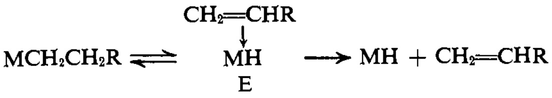
tive saturation. The generally accepted scheme for transition metal systems (eq 14) requires an empty co-



$$\mathrm{MCH_2CH_2R} \rightleftharpoons \underset{\mathrm{E}}{\overset{\overset{\mathrm{CH_2{=}CHR}}{\downarrow}}{\mathrm{MH}}} \longrightarrow \mathrm{MH} + \mathrm{CH_2{=}CHR} \quad (14)$$

ordination position, which is sometimes created by dissociation of another ligand.[92,93] Attempts in this laboratory to prepare $(C_5H_5)_3UH$ have so far been unsuccessful.

Additional Reactions. Over a period of several hours there was no evidence from pmr spectra that $(C_5H_5)_3UR$ compounds added to either acetone or CO_2 to produce the corresponding alkoxide[25] or carboxylate.[94] Thus, these uranium alkyls, though susceptible to attack by protonic reagents, appear to be poor nucleophiles.

Further studies of the chemical and structural characteristics of actinide alkyls and aryls are in progress.

Acknowledgments. We are grateful to the National Science Foundation for generous support of this work (GP-30623X) and to the Northwestern Materials Research Center for access to the Magnetic Properties Facility under Mr. J. Anderson. The R20-B nmr spectrometer was purchased with funds from the National Science Foundation and E. I. du Pont de Nemours and Co. We thank Professor J. L. Atwood for structural data on $(C_5H_5)_3UC_2C_6H_5$ in advance of publication.

Supplementary Material Available. Analytical data and infrared data for the compounds described here will appear, at the request of the Editor, following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20 × reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St. N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number JACS-73-5529.

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[92] (a) C. A. Tolman, *Chem. Soc. Rev.*, 1, 337 (1972). (b) That the *trihapto*allyl configuration could be as much as 8–9 kcal/mol above the monohapto configuration in $(C_5H_5)_3U(C_3H_5)$ supports this, though the steric requirements of E may be somewhat different.

[93] Thermal decomposition of the reaction product of UCl_4 + $4n\text{-}C_4H_9Li$ in diethyl ether or hexane yields butene and butane, but only traces of octane. These products appear to arise *via* β elimination: T. J. Marks and A. M. Seyam, submitted for publication.

[94] T. J. Marks, unpublished work.

Electron Transfer through Organic Structural Units. XIV. Linear Free Energy Relationships between the Chromium(II) and Vanadium(II) Reductions of Pentaamminecobalt(III) Derivatives[1]

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Contribution from the Department of Chemistry, Kent State University, Kent, Ohio 44242. *Received February 14, 1973*

Abstract: The specific rates of reduction of 23 pentaamminecobalt(III) complexes (containing a variety of aliphatic, aromatic, and heterocyclic ligands) with V^{2+} and Cr^{2+} are compared. The Cr(II) values cover a range of 10^8 and the V(II) values a range of 3×10^3. Outer-sphere reductions (at 25° and $\mu = 1.0$) conform to the relationship $\log k_{V^{2+}} = 1.10 \log k_{Cr^{2+}} + 1.85$. The slope near unity, like that observed for the corresponding Cr^{2+}–Eu^{2+} comparison, is in accord with Marcus's model. Values of $k_{V^{2+}}$ for the more rapidly reduced carboxylato complexes lie below 20 M^{-1} sec^{-1}, indicating that these are inner-sphere reductions with specific rates limited by the rate of ligand substitution in $V(H_2O)_6{}^{2+}$. Rates for the more slowly reacting carboxylato complexes, which are known to react with Cr^{2+} with transfer of the carboxylato group, fit the equation $\log k_{V^{2+}} = 0.40 \log k_{Cr^{2+}} + 0.22$. The latter linear free energy relationship, the first to be applied to redox series in which the bridging ligand is varied, is taken as an indication that the oxidants in this rate range oxidize V^{2+} *via* the inner-sphere mechanism. Several kinetic acidity patterns are common to the two reductants, and, when difference in such patterns arise, they are in accord with the substitution-related upper limit for inner-sphere reductions by V^{2+}; this limit generally masks accelerative chelating effects unless the chelating species is a major Co(III) component. Values of $\log k_{V^{2+}}$ for the aliphatic complexes are linear functions of Taft's steric substituent parameters, indicating that rates are related to the severity of nonbonded interaction between the side chain and the reducing center. Reductions, by V^{2+} (but not by Cr^{2+}), of the complexes of 2,4- and 2,5-pyridinedicarboxylic acid are autocatalytic, and the free dicarboxylic acids catalyze the outer-sphere V^{2+} reductions of $(NH_3)_6Co^{3+}$, $(NH_3)_5pyCo^{3+}$, and $(NH_3)_5(DMF)Co^{3+}$. These catalytic phenomena provide additional examples of rapid reduction of Co(III) by pyridine-derived radicals, formed, in the present case, by one-electron reduction of the free ligand with V^{2+}. The high specific rates for the catalyzed reductions ensure that the initial step is an outer-sphere one, and the observed inhibition of catalysis by V^{3+} points to the reversibility of this step.

Linear free energy relationships[2a] have been found to correlate reactivity patterns for electron transfer reactions in a number of instances where two or more reducing centers react, *via* outer-sphere mechanisms, with the same series of oxidants[2b] and have been ap-

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

[2] (a) For a broad survey of this area, see P. R. Wells, "Linear Free Energy Relationships," Academic Press, London, 1968. (b) The application of linear free energy relationships to outer-sphere redox reactions has been briefly but critically reviewed by D. P. Rillema, J. F. Endicott, and R. C. Patel, *J. Amer. Chem. Soc.*, 94, 394 (1972).

plied also to inner-sphere reaction series in which bridging ligands are kept constant but nonbridging ligands are altered.[3] Such relationships appear, however, to be much less generally applicable to comparisons of rates of inner-sphere reactions in which the bridging substituent changes.[4] Moreover, they would be expected to break down completely for rapid inner-sphere reductions by vanadium(II), the specific rates for which are now recognized to be determined principally by the rates of substitution about the reducing center.[3a,5]

In the present work, the reductions, by Cr^{2+}, of a variety of organic pentaamminecobalt(III) derivatives, having specific rates varying over a range of 10^8, are compared with the corresponding reductions by V^{2+}. For those cobalt(III) complexes which react with both reductants through outer-sphere mechanisms, values of $\log k_{Cr^{2+}}$ are, as would be anticipated, linearly related to those of $\log k_{V^{2+}}$. At the fast end of the kinetic scale, specific rates for V^{2+} cluster about the expected substitution-controlled upper limit. Of principal interest, however, is an intermediate region encompassing a number of the simpler aliphatic carboxylatocobalt(III) complexes which undergo inner-sphere reduction by Cr^{2+}.[6] Here again specific rates conform to a linear free energy relationship, the existence of which, in conjunction with the observed upper limit for V^{2+}, constitutes strong evidence that the reductions of monocarboxylatocobalt(III) complexes by V^{2+}, like those of the oxalato[5b] and azido[5d] complexes in the same series, are inner sphere.

Experimental Section

Materials. Aquopentaamminecobalt(III) perchlorate,[7a,8] chloropentaamminecobalt(III) perchlorate,[7a] chromium(II) solutions,[7a,b] vanadium(II) solutions,[3] and lithium perchlorate[4] were prepared as described. Analyses of Cr(II) solutions[7a] and vanadium(II) solutions[3,9] were as described. V(II) solutions were used within a few hours of their preparation to minimize reduction of ClO_4^-. Those cobalt(III) complexes not available from previous studies[7b] were prepared from the aquopentaammine perchlorate in water[7a] or the carbonatopentaammine nitrate[8] in diethylene glycol[4] as described.[10]

Kinetic Experiments. Rates were estimated from measurements of absorbance changes on the Cary 14 recording spectrophotometer[7b,11] or on the Durrum-Gibson stopped-flow spectrophotometer.[6b] Measurements for O-bound cobalt complexes were made at 502 nm, those for N-bound complexes at 475 nm. All reactions, except the autocatalytic V^{2+} reductions of the 2,5- and 2,4-pyridinedicarboxylato complexes mentioned below, were first order each in Co(III) and in reductant, but rate measurements were generally carried out under pseudo-first-order conditions with at least a tenfold excess of reductant. For a number of complexes having uncoordinated donor sites, rates were followed at three or more acidities in the range 0.12–1.0 M H^+. Ionic strengths were adjusted to near unity by addition of twice-recrystallized $LiClO_4$. Reactions were followed for at least 5 half-lives. Rate constants evaluated from successive half-life values 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 8%. Temperatures were kept at 25.0 ± 0.2° during the entire series of experiments. Specific rates for Cr^{2+} reductions of the *o*-formylbenzoato and 4-benzoylpyridine complexes measured on the stopped-flow spectrophotometer were significantly greater than earlier values[7b] obtained with syringe techniques; since a much greater fraction of the total reaction could be observed using stopped-flow, the present values for these complexes are considered to be more reliable.

The V^{2+} reductions of the 2,4- and 2,5-pyridinedicarboxylato complexes exhibited autocatalysis similar to that reported for the Cr^{2+} and Eu^{2+} reductions of the $(NH_3)_5Co^{III}$ complex of *trans*-1,2-bis(4-pyridyl)ethylene[11] and the Eu^{2+} reduction of the 4-carboxamidopyridine complex.[12] In these cases, decreases in absorbance were linear, rather than logarithmic, during most of the reaction and finally "curved off" during the last few per cent. Initial rates could be increased by addition of the free ligand and were very nearly proportional to its concentration. Moreover, these ligands and, more particularly, the N-methylated derivative of the 2,4-acid were found markedly to catalyze the V^{2+} reductions of $(NH_3)_6Co^{3+}$, $(NH_3)_5pyCo^{3+}$, and $(NH_3)_5(DMF)Co^{3+}$. Such catalyzed reductions when carried out with the N-methyl catalyst at or above the 10^{-3} M level, proceeded at specific rates well above 10^2 M^{-1} sec.$^{-1}$.[13]

Results and Discussion

Range of Rate Constants. Specific rates for reductions by V^{2+} are assembled and compared with those by Cr^{2+} in Tables I and II; rate constants in Table I appear to be independent of (H^+) in the range 0.1–1.0 M, whereas those in Table II exhibit some variation with acidity. Vanadium(II) values are in satisfactory agreement with specific rates for the benzoato (0.63),[6b] acetato (1.15),[6b] formato (3.63),[6b] and pyruvato (10.5 M^{-1} sec^{-1})[5b] reductions recently reported from other laboratories.

The range of rate constants for V^{2+} (about 10^3) is, as expected, much narrower than that for Cr^{2+}. At the fast end of the scale, the limit on inner-sphere V^{2+} rates (well below 10^2 M^{-1} sec^{-1}) imposed by ligand substitution at the reducing center[3a,5] is in effect. On the other hand, very slowly reacting Co(III) complexes, for which bridge mechanisms are structurally excluded, are reduced more slowly by Cr^{2+} than by V^{2+}, reflecting, in large part, the greater reorganizational barrier associated with removal of an antibonding e_g electron from Cr^{2+}.[14,15] Of the various patterns of H^+-de-

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[3] (a) P. R. Guenther and R. G. Linck, *J. Amer. Chem. Soc.*, **91**, 3769 (1969); (b) R. G. Linck, *Inorg. Chem.*, **9**, 2529 (1970).

[4] See, for example, E. R. Dockal, E. T. Everhart, and E. S. Gould, *J. Amer. Chem. Soc.*, **93**, 5661 (1971).

[5] (a) B. R. Baker, M. Orhanovic, and N. Sutin, *J. Amer. Chem. Soc.*, **89**, 722 (1967); (b) H. J. Price and H. Taube, *Inorg. Chem.*, **7**, 1 (1968); (c) C. Norris and F. R. Nordmeyer, *ibid.*, **10**, 1235 (1971); (d) K. W. Hicks, D. L. Toppen, and R. G. Linck, *ibid.*, **11**, 310 (1972).

[6] (a) H. Taube and E. S. Gould, *Accounts Chem. Res.*, **2**, 321 (1969); (b) M. B. Barrett, J. H. Swinehart, and H. Taube, *Inorg. Chem.*, **10**, 1983 (1971).

[7] (a) E. S. Gould and H. Taube, *J. Amer. Chem. Soc.*, **86**, 1318 (1964); (b) E. S. Gould, *ibid.*, **87**, 4370 (1965); **88**, 2983 (1966); **89**, 5792 (1967).

[8] F. Basolo and R. K. Murmann, *Inorg. Syn.*, **4**, 171 (1946).

[9] G. Telep and D. F. Boltz, *Anal. Chem.*, **23**, 901 (1951).

[10] Although the preparations from the carbonato nitrate in diethylene glycol[4] are superior to those from the aquo perchlorate in water for complexes of very lipophilic acids, aminobenzoic acids, and easily oxidizable carboxylic acids, the aqueous preparation[7a] gives purer products for complexes of the simpler carboxylic acids.

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

[12] C. Norris and F. R. Nordmeyer, *J. Amer. Chem. Soc.*, **93**, 4044 (1971).

[13] Our preliminary studies of these catalyzed outer-sphere reactions indicate that they are first order each in V(II), Co(III), and catalyst and are inhibited by added V(III). The reactions catalyzed by the 2,4- and 2,5-dicarboxylic acids proceed more raipdly at low than at high acidity, but the acid-dependence appears to be less sensitive to (H^+) than inverse-first order. Catalytic action by the *N*-methyl ligand is very nearly independent of (H^+). The 2,4-acid is approximately three times as effective in its catalytic action as the 2,5 under comparable conditions.

[14] (a) P. Dodel and H. Taube, *Z. Phys. Chem.* (*Frankfurt am Main*), **44**, 92 (1965); (b) see also F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967, p 611.

[15] An earlier suggestion[6a] that V^{2+} enjoys a kinetic advantage over Cr^{2+} in inner-sphere reduction of carboxyl-bound oxidizing centers as a result of favorable overlap between the t_{2g} electron and the π orbitals of the mediating unit cannot apply to the systems at hand, for this advantage persists unattenuated with outer-sphere oxidants.

Table I. Specific Rates for Vanadium (II) and Chromium(II) Reductions of Pentaamminecobalt(III) Complexes, $R(NH_3)_5Co^{III}$ [a]

R	$k_{V^{2+}}$	$k_{Cr^{2+}}$ [b]
Imidazole (I)	0.020	0.0014[c]
Pyrazole (II)	0.120	0.0021
Pyridine	0.240	0.0039
N,*N*-Dimethylformamide	0.35	0.0067
N,*N*-Dimethylnicotinamide (III)	1.38	0.029
Triethylacetato	0.127	0.0022
Trimethylacetato	0.22	0.0070
Trifluoroacetato	0.86	0.034
Benzoato	0.59	0.15
Salicylato (IV)	1.15	$0.11 + 0.03/(H^+)$
Biphthalato	1.20	$0.075 + 0.004/(H^+)$
p-Nitrobenzoato	0.50	
2-Pyridinecarboxylato (V)	0.94	$36/(H^+)$
4-Pyridinecarboxylato	1.01	$0.90 + 0.002/(H^+)$[d]
o-Formylbenzoato (VI)	1.24	90[c]
Formato	3.5	7.2
Glycolato (VII)	8.2	3.1
Maleato (VIII)	5.5	2×10^2
Pyruvato (IX)	10.5	1×10^4
4-Benzoylpyridine (X)	4.5	4.7×10^4 [c]

[a] Specific rates in M^{-1} sec^{-1} at 25°; $\mu = 1.0$. Reductions with V^{2+} independent of (H^+) in the range 0.1–1.0 *M*. $(Co^{III})_0 = 7 \times 10^{-5}$–$1 \times 10^{-3}$ *M*. $(V^{II})/(Co^{III}) = 10$–250; V^{2+} added to Co^{III}. Values for V^{2+} reductions are averages of two to five replicate runs; agreement between runs was better than 8%. [b] Specific rates for Cr^{2+} reductions taken from ref 4, 6a, 7b, and 11 unless otherwise indicated. [c] This work. [d] J. R. Barber, Jr., Ph.D. Thesis, Kent State University, 1973.

Table II. Kinetic Data for H^+-Dependent Vanadium(II) Reductions of Carboxylatopentaamminecobalt(III) Complexes

Organic ligand	(H^+)	k[a]
Acetato	0.90	1.09
	0.20	1.20
	0.10	1.25
p-Formylbenzoato	0.50	1.00
	1.00	1.12
	0.10[b]	2.16
	0.30[b]	2.4
	1.00[b]	3.0
	2.00[b]	3.6
	4.00[b]	4.8
2,3-Pyridinedicarboxylato[c]	1.00	5.5
	0.50	7.2
	0.20	8.6
	0.10	10.2

[a] Specific rates in M^{-1} sec^{-1} at 25°; $\mu = 1.0$ unless otherwise indicated. Reactions run under pseudo-first-order conditions with $(V^{II})/(Co^{III}) = 10$–250; $(Co^{III})_0 = 7 \times 10^{-6}$–$1 \times 10^{-3}$ *M*. V^{2+} added to Co^{III}. Specific rates are averages of two to five replicate runs; agreement between runs was better than 6%. [b] $\mu = 4.0$. [c] For evidence that Co^{III} is bound to the 2-, rather than to the 3-carboxyl in this ligand; see ref 4.

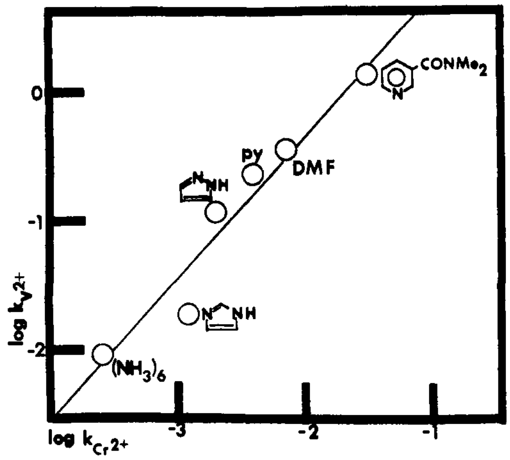
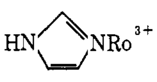


Figure 1. Log–log plot comparing the specific rates of outer-sphere reductions of pentaamminecobalt(III) complexes, $R(NH_3)_5$-Co^{3+}, by Cr^{2+} and V^{2+}. Rate constants have been adjusted to 25° and $\mu = 1.0$ (see ref 7). The least-squares line shown corresponds to the equation $\log k_{V^{2+}} = 1.10 \log k_{Cr^{2+}} + 1.85$.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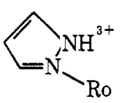
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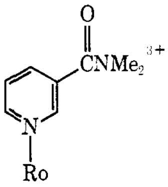
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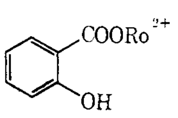
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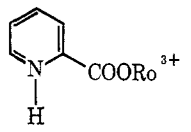
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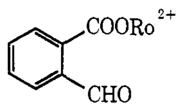
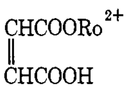
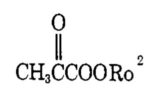
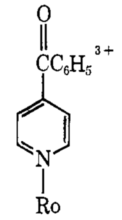

VI

$HOCH_2COORo^{2+}$
VII


$$\begin{matrix} CHCOORo^{2+} \\ \| \\ CHCOOH \end{matrix}$$
VIII


$$\overset{O}{\overset{\|}{CH_3C}}COORo^{2+}$$
IX


X

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

pendency observed for Cr^{2+}, a few persist, in muted form, for V^{2+}, whereas others seemingly vanish.

Correlation of Outer-Sphere Rates. The first five complexes in Table I are known[7b,16] to react with Cr^{2+} *via* outer-sphere mechanisms. Values of $\log k_{Cr^{2+}}$ for these derivatives, and that for $Co(NH_3)_6{}^{3+}$ as well,[14a] are compared with the corresponding values of $\log k_{V^{2+}}$ (Figure 1). The resulting close approach to a linear free energy relationship brings to mind similar comparisons of the specific rates of reduction of a series of Co(III) complexes by V^{2+} and Fe^{2+},[3a] reduction of a different Co(III) series by V^{2+} and $Ru(NH_3)_6{}^{2+}$,[2b] and oxidation of a series of Fe(II) complexes by Mn(III) and Ce(IV).[17,18] Although it has been emphasized[3a] that such a correlation does not guarantee that the two reagents being compared adopt the same mechanism when reacting with a common series, it would be expected to fail if there were a mechanistic change within the series for one reagent but not for the other. Since only outer-sphere reductions are possible for $Co(NH_3)_6{}^{2+}$ and $Co(NH_3)_5py^{3+}$, the observed linearity strongly indicates that the other Co(III) complexes having reactivities indicated in Figure 1 are also reduced by V^{2+} *via* the outer-sphere mechanism. As with Cr^{2+} reductions, bound imidazole (I), pyrazole (II), *N*,*N*-dimethylnicotinamide (III), and O-bound[16] DMF, despite the presence of outer un-

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(16) E. S. Gould, *J. Amer. Chem. Soc.*, **90**, 1740 (1968).

(17) (a) G. Dulz and N. Sutin, *Inorg. Chem.*, **2**, 917 (1963); (b) H. Diebler and N. Sutin, *J. Phys. Chem.*, **68**, 174 (1964).

(18) In some cases, log *k* values for the two reagents are not compared directly but are shown to be linearly related to a common function such as standard potential or free energy difference.

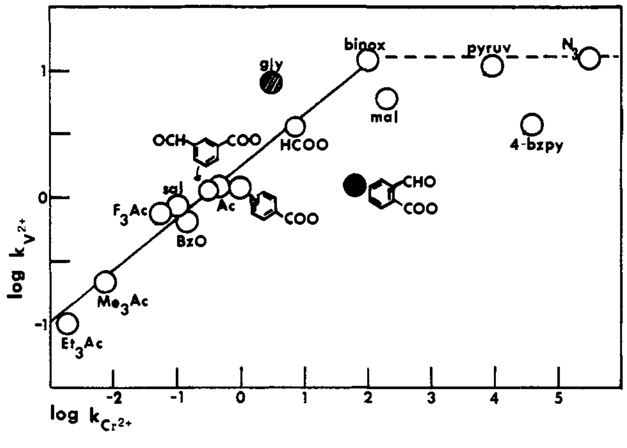

Figure 2. Log–log plot comparing the specific rates of inner-sphere reductions of pentaamminecobalt(III) complexes, $R(NH_3)_5Co^{2+}$, by Cr^{2+} and V^{2+}. Rate constants have been adjusted to 25° and $\mu = 1.0$ (see ref 7): sal = salicylato (IV), gly = glycolato (VIII), binox = binoxalato, mal = maleato (VIII), pyruv = pyruvato (IX), 4-bzpy = 4-benzoylpyridine (X). The diagonal line to the left of the "break-point" (the latter indicated by the dashed line) corresponds to the equation $\log k_{V^{2+}} = 0.40 \log k_{Cr^{2+}} + 0.22$. Neither the *o*-formylbenzoato (VI) nor the glycolato complex is included in the least-squares treatment because of the possibility of selective chelation effects (see ref 24a).

shared electron pairs, appear to be ineffective as bridges.[19–21]

Note that the slope of the least-squares line in Figure 1 is close to unity, *i.e.*, the specific rates for V^{2+} reductions are very nearly proportional to those for Cr^{2+} reductions. A similar proportionality has been reported for the same series of oxidants when reductions by Eu^{2+} and Cr^{2+} are compared[11] and appears to apply also to the corresponding reductions by Cr^{2+} and U^{3+}.[22] Although log–log plots having unit slope are in accord with Marcus's model[23] for reactions of the type at hand, a number of cases are known, some involving pairs of oxidants reacting with the same series of reductants,[17] others the reverse,[3a] where the reagents being compared exhibit significantly different sensitivities to structural alteration. Linck[3a] has attempted to relate such sensitivity to net free energy change, but the present experiments, in addition to those in other laboratories,[2b] point to instances in which reductants of widely different potential exhibit very similar sensitivities to changes in outer-sphere oxidants. It would appear that examination of additional systems is desirable for resolution of this point.

Carboxylato Complexes. Correlation of Inner-Sphere Rates below the Substitution-Controlled Limit. Of the remaining 17 oxidants listed in Tables I and II, all but the rapidly reduced 4-benzoylpyridine derivative (X) are carboxylate complexes, a number of which have been shown to undergo Cr^{2+} reduction *via* one or more variations of the inner-sphere path.[6,7a,24] The most slowly reduced member of the group for which the extent of ligand transfer has been critically examined[6b] is the trimethylacetateo complex, which oxidizes Cr^{2+} with at least 84% carboxyl transfer. The further progressive drop in $k_{Cr^{2+}}$ as the more sterically demanding triethylacetato and triphenylacetato[25] groups are substituted for trimethylacetato indicates that predominance of the inner-sphere path in Cr^{2+} reduction extends at least to the triethyl complex, for it has been shown that outer-sphere reductions of crowded Co(III) complexes by Cr^{2+} are subject to steric acceleration.[16]

The log–log plot comparing specific rates for reduction of carboxylatocobalt(III) complexes by Cr^{2+} with those by V^{2+} is given as Figure 2. Two distinct regions emerge. For those complexes reduced by Cr^{2+} at specific rates below about 50 M^{-1} sec^{-1} (at 25° and $\mu = 1$), values of log V^{2+} are linearly related to those of log Cr^{2+}, but the slope of the correlation line, 0.40, is very much less than that for the outer-sphere reactions (Figure 1). However, the very rapidly reacting Co(III) complexes, for which $k_{Cr^{2+}}$ lies in the range 50–300,000, oxidize V^{2+} at specific rates not greatly different for 10 M^{-1} sec^{-1}. The second (flat) region of the log–log plot is wholly expected, being similar to that reported for V^{2+}–Fe^{2+} comparisons by Grossman and Haim,[26] and once more reflects the circumstance that despite the effectiveness of the ligands as electron transfer bridges, maximal rates of inner-sphere reduction by V^{2+} are determined mainly by substitution at the reducing center. Slight variations in $k_{V^{2+}}$ in this region appear to be nonsystematic and are probably related, at least in part, to variations in the association constants of the various precursor complexes.[6a]

In contrast to the series considered by Linck,[3] who introduced variation in nonbridging ligands, the correlation constituting the linearly rising portion of Figure 2 involves variation in the bridging group and therefore is a stronger indication that the two reducing centers are operating through similar mechanisms. We suggest that the observed linear correlation for the slowly reacting carboxylato complexes, when considered along with the upper limit for $k_{V^{2+}}$ at the rapid end of the scale, constitutes compelling evidence that reduction *via* ligand transfer persists throughout the series for V^{2+}, as for Cr^{2+}.

Acidity Patterns. The proposed similarity in paths appears to introduce no major inconsistencies and is corroborated by the several kinetic acidity patterns which are perceived to be common to the two reductants. Moreover, when differences in such patterns arise, they are in accord with the upper limit for inner-sphere reductions by V^{2+}.

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[19] Although the structural requirement for redox bridging by organic groups has not yet been precisely defined, it is clear that a substantial degree of unsaturation must be associated with the "lead-in" atom. Thus, carboxamides bound to Co(III) through oxygen do not partake in bridging,[16] in contrast to N-bound formamide, which, as its conjugate base, mediates effectively.[20] The importance of conjugative relationships is emphasized by the observed sharp drop in the mediating action of MeOOC- and H_2NCO-substituted pyridines when the lead-in group is moved from the γ to the β position,[11,21] and further sterically related erosion of the mediating role has been noted by one of us[16] when crowding in the vicinity of the lead-in atom is increased. The rationale for nonbridging by imidazole and pyrazole is less straightforward but probably parallels that applied by Balahura and Jordan[20] to carboxamidocobalt(III) complexes.

(20) R. J. Balahura and R. B. Jordan, *J. Amer. Chem. Soc.*, **92**, 1533 (1970).

(21) F. Nordmeyer and H. Taube, *J. Amer. Chem. Soc.*, **90**, 1162 (1968).

(22) M. A. Miller, unpublished experiments, Kent State University, 1970. The ratio $k_{U^{3+}}/k_{Cr^{2+}}$ throughout the series was found to be 1×10^4.

(23) R. A. Marcus, *Annu. Rev. Phys., Chem.*, **15**, 155 (1964).

(24) (a) R. D. Butler and H. Taube, *J. Amer. Chem. Soc.*, **87**, 5597 (1965); (b) M. V. Olson and H. Taube, *Inorg. Chem.*, **9**, 2072 (1970).

(25) The triphenylacetato perchlorate in this series is nearly insoluble in water at room temperature. It is reduced by Cr^{2+} at a specific rate 6.8×10^{-4} M^{-1} sec^{-1} in a medium which is 25% (v/v) methanol, 0.1 M in $HClO_4$, and 0.9 M in $LiClO_4$ at 25°: J. R. Barber, Jr., Ph.D. Thesis, Kent State University, 1973.

(26) B. Grossman and A. Haim, *J. Amer. Chem. Soc.*, **93**, 6490 (1971).

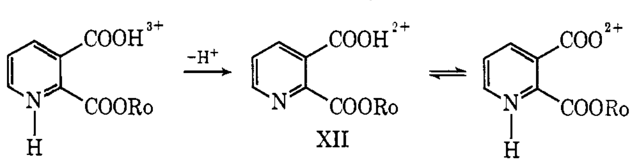
What appears to be the most striking of these differences relates to the reduction of the 2-pyridinecarboxylato complex (V), which is inverse-first order in (H$^+$) with Cr^{2+} but independent of acidity (in the range 0.1–1.0 M H$^+$) with V^{2+}. The rate law for Cr^{2+} reflects the exceptionally high reactivity of the conjugate base of this complex, for which a specific rate of 3.6×10^5 M^{-1} sec^{-1} may be calculated by taking pK_A for V as 4.0.[4] If, however, the usual substitution-controlled upper limit is assumed to apply to reduction of this conjugate base by V^{2+}, an inverse-acid term no greater than 40K_A or 0.004 sec^{-1} would be expected. This term would be overshadowed by the acid-independent term within the acidity range examined but would presumably be detectable at much lower acidities. The erosion of the inverse-acid paths in the reductions of the 4-pyridinecarboxylato, biphthalato, and salicylato complexes when V^{2+} is substituted for Cr^{2+} can be accounted for in much the same fashion.

Acid dependencies observed for the reductions of the acetato and *p*-formylbenzoato complexes (Table II) resemble those reported for the corresponding Cr^{2+} reductions,[6,7,27] whereas reduction of the 2,3-pyridinedicarboxylato derivative is similar to the reaction of this oxidant with Cu$^+$.[4] A generalized rate law embracing such situations, in which Co(III) is partitioned into a protonated and nonprotonated form, reduced at different specific rates,[6b,28] is

$$\text{rate} = [\text{V}^{\text{II}}][\text{Co}^{\text{III}}]\frac{kK_A + k'[\text{H}^+]}{K_A + [\text{H}^+]} \qquad (1)$$

where k and k' are the specific reduction rates of the deprotonated and protonated forms and K_A is the acidity constant for the oxidant. The K_A value reported by Barrett[6b] (4.0 M at $\mu = 1.0$) for the acetato complex corresponds to 25% conversion of this species to the less reactive protonated form in 1.0 M H$^+$ but only 2.5% conversion in 0.1 N H$^+$. Hence, the observed rate constant at the latter acidity closely approximates k, but the data for this complex are not sufficiently precise to allow a reliable estimate of k'.

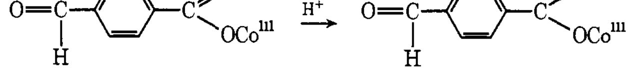
Rate data on the 2,3-pyridinedicarboxylato derivative, in conjunction with the known value of K_A for this complex (0.52 M at 25° and $\mu = 1.0$),[4] lead to specific reduction rates of 2.7 M^{-1} sec^{-1} for the protonated form, XI, and 11.2 for the nonprotonated form,[29] which exists as a mixture of microspecies XII and XIII. If it is assumed that XII, like the oxalato complex,[5b] is reduced at a specific rate near 40 M^{-1} sec^{-1} but that the specific rate for XIII, which cannot chelate in the same way, lies somewhat below 10 M^{-1} sec^{-1}, the observed rate constant, a weighted average for the two tautomeric oxidants, confirms earlier evidence[4,30] that the zwitterionic form XIII predominates in aqueous solutions of substituted pyridinecarboxylic acids of this sort.



XI, pK_A = 0.28 XII XIII

The difference in acidity patterns observed for the two closely related pyridinecarboxylato complexes V and XI emphasizes the point that the substitution-related upper limit for inner-sphere reduction by V^{2+} tends to mask chelation effects unless the chelating species is a major oxidizing component. The change in H$^+$-dependency when the second carboxyl group is incorporated into the complex V does not reflect an important difference in the reactivities of the respective conjugate bases, but merely that XI is much the stronger acid.

Like Zanella and Taube[27], we find that the reduction of the *p*-formylbenzoato complex (XIV) is accelerated by increasing acidity, and we have extended our measurements with this oxidant to $\mu = 4.0$. The higher ionic strength not only allows us to examine reactions at higher acidity but, in analogy with the acetato complex,[6b,31] should increase the basicity of the oxidant so that proportionately more of it is converted to the much more active protonated form XV, in the range studied.



XIV XV

Our data for this complex fit the equation (25°; $\mu = 4.0$)

$$\text{rate} = [\text{V}^{\text{II}}][\text{Co}^{\text{III}}](2.21 + 0.66[\text{H}^+]) \qquad (2)$$

Our first order H$^+$ term is considerably higher than Zanella's value, as would be anticipated at the higher ionicity.[32] The magnitude of this term falls well below that for the analogous reduction by Cr^{2+}, doubtless reflecting once again substitution-limiting reduction of XV by V^{2+}. An upper limit of 40 M^{-1} sec^{-1} for this path corresponds to a lower limit of -1.78 for the pK_A of XV.[33]

Although we have taken the linear free energy relationship applicable to the slower carboxylato complexes as evidence for mechanistic similarity, we cannot say whether it would persist if the bridging group were more drastically altered. Clearly, the array of ligands here chosen greatly favors the observed correlation; possible kinetic effects resulting from selective chelation have been minimized,[34] and the lead-in atom remains the same throughout. Despite the formal variation in the bridging ligands, the electron transfer path lies principally through the carboxyl group in each case. Note that the specific rates for reductions of the *m*-formylbenzoato[27] and 4-pyridinecarboxylato derivatives reasonably fit the correlation shown. Since intervention of a radical-cation intermediate has been suggested for the reactions of both of these complexes with Cr^{2+},[7a,27] the implication here is that any modifica-

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[27] A. Zanella and H. Taube, *J. Amer. Chem. Soc.*, **94**, 6403 (1972).

[28] A. Liang and E. S. Gould, *J. Amer. Chem. Soc.*, **92**, 6971 (1970).

[29] These specific rates may be conveniently obtained by plotting values of the sum (H$^+$) + K_A against (H$^+$). The slope of the resulting least-squares line is k', the intercept kK_A.

[30] R. W. Green and K. H. Tong, *J. Amer. Chem. Soc.*, **78**, 4896 (1956).

[31] A. Liang and E. S. Gould, *Inorg. Chem.*, **12**, 12 (1973).

[32] Note that the form of eq 2 is a simplification of eq 1, corresponding to measurements in which $K_A \gg \text{H}^+$.

[33] The lower limit given is 6–7 units more positive than the pK_A values for ordinary benzoic esters: see, for example, E. M. Arnett, *Progr. Phys. Org. Chem.*, **1**, 223 (1963). Similarly large decreases in acidity when (NH$_3$)$_5$Co$^{\text{III}}$ is substituted for an alkyl group have been noted in an earlier communication.[31]

[34] Although chelation has been shown to be important in the reduction of the salicylato complex by Cr^{2+}, its chief effects are felt in the inverse-acid path for this reaction.[22] The $k_{\text{Cr}^{2+}}$ taken for Figure 2 is that for the acid-independent term.

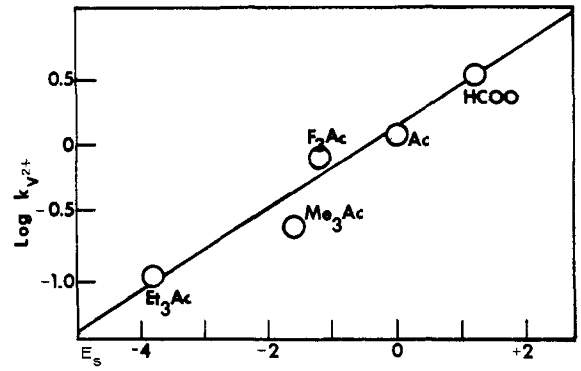

Figure 3. Correlation of specific rates of reduction, using V^{2+}, of aliphatic carboxylatopentaamminecobalt(III) complexes, $(NH_3)_5RCOOCo^{2+}$, with Taft's steric substituent parameters (E_s values).[36] Rate constants have been adjusted to 25° and $\mu = 1.0$ (see ref 7). The least-squares line shown corresponds to the equation $\log k_{V^{2+}} = 0.31E_s + 0.10$.

tion of the activation profile resulting from such intervention is of comparable importance for both reducing centers.

The structural features governing reduction rates of the aliphatic carboxylato complexes have been considered by several workers. Both Fraser[35] and Barrett, *et al.*,[6b] have attempted to relate rates of Cr^{2+} reduction to electron withdrawal by induction, but the latter authors and, earlier, one of us[7b] have noted that sensitivity to inductive effects within the series is slight and may be overshadowed by steric interactions. Indeed, values of log Cr^{2+} for the aliphatic complexes, which vary over a range of 10^4, have been found[7b] to be linearly related to Taft's[36] *steric* substituent parameters (E_s values)[37] and, as shown in Figure 3, specific rates for reductions by V^{2+} may be similarly correlated. It thus appears that for V^{2+}, as for Cr^{2+}, the major factor governing the trend in reaction rates is the severity of nonbonded interactions between the side chain and the reducing center.[38]

Catalyzed Reductions. Neither autocatalyzed reductions of carboxylatocobalt(III) complexes nor the catalysis, by pyridine derivatives, of the reductions of $(NH_3)_6Co^{3+}$, $(NH_3)_5pyCo^{3+}$, and $(NH_3)_5(DMF)Co^{3+}$ appear to have been reported with V^{2+} as the reductant. However, our observations of such catalytic phenomena are in close analogy with reports of corresponding behavior with Cr^{2+} and Eu^{2+},[11,12,39] and, like them, may be taken to reflect the intervention of a pyridine-derived radical which is generated from the catalyst by action of the reducing metal center and which rapidly reduces Co(III). Since specific rates may exceed 10^2 M^{-1} sec^{-1} for these catalyzed reductions, the initial formation of the radical must involve an outer-sphere reduction by V^{2+}. Inhibition of catalysis by added V(III)[13] points to the reversibility of this step. We find it interesting that the 2,4- and 2,5-pyridinedicarboxylato complexes exhibit autocatalysis in their reactions with V^{2+} but not with Cu^+ or Cr^{2+}.[4,40] It is suggested that Cu^+ is too weak a reductant to reduce the pyridine ring to a radical intermediate, whereas, with Cr^{2+}, the very rapid[40] uncatalyzed inner-sphere reactions predominate.

In summary, this report leaves unanswered two major (possibly related) questions: (a) in what manner is the kinetic sensitivity to structural change in the oxidant in a reaction series related to the identity of the reductant and to the reaction mechanism and (b) why is electron transfer through extended organic systems (remote attack) less usual for V^{2+} than for Cr^{2+}? On the credit side, we have added support to the view that for N- and O-bonded cobalt(III) complexes, reduction paths with V^{2+} very often parallel those with Cr^{2+}, but we stress that when more than one path is possible for a given oxidant, the mode of partition between paths may be different for the two reducing centers.

Acknowledgments. We thank Dr. John Barber, Jr., for samples of several of the complexes used. We are also indebted to Professors William Movius and John Endicott for valuable discussions.

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(35) R. T. M. Fraser, *Nature (London)*, **205**, 1207 (1965).

(36) R. W. Taft, Jr., "Steric Effects in Organic Chemistry," M. S. Newman, Ed., Wiley, New York, N. Y., 1956, p 598,

(37) The unimportance of inductive effects in the Cr(II) reduction of carboxylatopentaamminecobalt(III) complexes is underscored by a substantial body of data on meta- and para-substituted benzoato complexes. In the absence of remote attack, specific rates appear to be very nearly invariant, irrespective of the nature of the ring substituent.[6a,7]

(38) The greater sensitivity to structural change exhibited by the Cr^{2+} reductions in the carboxylato series remains a puzzling point, particularly in view[3a] of the circumstance that the thermodynamic driving force is greater for reductions by Cr^{2+} than those by V^{2+}.

(39) J. R. Barber, Jr., and E. S. Gould, *J. Amer. Chem. Soc.*, **93**, 4045 (1971).

(40) Preliminary studies by one of us (E. S. Gould, Kent State University, 1972) indicate that both the 2,4- and 2,5-pyridinedicarboxylato complexes are reduced by Cr^{2+} with a rate expression of the type rate = $k[Co^{III}][Cr^{II}][H^+]^{-1}$, with k values (25°, $\mu = 1.21$) estimated at 1.6×10^4 sec for the 2,4, and 1.7×10^3 sec^{-1} for the 2,5 complex. There is no hint of autocatalysis.