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Electron Transfer through Organic Structural Units. XVII. Reductions of Pentaamminecobalt(III) Complexes with Hexaammineruthenium(II). Partition of the Reduction of Carboxylatocobalt(III) Complexes into Outer- and Inner-Sphere Paths[1]

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The present treatment separates the reductions of carboxylatopentaamminecobalt(III) complexes by Cr^{2+}, Eu^{2+}, and V^{2+} into approximate outer- and inner-sphere fractions. log k values for outer-sphere reductions, with Cr^{2+} and Eu^{2+}, of complexes $R(NH_3)_5Co^{3+}$ (where R = NH_3, imidazole, pyrazole, pyridine, DMF, and dimethylnicotinamide) are linearly related to the corresponding log k values for $Ru(NH_3)_6{}^{2+}$: $\log k_{Ru} = 1.05 \log k_{Cr} + 2.30 = 1.05 \log k_{Eu} + 0.96$. A similar correlation links the Ru^{II} and V^{2+} series: $\log k_{Ru} = 1.05 \log k_V + 0.48$. These cross relations, when combined with measured rates for reductions of carboxylato complexes with $Ru(NH_3)_6{}^{2+}$, which are necessarily outer sphere, allow estimates of outer-sphere components of the reductions of 15 carboxylato complexes with Cr^{2+}, Eu^{2+}, and V^{2+}. The resulting partial rates (k^{OS} values) are 10^{-6}–10^{-1} times the observed specific rates for these reductions, the implication thus being that carboxylatocobalt(III) reductions by Eu^{2+} and V^{2+}, as well as those by Cr^{2+}, are predominantly inner sphere. Carboxylato groups are remarkably ineffective outer-sphere mediators; coordinated acetato is comparable to coordinated ammonia in this respect. Values of k^{OS} for the Cr^{2+} and V^{2+} reductions of the formato and acetato complexes agree closely with the outer-sphere rates reported for the corresponding reductions of dinuclear μ-carboxylato complexes of type XI. In contrast to outer-sphere reductions, for which electron supply at the oxidizing center appears to be important, rates of reaction of the carboxylatocobalt(III) complexes with the three aquated metal reductants are governed largely by the degree of nonbonded interaction between the carboxyl side chain and the reducing center, the rates for Cr^{2+} being much more sensitive to structural variation than those for Eu^{2+} or V^{2+}. It is suggested that with all three aquated reductants, steric crowding results in decreased values for the formation constants of the precursors but that with Cr^{2+}, bulky substituents also affect the rate of internal electron transfer by interfering with distortion of Cr–OH_2 bonds by water molecules in the second coordination sphere, a distortion which is necessary for nonzero overlap between the e_g orbitals of Cr(II) (one of which furnishes the reducing electron) and the π orbitals of the carboxyl bridge.

The reductions, using Cr^{2+}, of a large variety of carboxylatocobalt(III) complexes proceed predominantly *via* the inner-sphere path in one or more of its variations,[2] and the same appears to be true also for reactions with Cu^+,[3a] V^{2+},[3b] and Eu^{2+}.[3c] Each of these reactions, however, must have an outer-sphere component, however small. The latter is presumed to be less sensitive to structural variation than the inner-sphere portion and could conceivably become the major kinetic contributor if the bridged path were suitably retarded.[4] Only a few upper limits for the specific rates of such minor components have been estimated for Cr^{2+},[4,5] and none for the other reductants.

In the present work, we employ measured rates of reduction by $Ru(NH_3)_6{}^{2+}$ (an outer-sphere reagent under our conditions[6]) in conjunction with a series of observed linear free energy relationships applying to outer-sphere reductions, to estimate outer-sphere specific rates for reduction of a variety of carboxylato complexes using Cr^{2+}, Eu^{2+}, and V^{2+}. This study also affords a glimpse as to the manner in which outer-sphere rates vary with the structure of the carboxylato ligand. Although such variation is sizable, we find no case involving these aquo-substituted reductants in which this route predominates.

Experimental Section

Materials. Hexaammineruthenium(III) chloride, $(NH_3)_6RuCl_3$ (Matthey-Bishop), was purified by dissolving in a minimum volume of 0.01 *M* HCl, filtering off any residue, cooling the filtrate to 0°, and reprecipitating by slow addition of saturated LiCl solution. Solutions of $Ru(NH_3)_6{}^{2+}$ for rate experiments were prepared by taking a 0.04 *M* solution of the reprecipitated Ru(III) complex (in a solution 0.01 *M* in HCl containing enough LiCl to bring the ionic strength to 0.50), purging this solution with argon for 30 min in a cell stoppered with a rubber serum cap, and then injecting a known deficient amount of 1.0 *M* $CrCl_2$ or $EuCl_2$.[7] After 15 min, the resulting solution could be used for rate measurements. The concentration of Ru(II) was determined by the method of Endicott.[8] The known[9] reduction of ClO_4^- by $Ru(NH_3)_6{}^{2+}$ rules out the use of perchlorates as supporting electrolytes. All preparations and reactions of Ru(II) were carried out under a blanket of argon.

Cobalt(III) complexes, available as their perchlorates from previous studies,[3] were converted to their chlorides by passing their aqueous solutions through an anion-exchange column (AG2-X8, BioRad, 200–400 mesh) in the chloride form. Removal of solvent water by rotary evaporation at room temperature yielded the solid chlorides, which were dried *in vacuo*.[10]

Rate Measurements. Rates were estimated from measurements of absorbance decreases on the Cary 14 recording spectrophotometer.[3,4b] Readings were made at the low-energy maxima for the Co^{III} complexes near 500 nm. Reactions were run in a 1.0-cm cylindrical cell, except for those few having specific rates greater than 1.0 M^{-1} sec^{-1}, which were carried out in a 10.0-cm cell. Reactions were first order each in Co(III) and in Ru(II), but rate studies were generally performed under pseudo-first-order conditions with at least a tenfold excess of reductant. The initial value of (H^+) was generally 0.013

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[1] Sponsorship of this work by the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

[2] H. Taube and E. S. Gould, *Accounts Chem. Res.*, 2, 321 (1969).

[3] (a) E. R. Dockal, E. T. Everhart, and E. S. Gould, *J. Amer. Chem. Soc.*, 93, 5661 (1971); (b) J. C. Chen and E. S. Gould, *ibid.*, 95, 5539 (1973); (c) F.-R. F. Fan and E. S. Gould, *Inorg. Chem.*, 13, 2639 (1974).

[4] See, for example: (a) F. Nordmeyer and H. Taube, *J. Amer. Chem. Soc.*, 90, 1162 (1968); (b) E. S. Gould, *ibid.*, 90, 1740 (1968).

[5] M. B. Barrett, J. H. Swinehart, and H. Taube, *Inorg. Chem.*, 10, 1983 (1971).

[6] For a brief summary of the evidence of the outer-sphere character of reductions with $Ru(NH_3)_6{}^{2+}$ and answers to earlier reservations on the point, see D. P. Rillema, J. F. Endicott, and R. C. Patel, *J. Amer. Chem. Soc.*, 94, 394 (1972), footnote 54.

[7] (a) R. C. Patel and J. F. Endicott, *J. Amer. Chem. Soc.*, 90, 6364 (1968); (b) J. R. Pladziewicz, T. J. Meyer, J. A. Broomhead, and H. Taube, *Inorg. Chem.*, 12, 639 (1973). (c) In our hands, Ru(II) solutions prepared by reduction with $EuCl_2$ gave somewhat more satisfactory kinetic data than those prepared by reduction with $CrCl_2$.

[8] J. F. Endicott and H. Taube, *Inorg. Chem.*, 4, 437 (1965).

[9] T. W. Kallen and J. E. Earley, *Chem. Commun.*, 61 (1971).

[10] Satisfactory elemental analyses of the resulting formato, acetato, trifluoroacetato, trimethylacetato, and triethylacetato chlorides (Galbraith Laboratories) confirmed that this exchange of counterions proceeded without complication.

M, about 7 times the value of $(Co^{III})_0$. Since every Co^{III} reduced releases five molecules of NH_3, (H^+) dropped to less than 0.004 *M* during the course of each run. In no instance did distortion of the kinetic curve accompany this decrease in acidity; hence, rates may be taken to be independent of (H^+) in the range 0.004–0.013 *M*. Measurements were not extended to higher acidities, for here the picture may become complicated by acid-catalyzed aquation of $Ru(NH_3)_6^{2+}$.[11-13] As in the earlier Cu^+ studies,[3a] Co^{III} was added to the reductant. Ionic strengths were adjusted to 0.5 by addition of LiCl. Reactions were followed for at least 5 half-lives. Rate constants evaluated from successive half-life periods within a single run agreed to within 5%; no trends indicative of systematic errors were noted, and average values did not differ significantly from values obtained from least-squares treatment of logarithmic plots of absorbance differences against reaction time. Specific rates obtained from replicate runs checked to better than 7%. Temperatures were kept at 25.0 ± 0.2° during the entire series of experiments.

Stoichiometry Studies. Stoichiometry experiments, in which deficiency quantities of $Ru(NH_3)_6^{2+}$ were treated with representative cobalt(III) complexes, were carried out in a manner analogous to that earlier described for Cr^{2+} reductions.[14] Yields of Co^{2+} of 99–100% were obtained from reductions of the formato, fluoroacetato, trifluoroacetato, glycolato, benzoylformato, and *N,N*-dimethylnicotinamide complexes of $(NH_3)_5Co^{III}$ in 0.013 *M* HCl.

Results and Discussion

Range of Specific Rates. Rate constants for reductions by $Ru(NH_3)_6^{2+}$ are assembled and compared with those for reductions by Eu^{2+}, Cr^{2+}, and V^{2+} in Tables I and II. The specific rate for the triethylacetato complex appears to be the lowest Co(III)–Ru(II) value thus far reported and may be compared to rate constants near 10^3 M^{-1} sec^{-1} recorded for the halopentaamminecobalt(III) species.[13a] The span bracketed by these extremes (about 10^5) is considerably narrower than the corresponding ranges for Eu^{2+} (10^7) and Cr^{2+} (nearly 10^{10});[3c] more important, reduction rates for the carboxylato complexes cover a range of only 10^2 with $Ru(NH_3)_6^{2+}$, reflecting the denial to this reductant[6] of each of the several rate-enhancing variants of the inner-sphere path.[15]

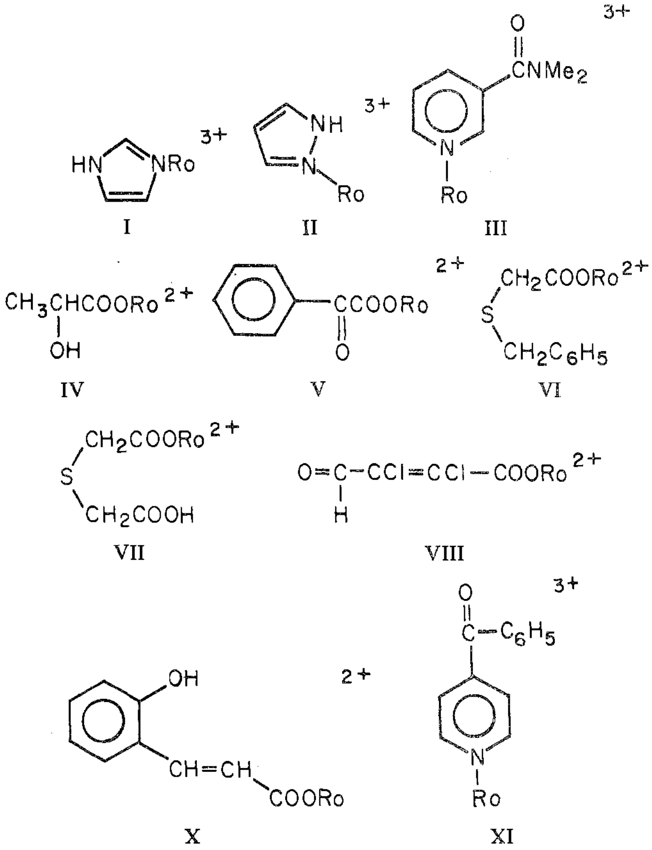
Structure-Reactivity Correlations. Although a number of workers have considered the influence of oxidant-bound ligands on the rates of outer-sphere reactions,[16] no quantitative treatment applicable both to gross changes and to fine alteration of ligand structure has as yet appeared. Marcus[17] has emphasized that specific rates of outer-sphere reactions should be closely related to respective free energy changes, and Earley,[16a] Endicott,[6] and Sutin,[18] among others, have described reaction series in which values of log *k* are found to be linear functions of $\Delta G°$. The difficulty in measuring free energy changes associated with irreversible reductions of substitution-inert $(NH_3)_5Co^{III}$ complexes militates against direct confirmation of such a relationship in the present series (although there are indirect indications that it is applicable, at least in part). Correlation of rates with ligand field strengths, as estimated, for example, from the frequencies associated with d–d transitions in the oxidant,[19] although perhaps appropriate for a series in which the ligand environment of the metal center undergoes substantial change, is not of use here since the various carboxylato complexes exhibit very nearly the same absorption maxima[14] (as do the various pyridine complexes[20]).

Linck[16b] has commented upon the importance of σ-bonding strengths of ligands, as reflected by their relative basici-

Table I. Reductions of Pentaamminecobalt(III) Complexes $R(NH_3)_5Co^{3+}$, Having Nonbridging Ligands, with $Ru(NH_3)_6^{2+}$, Cr^{2+}, and V^{2+} [a]

R	k_{Ru}[b]	k_{Eu}[c,d]	k_{Cr}[c,d]	k_V[c,e]
Ammonia	0.024	0.0030	2.2×10^{-4}	0.010
Imidazole (I)	0.037	0.0063	3.5×10^{-4}	0.020
Pyrazole (II)	0.23	0.034	2.3×10^{-3}	0.120
Pyridine	0.67	0.083	4.0×10^{-3}	0.24
N,N-Dimethylformamide[f]	1.2	0.13	7.0×10^{-3}	0.35
N,N-Dimethylnicotinamide (III)	3.7	0.45	3.0×10^{-2}	1.38

[a] Specific rates in M^{-1} sec^{-1} at 25°. [b] $(H^+)_0 = 0.013$ *M*, $(Ru^{II}) = 0.002–0.03$ *M*, $(Co^{III})_0 = 2 \times 10^{-3}$ *M*, $\mu = 0.50$; supporting electrolyte LiCl. [c] $(H^+) = 1.0$ *M*, $\mu = 1.1$; perchlorate medium. [d] E. R. Dockal and E. S. Gould, *J. Amer. Chem. Soc.*, 94, 6673 (1972). [e] See ref 3b. [f] O-bound Co^{III} (see ref 4b).



Ro = "roseo" = $(NH_3)_5Co^{III}$

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(11) (a) P. C. Ford, J. Retz, J. R. Kuempel, and H. Taube, *Inorg. Chem.*, 7, 1976 (1968); (b) A. Zanella and H. Taube, *J. Amer. Chem. Soc.*, 94, 6403 (1972).

(12) Early specific rates recorded for the reduction of carboxylatocobalt(III) complexes, presumably by $Ru(NH_3)_6^{2+}$, appear to be about one order of magnitude too great, due very probably to substantial aquation of the reductant to the more rapidly reacting $Ru(NH_3)_5H_2O^{2+}$. Thus, Endicott[13a] reported a specific rate of 0.6 ± 0.1 M^{-1} sec^{-1} for reduction of the binoxalato complex of $(NH_3)_5Co^{III}$ (in 0.004 *M* HCl with Co^{III} in excess), whereas Price[13b] assigned a rate constant of 0.027 to this reaction (in 0.0073 *M* HCl with Ru^{II} in excess).

(13) (a) J. F. Endicott and H. Taube, *J. Amer. Chem. Soc.*, 86, 1686 (1964); (b) H. J. Price and H. Taube, *Inorg. Chem.*, 7, 1 (1968).

(14) E. S. Gould and H. Taube, *J. Amer. Chem. Soc.*, 86, 1318 (1964).

(15) Note, however, that this 10^2-fold rate variation, resulting from structural modifications at sites well removed from the oxidizing metal center, is substantially greater than the 30-fold variation observed for the Cr(II) reductions of nitrile derivatives of $(NH_3)_5Co^{III}$ by R. J. Balahura, G. B. Wright, and R. B. Jordan, *J. Amer. Chem. Soc.*, 95, 1137 (1973), and regarded by these authors as being too large to be consistent with outer-sphere reduction.

(16) For recent reviews see: (a) J. E. Earley, *Progr. Inorg. Chem.*, 13, 243 (1970); (b) R. G. Linck, *MTP (Med. Tech. Publ. Co.) Int. Rev. Sci.: Inorg. Chem., Ser. One,* 9, 303 (1972).

(17) (a) R. A. Marcus, *J. Chem. Phys.*, 24, 970 (1956); (b) *Annu. Rev. Phys. Chem.*, 15, 155 (1964).

(18) G. Dulz and N. Sutin, *Inorg. Chem.*, 2, 917 (1963).

(19) T. J. Williams and C. S. Garner, *Inorg. Chem.*, 9, 2058 (1970).

(20) E. S. Gould, *J. Amer. Chem. Soc.*, 89, 5792 (1967).

Table II. Reductions of Pentaamminecobalt(III) Complexes $R(NH_3)_5Co^{III}$, Having Bridging Ligands, with $Ru(NH_3)_6^{2+}$, Eu^{2+}, Cr^{2+}, and V^{2+}[a]

R	k_{Ru}[b]	k_{Eu}[c,d]	k_{Cr}[c,e]	k_V[c,f]	k^{OS}(calcd)[g] Cr^{2+}	Eu^{2+}	V^{2+}	Fraction OS Cr^{2+}	Eu^{2+}	V^{2+}
Triethylacetato	0.0072	0.068	0.0022	0.127	6×10^{-5}	0.0011	0.004	0.03	0.016	0.029
Trimethylacetato	0.0087	0.18	0.0070	0.22	7×10^{-5}	0.0014	0.004	0.011	0.008	0.018
Acetato	0.022	1.7	0.35	1.25	2×10^{-4}	0.003	0.009	6×10^{-4}	0.002	0.007
Formato	0.092	16	7.2	3.5	7×10^{-4}	0.012	0.04	9×10^{-5}	8×10^{-4}	0.011
Fluoroacetato	0.087	3.8	0.12		6×10^{-4}	0.012		0.005	0.003	
Trifluoroacetato	0.18	1.3	0.034	0.86	0.0013	0.024	0.07	0.038	0.018	0.09
Trichloroacetato	0.25	0.82				0.033			0.04	
Glycolato	0.047	88	3.1	8.2	4×10^{-4}	0.007	0.02	1×10^{-4}	8×10^{-5}	0.003
Lactato (IV)	0.047	91	6.7		4×10^{-4}	0.007		5×10^{-5}	7×10^{-5}	
Benzoylformato (V)	0.31	3.7×10^4				0.041			1×10^{-6}	
S-Benzylthioglycolato (VI)	0.041	1.84	5.3	1.64	3×10^{-4}	0.006	0.02	6×10^{-5}	0.003	0.012
Thiodiglycolato (VII)	0.050	18	150		5×10^{-4}	0.007		3×10^{-6}	4×10^{-4}	
Oxydiacetato	0.17	490	0.27		0.0012	0.023		4×10^{-3}	4×10^{-5}	
Mucochlorato (VIII)	0.55	130				0.070			5×10^{-4}	
o-Hydroxycinnamato (IX)	0.035	1.95	1.30		3×10^{-4}	0.0050		2×10^{-4}	0.003	
4-Benzoylpyridine (X)	4.5		4.7×10^4	4.5	0.027		1.5	6×10^{-7}		0.33

[a] Specific rates in M^{-1} sec^{-1} at 25°. [b] $(H^+) = 0.013\ M$, $(Ru^{II}) = 0.002$–$0.03\ M$, $(Co^{III})_0 = 2 \times 10^{-4}$–$2 \times 10^{-3}\ M$, $\mu = 0.50$; supporting electrolyte LiCl. [c] $(H^+) = 0.1\ M$, $\mu = 1.0$; supporting electrolyte $LiClO_4$. [d] See ref 3c. [e] Values mainly from ref 2 and 3c and work cited therein. [f] See ref 3b. [g] Estimated specific rates for outer-sphere (OS) reduction, calculated from eq 1 and 2.

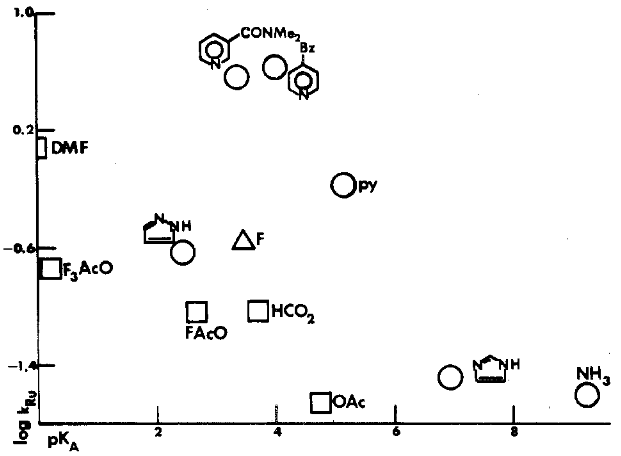

Figure 1. Plot of log k for $Ru(NH_3)_6^{2+}$ reductions of pentaamminecobalt(III) complexes $R(NH_3)_5Co^{III}$ *vs.* pK_A values for ligand R. Reaction conditions for Ru^{II} reductions are listed in Tables I and II. Note that despite the general scatter, the nitrogen-bound ligands (○), except for pyrazole, fall near one line, and the oxygen-bound ligands (□) near another.

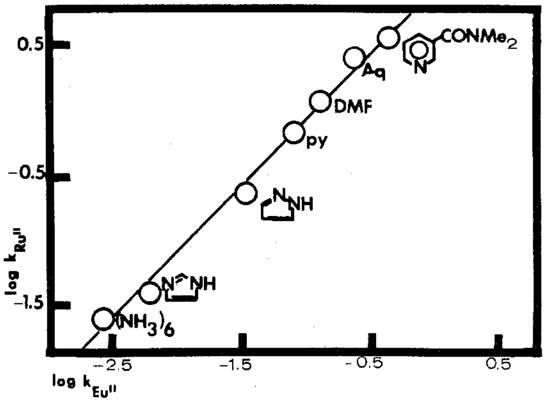

Figure 2. log–log plot comparing the specific rates of outer-sphere reductions of pentaamminecobalt(III) complexes $R(NH_3)_5Co^{3+}$, by $Ru(NH_3)_6^{2+}$ and Eu^{2+}. Reaction conditions are listed in Tables I and II. The least-squares line shown corresponds to the equation $\log k_{Ru^{II}} = 1.05 \log k_{Eu^{2+}} + 0.96$.

ties toward H_{aq}^+, but both he[21] and Endicott[7a] have pointed out that a quantitative correlation of rates with basicities, embracing a broad range of ligand structures, is not to be expected. The scatter of points in Figure 1 indeed underlines the limitations of this approach when applied to several types of substituent, but the treatment appears to hold up reasonably if ligands of only one type (substituted pyridines or substituted carboxylato groups) are being compared.[22] Probably the most astonishing facet of the present work is the observed ineffectiveness of the ordinary carboxylato groups as outer-sphere mediators; note, for example, that $Ru(NH_3)_6^{2+}$ reduces $(NH_3)_5CoOAc^{2+}$ and $(NH_3)_6Co^{3+}$ at nearly the same specific rate, despite the marked difference in basicity between OAc^- and NH_3.

The oxidants listed in Table I are known to react with Cr^{2+}, Eu^{2+}, and V^{2+} without intervention of bridged intermediates.[3b,23] The k_{Ru} values in this group are very nearly proportional to the corresponding k_{Eu} and k_{Cr} values, and a similar proportionality exists with the k_V values. The Ru^{II}-Eu^{2+} correlation is shown as Figure 2, with the least-squares line representing the relationship

$$\log k_{Ru} = 1.05 \log k_{Eu} + 0.96 \qquad (1)$$

Similar correlations with Cr^{2+} and V^{2+} yield

$$\log k_{Ru} = 1.05 \log k_{Cr} + 2.30 = 1.05 \log k_V + 0.48. \qquad (2)$$

Thus, although the structural types employed as the "sixth ligand" within this group of oxidants include three different aromatic heterocyclic systems, a nonaromatic N-bound ligand, and an O-bound amide, we are nevertheless dealing with systems which are well behaved in the Marcus sense,[17] *i.e.*, systems in which variations in $\Delta G^{\ddagger}$ resulting from the alteration of the ligand environment at one center operate independently of the coreagent.[24]

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(21) C. Bifano and R. G. Linck, *J. Amer. Chem. Soc.*, **89**, 3945 (1967).

(22) Note that in the pyridine series the 3-$CONMe_2$ complex is reduced by $Ru(NH_3)_6^{2+}$ at nearly the same rate as the 4-COC_6H_5 derivative. Since the "lead-in" function associated, in inner-sphere reactions, with unsaturated donor groups does not operate here, selective conjugative relationships, as observed for reductions with Cr(II),[2] should play no part with Ru(II).

(23) E. R. Dockal and E. S. Gould, *J. Amer. Chem. Soc.*, **94**, 6673 (1972).

(24) Although log–log plots having unit slope were predicted by Marcus,[16b] sizable departures have been reported, even when the two reaction series being compared utilize outer-sphere mechanisms.[17,25] Slopes different from unity are usual when one[26] or both[3b] series are inner sphere.

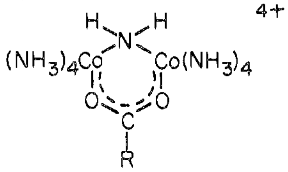
(25) H. Diebler and N. Sutin, *J. Phys. Chem.*, **68**, 174 (1964).

Reduction of Carboxylato Complexes. Outer-Sphere Components for Multipath Reactions. Values of k_{Ru} for carboxylatocobalt(III) derivatives are listed at the left of Table II. Within this series, only the single trend already noted for N-bound oxidants[21] is conspicuous—electron withdrawal from $\mathrm{Co^{III}}$ facilitates reaction. Halogenation of the side chain or incorporation of a carbonyl function accelerates, whereas substitution of methyls for α hydrogens retards. On this basis, we would further expect the reductions of such complexes as acetato and levulinato, which undergo measurable protonation at acidities below 1 M,[5,14] to exhibit hydrogen ion catalysis. Although the acid-catalyzed aquation of $\mathrm{Ru(NH_3)_6}^{2+}$ complicates confirmation of this point,[11] such catalysis has been reported for reduction of $\mathrm{(NH_3)_5CoF^{2+}}$.[7a] In the carboxylato series there is no perceptible similarity in pattern between the values of k_{Ru} and the observed values of k_{Cr}, k_{Eu}, or k_{V}.

Our interest in these carboxylatocobalt(III)–ruthenium(II) rates lies principally in their use, in combination with the correlations expressed here as eq 1 and 2, to estimate outer-sphere specific rates for reduction of these same complexes by $\mathrm{Cr^{2+}}$, $\mathrm{Eu^{2+}}$, and $\mathrm{V^{2+}}$ and thus compare them to measured specific rates. These calculated outer-sphere components (k^{os} values) are listed in Table II, as is the fraction of each reaction proceeding by the outer-sphere path.

The generally approximate nature of such extrathermodynamic relationships[27] obviously limits the precision of the treatment employed; nevertheless, several points emerge. The outer-sphere values for the $\mathrm{Cr^{2+}}$ series bolster Barrett's conclusion[5] that even the least reactive carboxylatocobalt(III) complexes are reduced mainly *via* carboxyl bridging,[28] with the distribution between paths becoming still more one-sided for the more rapid derivatives. Moreover, the magnitudes of the outer-sphere components for $\mathrm{V^{2+}}$ and $\mathrm{Eu^{2+}}$ add substantially to earlier indirect evidence[3b,c,13b,16b] that the inner-sphere path predominates with these reductants as well.

The reality of our k^{OS} values is confirmed by comparison with specific rates reported by Scott and Sykes[29] for reduction of μ-carboxylato complexes of type XI, to which the inner-sphere path is forbidden because the carbonyl oxygen is blocked off by coordination. With both the μ-acetato and μ-formato complexes, values of k_{Cr} and k_{V} are very nearly twice the corresponding k^{OS} values in Table II. When it is further noted that the complexes reduced by these authors contain two cobalt(III) centers and that the (inner-sphere) reduction of the second $\mathrm{Co^{III}}$ is sufficiently rapid that the first reduction is rate determining, the agreement between their values and ours is remarkably close.



XI ($\mathrm{R = H, CH_3}$)

The carboxylato reduction patterns for the aquated metal centers, although dissimilar to the pattern for $\mathrm{Ru(NH_3)_6}^{2+}$, closely resemble each other. Indeed, among the slower oxidations,[30,31] observed values for log k_{Cr}, log k_{Eu}, and log k_{V} are linearly related not only to each other[3b,c] (albeit with nonunit slopes) but also to Taft's steric substituent parameters.[32] Thus, in contrast to outer-sphere reductions, for which electron supply by the ligand appears to be important, the simpler inner-sphere reductions proceed at rates governed in considerable measure by the degree of nonbonded interaction between the carboxyl side chain and the reducing center.

It is appropriate to consider here the $\mathrm{Eu^{2+}}$ reduction of the conjugate acid of the acetato complex, to which a specific rate 0.25 M^{-1} sec^{-1} (25°, $\mu = 4.0$) has been assigned.[3c] If it is assumed that protonation ties off the lead-in carbonyl function, then this reduction may be taken as outer sphere. The rate constant, although considerably greater than the k^{OS} values for $\mathrm{Eu^{2+}}$ in Table II, nevertheless remains reasonable in view of the severity of electron withdrawal resulting from protonation of the ligand.[33,34]

The present results underscore several of the factors which control the distribution between paths in a reaction series where two mechanisms are possible. Among the oxidants in Table II, the outer-sphere component is greatest for the $\mathrm{V^{2+}}$ reduction of the 4-benzoylpyridine complex (X); this reflects mainly the substitution-controlled upper limit (near 40 M^{-1} sec^{-1}) for inner-sphere reductions by V(II)[31] and merely represents, in miniature, what has previously been observed, in more striking fashion, with other reactions of this reducing center.[35] More generally, the inner-sphere fraction dwindles as the lead-in site becomes more crowded, as electron density shifts from the oxidizing center, and as conjugation between possible lead-in functions and the electron-transfer terminus is disrupted. Thus, among the aliphatic ligands, the outer-sphere fraction is maximized by substitution of bulky but electron-withdrawing halogen atoms α to the carboxyl.[36] More pronounced trends appear among $\mathrm{Cr^{2+}}$ reductions in the pyridine series where, for example, the outer-sphere fraction increases from about 0.001 to 0.3 when a $\mathrm{CONH_2}$ substituent, a lead-in group, is moved from

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(26) P. R. Guenther and R. G. Linck, *J. Amer. Chem. Soc.*, 91, 3769 (1969).

(27) See, for example, P. R. Wells, "Linear Free Energy Relationships," Academic Press, London, 1968, pp 1-56.

(28) Our k^{OS} values lie well below the upper limits given by Barrett, *et al.*,[5] for $\mathrm{Cr^{2+}}$ reduction of the trimethylacetato (0.0011 M^{-1} sec^{-1}) and acetato (0.018 M^{-1} sec^{-1}) complexes under corresponding conditions.

(29) K. L. Scott and A. G. Sykes, *J. Chem. Soc., Dalton Trans.*, 1832 (1972).

(30) Rate comparisons involving reductions slower than that of the formato complex in this series are generally not complicated by the substitution-controlled upper limit for V(II)[13b,26,31] nor by selective chelation effects.[3c]

(31) (a) B. R. Baker, M. Orhanovic, and N. Sutin, *J. Amer. Chem. Soc.*, 89, 722 (1967); (b) C. Norris and F. R. Nordmeyer, *Inorg. Chem.*, 10, 1235 (1971).

(32) (a) R. W. Taft, Jr., in "Steric Effects in Inorganic Chemistry," M. S. Newman, Ed., Wiley, New York, N. Y., 1956, p 598. (b) A newer scale of steric substituent constants has been proposed by R. Fellous and R. Luft, *J. Amer. Chem. Soc.*, 95, 5593 (1973). However, these authors have considered too narrow a variety of substituents to allow correlation of the reduction series at hand.

(33) (a) Protonation of acetic acid, for example, enhances its acidity by more than 10 pK units: E. M. Arnett, *Progr. Phys. Org. Chem.*, 1, 339 (1963). (b) Preliminary experiments by Mrs. Jean Thomas, Kent State University, 1973, yield a specific rate 1.15 M^{-1} sec^{-1} (25°, $\mu = 4.0$) for the V(II) reduction of the protonated acetato complex (likewise outer sphere). The ratio $k_{\mathrm{V}}/k_{\mathrm{Eu}}$ for this species thus lies close to the corresponding ratios (at $\mu = 1.0$) for the outer-sphere oxidants in Table I. The value of k_{Cr} may be estimated as 0.01 M^{-1} sec^{-1} at $\mu = 4.0$ but has not yet been observed experimentally.[5,34]

(34) A. Liang and E. S. Gould, *Inorg. Chem.*, 12, 12 (1973).

(35) Reduction by $\mathrm{V^{2+}}$, of *trans*-$\mathrm{Co(en)_2H_2OCl^{2+}}$ ($k = 2.60 \times 10^2$ M^{-1} sec^{-1} at 25° and $\mu = 1.0^{26}$),[2] for example, must have an outer-sphere component at least 85% of the total. Even more dramatically, reduction of the pyrazine derivatives of $\mathrm{(NH_3)_5Ru^{III}}$, which proceeds at a specific rate greater than 10^6 (W. Movius and R. G. Linck, unpublished experiments, University of California, San Diego, Calif., 1969), can have an inner-sphere fraction no greater than 4×10^{-5}, despite the presence of the possible lead-in site at the uncoordinated ring nitrogen.

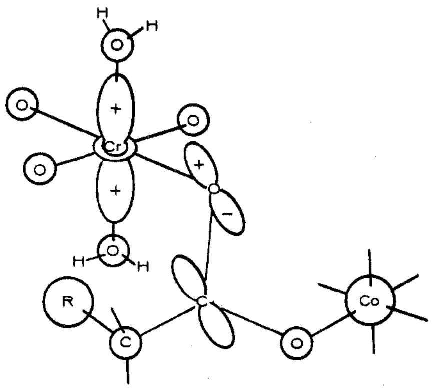

Figure 3. Precursor complex for inner-sphere reduction of a carboxylatocobalt(III) complex by $Cr(H_2O)_6^{2+}$. The reducing electron from Cr(II) is taken as arising from the d_{z^2} orbital shown. Note the zero overlap between this orbital and the acceptor carboxyl π orbital unless the coordination sphere of Cr(II) is subjected to distortion which is unsymmetric with respect to the carboxyl plane.

the γ to the less effectively conjugated β position[4a,37] and rises still further to above 0.90 when crowding in the vicinity of the amide oxygen is increased by N-methylation.[4b]

The drop in inner-sphere rates with increased steric crowding may reasonably by attributed in part to lower values for the formation constants of the precursor, a trend which would be expected to be quite similar for the three dipositive aquated reductants. Since, however, the rates for Cr^{2+} (where, for example, the formato and triethylacetato values span a range of 3300) are much more sensitive than those for V^{2+} and Eu^{2+} (for which the corresponding ranges are 27 and 230), we suspect the operation of an additional effect with this d^4 center. The mismatch of orbital symmetry between the e_g orbitals of octahedrally coordinated Cr(II) (one of which furnishes the reducing electron) and the π orbitals of the carboxylato bridge[2] does not extend to V^{2+}, which transfers a t_{2g} electron, nor to the 4f electron lost from Eu^{2+}.[38] As shown in Figure 3, there will be zero overlap between the appropriate Cr^{2+} and carboxyl orbitals (hence, minimal redox bridging) unless the ligand environment about Cr(II) is subjected to distortion which is unsymmetric with respect to the carboxyl plane. Since such distortion can occur most readily by the stretching or breakage of a $Cr-OH_2$ bond above or below this plane and, hence, is aided by interaction with water molecules in the second coordination sphere, it should be adversely affected by the presence of nearby lipophilic groups which serve to disarrange the solvent ordering.

On the other hand, properly oriented polar substituents which can hydrogen bond to one of the primary-sphere water molecules furthest removed from the carboxyl plane may facilitate reaction. This appears to be a reasonable mode of action for α-SR groups in Co(III)-bound carboxyl. Such groups have long been known to increase k_{Cr}[39] but not k_V or k_{Eu}.[3c] However, in no case has evidence for a chelated product or intermediate having an S-Cr^{III} bond been obtained for a reaction of this type, although it is anticipated that such a species, if formed, should undergo aquation only slowly.[40-42]

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Registry No. $Ru(NH_3)_6^{2+}$, 19052-44-9; $Co(NH_3)_6^{3+}$, 14695-95-5; imidazolepentaamminecobalt(III), 38716-02-8; pyrazolepentaamminecobalt(III), 38671-07-7; pyridinepentaamminecobalt(III), 31011-67-3; *N,N*-dimethylformamidepentaamminecobalt(III), 38686-44-1; *N,N*-dimethylnicotinamidepentaamminecobalt(III), 31011-70-8; triethylacetatopentaamminecobalt(III), 51965-36-7; trimethylacetatopentaamminecobalt(III), 33887-25-1; acetatopentaamminecobalt(III), 16632-78-3; formatopentaamminecobalt(III), 19173-64-9; fluoroacetatopentaamminecobalt(III), 51965-33-4; trifluoroacetatopentaamminecobalt(III), 19173-66-1; trichloroacetatopentaamminecobalt(III), 19998-53-9; glycolatopentaamminecobalt(III), 31279-86-4; lactatopentaamminecobalt(III), 34464-03-4; benzoylformatopentaamminecobalt(III), 49861-82-7; *S*-benzylthioglycolatopentaamminecobalt(III), 46923-07-3; thiodiglycolatopentaamminecobalt(III), 51965-32-3; oxydiacetatopentaamminecobalt(III), 45160-35-8; mucochloratopentaamminecobalt(III), 51965-35-6; *o*-hydroxycinnamatopentaamminecobalt(III), 46913-88-6; 4-benzoylpyridinepentaamminecobalt(III), 42582-66-1; Cr^{2+}, 22541-79-3; Eu^{2+}, 16910-54-6; V^{2+}, 15121-26-3.

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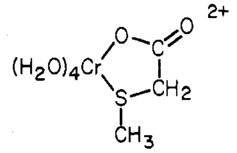
(36) It is likely that the outer-sphere fractions for reductions of the triphenylacetato complex in this series (having three electron-attracting phenyl groups α to carboxyl) are considerably larger than those for the triethyl and trimethyl derivatives. The triphenylacetato perchlorate, which is nearly insoluble in water at room temperature, exhibits a k_{Cr} value of 6.8×10^{-4} M^{-1} sec^{-1} in 25% (v/v) methanol (25°, $\mu = 1.0$): J. R. Barber, Jr., Ph.D. Thesis, Kent State University, 1973.

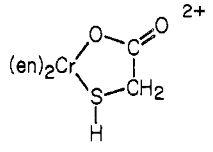
(37) No value of k^{OS} was reported by Nordmeyer and Taube[4a] for the γ isomer. From our k_{Ru} values for the 4-COC_6H_5 and the 3-$CONMe_2$ complexes in the pyridine series, we suggest a specific rate near 0.014 M^{-1}, the k^{OS} observed at 25° for the β isomer.

(38) See, for example, H. G. Friedman, Jr., G. R. Choppin, and D. G. Feuerbacher, *J. Chem. Educ.*, **41**, 354 (1964).

(39) E. S. Gould, *J. Amer. Chem. Soc.*, **87**, 4730 (1965); **88**, 2983 (1966).

(40) We suggest that a species such as XII will be at least as stable to aquation as the protonated complex XIII, for which a first-order rate constant of 0.011 sec^{-1} (25°, $\mu = 4.0$) has been reported.[41]


XII


XIII

(41) C. J. Weschler and E. Deutsch, *Inorg. Chem.*, **12**, 2682 (1973). For related data, see also R. H. Lane and L. E. Bennett, *Chem. Commun.*, 491 (1971).

(42) We are indebted to the referee who pointed out that the reported k_{Ru} value,[13a] 3.0 M^{-1} sec^{-1}, for reduction of $(NH_3)_5Co$-H_2O^{3+}, in conjunction with our eq 2, leads to a $k^{OS}{}_{Cr}$ value of 0.018 for this oxidant, in agreement with the upper limit 0.1 M^{-1} sec^{-1} estimated by D. L. Toppen and R. G. Linck, *Inorg. Chem.*, **10**, 2635 (1971).