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Electron Transfer through Organic Structures. 26. Mediation by Pyridylacrylate and Related Ligands[1]

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Received January 3, 1977 AIC70003+

Specific rates and acidity patterns for reduction, using Cr^{2+}, of 11 pentaamminecobalt(III) derivatives having pyridylacetato, pyridylacrylato, and related ligands are compared to rates with Eu^{2+} and V^{2+}. Reductions with the latter two centers are acid independent, and specific rates unexceptional. The Cr^{2+} reduction of the 2-pyridylacetato complex, I, in which conjugation between donor centers is broken, exhibits an inverse-acid path, for which the bimolecular rate constant is 1.1×10^3 M s^{-1}, leading to a chelated product. Comparisons with other systems indicate that the $10^{2.6}$-fold rate difference between the reduction of I and the highly conjugated 2-pyridinecarboxylato complex, VII, can be attributed wholly to the more stable precursor formed by the latter and that the specific rates of internal electron transfer in the two systems are nearly the same. The Cr^{2+} reductions of the 2- and 4-pyridylacrylato complexes, which cannot partake in chelation, also show substantial $[H^+]^{-1}$ components but yield carboxyl-bound Cr(III) products, irrespective of the degree of protonation in the activated complex. In each of several instances, reduction of a $-COOCo^{III}$ derivative of pyridine has proceeded by attack at carboxyl, even when the pyridine nitrogen is unblocked and lies in conjugation with the Co^{III} center. A similar conclusion applies, with less certainty, to Cr^{2+} reduction of the 4-pyridinecarboxylato complex VIII. Rate enhancements in the acid-independent components in the chromium(II)–pyridylacrylato reactions may be attributed to a transition state having radical–cation character, but this is probably not the case for the more marked increases observed for the inverse-acid paths. The source of the latter accelerations remains in doubt.

A substantial segment of the early work demonstrating the inner-sphere path for electron transfer utilized cobalt(III) complexes of α,β-unsaturated carboxylic acids.[2] Although the conclusions resulting from some of these experiments were subsequently modified,[3] such studies gave impetus to the notion that electron transfer could proceed through an extended portion of an organic molecule. The use of ligands having the pyridine residue added detail to the picture and resulted first in indications[4] then, finally, in demonstration[5] that electron transfer could occur through this heterocyclic unit.

The present study, which deals principally with bridging carboxylato groups having both α,β-unsaturation and the pyridine ring system, leads in part to reinterpretation of earlier results.

Experimental Section

Materials. Solutions of Eu(II),[6] Cr(II),[4a] and V(II)[7] were prepared and analyzed as described. Carbonatopentaamminecobalt(III) nitrate[4a] and lithium perchlorate[8] were prepared as described. 4-Pyridylacrylic acid was prepared by the method of Marvel;[9] its *N*-methyl derivative and the corresponding methyl derivative of 2-pyridylacetic acid were prepared by the methylation procedure of Meyer.[4a,10] Other ligands (Aldrich, Pfaltz and Bauer, or K&K products) were used as received.

Preparation of Complexes. Those cobalt(III) complexes not available from previous studies[11] were prepared from the aquopentaammine perchlorate in water[4a] or the carbonatopentaammine nitrate in diethylene glycol[8] as described. The principal impurity in these preparations, as in a number of earlier ones,[4a,11b] was the parent carboxylic acid. Such contamination leads to particular difficulty in the studies of the reductions of 2- and 4-pyridylacrylato complexes with Cr^{2+}, which reacts rapidly also with the parent acids, forming strongly absorbing products. A final purification, resulting in very pure complexes, could be carried out by dissolving the complex in a minimum volume of water, carefully adding cation-exchange resin (Bio-Rad 50W-X2, 200–400 mesh, in the H^+ form) in increments with stirring until the solution became colorless. The liquid was then discarded and the resin washed several times with water. The desired complex was then eluted from the resin by stirring with a minimum volume of 8 M $HClO_4$, and the solution was cooled at 0 °C for 60 min, depositing microcrystals. Elemental analyses of complexes prepared here for the first time appear in Table I.

Rate Measurements. Rates were estimated from measurements of absorbance changes on the Cary 14 recording spectrophotometer as described.[6] Measurements were made at 502 nm. Reactions were first order each in Co(III) and reductant but were generally carried out under pseudo-first-order conditions with at least a tenfold excess of reductant. Reductions using Cr(II) were carried out in both 1.0 and 0.10 M $HClO_4$ and when specific rates were found to vary with $[H^+]$ at three or more additional acidities. Rates of reduction by Eu^{2+} and V^{2+} were independent of $[H^+]$ in the present series. Ionic strength was adjusted to near unity by addition of twice-recrystallized $LiClO_4$. Reactions were followed for at least five half-lives. Rate constants evaluated from successive half-life values within a single run agreed to within 4%; no trends indicative of systematic errors were noted, and average values did not differ significantly from those obtained from least-squares treatment of logarithmic plots of absorbance differences against reaction time. Specific rates obtained from replicate runs checked to within 7%. Autocatalysis, similar to that reported for related systems,[6,12] was encountered in the Eu^{2+} reductions of the 2- and 4-pyridylacrylato complexes (Table IV) and in the Eu^{2+} and V^{2+} reductions of the *N*-methyl-2,5-pyridinecarboxylato complex (V) but in none of the other reactions. Temperatures were kept at 25.0 ± 0.2 °C during the entire series of experiments.

Spectra of the Products. The visible spectra of the chromium(III) products formed in the reductions of the 2-pyridylacetato and the 2- and 4-pyridylacrylato complexes with Cr^{2+} were taken, at a number of acidities, by adding successive known quantities of reductant to an excess of oxidant, waiting for reaction to stop, and subtracting the

Table I. Analyses of Pentaamminecobalt(III) Trisperchlorates, $RCo(NH_3)_5(ClO_4)_3$

R	% calcd			% found		
	Co	C	H	Co[a]	C	H
2-Pyridylacetato (I)	10.1	14.5	3.80	9.7	14.5	3.90
4-Pyridylthioacetato (II)	10.1	13.7	3.70	10.1	14.0	3.58
2-Pyridylacrylato (III)	9.9	16.2	3.72	9.9	16.0	3.85
4-Pyridylacrylato	9.9	16.2	3.72	9.8	15.8	3.60
N-Methyl-4-pyridylacrylato (IV)	9.7	17.8	3.96	10.1	14.0	3.58
N-Methyl-2,5-pyridinedicarboxylato (V)	9.3	15.2	3.49	9.3	15.5	3.35

[a] See ref 4a.

Table II. pK_A Values for Pentaamminecobalt(III) Complexes, $RCo(NH_3)_5^{3+}$

R	pK_A[a]
2-Pyridylacetato (I)	5.6
4-Pyridylthioacetato (II)	5.9
2-Pyridylacrylato (III)	4.7
4-Pyridylacrylato	5.1

[a] In 1.0 M aqueous $LiClO_4$, 25 °C.

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

R	k_{Eu}	k_V
2-Pyridylacetato (I)	1.47	0.34
3-Pyridylacetato	0.96	0.53
N-Methyl-2-pyridylacetato	0.95	0.44
4-Pyridylthioacetato (II)	1.53	0.87
2-Pyridylacrylato (III)	*b*	0.98
3-Pyridylacrylato	3.0	1.12
4-Pyridylacrylato	*b*	0.98
N-Methyl-4-pyridylacrylato (IV)	*b*	1.08
β-Styrylacrylato (VI)	2.1	1.03
N-Methyl-2,5-pyridinedicarboxylato (V)	*b*	*b*
Acetato	1.47[c]	1.09[c]
Benzoato	0.83[d]	0.59[d]
Acrylato	1.60[d]	0.82[d]
p-Hydroxycinnamato	2.4[d]	0.79[d]

[a] Specific rates are in M^{-1} s^{-1} at 25 °C. Reactions were carried out in 1.0 M $HClO_4$ unless otherwise indicated. $[Co^{III}]_0 = 7 \times 10^{-5}$ to 1×10^{-3} M. $[Red]/[Co^{III}] = 10$–100. Specific rates given are averages of three to five replicate runs; agreement between runs was better than 7%. [b] Autocatalytic reaction. [c] Reduction was retarded at high acidities (see, for example, ref 12c). Value given here is the limiting specific rate at low acidities. [d] Reference 13.

known absorbancies of the Co(III) complex remaining and Co^{2+} formed. Agreement between spectra calculated at various stages of such "titrations" was good, but became poorer beyond the equivalence point as a result of secondary reactions. Maxima for the Cr(III) product from the 2-pyridylacetato reaction shifted substantially toward the ultraviolet as the acidity of the reduction medium was decreased, lying at 567 (ε 22.7) and 413 nm (24.5) in 1.0 M $HClO_4$ and at 545 (ε 26.3) and 402 nm (23.2) in 0.049 M H^+. In contrast, the spectra of the pyridylacrylato products were very nearly independent of the reaction medium. That from reduction of the 2-complex in 1 M $HClO_4$ exhibited maxima at 410 (ε 28.3) and 570 nm (27.4) whereas that from reduction at $[H^+] = 0.047$ M showed maxima at 407 (ε 29.4) and 565 nm (28.0). Similarly, reduction of the 4-complex in 1 M $HClO_4$ gave a Cr(III) product absorbing at 407 (ε 29.4) and 568 nm (28.1), whereas reduction at $[H^+] = 0.061$ M yielded maxima at 406 (ε 29.4) and 573 nm (30.8). The appearance of isosbestic points at 434 and 556 nm for the 2-isomer and at 445 and 550 nm for the 4-isomer is evidence against secondary conversions during the pyridylacrylato reductions (with Co(III) in excess). A still more sensitive indication is the constancy of the absorbance ratios A_{570}/A_{530} for the Cr(III) products throughout the progress of the reactions, as well as the invariance of the corresponding 570/540, 570/550, and 570/560 ratios.

Results and Discussion

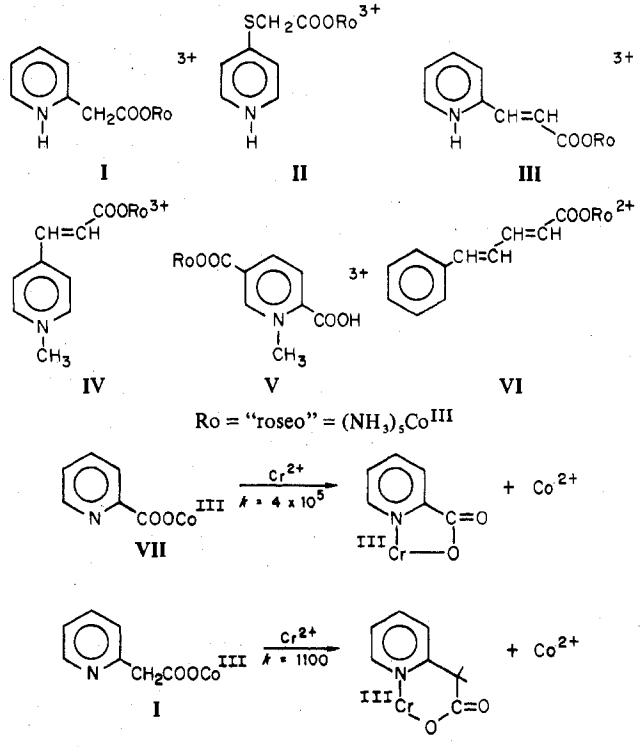
Kinetic data are summarized in Tables III and IV. Specific rates for reductions by V^{2+} and Eu^{2+} (k_V and k_{Eu} values, Table III) are generally independent of acidity and fall well within the ranges typical of the usual inner-sphere reductions by these metal centers.[6b,12c,13] The autocatalysis observed for four of the reductions by Eu^{2+} and one by V^{2+} is attributable to catalysis of the primary process by the free ligand released during the progress of the reaction. Detailed studies of redox catalysis by 4-pyridylacrylic acid and by closely related pyridine derivatives in similar systems have recently been reported.[14]

Reductions by Cr^{2+} (k_{Cr} values, Table IV) display rather more diversity. The inverse-acid term contributing to the reduction of the 2-pyridylacetato complex, I ($k_{obsd} = 0.060 + 0.0027\ [H^+]^{-1}$), and constituting the major reaction path at acidities below 0.045 M, may be taken to reflect chelation in the transition state in the manner already described for the corresponding reductions of the 2-pyridinecarboxylato,[4a] VII, and salicylato[15] complexes. The observed shift toward the ultraviolet by the absorption peaks of the Cr(III) products as the acidity of the reaction medium is decreased confirms the growing importance of an N-coordinated route. The bimo-

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

R	H^+, M	k_{Cr}
2-Pyridylacetato (I)[c]	0.70	0.064
	0.50	0.067
	0.30	0.074
	0.10	0.091
	0.070	0.107
	0.040	0.122
N-Methyl-2-pyridylacetato	1.0	0.098
	0.10	0.107
3-Pyridylacetato	0.80	0.13
	0.080	0.13
4-Pyridylthioacetato (II)	1.0	0.098
	0.10	0.103
2-Pyridylacrylato (III)	1.0	3.6
	0.10	3.7
	0.020	5.4
	0.0040	11.2
3-Pyridylacrylato	1.0	0.99
	0.10	1.03
4-Pyridylacrylato	1.0	2.6
	0.50	3.3
	0.10	4.1
	0.025	9.2
	0.012	12.3
4-Pyridinecarboxylato[b]	0.45	0.86
	0.0090	1.56
	0.0053	1.83
	0.0031	2.3
N-Methyl-4-pyridylacrylato (IV)	1.0	2.0
	0.10	2.4
β-Styrylacrylato (VI)	1.0	0.93
	0.10	1.37
N-Methyl-2,5-pyridinedicarboxylato (V)	1.0	18.0
	0.10	61

[a] Specific rates are in M^{-1} s^{-1}. Reaction conditions are analogous to those for reductions in Table III. $\mu = 1.0$; supporting electrolyte was $LiClO_4$. [b] $\mu = 0.46$. Specific rates were taken early in the reaction to minimize effects of autocatalysis. Data on this complex are from the Ph.D. Thesis of J. R. Barber, Jr., Kent State University, 1973. [c] $\mu = 1.30$.



I II III

IV V VI

VII

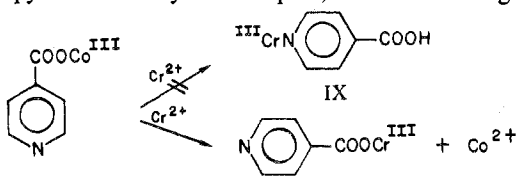
lecular rate constant for this inverse-acid path, pertaining to reduction of the deprotonated (dipositive) form of the oxidant, is obtained by dividing the coefficient of the $[H^+]^{-1}$ term by K_{HA} (Table II). The resulting quotient, 1100 M^{-1} s^{-1}, lies 2.6 powers of 10 below the corresponding bimolecular constant (4×10^5 M^{-1} s^{-1})[4a,8] for reduction of the 2-pyridinecarboxylato complex, VII, in which the ring nitrogen is conjugated with $-COOCo^{III}$. This reactivity difference may arise from a difference in association constants of the Co(III)–Cr(II) precursor complexes, from different rates of internal electron transfer within the precursor, or from a combination of the two effects. However, Faure reports that association constants of the complexes formed from 2-pyridylacetic acid and dipositive transition metal ions are uniformly 3 pK units below those for the corresponding complexes of 2-pyridinecarboxylic acid,[16] a decrement which undoubtedly reflects loss of conjugation and puckering of the ring. If the same difference is taken to apply to the precursors under consideration, we may conclude that internal electron transfer in the two systems occurs at very nearly the same specific rate and that there is thus no significant acceleration attributable to electron transfer through the pyridine nitrogen in the fully conjugated system.

Of principal interest are the Cr^{2+} reductions of the 2- and 4-pyridylacrylato complexes, which, like the 2-pyridylacetato derivative, proceed by rate laws featuring a substantial $[H^+]^{-1}$ term. Least-squares treatments of the acrylato rate data lead to the relationship $k_{obsd} = 3.7 + 0.030/[H^+]$ for the 2-complex III and $k_{obsd} = 3.1 + 0.12/[H^+]$ for the 4-isomer. The inverse acid component accounts for major fractions of the reactions at low acidities but is not observed for the 3-acrylato isomer, in which the side chain lies out of conjugation with the ring nitrogen. The $[H^+]^{-1}$ term is again associated with deprotonation of nitrogen, for it disappears on N-methylation, IV. Bimolecular rate constants for the inverse-acid paths are 1.5×10^3 M^{-1} s^{-1} for the 2-pyridylacrylato and 1.5×10^4 M^{-1} s^{-1} for the 4-pyridylacrylato derivative.[17] Note, however, that the structures of both pyridylacrylato complexes rule out the intervention of chelated transition states in reduction.

In these chromium(II)–pyridylacrylato reactions, alteration of the distribution between reaction paths resulting from variation in acidity does not appreciably change the ligand field spectrum of the Cr(III) product. Specifically, the product from reduction of the 4-isomer in 1 M $HClO_4$ (where 96% of the reaction proceeds by the acid-independent path) is virtually identical with that in 0.061 M $HClO_4$ (where 60% of the reaction proceeds by the inverse-acid path).[18] Similarly, reduction of the 2-derivative in 1 M $HClO_4$ (99% by the acid-independent path) yields what appears to be the same product as reduction in 0.047 M H^+ (58% inverse acid[18]). Absorption maxima are in the range characteristic of carboxylato derivatives of $(H_2O)_5Cr^{III}$,[4a] and there is no indication of a shift toward the ultraviolet (generally 10–20 nm) which is known[4a,5,6] to occur when a heterocyclic nitrogen donor replaces the more weakly coordinating carboxyl group. Moreover, the possibility of a secondary reaction, in which an N-coordinated Cr(III) product undergoes isomerization to a carboxyl-coordinated product appears to be ruled out by the appearance of isosbestic points during the progress of the reactions and by the observed constancy of absorbance ratios in those spectral regions most sensitive to alterations of the donor center. We may then conclude that attack by Cr^{2+} in the inverse-acid path, as well as in the acid-independent path, is mainly, if not exclusively, at the coordinated carboxyl.

Our chromium(II)–acrylato results find common ground with the comparisons between k_{Cr} values of complexes I and VII, for in each system the evidence is that reduction of a $-COOCo^{III}$ derivative of pyridine has proceeded by electron transfer through the "adjacent" carboxyl even when the pyridine nitrogen is nonprotonated and lies in conjugation with the Co^{III} center.[19] Although this conclusion was derived from experiments with Cr^{2+}, it is almost certainly applicable also to reductions with the "harder" metal centers Eu^{2+}, V^{2+}, and Ti^{3+}.

It is appropriate here to reconsider the Cr^{2+} reduction of the 4-pyridinecarboxylato complex, VIII. Although this



VIII X

reaction is complicated by an autocatalytic path,[12b] experiments under conditions where such autocatalysis is minimal (Table IV) confirm the existence of an inverse-acid contribution, as do recent reports from other laboratories.[20,29c] Observation of this component led to the initial proposal[4a] that electron transfer could occur through a nitrogen in conjugation with the oxidizing center, but the magnitude of this contribution (a bimolecular rate constant close to 5×10^2 M^{-1} s^{-1} at μ = 0.46) can no longer be interpreted in this way since the corresponding term is even greater for the pyridylacrylato complexes which our experiments show to be reduced by attack at carboxyl. Attack at nitrogen should lead to the ring-bound complex IX as the primary Cr(III) product, but only the $-COOCr^{III}$ product, X, was found, both in the original work[4a] and in a later study.[20]

The early suggestion that an $N-Cr^{III}$ product was converted to $-COOCr^{III}$ by the action of unreacted Cr(II) in a second electron transfer through the ring system, although not completely eliminated,[21-24] may be considered extremely unlikely in view of present evidence against such isomerization in both the 2- and 4-acrylato reductions. For it is difficult to see how 4-pyridinecarboxylato, a less effective mediator than 2- and 4-pyridylacrylato for the Cr(II)–Co(III) system, can nevertheless become more effective for Cr(II)–Cr(III) electron transfer reactions by which Cr^{2+}-catalyzed interconversions of Cr(III) products in large part proceed.[5,25] Further examination of the Cr(III) products of reduction of VIII at very low acidities (where the inverse-acid path constitutes the major uncatalyzed route) is, in principle, desirable, but under such conditions complications from autocatalysis become severe.

Since rate enhancements in the chromium(II)–pyridylacrylato reactions can be ascribed neither to chelation nor to electron transfer through the pyridine ring, the accelerations fall into the category denoted by Taube[26] as pendant group effects, i.e., instances in which conjugation facilitates inner-sphere reduction although the conjugated system does not lie in the line of electron transfer. Granted that this classification is convenient, the wide variation in the magnitudes of such enhancements and the differences in H^+ dependencies within this group[27,28] lead us to suspect the operation of more than one mechanistic feature.

The acid-independent terms in the pyridylacrylato reactions are 15–20 times the specific rates observed for straightforward Cr(II)–Co(III) reactions mediated by arylcarboxylato groups (k = 0.1–0.2 M^{-1} s^{-1} at 25 °C, μ = 1.0).[4] Similar, but less intense, rate enhancements noted for the 4-pyridinecarboxylato complex and its N-methyl derivative prompted the suggestion in 1964 that electron transfer in such cases occurred mainly by initial reduction of the ligand to a conjugated radical bound both to Co(III) and Cr(III).[4a,25] Additional evidence for such a "radical-ion" or "chemical" mechanism has since appeared,[5,29] but such radical intermediates have not yet been detected in inner-sphere Cr(II)–Co(III) reactions mediated by substituted pyridines.[30] Although it is reasonable to assign

the radical–ion mechanism to the acid-independent path for the 2- and 4-pyridylacrylato reactions, this description almost certainly does not extend to the $[H^+]^{-1}$ components, for it has been shown that deprotonation of pyridinecarboxylato species heightens the thermodynamic barrier to one-electron reduction,[31] whereas in our $(NH_3)_5Co^{III}$ systems, deprotonation has been found to facilitate reduction. Thus, the precise nature of rate enhancements by the pyridylacrylato groups and the manner in which the effect is blocked off by N-protonation or methylation remain the most perplexing points in this study.[32]

The very slight acid dependence observed for the Cr^{2+} reduction of the β-styrylacrylato derivative (VI) very probably represents a kinetic medium effect, for the reduction of such unsaturated complexes by this metal center (but not by V^{2+}, Eu^{2+}, or $Ru(NH_3)_6^{2+}$) have been found to be unusually sensitive to changes in the supporting electrolyte.[13]

Acknowledgment. The authors are grateful to Professor Francis Nordmeyer for valuable discussions and for making known his experimental data prior to publication.

Registry No. (2-Pyridylacetato)$Co(NH_3)_5(ClO_4)_3$, 62816-18-6; (4-pyridylthioacetato)$Co(NH_3)_5(ClO_4)_3$, 62816-15-3; (2-pyridylacrylato)$Co(NH_3)_5(ClO_4)_3$, 62816-12-0; (4-pyridylacrylato)$Co(NH_3)_5(ClO_4)_3$, 62851-11-0; (*N*-methyl-4-pyridylacrylato)$Co(NH_3)_5(ClO_4)_3$, 62816-01-7; (*N*-methyl-2,5-pyridinedicarboxylato)$Co(NH_3)_5(ClO_4)_3$, 62851-27-8; (3-pyridylacetato)$Co(NH_3)_5^{3+}$, 62815-99-0; (*N*-methyl-2-pyridylacetato)$Co(NH_3)_5^{3+}$, 62815-98-9; (3-pyridylacrylato)$Co(NH_3)_5^{3+}$, 62851-14-3; (β-styrylacrylato)$Co(NH_3)_5^{2+}$, 52950-74-0; (acetato)$Co(NH_3)_5^{2+}$, 16632-78-3; Eu(II), 16910-54-6; Cr(II), 22541-79-3; V(II), 15121-26-3.

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(17) Reservations as to the reality of specific rates obtained in this way for systems in which deprotonation need not precede Cr(II)-coordination have been expressed by Liang[15a] and by Martin.[15b] For a divergent view, see A. Haim, *Acc. Chem. Res.*, **8**, 264 (1975).
(18) In calculating the distribution between reaction paths at low acidities, account must be taken of consumption of H^+ by ammonia released in the reaction. In such instances, the inverse-acid path becomes more important as the reaction progresses. Rates could not be measured in solutions where $[H^+]_0$ was less than $5[Co^{III}]_0$, for under such conditions acid becomes depleted, and metal hydroxides precipitate.[15a] This circumstance prevents extension of the acrylato measurements to systems in which the inverse-acid path is even more predominant.
(19) Similarly, R. J. Balahura, *Inorg. Chem.*, **13**, 1350 (1974), has shown that reduction, using Cr^{2+}, of the NH_2-bound Co(III) derivative of 4-pyridinecarboxamide features electron transfer through the amide side chain, rather than through heterocyclic nitrogen.
(20) H. Spieker and W. Wieghardt, *Inorg. Chem.*, **15**, 909 (1976).
(21) Although the $(H_2O)_5Cr^{III}$ derivative IX has not yet been described, Nordmeyer[22] has prepared its $(NH_3)_5Co^{III}$ analogue. Preliminary studies[23] indicate that this is reduced by Cr^{2+} at a specific rate near 10 M^{-1} s^{-1} (25 °C, μ = 1.0) with a negligible inverse-acid contribution. We can then set the upper limit for reaction of IX with Cr^{2+} at 1 M^{-1} s^{-1}.[24]
(22) C. Norris and F. R. Nordmeyer, *Inorg. Chem.*, **10**, 1235 (1971).
(23) F. R. Nordmeyer, unpublished experiments, University of Rochester, 1970.
(24) Nordmeyer and Taube[5] have pointed out that the reductions, with Cr^{2+}, of $(NH_3)_5Co^{III}$ derivatives proceed with specific rates 10^1 to 10^7 times as great as those of the corresponding reactions with $(H_2O)_5Cr^{III}$ derivatives under comparable conditions.
(25) Reductions of the 4-pyridinecarboxylato complex by V(II)[12c] and Eu(II)[6b] exhibit no inverse-acid path in the range 0.05–1.0 M H^+. For evidence that electron transfer occurs through the ring during reaction of this oxidant with $Fe(CN)_5OH_2^{3-}$ at pH 8, see J.-J. Jwo and A. Haim, *J. Am. Chem. Soc.*, **98**, 1172 (1976).
(26) H. Taube and E. S. Gould, *Acc. Chem. Res.*, **2**, 321 (1959).
(27) Magnitudes of pendant group accelerations of inner-sphere Cr(II)–Co(III) reactions are less than tenfold with substituted cinnamato ligands[13] but approach 10^5 with pyruvato.[28] Although most reactions accelerated by such groups have acid-independent rate laws, a few (such as those in the present study) exhibit an inverse-acid dependence and still others feature a first-order $[H^+]$ term.[3]
(28) H. J. Price and H. Taube, *Inorg. Chem.*, **7**, 1 (1968).
(29) (a) E. S. Gould, *J. Am. Chem. Soc.*, **87**, 4730 (1965); (b) H. Diaz and H. Taube, *Inorg. Chem.*, **9**, 1304 (1970); (c) M. M. Itzkowitz and F. R. Nordmeyer, *ibid.*, **14**, 2124 (1975).
(30) For descriptions of related radical intermediates, see, for example, (a) M. Z. Hoffman and M. Simic, *J. Am. Chem. Soc.*, **94**, 1757 (1972); (b) E. S. Gould, *ibid.*, **94**, 4360 (1972); (c) H. Cohen and D. Meyerstein, *Isr. J. Chem.*, **12**, 1049 (1974).
(31) U. Bruhlmann and E. Hayon, *J. Am. Chem. Soc.*, **96**, 6169 (1974), estimate, for example, that protonation in aqueous solution renders nicotinamide more strongly oxidizing by 0.8 V, whereas Cohen and Meyerstein[30c] calculate the protonated form of isonicotinamide to be more strongly oxidizing than the nonprotonated by about 0.1 V.
(32) A reviewer has suggested that the lower specific rates associated with reductions of our protonated forms may reflect: (1) a greater electrostatic barrier to approach of Cr^{2+} to the protonated oxidant; (2) retardation, by protonation, of internal electron transfer from the organic radical center of the radical intermediate to Co(III); or (3) a combination of these effects. This does not explain, however, why protonation accelerates reduction in Hurst's systems,[3] which appear to be formally analogous to ours.