nitrogen temperatures.

These results point to fundamental differences between solution polymerization and electropolymerization.

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Registry No. $[Ru(vbpy)_3(PF_6)_2]/[Os(vbpy)_3(PF_6)_2]$ (copolymer), 137768-23-1.

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Kinetics of the Aqueous Cobalt(II)/Cobalt(III)/EDTA System at Variable Pressure[1]

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The effect of pressure on the rate of the redox exchange reaction of $Co^{III}(EDTA)^-$ with $Co^{II}(HEDTA)OH_2^-$ at 85 °C, pH 2.0, and ionic strength 0.5 mol L^{-1} is described by a volume of activation $\Delta V_{ex}^* = -3.2 \pm 0.3$ cm^3 mol^{-1} which is apparently constant to within the experimental uncertainty over the range 0.1–228 MPa. This value is consistent with predictions based on Marcus–Hush theory for a nonadiabatic, outer-sphere exchange mechanism in which ring closure and loss of coordinated water occur in $Co(HEDTA)OH_2^-$ prior to electron transfer. For the conversion of $Co^{III}(EDTA)^-$ to $Co^{III}(HEDTA)OH_2$, $\Delta V_o^* = +3.5 \pm 0.7$ cm^3 mol^{-1} at 25.0 °C in aqueous $HClO_4$ (1.0 mol L^{-1}), while for the reverse reaction the corresponding parameter $\Delta V_c^* = +6.7 \pm 0.7$ cm^3 mol^{-1}. It is argued that the transition state for the forward reaction occurs early in the ring-opening step, following closely upon or concurrently with protonation of the carboxyl group.

The EDTA complex of cobalt(II) continues to be of considerable interest as a reductant in mechanistic studies, particularly where stereochemical information is sought, since the $Co^{III}(EDTA)^-$ product is chiral and nonlabile.[6-9] The detailed mechanism of electron transfer, however, is not easily assigned, since the Co^{II} complex is labile and consequently there exists the possibility of inner-sphere as well as outer-sphere paths. Further kinetic and mechanistic complications arise because aqueous $Co^{II}(EDTA)^{2-}$ exists predominantly as the sexidentate complex only at pH >4.5; in more acidic solutions, the quinquedentate form $Co(HEDTA)OH_2^-$, with one aqua ligand and a protonated pendant carboxylate function with $pK_a \simeq 3$ becomes important and is the dominant form at pH 2.0.[10-12] The Co^{III}–EDTA complex behaves similarly, but at 25 °C at least, the dominant form is $Co(EDTA)^-$ at all pH >0, and the quinquedentate–sexidentate interconversion is slow;[10d,e] complicated pH dependences of the rates of reactions in which this complex is the oxidant can therefore result.[13]

In general, it seems that outer-sphere electron transfer prevails in reactions in which the Co^{II}–EDTA species are the reductants,[6,11,12] even in the curious case of the reduction of $Fe(CN)_6^{3-}$ by $Co(EDTA)^{2-}$ in which a cyano-bridged Co–Fe complex actually forms but represents a "dead end" as far as the formation of free $Co^{III}(EDTA)^-$ is concerned.[14] On the other hand, Lappin and co-workers[6b] give evidence that implies the operation of an inner-sphere mechanism in the oxidation of the Co^{II}–EDTA species by an iron(III) bis(oxime imine) complex below pH 4—the Co^{III} product in this case, however, is $Co(EDTA)OH_2^-$, rather than the usual $Co(EDTA)^-$.

Our interest in the kinetics of electron transfer between the Co^{II} and Co^{III} EDTA complexes stems from the particular need for more data on the effects of pressure on the rates of anion–anion self-exchange reactions in solution.[15,16] We present here measurements of the pressure dependence of the kinetics of the "self-exchange" reaction of the Co^{III} and Co^{II} EDTA complexes in aqueous solution at pH 2.0

$$^{60}Co(HEDTA)OH_2^- + Co(EDTA)^- \overset{k}{\rightleftharpoons} {}^{60}Co(EDTA)^- + Co(HEDTA)OH_2^- \quad (1)$$

and show that the results are consistent with a nonadiabatic outer-sphere electron-transfer mechanism, in terms of our adaptation[15,16] of Marcus–Hush theory. The term "self-exchange" is used rather loosely here, as the Co^{III} and Co^{II} complexes differ in the denticity and protonation of the EDTA ligands under the conditions of our variable-pressure experiments. The self-exchange of Co^{II} and Co^{III} EDTA complexes was first studied by Adamson and Vorres[17] at pH 2.0 (where reaction 1 specifically prevails) using a ^{60}Co tracer; later, Im and Busch[12] followed the electron transfer over the pH range 2.0–4.0 using optical activity and showed that a second reaction path, direct exchange between $Co(EDTA)^-$ and $Co(EDTA)^{2-}$, becomes important at the higher pH values. Our radiochemical measurements confirm and extend these results.

The tendency of the carboxylate groups of coordinated EDTA to protonate and the metal ion to aquate (i.e., for ring opening to occur) in acidic solutions[10-12] must be considered in any study of the electron-transfer reaction (1). In this connection, we also report here measurements of the effects of pressure on the rate and equilibrium constants for ring-opening (k_o) and -closing (k_c) in $Co^{III}(EDTA)^-$ (eq 2) and consider their mechanistic implications.

$$Co^{III}(EDTA)^- + H^+ + H_2O \underset{k_c}{\overset{k_o}{\rightleftharpoons}} Co^{III}(HEDTA)OH_2 \quad (2)$$

Experimental Section

Materials. Metallic cobalt-60 (Australian Atomic Energy Commission, Lucas Heights) was dissolved in nitric acid (7 mol L^{-1}), and from this stock solution were obtained more dilute solutions with a specific activity of about 30 MBq mL^{-1}. One or two drops of this tracer solution were sufficient to label the reactant solutions to a suitable level of activity; the concentration of additional cobalt(II) introduced in this way was negligible ($\simeq 10^{-7}$ mol L^{-1}).

$Na[Co(EDTA)]\cdot 4H_2O$ was made by the method described for the potassium salt by Dwyer et al.,[18] and its purity was confirmed by CHN microanalysis. Concentrations of $Co(EDTA)^-$ in solutions were determined spectrophotometrically (molar absorbance 219 ± 1 L mol^{-1} cm^{-1} at 382 nm). $Co(ClO_4)_2$ was made by fuming $CoCl_2\cdot 6H_2O$ with concentrated $HClO_4$ until no Cl^- was detectable with $AgNO_3$; stock solutions were made up in $HClO_4$ (0.005 mol L^{-1}) and analyzed for Co content by electrodeposition on Pt electrodes. Solutions of the Co^{II}–EDTA complex for kinetic studies were prepared at the beginning of each run by mixing solutions of $Co(ClO_4)_2$ and a 35% excess of Na_2H_2EDTA, so that at least 99% of the Co^{II} was complexed by the EDTA. Water for all stock solutions and reaction mixtures was demineralized and redistilled from alkaline permanganate and then acidified dichromate solutions. All other materials were of analytical reagent grade.

Electron-Transfer Kinetics. Reaction mixtures were prepared by mixing 10.0 mL of 0.1 mol L^{-1} $Co(ClO_4)_2$ with 10.0 mL of 0.13 mol L^{-1} Na_2H_2EDTA solution and adding 20.0 mL of Na[Co(EDTA)] followed by 10.0 mL of 2.0 mol L^{-1} $NaClO_4$ solution to adjust the ionic strength I to 0.5 mol L^{-1}.[19] One or two drops of ^{60}Co tracer solution were added, giving a total activity of about 0.7 MBq, and the pH was adjusted to 2.00 with a few drops of $HClO_4$ or NaOH solution. For runs at atmospheric pressure, the reaction mixture was placed in a stoppered glass flask in a thermostat bath (±0.1 °C); for runs at elevated pressures, the solutions were loaded into a poly(methyl methacrylate) syringe in a thermostated pressure vessel, as described elsewhere.[20] It was established that the nature of the vessel and the surface area exposed to the sample had no significant effects on the reaction rate; the high-pressure sampling capillary, however, had to be of Pt/Ir alloy, rather than stainless steel, which was found to react, causing some loss of Co^{III} (cf. Jones et al.[21]). It was unnecessary to exclude air. The pH and the optical absorbance at 382 nm were checked at the end of each run and were unchanged within the accuracy of the measurements (±0.01 in pH, ±1% in $[Co^{III}]$); the changes reported by Adamson and Vorres,[17] and attributed by them to decomposition of the Co^{III} complex, were not observed.

At selected times, 2.0-mL aliquots of the reaction mixture were quenched by discharging them into 3 mL of 4 mol L^{-1} perchloric acid (which aquated the labile Co^{II} complex but not the inert Co^{III}) containing some Co^{2+} carrier and passed through a column of Zeo-carb 225 cation-exchange resin in the H^+ form. The Co^{III} fraction passed directly through the column and was collected; the Co^{II} fraction was eluted with concentrated HCl as $CoCl_4^{2-}$. Separation of the Co^{III} from the Co^{II} by this method was shown to be >99% complete. The activities of both fractions were measured with a Philips PW4119 scintillation detector, using a well-type Tl-activated NaI scintillation crystal. Since the reac-

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Table I. Rate Constants for Electron Transfer between Co^{III}– and Co^{II}–EDTA Complexes in Aqueous Solution[a]

P/MPa	$k_{ex}/10^{-4}$ L mol^{-1} s^{-1} [b]	no. of runs	P/MPa	$k_{ex}/10^{-4}$ L mol^{-1} s^{-1} [b]	no. of runs
0.1	1.78	9	186.1	2.17	1
110.3	2.00	2	207.0	2.22	2
158.5	2.03	1	228.0	2.28	4
172.2	2.17	2			

[a] 85.0 °C; pH 2.00; $[Co^{III}] = 0.0288$ mol L^{-1}; $[Co^{II}] = 0.0186$ mol L^{-1}; $I = 0.5$ mol L^{-1} ($NaClO_4$). [b] ±4.7%.

tions were very slow, the infinite-time activities were calculated from the mass balance.

Effect of Pressure on the $Co^{III}(EDTA)^-$–$Co^{III}(HEDTA)OH_2$ Interconversion. The rate of approach of reaction 2 to equilibrium, starting from a solution of $Na[Co(EDTA)]\cdot 4H_2O$ in 1.0 mol L^{-1} $HClO_4$, was studied spectrophotometrically with a Unicam SP800 double-beam spectrophotometer fitted with an SP850 scale expansion accessory (since the absorbance changes were never more than 0.07) and the thermostated (±0.1 °C) high-pressure optical assembly described elsewhere.[22] Although the use of the high-pressure optical cell afforded the convenience and precision of continuous in situ *rate* measurements, absorbances measured with this apparatus were intrinsically pressure-dependent. Accordingly, the compositions of the solutions *at equilibrium* were derived from spectrophotometric measurements made at atmospheric pressure with conventional cuvettes containing samples of the reaction mixtures that had been equilibrated at the desired pressure in the syringe assembly described above. Absorbance measurements were made at 500 nm, where the molar absorbances of $Co(EDTA)^-$ and $Co(HEDTA)OH_2$ are 235 and 134 L mol^{-1} cm^{-1}, respectively, at 0.1 MPa and 25.0 °C.[10c] For the kinetic experiments made in the pressurizable optical cell, continuous absorbance recordings were begun 7–10 min after pressurization, to allow temperature perturbations to subside.

Results

Self-Exchange Reaction. Measurements of the fraction f of ^{60}Co exchange at times t confirmed[12,17] that the rate R of reaction 1 obtained from the McKay equation

$$R = -[Co^{II}][Co^{III}][\ln [(1 - f)/([Co^{II}] + [Co^{III}])]]t \quad (3)$$

was first order in each of $[Co^{II}]$ and $[Co^{III}]$ at a given pH, and the apparent second-order rate constant, k_{ex} was reproducible to ±7% (at pH 2.0). Any errors in the initial activity due to "zero-time exchange" during thermal equilibration amounted to no more than 2%.

Preliminary studies at 100 °C and pH 2.0–6.2 gave good agreement with the data of Im and Busch,[12] and the existence of plateaus in k_{ex} at pH 2.0 (where the reactive Co^{II} species is $Co(HEDTA)OH_2^-$, as in reaction 1) and at pH >4 (reactive species $Co(EDTA)^{2-}$ and $Co(EDTA)^-$) was confirmed. However, decomposition with precipitation of a Co oxide or hydroxide occurred above pH 4, and attention was therefore focused upon reaction 1 at pH 2.0, at which acidity it can be calculated[12] that reaction 1 accounts for over 97% of the overall reaction rate. Thus, k_{ex} at pH 2.0 may be identified with k for reaction 1, within the experimental uncertainty. Preliminary experiments at variable temperature gave $k_{ex} = (1.78 \pm 0.08) \times 10^{-4}$ L mol^{-1} s^{-1} at pH 2.0 (85.0 °C) and an activation enthalpy ΔH^* of about 90 kJ mol^{-1} (cf. $k = 1.98 \times 10^{-4}$ L mol^{-1} s^{-1}, $\Delta H^* = 96 \pm 8$ kJ mol^{-1}, and $\Delta S^* = -50 \pm 23$ J K^{-1} mol^{-1}, calculated from the data of Im and Busch[12] for reaction 1).[19]

Values of k_{ex} at 85.0 °C and pH 2.0 as a function of pressure are presented in Table I and are adequately summarized, within the experimental uncertainties, by the linear equation

$$\ln (k_{ex}^P/k_{ex}^0) = -P\Delta V_{ex}^*/RT \quad (4)$$

with the apparent volume of activation $\Delta V_{ex}^* = -3.2 \pm 0.3$ cm^3 mol^{-1}. No correction of k_{ex} for compression was necessary, since a pressure-independent concentration scale was used.[19,23] Since theory[16] indicates that the ln k_{ex} vs P plot should be curved (see Discussion and Figure 1), this apparent volume of activation is better regarded as a mean taken over the pressure range.

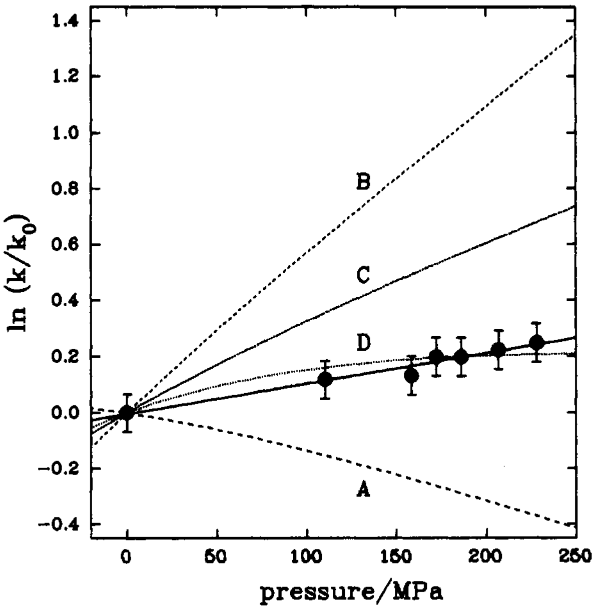

Figure 1. Pressure dependence of observed and calculated relative rate constants for electron transfer between $Co^{II}(HEDTA)OH_2^-$ and $Co^{III}(EDTA)^-$ at 85.0 °C and $I = 0.5$ mol L^{-1} ($k_0 = 1.78 \times 10^{-4}$ L mol^{-1} s^{-1}). Solid line: linear regression of experimental data (filled circles; k_{ex} taken to be identical to k for the exchange reaction (1)). Broken curves A–C: k/k_0 values calculated for adiabatic electron transfer via mechanisms A–C, respectively (see text);[16] in the notation of ref 16, $r_1 = 398$ pm, $r_2 = 413$ pm, $\sigma_0 = 811$ pm, $a = 700$ pm, and $\Delta V_{IR}^* = 0.6$ cm^3 mol^{-1}. Curve D: mechanism A with nonadiabatic electron transfer (distance scaling factor α set at 13 nm^{-1}).

Table II. Pressure Dependences of the Rate and Equilibrium Constants for Acid-Dependent Ring Opening and Closing in Aqueous $Co(EDTA)^-$ [a]

P/MPa	K/L mol^{-1}	k_{obs}[b]$/10^{-4}$ s^{-1}	$k_o/10^{-4}$ L mol^{-1} s^{-1}	$k_c/10^{-4}$ s^{-1}
0.1	1.28	5.28 ± 0.30	2.96	2.32
68.9	1.68	4.98 ± 0.52	3.12	1.86
137.9	2.20	4.05 ± 0.32	2.79	1.26
206.8	2.89	3.62 ± 0.57	2.69	0.93

[a] 25.0 °C; $[Co^{III}] \simeq 1.5 \times 10^{-3}$ mol L^{-1}; $I \simeq [HClO_4] = 1.00$ mol L^{-1}. [b] Averages of eight or nine runs at each pressure.

The $Co^{III}(EDTA)^-$–$Co^{III}(HEDTA)OH_2$ Equilibrium. The optical absorbance A_t at time t changed according to the usual first-order rate equation

$$\ln [(A_0 - A_\infty)/(A_t - A_\infty)] = k_{obs}t \quad (5)$$

in which the rate constant k_{obs} for the approach to equilibrium is given by

$$k_{obs} = k_o[H^+] + k_c \quad (6)$$

(cf. eq 2; $[H^+] = 1.0$ mol L^{-1}). Evaluation of k_c and k_o at various pressures P required determination of the equilibrium constant K ($=k_o/k_c$) for reaction 2 as a function of P, and this was done through replicate measurements of the optical absorbance at atmospheric pressure of solutions that had been equilibrated at 0.1 and 180 MPa. Since the effect of P on the absorbance of equilibrated solutions was only −3.14% ± 0.50% from 0.1 to 180 MPa, measurements were made for only these two pressures, and the values of K at other P were obtained from the relationship

$$\ln K_P = \ln K_0 - P\Delta V/RT \quad (7)$$

in which $K_0 = 1.28$ L mol^{-1} and ΔV, the molar volume change for reaction 2, is -3.2 ± 0.5 cm^3 mol^{-1}, at 25.0 °C and ionic strength $I = 1.0$ mol L^{-1}.

Values of the rate and equilibrium constants for reaction 2 at various pressures are collected in Table II. The data for 0.1 MPa

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are in excellent agreement with those of Dyke and Higginson[10c] for the same conditions. Assumption of linear dependences of ln k_o and ln k_c on P (cf. eq 4) gave volumes of activation $\Delta V_o^\ddagger = +3.5 \pm 0.7$ and $\Delta V_c^\ddagger = +6.7 \pm 0.7$ $\text{cm}^3\ \text{mol}^{-1}$ for the ring-opening and -closing directions, respectively, of reaction 2.[19] Again, no compressional correction is necessary or desirable.[23]

Discussion

Ring Opening and Closure. The protonation of a carboxylate function and aquation in $\text{Co}^{\text{III}}(\text{EDTA})^-$ (reaction 2) are accompanied by a volume change ΔV of -3.2 $\text{cm}^3\ \text{mol}^{-1}$ at 25 °C and $I = 1.0$ mol L^{-1}. For the cobalt(II) analogues Co(EDTA)^{2-} and Co(HEDTA)OH_2^- in aqueous solution, Yoshitani[24] reports molar volume data that give $\Delta V = -7.0$ $\text{cm}^3\ \text{mol}^{-1}$ for the reaction

$$\text{Co}^{\text{II}}\text{EDTA}^{2-} + \text{H}^+ + \text{H}_2\text{O} \rightleftharpoons \text{Co}^{\text{II}}(\text{HEDTA})\text{OH}_2^- \quad (8)$$

at infinite dilution, 25 °C, and 0.1 MPa. Precise comparison of this ΔV value with that measured for reaction 2 cannot be made because of the high ionic strength and reduced importance of electrostriction of water in the latter case, but it appears that ΔV for reaction 2 is somewhat more positive than might be expected on this basis. It should be noted, however, that the experimental ΔV for reaction 2 was obtained over a 180-MPa pressure range, and the scatter of the data may conceal a dependence on pressure; if so, then the true value at 0.1 MPa may be considerably more negative.

The mechanism of reaction 2 in the forward (k_o) direction must involve at least three processes: ring opening to form a pendant carboxylate arm, protonation of this arm, and entry of a water molecule into the first coordination sphere of Co^{III}. These may or may not be concerted or occur in this order, but we know from the rate equation[10c] that the proton is present in the transition state for the rate-determining step. Presumably, protonation of the carboxylate function is a prerequisite for the inhibition of prompt reclosure of any ring that might open spontaneously, and hence for an observable reaction. The nearest analogue for the protonation of a carboxylate function in Co(EDTA)^- for which volume change measurements are available is the protonation of Co(EDTA)^{2-}

$$\text{Co(EDTA)}^{2-} + \text{H}^+ \rightleftharpoons \text{Co(HEDTA)}^- \quad (9)$$

for which Yoshitani[25] finds $\Delta V_{\text{H}} = +3.5$ $\text{cm}^3\ \text{mol}^{-1}$ at infinite dilution; the corresponding quantity for the protonation of Co(EDTA)^- may be slightly less positive ($+2 \pm 1$ $\text{cm}^3\ \text{mol}^{-1}$) because of the reduced influence of electrostriction but still is close to $\Delta V_o^\ddagger$ ($+3.5 \pm 0.7$ $\text{cm}^3\ \text{mol}^{-1}$).

Combination of Yoshitani's data[24,25] for reactions 8 and 9 indicates that the addition of an aqua ligand to $\text{Co}^{\text{II}}(\text{HEDTA})^-$ is accompanied by a volume change ΔV_{aq} of -10.5 $\text{cm}^3\ \text{mol}^{-1}$. This value is gratifyingly similar to those obtained for the addition of an aqua ligand to simple aqueous cations by a semiempirical approach[26] which also showed that such volume changes were almost independent of the oxidation state of the metal ion. Thus, it can be confidently expected that the transfer of a water molecule from bulk solvent to the first coordination sphere of the Co^{III} analogue Co(HEDTA)^0 will also result in a volume change of close to -10.5 $\text{cm}^3\ \text{mol}^{-1}$. Consequently, the observed value of $\Delta V_o^\ddagger$ ($+3.5$ $\text{cm}^3\ \text{mol}^{-1}$) rules this out as an initial, rate-determining step for the forward reaction.

Allowance for the effect of protonation leaves only a small volume change ($\simeq +1$ to $\simeq +3$ $\text{cm}^3\ \text{mol}^{-1}$) that can be attributed to ring opening in the transition state. Ring opening might naively be expected to give rise to a substantial expansion because a bond is broken and a pendant arm set free, but in fact small ring structures almost always have *larger* molar volumes than the corresponding open chains (mainly because access of other molecules to the space enclosed by the ring is sterically inhibited),[27] so that ring opening may result in only a small net expansion or even a contraction. To clarify this, we may consider the *reverse* of reaction 2, for which microscopic reversibility requires that $\Delta V_c^\ddagger$ ($+6.7$ $\text{cm}^3\ \text{mol}^{-1}$) be attributed to the release of the aqua ligand from $\text{Co}^{\text{III}}(\text{HEDTA})\text{OH}_2$ (volume change $+10.5$ $\text{cm}^3\ \text{mol}^{-1}$, estimated as above) offset by a contribution of -3.8 $\text{cm}^3\ \text{mol}^{-1}$ from some degree of ring closure, since the rate equation[10c] confirms that the ionizable proton is still present in the transition state. These volume data, taken at face value, imply that ring closure is some 80% complete in the transition state.

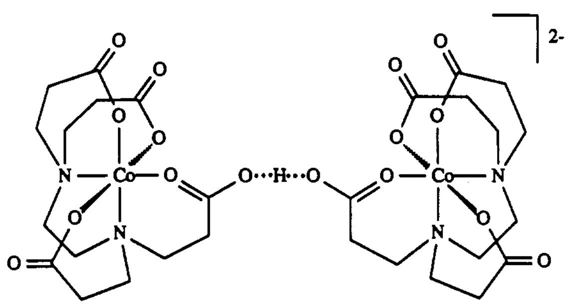

Figure 2. Proposed transition state for electron transfer between $\text{Co}^{\text{II}}(\text{HEDTA})\text{OH}_2^-$ and $\text{Co}^{\text{III}}(\text{EDTA})^-$ (mechanisms A and D).

Thus, on the basis of the rate equation and pressure effects, i.e., of contributions to $\Delta V_c^\ddagger$ and $\Delta V_o^\ddagger$, we can infer that the transition state for reaction 2 is $\{\text{Co}^{\text{III}}(\text{HEDTA})\}^\ddagger$ in which the extent of ring opening is minor.

Electron-Exchange Reaction. The rate equation and pH profile indicate that the composition of the transition state for reaction 1 at pH 2.0 is $\{\text{Co}_2(\text{EDTA})_2\text{H}(\text{H}_2\text{O})_n{}^{2-}\}^\ddagger$; n cannot be determined unequivocally in aqueous solution by conventional kinetic means. The principle of microscopic reversibility, as applied to the exchange reaction (1), requires either that the transition state for electron transfer be symmetrical or that the reaction proceed by two parallel paths of exactly equal importance with "mirror-image" free energy profiles.[28] In either case, this means either that $\text{Co}^{\text{II}}(\text{HEDTA})\text{OH}_2^-$ loses its aqua ligand en route to the transition state or that $\text{Co}^{\text{III}}(\text{EDTA})^-$ gains one.

In Figure 1, predictions of the pressure dependence of ln (k/k_0) according to four alternative mechanisms (A–D) are compared with the experimental results. The theoretical effect of pressure on ln k for reaction 1 (identifiable at pH 2.0 with ln k_{ex}) was calculated on the basis of Marcus–Hush theory as described elsewhere,[16] by taking the effect of internal (metal–ligand) reorganization to be equivalent to a contribution $\Delta V_{\text{IR}}^\ddagger$ of $+0.6$ $\text{cm}^3\ \text{mol}^{-1}$ to the activation volume[15] but with no allowance for depletion of the reactant pool through ion pairing.[29]

Mechanism A. The water ligand in $\text{Co}^{\text{II}}(\text{HEDTA})\text{OH}_2^-$ (but not the proton) is lost in a rapid initial step; the data of Yoshitani[24,25] indicate that a volume change $-\Delta V_{\text{aq}} = +10.5$ $\text{cm}^3\ \text{mol}^{-1}$ accompanies this process (at 0.1 MPa and 25 °C). Adiabatic electron transfer between $\text{Co}^{\text{II}}(\text{HEDTA})^-$ and $\text{Co}^{\text{III}}(\text{EDTA})^-$ then occurs through the symmetrical transition state shown in Figure 2, as originally suggested by Im and Busch.[12] This scenario is appealing in that Co(HEDTA)OH_2^- and Co(EDTA)^- are known to be the predominant forms of the Co^{II} and Co^{III} complexes under our experimental conditions, and the Co^{II} complex is substitutionally labile. Combination of ΔV_{aq} with the pressure effect on the electron-transfer rate calculated[16] for this model, however, predicts a substantial *retardation* of the overall reaction by increasing pressure (mean $\Delta V_{\text{ex}}^\ddagger \simeq +4.7$ $\text{cm}^3\ \text{mol}^{-1}$ over the pressure range), and Figure 1 shows that this is quite inconsistent with the experimental data ($\Delta V_{\text{ex}}^\ddagger = -3.2 \pm 0.3$ $\text{cm}^3\ \text{mol}^{-1}$). Although the ΔV_{aq} value for Yoshitani's work[24,25] refers to 0.1 MPa and

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(29) Since the reactant anions are fairly large and are of low charge, the contribution of ion pairing to $\Delta V_{\text{ex}}^{\ddagger}$[16] is small ($-0.4$ $\text{cm}^3\ \text{mol}^{-1}$ at most) and may be neglected.

25 °C, it is unlikely to be sufficiently different at 85 °C and 200 MPa to account for this disagreement.

Mechanism B. $Co^{III}(EDTA)^-$ aquates to form $Co(EDTA)OH_2^-$ in an initial step with a volume change ΔV_{aq} of about −10.5 $cm^3\ mol^{-1}$ (estimated as explained above); adiabatic electron transfer then occurs between $Co^{III}(EDTA)OH_2^-$ and $Co^{II}(HEDTA)OH_2^-$. Ring opening and aquation in $Co^{III}(EDTA)^-$, however, require prior protonation if the initial step is to be fast enough under the conditions of the electron-transfer experiments, and the rate equation for reaction 1 shows that this does not occur. In any event, the acceleration of reaction 1 predicted on this basis is far too strong (curve B, Figure 1; calculated average $\Delta V_{ex}^{\ddagger} \simeq -16$ $cm^3\ mol^{-1}$).

Mechanism C. $Co^{III}(HEDTA)OH_2^0$ forms as in reaction 2 (which is some 700 times as fast[10e] as the exchange rate at 85 °C, pH 2.0, and the relevant $[Co^{II}]$;[12] measured volume change at 25 °C = −3.2 $cm^3\ mol^{-1}$) and undergoes adiabatic electron exchange with the predominant Co^{II} species, $Co^{II}(HEDTA)OH_2^-$. This nicely symmetrical model, however, would require first-order dependence of the measured electron-transfer rate on $[H^+]$ at pH 2.0 and below, whereas the pH profile shows a plateau in rate in this region. Furthermore, this model predicts an excessive pressure acceleration (curve C in Figure 1; average $\Delta V_{ex}^{\ddagger} \simeq -9.0$ $cm^3\ mol^{-1}$ over the pressure range).

Mechanism D. The reaction proceeds as in mechanism A, which is the most likely pathway, but is *nonadiabatic*. In the simplest treatment,[16] this additional constraint requires only the introduction of a distance-scaling parameter α for calculation of the pressure effect on the reaction rate. In practice, α is not easily predictable from theory with the required precision, so it may be introduced as an adjustable parameter to fit the experimental data to within the error bars. This is done in curve D of Figure 1, for which $\alpha = 13 \pm 1\ nm^{-1}$—a value that is midrange for reactions of this type[31] and is similar to that (16–19 nm^{-1}) estimated in the same way for the $Co(en)_3^{3+/2+}$ exchange.[30]

Two further possibilities may be considered: an inner-sphere electron-transfer mechanism involving one of the carboxylate groups of the two EDTA ligands as a ligand bridge, and H atom transfer rather than electron transfer in mechanism A (cf. Figure 2). The first may be discounted because there was no evidence of bridging-ligand trapping by the newly formed Co^{III} center to give a binuclear complex; the Co^{III} and Co^{II} fractions separated cleanly after exchange. The second remains a real possibility, but at present it is not possible to say how it would be manifested in terms of pressure effects, and accordingly it has not been considered further.

Thus, if it is accepted that the exchange process at pH 2 is of the outer-sphere type, then the kinetic effect of pressure is consistent with nonadiabatic electron transfer between the predominant Co species in solution, $Co^{III}(EDTA)^-$ and $Co^{II}(HEDTA)OH_2^-$, following rapid deaquation of the latter (mechanism D). This places reaction 1 in the same mechanistic category as the $Co(en)_3^{3+/2+}$ exchange in water, for which the strong acceleration by pressure has been ascribed to nonadiabaticity of electron transfer.[30,32] Significantly, both the $Co(en)_3^{3+/2+}$ and the $Co(EDTA)^-/Co(HEDTA)OH_2^-$ exchanges are much slower than the analogous $Co(sep)^{3+/2+}$ and $Co([9]aneS_3)_2^{3+/2+}$ reactions, the rates and volumes of activation of which are consistent with full adiabaticity.[32,33]

On a final note of caution, we remark that all of these models predict that plots of ln (k/k_0) vs P for outer-sphere electron transfer should be distinctly curved,[16] yet the experimental data seem to be better represented by a linear regression. Similar seemingly excessive curvatures of theoretical ln (k/k_0) vs P plots have been noted in several cases and may reflect a basic inadequacy of the theory.[16]

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Registry No. $Co^{III}(EDTA)^-$, 15136-66-0; $Co^{II}(HEDTA)OH_2^-$, 14024-68-1.

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Solution IR Spectroscopic Studies of *cis*-Dioxomolybdenum(VI) Complexes

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Series of *cis*-dioxo–MoL·DMF complexes have been investigated using FT-IR spectroscopy in DMF solution. The ligands (L) used are obtained from Schiff base condensation of 5-X–salicylaldehyde (X = NO_2, Cl, Br, H, OCH_3) with *o*-aminophenol, *o*-aminobenzenethiol, 2-aminoethanol, 2-aminoethanethiol, 2-amino-5-nitrophenol or 2-amino-4-nitrophenol. Correlations were observed between the antisymmetric Mo═O stretching vibration (ν_{as}(Mo═O)), the Hammett parameter (σ_p) for the X substituent on the salicylaldehyde ligand fragment, and the specific rate constant (k_1) for oxygen atom transfer between $Mo^{VI}O_2$(5-X-SSP) or $Mo^{VI}O_2$(5-X-SSE) and $PEtPh_2$. The observed variation in ν_{as}(Mo═O) as the ligand structure is systematically altered reflects changes in the relative energy of the oxo O π^* antibonding orbital. We propose that this energy change contributes to the activation energy in the oxygen atom transfer reaction with $PEtPh_2$. Our results support the proposed reaction mechanism of donation of the phosphorus lone-pair electrons into the oxo O π^* antibonding orbital.

Introduction

A number of redox enzymes are known to be dependent on molybdenum for physiological activity. Some of these enzymes include nitrate reductase, xanthine oxidase, sulfite oxidase, and aldehyde oxidase. Extended X-ray absorption fine structure (EXAFS) spectroscopy studies[1–4] have implicated sulfur and

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