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Rates of Reduction of Tris(cyclohexanediamine)cobalt(III) and Tris(ethylenediamine)cobalt(III) Ions. A Search for Steric Effects in Outer-Sphere Electron Transfer

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The rates of reduction of tris(cyclohexanediamine)cobalt(III) and tris(ethylenediamine)cobalt(III) ions were measured under identical conditions in aqueous solutions using as reducing agents (A) tris(bipyridine)chromium(II) ion in 0.1 M chloride medium, (B) hexaaquavanadium(II) ion in 0.1 M trifluoroacetate medium, and (C) chloropentaammineruthenium(II) ion in 0.1 M chloride medium. The rate constants ($M^{-1}\ s^{-1}$) at 25 °C, activation enthalpies (kJ mol^{-1}), and activation entropies (J $deg^{-1}\ mol^{-1}$), in that order, are as follows: for $Co(chxn)_3^{3+}$: (A) 40 ± 2, 54 ± 2, -32 ± 6; (B) $(2.6 \pm 0.1) \times 10^{-4}$, 62 ± 4, -106 ± 12; (C) $(3.8 \pm 0.1) \times 10^{-3}$, 74 ± 2, -44 ± 4; for $Co(en)_3^{3+}$: (A) 35 ± 2, 47 ± 3, -59 ± 10; (B) $(4.6 \pm 0.1) \times 10^{-4}$, 59 ± 2, -110 ± 4; (C) $(6.2 \pm 0.5) \times 10^{-3}$, 72 ± 2, -47 ± 4. The results for reduction by ruthenium(II) are given as apparent rate constants, ignoring the equilibrium with the $Ru(NH_3)_5H_2O^{2+}$ species, which does not reduce the cobalt(III) complexes. There are no significant differences between the two complexes which could be ascribed to steric effects on electron transfer. Analysis of the results using the Marcus–Hush theory of outer-sphere electron transfer indicates either that the electron transfer occurs by a common mechanism with the reducing agent oriented along the threefold axis of the complex or that the probabilities of electron transfer through the cyclohexanediamine and ethylenediamine ligands are equal.

Introduction

Despite numerous studies of outer-sphere electron-transfer reactions, there is surprisingly little evidence on how steric factors affect the probability of electron transfer.[2] For example, while it is commonly believed that the conjugation of the phenanthroline ligand promotes the rate of electron transfer between $Fe(phen)_3^{3+}$ and $Fe(phen)_3^{2+}$ by the delocalization of metal electron density onto the ligands, alternative explanations are possible and have not been excluded. It is now known from crystal structure determinations that the iron–nitrogen distances in the two complexes are identical,[3] thus eliminating the inner-sphere reorganization energy requirement for electron transfer. Would the rate of electron transfer be equally rapid between complexes with saturated ligands of similar size with equal bond lengths in both oxidation states; i.e., are saturated ligands equally effective for electron transfer? Only recently has some evidence been reported that cyclohexyl substitution on the periphery of the phenanthroline ligand reduces the rate of electron exchange compared with that of the phenyl substituted complexes by more than a factor of 10.[4] These results were interpreted as indicating that the cyclohexyl group conducts electrons less well than the phenyl group in the electron-transfer process.

To examine this question we have taken advantage of the observation[5] that the reduction potentials of tris(ethylenediamine)cobalt(III) and tris(cyclohexanediamine)cobalt(III) differ by only 20 mV. By reducing both of these complexes under identical conditions using various different reducing agents, any marked difference due to the increased size of the cyclohexyl ligand should be apparent, since there is little difference between the complexes in the overall free-energy change for reduction.

Experimental Section

Materials. Trifluoromethylsulfonic acid (3M Co.) was purified by distillation with an equimolar quantity of water to give the stable solid monohydrate acid.[6] Melts of this solid (mp 34 °C, 3.5 M) were used to prepare dilute solutions of the acid.

Vanadyl trifluoroacetate solutions were prepared from solutions of vanadyl sulfate (Fisher) in trifluoroacetic acid and solutions of barium trifluoroacetate obtained from reagent grade barium carbonate and trifluoroacetic acid.

Hexaaquavanadium(II) trifluoroacetate solutions were obtained by zinc amalgam reduction of $VO(CF_3CO_2)_2$ solutions in 0.1 M CF_3CO_2H. The solutions were characterized by their visible absorption spectra[7] and by determination of the vanadium(II) concentration by reduction of a solution of $[Co(NH_3)_5Br]Br_2$,[8] followed by analysis of the cobalt(II) produced spectrophotometrically using the thiocyanate method.[9] Solutions prepared in this manner gave reproducible kinetics results, but solutions prepared by zinc amalgam reduction of V_2O_5 (Baker reagent grade) in 0.1 M CF_3CO_2H were found to give erratic results.

Chloropentaammineruthenium(II) solutions were prepared by zinc amalgam reduction of $[Ru(NH_3)_5Cl]Cl_2$ obtained[10] from $[Ru(NH_3)_6]Cl_3$ (Johnson Matthey Chemicals, Ltd.). Solutions of varying ruthenium(II) concentrations were prepared with NaCl and HCl, such that the total chloride ion concentration was 0.10 M and $[H^+]$ was 0.020 M, and were analyzed spectrophotometrically as $Ru(NH_3)_5py^{2+}$.[11]

Aquapentaammineruthenium(III) fluoroborate was prepared by a procedure similar to that of Stritar for preparation of the perchlorate salt.[12]

Tris(bipyridine)chromium(II) solutions were prepared by dissolving a weighed quantity of $[Cr(bpy)_3](ClO_4)_2$[13] in a 2×10^{-3} M solution of bipyridine adjusted to pH ~4 with HCl.

Tris(ethylenediamine)cobalt(III) trifluoromethanesulfonate was prepared by addition of ice-cold 5 M CF_3SO_3H to a concentrated solution of $[Co(en)_3]Cl_3$[14] until no further precipitation occurred. The mixture was heated on a steam bath until all of the precipitate dissolved, the solution was cooled slowly to salt–ice bath temperature, and then the product was collected by filtration and washed with 95% ethanol until the washings were nearly colorless and then with absolute alcohol and anhydrous ether. The product was recrystallized by dissolving in a minimum amount of hot water, adding concentrated CF_3SO_3H until precipitation occurred, and then treating as above. Anal. Calcd for $CoC_9H_{24}N_6F_9S_3O_9$: H, 3.53; C, 15.75; N, 12.24; Co, 8.59. Found: H, 3.45; C, 15.76; N, 12.31; Co, 8.65.

Tris(*trans*-1,2-diaminocyclohexane)cobalt(III) chloride monohydrate was prepared in a manner analogous to that used for the ethylenediamine complex. The chloride salt was converted to the trifluoromethanesulfonate salt by dissolving in boiling water and adding concentrated CF_3SO_3H. Anal. Calcd for $CoC_{21}H_{44}N_6F_9O_{10}S_3$: C, 29.10; H, 5.12; N, 9.70; Co, 6.80. Found: C, 29.08; H, 4.96; N, 9.64; Co, 6.97.

Methods. Spectra were recorded on a Beckman Acta V spectrophotometer. Kinetic measurements were performed either on a Gilford Model 2000 multiple sample absorbance recorder attached to a Beckman DU monochromator or on a Varian Techtron Model 635 spectrophotometer. Solutions were prepared using standard syringe techniques under an atmosphere of argon or nitrogen.

In the reductions with vanadium(II), solutions were prepared so that the final CF_3COO^- concentration was always 0.10 M and the initial H^+ concentration was about 0.09 M. The initial concentrations of the trifluoromethanesulfonate salts of the cobalt(III) complexes

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Table I. Second-Order Rate Constants k ($M^{-1}\ s^{-1}$)

		Oxidant	
Reductant	T, °C	$Co(en)_3{}^{3+}$	$Co(chxn)_3{}^{3+}$
$Cr(bpy)_3{}^{2+}$	10.0	12	12
	25.0	35 ± 2	40 ± 2
	40.0	93	121
V^{2+}	25.2	$(4.6 \pm 0.1) \times 10^{-4}$	$(2.6 \pm 0.1) \times 10^{-4}$
	34.8	9.4×10^{-4}	5.8×10^{-4}
	44.3	20×10^{-4}	12×10^{-4}
$Ru(NH_3)_5Cl^{+}$ [a]	17.0	2.7×10^{-3}	1.6×10^{-3}
	25.0	$(6.2 \pm 0.5) \times 10^{-3}$	$(3.8 \pm 0.1) \times 10^{-3}$
	35.0	16×10^{-3}	10×10^{-3}

[a] Apparent second-order rate constants. See text.

were (3–4) × 10^{-3} M, near the solubility limit in this medium, and the initial concentrations of vanadium(II) were (6–8) × 10^{-3} M. The reactions were observed spectrophotometrically at the absorbance maxima of 467 nm for $Co(en)_3{}^{3+}$ and 471 nm for $Co(chxn)_3{}^{3+}$ for up to 24 h, which still represented only 20% completion of the reduction. The absorbance–time data were analyzed using a nonlinear least-squares program to fit an integrated second-order rate law and independently determined extinction coefficients.[15]

In the reductions with ruthenium(II) the chloride ion concentration was maintained at 0.10 M with NaCl and the initial acid concentration was 2.0 × 10^{-2} M. The reactions occurred under second-order conditions with initial unequal concentrations in the range (3–10) × 10^{-3} M with either cobalt(III) or ruthenium(II) in excess, using the chloride salts of the cobalt(III) complexes. Again the absorbance–time data at 467 or 471 nm were analyzed using an integrated second-order rate law.

In the reductions with $Cr(bpy)_3{}^{2+}$ a medium of 0.1 M NaCl with 2 × 10^{-3} M bipyridine at pH 4.4 was employed. Pseudo-first-order conditions were used with initial concentrations of (4–40) × 10^{-4} M of the chloride salts of the cobalt(III) complexes and initial $[Cr(bpy)_3]^{2+}$ concentrations of (4–40) × 10^{-5} M. The reactions were observed at 562.5 nm, an absorbance maximum for $Cr(bpy)_3{}^{2+}$. Linear least-squares analyses were used to obtain the pseudo-first-order rate constants from the absorbance–time data and the second-order rate constants from the dependence of these on the cobalt(III) concentration.

Results

The second-order rate constants for the reduction of $Co(en)_3{}^{3+}$ and $Co(chxn)_3{}^{3+}$ by $Cr(bpy)_3{}^{2+}$, V^{2+}, and $Ru(NH_3)_5Cl^{+}$ under the conditions described in the Experimental Section are given in Table I. Specific aspects of the particular reactions are described below.

Reduction with $Cr(bpy)_3{}^{2+}$. The kinetics of these reactions were studied using pseudo-first-order conditions with an excess of the cobalt(III) oxidants. The reactions were complicated only by the need to maintain the reducing agent in a weak bipyridine buffer to obtain stable solutions. No dependence of the rate on the pH between 3.6 and 4.6 was observed. First-order plots linear to 4 half-lives were obtained. A linear dependence of the pseudo-first-order rate constants on the cobalt(III) concentration was observed at 25 °C.

The reduction of $Co(en)_3{}^{3+}$ with $Cr(bpy)_3{}^{2+}$ has been studied twice previously, both times in 0.1 M NaCl as used here. Zwickel and Taube[16] determined a rate constant of 37 $M^{-1}\ s^{-1}$ at 25 °C, within experimental error of the value found in this work. Ulstrup[17] obtained a value of 25 $M^{-1}\ s^{-1}$ in studies using an equilibrium mixture of two chromium(II) reducing agents.

Reduction with V^{2+}. The kinetics of these reactions were studied in a 0.1 M trifluoroacetate medium. Perchlorate was avoided due to its reduction by both V^{2+} and V^{3+}, and trifluoromethanesulfonic acid could not be used due to the low solubility of its cobalt(III) salts. The rate constant for reduction of $Co(en)_3{}^{3+}$ by V^{2+} in 1.0 M perchlorate media at 25 °C has been reported[18] to be ~2 × 10^{-4} $M^{-1}\ s^{-1}$ using 0.5 M $HClO_4$ and $NaClO_4$ and, more recently,[19] 7.2 × 10^{-4} $M^{-1}\ s^{-1}$ using 0.1 M $HClO_4$ and $LiClO_4$ to maintain the ionic strength at 1.0 M.

Reduction with $Ru(NH_3)_5Cl^{+}$. Attempts were made initially to use $Ru(NH_3)_6{}^{2+}$ as a reducing agent for the cobalt(III) complexes. However, induction periods were observed in the kinetics experiments on the reduction of $Co(en)_3{}^{3+}$. These disappeared when the $Ru(NH_3)_6{}^{2+}$ solutions were aged for several hours in 3 × 10^{-3} M HCl. Spectrophotometric analysis of the aged solutions treated with excess pyridine provided evidence for the presence of a pentaammineruthenium(II) species.[20] That $Ru(NH_3)_5H_2O^{2+}$ is not the reducing agent, however, was demonstrated by attempts to reduce $Co(en)_3{}^{3+}$ with ruthenium(II) solutions prepared by Zn(Hg) reduction of $[Ru(NH_3)_5H_2O](BF_4)_3$ in HBF_4. No reduction was observed over a period of 14 h.

In the presence of 0.1 M Cl^-, however, solutions of $Ru(NH_3)_5H_2O^{2+}$ reduce both cobalt(III) complexes slowly without induction periods. Evidence for the formation of $Ru(NH_3)_5Cl^{2+}$ as the ruthenium(III) product was obtained by spectrophotometry. The absorbance increase at 327 nm, a maximum for $Ru(NH_3)_5Cl^{2+}$, was proportional to the decrease at 467 nm, a maximum for $Co(en)_3{}^{2+}$, in a 1:1 ratio of the respective extinction coefficients. This in itself does not require that $Ru(NH_3)_5Cl^{+}$ be the active reducing agent, since $Ru(NH_3)_5Cl^{2+}$ could be formed from $Ru(NH_3)_5H_2O^{3+}$ and Cl^- after the redox reaction. This mechanism is eliminated, however, by the two observations (i) that $Ru(NH_3)_5H_2O^{2+}$ in the absence of Cl^- does not reduce $Co(en)_3{}^{3+}$ and (ii) that the reduction of $Co(en)_3{}^{3+}$ is irreversible due to the rapid acid hydrolysis of the initial $Co(en)_3{}^{2+}$ product. Although anation by Cl^- of $Ru(NH_3)_5H_2O^{3+}$ could shift the $Ru(NH_3)_5Cl^{2+}/Ru(NH_3)_5H_2O^{2+}$ redox potential[21] to allow reduction by $Ru(NH_3)_5H_2O^{2+}$, this anation reaction is too slow[22] to compete with the acid hydrolysis of $Co(en)_3{}^{2+}$. Hence the anation reaction cannot influence the thermodynamics of the redox reaction. The available evidence thus indicates that $Ru(NH_3)_5Cl^{+}$ is the active reducing agent under the conditions used. This conclusion is consistent with the relative redox potentials of the three ruthenium(II) species, since $Ru(NH_3)_5Cl^{+}$ is approximately 0.1 V more powerful a reducing agent than the other two complexes.[23]

The kinetics of the redox reactions were, therefore, studied using Zn(Hg) reduced solutions of $[Ru(NH_3)_5Cl]Cl_2$ in 0.1 M Cl^-. Since the equilibrium constant for reaction 1 is not

$$Ru(NH_3)_5H_2O^{2+} + Cl^- \rightleftharpoons Ru(NH_3)_5Cl^{+} + H_2O \qquad (1)$$

known for the conditions of these experiments, the experimental second-order rate constants are apparent rate constants determined from the rate law

$$-d[Co^{III}]/dt = k_{app}[Co^{III}][Ru^{II}] \qquad (2)$$

Identical conditions were employed for the reduction of both $Co(en)_3{}^{3+}$ and $Co(chxn)_3{}^{3+}$ so that direct comparison of these rate constants is appropriate. If the equilibrium constant of 1.4 M^{-1} for (1) measured[21] in 0.1 M $HClO_4$ is used, the actual rate constants for reduction by $Ru(NH_3)_4Cl^{+}$ at 25 °C are obtained by multiplying k_{app} by 8.

Discussion

There are no substantial differences between the rates of reduction of $Co(en)_3{}^{3+}$ and $Co(chxn)_3{}^{3+}$ measured under identical conditions, whether $Cr(bpy)_3{}^{2+}$, or $V(H_2O)_6{}^{2+}$, or $Ru(NH_3)_5Cl^{+}$ is used as the reducing agent. These reductants were chosen because they have markedly different ligand characteristics; they have rates of reduction that differ by 10^5. In each case the activation enthalpies and entropies for reduction of both Co(III) complexes are very similar (Table II), indicating that the equality of the rates persists over a wide temperature range and is not an artifact of the temperature

Table II. Activation Free Energies, Enthalpies, and Entropies for Reduction of $Co(en)_3^{3+}$ and $Co(chxn)_3^{3+}$ at 25 °C

	$\Delta G^{\ddagger}$, kJ mol^{-1}	$\Delta H^{\ddagger}$, kJ mol^{-1}	$\Delta S^{\ddagger}$, J mol^{-1} deg^{-1}
	$Cr(bpy)_3^{2+}$		
$Co(en)_3^{3+}$	64	47 ± 3	−59 ± 10
$Co(chxn)_3^{3+}$	64	54 ± 2	−32 ± 6
	V^{2+}		
$Co(en)_3^{3+}$	92	59 ± 2	−110 ± 4
$Co(chxn)_3^{3+}$	93	62 ± 4	−106 ± 12
	$Ru(NH_3)_5Cl^+$		
$Co(en)_3^{3+}$	86	72 ± 2	−47 ± 4
$Co(chxn)_3^{3+}$	87	74 ± 2	−44 ± 4

of measurement. These observations suggest a common mechanism for the reduction of the two Co(III) complexes. Any mechanism which would lead to a significant difference between the complexes can be excluded.

Both of the reactions most probably occur by outer-sphere electron transfer. The Co(III) complexes are substitution inert within the time period of the redox reactions and the ligands are not capable of a bridging role. Consequently, the relative rates can be analyzed in terms of the Marcus–Hush theory of outer-sphere electron-transfer reactions.[24] The rate constant for a reaction is given by (3) where κ is the probability factor

$$k = \kappa Z \exp(-\Delta G^*/RT) \tag{3}$$

for electron transfer in the activated complex, Z, the collison frequency for uncharged reactants, and ΔG^*, the free energy required to form the activated complex from separated reactants. This is given by (4) where the terms will be defined as they are discussed.

$$\Delta G^* = W + \frac{\lambda_o}{4} + \frac{\lambda_i}{4} + \left[\frac{\Delta G^\circ + W_p - W}{2}\right] + \left[\frac{(\Delta G^\circ + W_p - W)^2}{4(\lambda_o + \lambda_i)}\right] \tag{4}$$

The work term, W, involves the energy required to bring the reactants together and, hence, depends on the effective radii of the complexes. The effective radii depend on the relative orientation of the reactants. Two limiting mechanisms will be considered: an *equatorial approach* mechanism in which the reducing agent approaches the Co(III) complex in an equatorial plane perpendicular to its threefold axis and an *axial approach* mechanism in which electron transfer occurs along the threefold axis. The relative sizes of the two Co(III) complexes are illustrated in Figure 1, generated from published crystal structures,[25] in which it is apparent that the effective radii of the two complexes along the threefold axes are equal, whereas the $Co(chxn)_3^{3+}$ complex is substantially longer in the equatorial plane. The effective equatorial radii were determined by calculating the largest possible Co–C distance and adding 2.2 Å for the sum of the C–H bond length and the van der Waals radius of the hydrogen atom. The values so determined are 5.0 Å for $Co(en)_3^{3+}$ and 7.5 Å for $Co(chxn)_3^{3+}$. The effective axial radii were taken as 3.4 Å for both complexes, being the sum of the distance from the cobalt to the axial octahedral face plus the N–H bond distance and the van der Waals radius of the hydrogen atom. The effective radii of the reducing agents were taken[26] to be 7.0 Å for $Cr(bpy)_3^{2+}$, 3.6 Å for $V(H_2O)_6^{2+}$, and 4.2 Å for $Ru(NH_3)_5Cl^+$, assuming contact in the last case along the Ru–Cl axis.

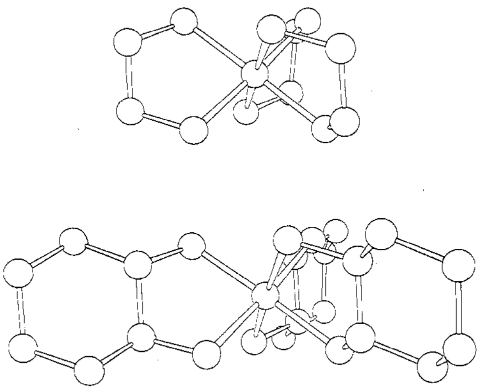

Figure 1. ORTEP drawing of $Co(en)_3^{3+}$ and $Co(chxn)_3^{3+}$ generated using published crystallographic data.[25]

The work term also depends, in an uncertain way,[27] on the ionic strength of the medium, which for each of the reactions studied was maintained at 0.1 M. Haim and Sutin[28] have observed that good agreement between some calculated and observed rate constants for electron transfer between oppositely charged ions could be obtained by using the mean of the work terms calculated for zero ionic strength and for the ionic strength actually used. Following this procedure, the values listed in Table III are obtained from equation 5, where Z_1 and Z_2 are the charges on the two reactants and d is the distance of closest approach. For the equatorial approach mechanism the smaller ethylenediamine complex has the larger work terms, but the differences between the two complexes are small and the ionic strength correction is smaller still, involving less than 0.4 kJ mol^{-1} difference between the complexes.

$$W = \frac{Z_1 Z_2 e^2}{\epsilon d} \exp(-\kappa d) \tag{5}$$

The outer-sphere reorganization energy λ_o also depends on the radii of the two reactants. This term, *assuming spherical reactants*, is given by (6), where r_1 and r_2 are the effective radii

$$\lambda_o = e^2 \left[\frac{1}{2r_1} + \frac{1}{2r_2} - \frac{1}{d}\right]\left[\frac{1}{D_{op}} - \frac{1}{D_s}\right] \tag{6}$$

of the two reactants, d is the distance between the centers in

Table III. Calculated Work and Outer-Sphere Reorganization Energies and Energy Differences (kJ mol^{-1})

	$Cr(bpy)_3^{2+}$			$V(H_2O)_6^{2+}$			$Ru(NH_3)_5Cl^+$		
	en	chxn	Δ	en	chxn	Δ	en	chxn	Δ
W^{eq} ($\mu = 0$)	8.83	7.28	1.55	12.30	9.54	2.76	5.77	4.52	1.25
W^{eq} ($\mu = 0.1$)	2.51	1.59	0.92	5.02	3.01	2.01	2.22	1.34	0.88
W^{eq} (mean)	5.67	4.44	1.23	8.66	6.28	2.38	3.99	2.93	1.06
W^{ax} ($\mu = 0$)	10.17	10.17	0	15.10	15.10	0	6.99	6.99	0
W^{ax} ($\mu = 0.1$)	3.43	3.43	0	7.28	7.28	0	3.14	3.14	0
W^{ax} (mean)	6.80	6.80	0	11.19	11.19	0	5.06	5.06	0
$\lambda_o^{eq}/4$	16.57	13.01	3.56	23.05	21.76	1.29	20.79	18.87	1.92
$\lambda_o^{ax}/4$	23.05	23.05	0	26.94	26.94	0	25.31	25.31	0
$\Delta(\Delta G^\circ)/2$			−0.97			−0.97			−1.32
$\Delta(\Delta G^*)^{eq}{}_{W+\lambda}$			4.79			3.67			2.98
$\Delta(\Delta G^*)^{eq}$			3.82			2.70			1.66

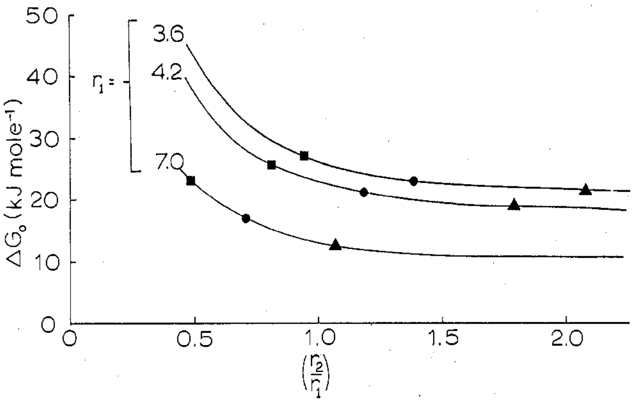

Figure 2. Plot of the outer-sphere reorganization energy as a function of radius ratio of the two reactants, evaluated for the radii r_1 of the three reducing agents used in this study: ●, values for equatorial reduction of $Co(en)_3^{3+}$; ▲, values for equatorial reduction of $Co(chxn)_3^{3+}$; ■, values for axial reduction.

the activated complex, D_{op} is the optical frequency dielectric constant (square of the refractive index), and D_s is the static (low-frequency) dielectric constant. We will again assume that $d = r_1 + r_2$, i.e., that the complexes must be in contact for electron transfer.[29] The dependence of λ_o on the ratio of the radii of the two complexes (r_2/r_1) evaluated for the radii of the three reducing agents, r_1, is shown in Figure 2.

From Figure 2 we note first that λ_o decreases with increasing size of the reducing agent. For a given reducing agent λ_o also decreases as the relative size of the oxidant increases, but above a ratio r_2/r_1 of about 1.5 no further decrease occurs. In other words, if one species is more than about 50% larger than the other, then the outer-sphere reorganization energy is dominated by the smaller species and further increase in the size of the larger species has no further effect. Marked on Figure 2 are the points appropriate for the two oxidants used in this study, assuming an equatorial approach mechanism. It is apparent that both cobalt complexes are sufficiently larger than the smaller reductants V^{2+} and $Ru(NH_3)_5Cl^+$ and that the differences in their relative size are insignificant. Only for the largest reductant, $Cr(bpy)_3^{2+}$, is an appreciable difference in outer-sphere reorganization energy predicted. The calculated energy differences are listed in Table III.

Any difference in the inner-sphere reorganization energy between the two cobalt(III) complexes is difficult to assess. Similar ligand fields and metal–ligand bond strengths are indicated, insofar as the visible absorption spectra and the redox potentials of the two complexes are nearly identical. This suggests that the energy required to expand the cobalt coordination sphere prior to electron transfer would be similar for both complexes, but no quantitative estimate can be made.

There is a small contribution to a difference in predicted rates from a difference in $\Delta G°$. When measured under comparable conditions, the redox potentials of the two cobalt(III) complexes differ by 20 mV, with $Co(chxn)_3^{3+}$ being the more difficult to reduce.[5] There is no difference between the work terms of reactants, W, and products, W_p, with both $V(H_2O)_6^{2+}$ and $Cr(bpy)_3^{2+}$ reductants since the charge products before and after electron transfer are identical (2 × 3). For $Ru(NH_3)_5Cl^+$ the charge product increases from 3 to 4 and a small correction is applied to the $\Delta(\Delta G°)$ value, using work terms adjusted for an intermediate ionic strength, as described above. Finally, the last term in (4) is negligible, for it contributes only in cases of rapid reactions (small $\lambda_o + \lambda_i$) with a large favorable free energy change ($\Delta G°$).

In summary, the outer-sphere electron-transfer theory contains three terms which can differ between $Co(en)_3^{3+}$ and $Co(chxn)_3^{3+}$. The overall free-energy change $(\Delta(\Delta G°)/2)$ favors slightly more rapid reduction of $Co(en)_3^{3+}$, with a predicted rate constant ratio k_{chxn}/k_{en} of 0.68. Since the effective radii of the two complexes are identical along the threefold axis, this ratio of rate constants is predicted for the axial approach mechanism, independent of the size of the reducing agent (but altered slightly to 0.59 due to work term differences for $Ru(NH_3)_5Cl^+$). For the equatorial approach mechanism, the larger radius of $Co(chxn)_3^{3+}$ results in smaller work terms and outer-sphere reorganization energies $(\Delta(\Delta G^*)^{eq}{}_{W+\lambda})$ by factors of 6.8 for $Cr(bpy)_3^{2+}$, 4.4 for $V(H_2O)_6^{2+}$, and 3.3 for $Ru(NH_3)_5Cl^+$, varying with the size and charge of the reducing agents. Combining these terms with the free-energy change gives $\Delta(\Delta G^*)^{eq}$ with predicted rate constant ratios (k_{chxn}/k_{en}) of 4.6, 3.0, and 1.9 for the three reducing agents. Hence, for the axial approach mechanism a constant ratio <1 is predicted, while for the equatorial approach mechanism variable ratios >1 are predicted.

These differences predicted between the two mechanisms are small and undoubtedly within the expected uncertainties of the theoretical model. These include medium effects on electrode potentials and $\Delta G°$, ionic strength corrections to work terms, uncertain inner-sphere contributions, and the general assumptions of spherical ions in a continuous dielectric. Neither mechanism predicts rate constant ratios in precise agreement with the observed ratios of 1.1, 0.57, and 0.61. The predictions of the equatorial approach mechanism are in agreement with the observations that reduction of the larger $Co(chxn)_3^{3+}$ is relatively faster with the larger $Cr(bpy)_3^{2+}$ reductant. On the other hand, the range of observed activation free-energy differences among the three reductants is only 2 kJ mol^{-1} (a factor of 2 in rate constants), in adequate agreement with the predictions of a common axial approach mechanism.

The results thus do not reveal specific steric effects on these electron-transfer reactions. They do require, however, *either* that a common axial approach mechanism occurs *or* that the electron-transfer probability through the cyclohexyldiamine ligand is equal to that through the smaller ethylenediamine ligand. This is not a trivial conclusion, for the smaller effective radii of the cobalt complexes in the axial approach mechanism result in larger activation free energies due to increased work (W^{ax}) and outer-sphere reorganization terms (λ_o^{ax}) (Table III). These correspond to rate differences of 20–150 between the axial and equatorial approaches, depending on the complex and reducing agent. Thus, if electron transfer through the ligands by the equatorial approach is forbidden, reaction by the axial approach requires this additional free energy. It follows that electron transfer through the ligands must be nonadiabatic by at least these factors (20–150) to impose the requirement of the higher energy axial approach mechanism. These factors apply to both ethylenediamine and cyclohexanediamine, for our results exclude the interpretation that one complex, e.g., $Co(en)_3^{3+}$, reacts by an equatorial approach mechanism and the other, i.e., $Co(chxn)_3^{3+}$, requires an axial approach. Hence, within the limitations of the analysis, we conclude that electron transfer through the two ligands is either equally probable or nonadiabatic.

Several results in the literature are related to this question of mechanism. The rate of electrochemical transfer has been found to decrease with increasing ligand size in the order $Co(en)_3^{3+} > Co(pn)_3^{3+} > Co(bn)_3^{3+} > Co(chxn)_3^{3+}$, but the rate differences are small and parallel the decrease in reduction potential.[5] Hence, the electrochemical results are consistent with either mechanism and similarly suggest that the probabilities of electron transfer through en and chxn are equal if an equatorial mechanism were to occur for electrochemical transfer at a platinum electrode.

The ability of cyclohexyl groups to mediate electron transfer has been investigated in two recent studies. One, mentioned in the Introduction, compared the effect of phenyl and cyclohexyl substituents on the rate of electron transfer between substituted phenanthroline complexes of iron(II) and iron(III).[4] A reduction of the rate by more than a factor of 10 was observed. In the second study the rate of intramolecular electron transfer between α-naphthylmethyl groups substituted in *trans*-1,4-cyclohexane was measured and compared with the similar rate between α-naphthylmethyls at the ends of a flexible four-carbon methylene chain.[30] The rate in the rigid cyclohexane derivative is 5 times slower, implying that the probability of electron transfer through several methylene groups is not unity. This suggests that in the present work an axial approach mechanism occurs, since a difference in electron-transfer probability between ethylenediamine and cyclohexanediamine should be observed at least in different activation parameters, reflecting the probability of electron transfer.

An obvious test of these conclusions is to examine electron transfer in a complex in which the axial approach is also sterically hindered. A suitable complex was not available when this work was in progress. The recently synthesized[31] Co(sepulchrate) ion appears to satisfy this requirement, but it is remarkable that the rate of electron exchange between its cobalt(II) and cobalt(III) complexes is 10^5 greater than between the tris(ethylenediamine) complexes! This suggests that other factors must be considered and that the role of ligands in electron transfer requires further investigation.

Finally, a comparison of the rates of reduction among the three reducing agents is possible. Since both cobalt(III) complexes are reduced at the same rate, only one of these need be discussed. In a recent article[32] the Marcus cross-reaction relationship was applied to the reduction of $\mathrm{Co(en)_3}^{3+}$ by $\mathrm{V(H_2O)_6}^{2+}$ and $\mathrm{Cr(bpy)_3}^{2+}$. For the former good agreement between observed and calculated rate constants is found, while for the latter the unmeasured self-exchange rate constant for $\mathrm{Cr(bpy)_3}^{2+/3+}$ is estimated to be $1.1 \times 10^9\ \mathrm{M^{-1}\ s^{-1}}$. From our results the self-exchange rate for $\mathrm{Ru(NH_3)_5Cl}^{+/2+}$ can be estimated, using the redox potential of -0.042 V[21] and making a correction to the measured rate constant for the equilibrium 1. The value of $3 \times 10^5\ \mathrm{M^{-1}\ s^{-1}}$ so obtained is reasonable for electron exchange between low-spin ruthenium(II) and ruthenium(III) complexes. In conclusion, our results, of course, imply that the self-exchange reactions of $\mathrm{Co(en)_3}^{3+/2+}$ and $\mathrm{Co(chxn)_3}^{3+/2+}$ occur at the same rate.

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Registry No. $\mathrm{Co(en)_3}^{3+}$, 14878-41-2; $\mathrm{Co(chxn)_3}^{3+}$, 41970-05-2; $\mathrm{Cr(bpy)_3}^{2+}$, 17632-84-7; V^{2+}, 15121-26-3; $\mathrm{Ru(NH_3)_5Cl}^{2+}$, 21560-19-0; $\mathrm{[Co(en)_3](CF_3SO_3)_3}$, 66416-81-7; $\mathrm{[Co(chxn)_3](CF_3SO_3)_3}$, 66416-80-6.

References and Notes

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