Electron Transfer through Organic Structural Units. XV. Rapid Chromium(II) Reductions of Pentaamminecobalt(III) Derivatives[1]

Edwin S. Gould

Contribution from the Department of Chemistry, Kent State University, Kent, Ohio 44242. Received July 26, 1973

Abstract: The specific rates of reduction, with Cr^{2+}, of 11 pentaamminecobalt(III) complexes, featuring several of the most effective organic mediating groups reported, have been measured using stopped-flow spectrophotometry. Most of these values fall between 90 and 80,000 M^{-1} sec^{-1} (25°, $\mu = 1.22$). Reduction of the *p*-formylcinnamato complex III proceeds through a short-lived intermediate having a decay constant of 7.6 sec^{-1} at 25°; this intermediate is similar to that described[9] for reduction of the *p*-formylbenzoato complex, which has been assigned a structure having a $-C=OCr^{III}$ linkage, and its appearance strongly supports a reduction mechanism in which Cr^{2+} attacks at the "remote" aldehydo oxygen. The specific rate for this complex is $(2.6 \times 10^2) + (1.8 \times 10^3[H^+])$, the first-order acid term being the greatest thus far recorded for a reduction of this type. No evidence for the intervention of a carbonyl–chromium(III) intermediate is obtained in the reduction of a *o*-formylbenzoato (I) or a pyruvato (XII) complex under conditions most favorable for detection. Hence, despite the high specific rates for I and XII, it is very unlikely that electron transfer occurs through the carbonyl group in these cases. Reduction of the 5-uracilcarboxylato complex (XI), in which $-COOCo^{III}$ lies adjacent to an oxo group, is 10^3 times as rapid as reduction of the 6-isomer, in which $-COOCo^{III}$ is adjacent to a less basic nitrogen center and gives a chelated Cr(III) product. Data for the β-styrylacrylato complex (IV) point to two reducible forms of this complex, equal quantities of which are present in 0.6 M HClO$_4$; the protonated form is reduced with a specific rate of 0.49, the nonprotonated form with a rate near 1.73 M^{-1} sec^{-1}. Despite extended conjugation in this complex, rate enhancement is slight, presumably reflecting the absence of a second polar center. The very rapid reductions of the pyridinedicarboxylato complexes (VI–IX) are strongly acid dependent and yield chelated Cr(III) products. Kinetic behavior here indicates that reductions of the diprotonated (tripositive) forms of these complexes are negligibly slow but that rapid reductions are occurring at the nonprotonated level and, except possibly for the 2,6 complex, at the monoprotonated level as well. The inverse acid specific rates associated with the nonprotonated paths are the largest values of this sort recorded to date. It is probable that the inverse acid paths stem principally from proton loss from the chelated monoprotonated precursors (*e.g.*, XXIV) rather than from direct reduction of the nonprotonated oxidants. The pyridinedicarboxylato complexes appear to constitute the first example in which ionization of a nonparticipating carboxyl accelerates electron transfer. It is proposed that this rate enhancement reflects the partition of the monoprotonated, but not the nonprotonated, oxidant into tautomers (*e.g.*, XXII and XXIII), with the unreactive zwitterion-like form, XXII, predominant. The acceleration resulting from deprotonation is most marked for the 2,6-dicarboxylato complex where the tautomeric equilibrium at the monoproton level would be expected to be the most one-sided.

Early studies dealing with bridging action by bound organic ligands in inner-sphere electron transfer reactions[2] predated the wide availability of stopped-flow kinetic devices. Although such investigations pointed to remarkably facile mediation of electron transfer by diverse heterocyclic systems, attempted measurements of specific rates led only to lower limits in a number of cases. This paper describes a reinvestigation of certain of the very fast reductions, with Cr(II), of pentaamminecobalt(III) complexes. Attention is centered mainly about pyridine derivatives, but information is included about various related systems as well. The oxidants chosen, which feature several of the most effective mediating groups known, exhibit, in their reactions, some unexpected facets.

Experimental Section

Materials. Aquopentaamminecobalt(III) perchlorate,[2a,3] chromium(II) solutions,[4] and lithium perchlorate[5] were prepared as described. Those cobalt(III) complexes not available from previous studies[2,4,5] were prepared from the aquopentaammine perchlorate in water[2a] or from the carbonatopentaammine nitrate[3] in diethylene glycol as described.[5] Analyses of complexes not previously characterized appear in Table I. Except for *p*-formyl-

Table I. Carboxylatopentaamminecobalt(III) Perchlorates, RCo(NH₃)₅(ClO₄)₂

R	⎯Calcd, %⎯			⎯Found, %⎯		
	C	H	Co	C	H	Co^a
p-Formylcinnamato (III)	23.1	4.1	11.3	22.9	4.0	10.8
β-Styrylacrylato (IV)	25.6	4.8	10.4	24.4	4.0	10.1
2,3-Pyridinedicarboxylato (VII)	16.5	3.7	11.6	16.5	3.8	11.7
6-Uracilcarboxylato (X)^b	12.1	4.0	11.6	12.6	4.2	11.0

^{a} See ref 2a. ^{b} Calcd: N, 19.6; Cl, 14.2. Found: N, 18.8; Cl, 14.0.

cinnamic acid, which was prepared by the procedure of Wiley,[6] carboxylic acid ligands were Aldrich product and were used as received.

Kinetic Experiments. Rates were estimated from measurements of absorbance changes, using, in most cases, the Durrum-Gibson

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

(2) See, for example, (a) E. S. Gould and H. Taube, *J. Amer. Chem. Soc.*, **86**, 1318 (1964); (b) E. S. Gould, *ibid.*, **87**, 4370 (1965).

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

(4) E. S. Gould, *J. Amer. Chem. Soc.*, **88**, 2983 (1966); **89**, 5792 (1967).

(5) E. R. Dockal, E. T. Everhart, and E. S. Gould, *J. Amer. Chem. Soc.*, **93**, 5661 (1971).

(6) R. H. Wiley and P. H. Hobson, *J. Amer. Chem. Soc.*, **71**, 2430 (1949).

stopped-flow spectrophotometer. Measurements were made at 475 nm for the benzoylpyridine complex, at 573 nm for the 2,6-pyridinedicarboxylato complex (the low energy maximum for the Cr(III) product[2a]), and at 502 nm for the other oxidants. All reactions were first order each in Co(III) and in reductant, but rate measurements were carried out under pseudo-first-order conditions. Specific rates were independent of the reagent taken in excess but were somewhat more reproducible when Cr(II) was in excess. Rates were generally followed at four or more acidities in the range 0.06–1.20 M H$^+$. Ionic strengths were adjusted to near 1.2 M by addition of twice recrystallized LiClO$_4$. Replicate oxidations, with the same pair of master solutions, were carried out until decay curves for three consecutive runs superimposed. Rate constants, obtained from logarithmic plots of absorbance differences against reaction time, agreed to better than 4% for runs with different master solutions if half-life periods were 10 msec or greater. For even faster reactions, instrument noise was more troublesome and reproducibility between runs accordingly less. Rate constants for reactions having half-life periods less than 2 msec could not be estimated reliably.[7] Temperatures were kept at 25.0 ± 0.2° during the entire series of experiments. No evidence for autocatalysis, as reported for related systems by Norris[8a] or Barber,[8b] was obtained.

Absorbance curves for the reductions of the o-formylbenzoato (I), p-formylcinnamato (III), pyruvato (XII), and 4-benzoylpyridine (V) complexes were examined in the spectral region 280–360 nm in an effort to detect the growth and decay of an intermediate of the type described by Zanella[9] for reduction of the corresponding p-formylbenzoato complex. No evidence for the intervention of such an intermediate was obtained with the o-formylbenzoato, 4-benzoylpyridine, or pyruvato reductions, but the reaction of the p-formylcinnamato complex resulted in a very sharp rise in absorbance at 320 nm, then a fall. With (Co^{III})$_0$ = 2.4 × 10^{-5} M, (Cr^{2+}) = 0.010 M, and (H$^+$) = 1.20 M, for example, the maximum absorbance occurred at 0.08 sec, and the reaction curve at 320 nm, at which wavelength the intermediate absorbed much more strongly than either reactants or products, could be shown[10] to be a superposition of two consecutive first order (or pseudo-first-order) reactions with rate constants at 20 and 7.6 sec^{-1}. The first of these components was proportional to (Cr^{2+}) and corresponded numerically to the disappearance of Co^{III} as measured at 502 nm, whereas the second component was nearly independent of (Cr^{2+}) at concentrations of the latter below 0.02 M but was accelerated significantly at high (Cr^{2+}). The absorption maximum of the intermediate species was found to lie near 305 nm (ϵ 3 × 10^4).[11]

Results and Discussion

Kinetic data are summarized in Table II. Specific rates lie between 1 and 80,000 M sec^{-1}. Values below this range are more conveniently measured using conventional mixing procedures, whereas values near the upper limit appear to be the maximum reported for organic (NH$_3$)$_5$Co^{III} derivatives.[12] The rate constant here recorded for the o-formylbenzoato complex (I) is significantly greater than the earlier value[2b] obtained

(7) Secondary reactions associated with Cr(II) reductions of keto-substituted pyridine complexes, especially at high acidities, have been described;[4] these reactions caused no difficulty in reductions of the 4-benzoylpyridine complex carried out at acidities below 0.8 M. In the reductions of the 2,3- and 2,5-pyridinedicarboxylato complexes with excess Cr^{2+}, gradual slight decreases in absorbance led to some drift in the "infinity reading." These drifts, possibly reflecting slow reductions of a minor fraction of 3- or 5-carboxyl-bound cobalt(III), did not seriously complicate measurements of the fast reductions of cobalt(III) bound to the 2-carboxyl with either complex.

(8) (a) C. Norris and F. R. Nordemeyer, *J. Amer. Chem. Soc.*, **93**, 4044 (1971); (b) J. R. Barber, Jr., and E. S. Gould, *ibid.*, **93**, 4045 (1971).

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

(10) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, Wiley, New York, N. Y., 1961, p 167.

(11) With (Co^{III})$_0$ = 2.4 × 10^{-5} M, (Cr^{2+}) = 0.010 M, and (H$^+$) = 1.20 M, the maximum conversion of oxidant to intermediate is estimated[10] as 54%.

(12) (a) Specific rates for Cr^{2+} reductions of halogenopentaamminecobalt(III) complexes lie in the range 10^5 to 3 × 10^6 M sec^{-1}: J. P. Candlin and J. Halpern, *Inorg. Chem.*, **4**, 766 (1965). (b) For evidence that values greater than 10^8 assigned to reduction of salicylato derivatives in this series[2a] are not correct, see A. Liang and E. S. Gould, *J. Amer. Chem. Soc.*, **92**, 6791 (1970).

Table II. Kinetic Data for Chromium(II) Reductions of Pentaamminecobalt(III) Complexes, R(NH$_3$)$_5$Co^{III} [a]

Organic ligand, R	(H$^+$), M	k[b]
o-Formylbenzoate (I)	0.24	90
	0.60	91
	1.20	97
2-Carboxy-4'-bromobenzophenone (II)	1.20	12.7
p-Formylcinnamato (III)	0.12	4.1 × 10^2
	0.24	6.8 × 10^2
	0.60	13.2 × 10^2
	1.20	24 × 10^2
β-Styrylacrylato (IV)	0.01	1.73[c]
	0.12	1.52
	0.60	1.10
	1.20	0.89
4-Benzoylpyridine (V)	0.12	4.5 × 10^4
	0.60	5.0 × 10^4
2,5-Pyridinedicarboxylato (VI)	0.11	12.7 × 10^3
	0.25	6.1 × 10^3
	0.60	2.84 × 10^3
	1.20	1.52 × 10^3
2,3-Pyridinedicarboxylato (VII)	0.11	62 × 10^2
	0.25	35 × 10^2
	0.60	14.5 × 10^2
	1.20	7.9 × 10^2
2,4-Pyridinedicarboxylato (VIII)	0.24	8 × 10^4
	0.60	2.7 × 10^4
	1.20	1.3 × 10^4
2,6-Pyridinedicarboxylato (IX)	0.24	6 × 10^4
	0.32	4.5 × 10^4
	0.60	2.8 × 10^4
	0.72	2.3 × 10^4
	0.80	1.9 × 10^4
	0.90	1.7 × 10^4
	1.20	1.1 × 10^4
6-Uracilcarboxylato (X)	0.24	0.98
	0.60	0.98
	1.20	1.07[c]
5-Uracilcarboxylato (XI)	0.24	1.10 × 10^3
	1.20	1.09 × 10^3

[a] Specific rates in M^{-1} sec^{-1} at 25°; μ = 1.22. (Co^{III})$_0$ = 5 × 10^{-5} to 1.5 × 10^{-3}; (Cr^{II}) = 0.005–0.05. Except for the very rapid reductions of complexes V, VIII, and IX (see Experimental Section) agreement between independent runs was better than 5%. [b] k defined as $-d(\text{Co}^{III})/dt(\text{Co}^{III})^{-1}(\text{Cr}^{II})^{-1}$. [c] Values determined on Cary spectrophotometer.
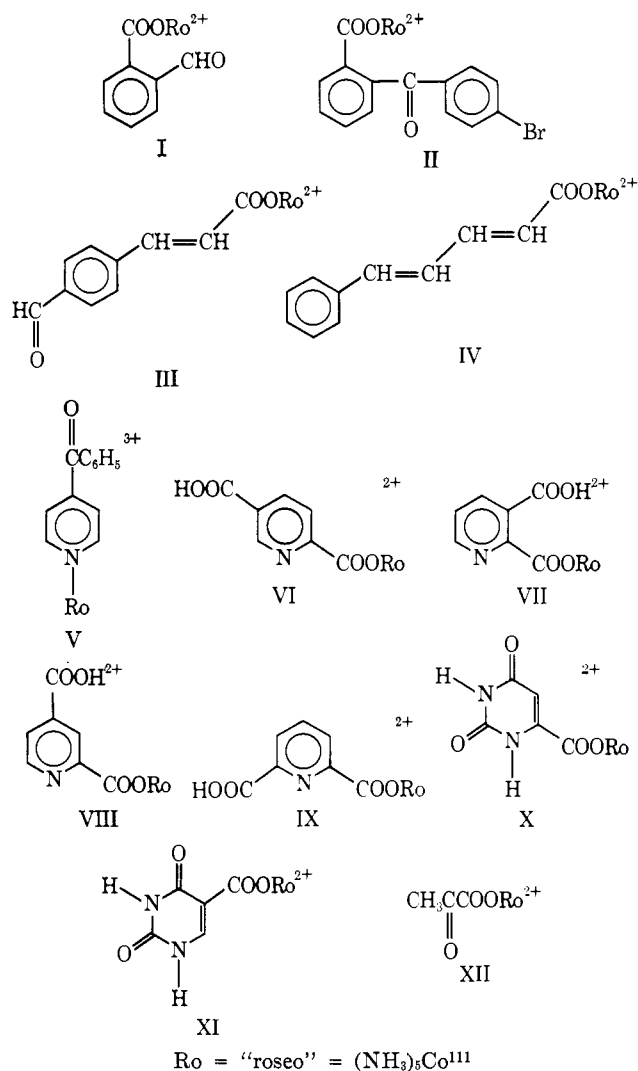
using syringe techniques and Cr^{2+} concentrations less than 10^{-3} M. Since a much greater fraction of the total reaction could be observed using stopped-flow techniques and since experiments at higher (Cr^{2+}) are less sensitive to traces of oxygen, the present value for this complex is considered the more reliable.

Past characterizations[2] of the Cr(III) products from reductions of the o-formylbenzoato (I), 5-uracilcarboxylato (XI), and the various pyridinedicarboxylato complexes have established inner-sphere paths for these reactions, and the relatively high specific rates[13] for the remaining carboxylato complexes in this report allow us to infer a bridge mechanism for these as well.

Rate Enhancement by Carbonyl Substituents. Shortly after the early reports[2,14] that striking increases in reduction rates may result from introduction of a carbonyl group in conjugation with –COOCo^{III}, a distinction was drawn[2a] between two modes of accelerative action. When the carbonyl lies remote from Co^{III}, the rate law for reduction by Cr^{2+} includes a substantial

(13) For evidence that outer-sphere reductions of carboxylatocobalt-(III) complexes by Cr^{2+} occur at specific rates in the range of 10^{-4}–10^{-3} M sec^{-1} at 25°, see K. L. Scott and A. G. Sykes, *J. Chem. Soc., Dalton Trans.*, 1832 (1972).

(14) R. T. M. Fraser, *J. Amer. Chem. Soc.*, **83**, 4920 (1961).

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

curves for the reduction of complex III, recorded in the region 280–330 nm, indicate the intervention of a Cr(III) intermediate very similar to Zanella's. The intermediate from III exhibits an absorption maximum near 305 nm ($\epsilon = 3 \times 10^4$) and a decay constant of 7.6 sec^{-1} at 25°, whereas λ_{max} of XIV is reported[9] as 290 nm ($\epsilon = 1.9 \times 10^4$) and its decay constant as 24 sec^{-1}. Like Zanella's intermediate, the intermediate from reduction of III decays at a rate nearly independent of (Cr^{2+}) at concentrations of the latter below 0.02 M, but this decay appears to be accelerated, in a manner not yet understood, at high (Cr^{2+}) values. It therefore is very likely indeed that in the reduction of the p-formylcinnamato complex, III, the attack by the reducing center occurs initially at the aldehydo oxygen and that the intermediate observed is a carbonyl-bound Cr(III) species vinylogous to XIV.

The manner in which conjugated carbonyl groups facilitate electron transfer in cases where reduction is acid independent is less well defined. In most such instances the carbonyl lies close enough to the Co(III) center to prompt consideration of a chelated transition state such as XV, proposed earlier,[2] but with some

misgivings,[2b] for the reductions of o-formyl- and o-keto-benzoato complexes, which yield nonchelated benzoato-chromium(III) products (XVI). If reduction were to occur through XV, the initial product should be a Cr(III) chelate, which would then be expected to undergo aquation to XVI. However, absorbance curves for the reductions of the o-formylbenzoato (I) and pyruvato (XII) complexes, when here examined under conditions found to be most favorable for detection of carbonyl-bound chromium(III) intermediates from XIII and III, give no hint of the intervention of such intermediates in the acid-independent reductions.[16] The reduction of

term first order in H$^+$, and, in at least some cases, Cr(H$_2$O)$_6^{3+}$ is the chief Cr(III) product. However, when the carbonyl group is moved closer to –COOCo^{III}, reduction yields a carboxylatochromium(III) product, at a rate independent of acidity. Further details pertaining to the reduction of the p-formylbenzoato complex (XIII), a prototype oxidant in the "remote"
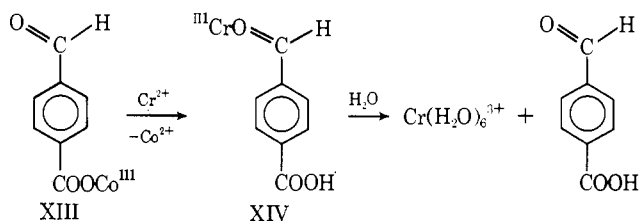
category, were recently furnished by Zanella,[9] who reported the observation of a short-lived reaction intermediate, the properties of which correspond to the carbonyl-bound Cr(III) product, XIV. In the present series, the reduction of the more fully conjugated p-formylcinnamato complex, III, closely follows this pattern. Data for this complex fit the equation

rate = [Cr^{2+}][Co^{III}]($2.6 \times 10^2 + 1.8 \times 10^3$[H$^+$])   (1)

(at 25° and $\mu = 1.2$), the second term of which features the highest first-order acid specific rate thus far reported for reductions of this type.[15] Moreover, absorbance

(15) Zanella[9] reports the specific rate of reduction of complex XIII as 53 + 380(H$^+$) M^{-1} sec^{-1} under conditions comparable to those used here. Unpublished experiments by F. Fan (Kent State University, 1973) indicate that the p-formylcinnamato complex is reduced with Eu^{2+} (25°, $\mu = 1.0$) with a rate constant 4.2 + 3.0(H$^+$) M^{-1} sec^{-1}. This appears to be the first Eu^{2+} reduction reported clearly exhibiting a first-order acid term.
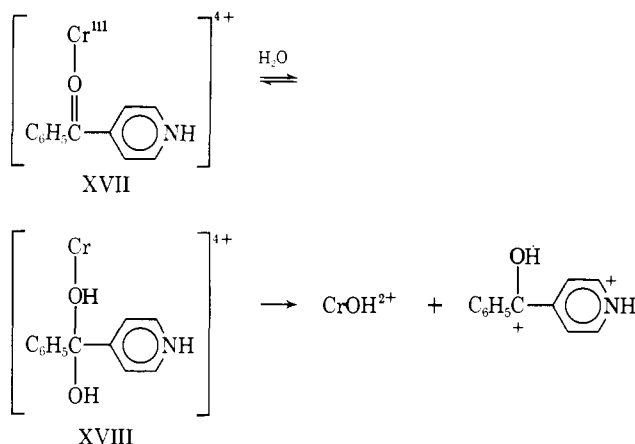
(16) (a) Failure to observe an intermediate in the reduction of the pyruvato complex has also been reported by H. J. Price and H. Taube, *Inorg. Chem.*, 7, 1 (1968). It appears, however, that these workers searched in the visible, whereas absorbance changes associated with metal ion coordination at the carbonyl group (and the reverse process) would be expected to be greatest in the region 250–320 nm.[9] (b) No search for a carbonyl-bound Cr(III) product was made in the reduction of the complex of 2-carboxy-4'-bromobenzophenone (II). The relatively low specific rate in this case militates against detection of an intermediate having decay properties similar to those of XIV.

the very reactive pyruvato complex ($k = 1 \times 10^4$)[16a] is particularly instructive. If this reaction passes through an intermediate having a decay constant near 10 sec^{-1} (i.e., comparable to that of XIV), the degree of conversion to this intermediate would be 78% after a reaction time of 0.03 sec under the conditions used; hence, it would almost certainly be detected. Since the present experiments argue strongly against a chelated precursor complex in the rapid reductions of carbonyl derivatives I and XII (and, by inference, complex II as well), electron transfer through the carbonyl group is, in effect, ruled out, and rate enhancement is best attributed to stabilization of a radical–cation transition state (in which the unpaired electron is delocalized over the conjugated system) lying between the Co(III)–Cr(II) precursor complex and the initial Co(II)–Cr(III) product. Such stabilization was proposed in 1964 in connection with studies of pyridine-4-carboxylato systems,[2a] and supporting evidence has since accumulated.[16a,17] The reductions of the o-formylbenzoato and pyruvato complexes, as well as that of the closely related glyoxalato derivative,[16a] appear to constitute especially striking examples of this mode of action.[18–21]
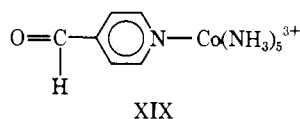
Still another mode of rate enhancement evidently operates during the reduction of the 5-uracilcarboxylato complex (XI), in which the "neighboring oxo group" at

(17) (a) F. Nordmeyer and H. Taube, J. Amer. Chem. Soc., 90, 1162 (1968); (b) H. Taube and E. S. Gould, Accounts Chem. Res., 2, 321 (1969); (c) E. S. Gould, J. Amer. Chem. Soc., 94, 4360 (1972).
(18) The very rapid reduction of the 4-benzoylpyridine derivative (V) has been shown ultimately to yield Cr(H$_2$O)$_6$$^{3+}$ and the free ligand.[4] Spectral profiles of this reaction give no indication of the intervention of Cr(III)–carbonyl intermediate XVII. This result can be reconciled

XVII

XVIII

with earlier evidence[4,19] that this is an inner-sphere reaction only if XVII were to undergo aquation rapidly enough to evade detection. It is recognized that the unimolecular heterolysis of C–O bonds in alkyl arenesulfonates may be accelerated by several orders of magnitude in polar solvents by incorporation of an aromatic ring α to the reaction center.[20] In much the same way, heterolysis of the C–OCr bond in XVIII, which is in mobile equilibrium with XVII,[21] would be expected to occur much more rapidly than the corresponding process for the hydrate of XIV. A rate enhancement of 10^3 is not unreasonable,[20] leading to an estimated decay constant near 10^4 sec^{-1} for XVII. The maximum degree of conversion would then be about 1% and would occur only 0.5 msec reaction time. Similar studies of the reduction of XIX, the carboxaldehyde analog of V, are in progress.

XIX

(19) J. C. Chen and E. S. Gould, J. Amer. Chem. Soc., 95, 5539 (1973).
(20) See, for example, A. Streitwieser, Jr., Chem. Revs, 56, 607 (1956).
(21) D. Samuel and B. L. Silver, Advan. Phys. Org. Chem., 3, 149 (1965).

the 4-position forms a portion of an amide-like unit. The Cr(III) product here has been identified as a chelate,[2b] and the parent carboxylic acid, unlike carbonyl-substituted benzoic acids and pyridinecarboxylic acids, is not reduced with Cr^{2+}, even on long standing.[2b] Hence the rapidity of reduction must be attributed almost solely to chelation in the activated complex, as appears to be the case with the malonato[22] and glycolato[23] complexes. Note that when the –COOCo^{III} substituent is moved from the 5- to the 6-position (X), rate enhancement virtually disappears although chelation involving the 1-nitrogen is, in principle, possible. The marked contrast in rates for the two isomers is in accord with Katritzky's evidence that the 4-oxo group in uracil is considerably more basic than either of the ring nitrogens.[24]

Despite a high degree of conjugation, the β-styrylacrylato complex (IV) is reduced slowly. The acidity pattern for this derivative resembles those for a number of α,β-unsaturated carboxylato complexes described by Liang,[25] and the treatment of data and interpretation called upon in those cases apply here as well. The present data point to two reducible forms of this complex, a protonated form having a specific rate of reduction of 0.49 M^{-1} sec^{-1} and a nonprotonated form with a rate near 1.73 M^{-1} sec^{-1}; equal quantities of the two forms are present in 0.60 M HClO$_4$. The similarity of these limiting specific rates to those for Liang's complexes, in which conjugation is less extended, reminds us that although conjugation may enhance reduction rates slightly, the most marked accelerations require the presence of a second polar center which need not, however, serve as a bridge.

Pyridinedicarboxylato Complexes. Dockal[5] has shown that reductions, with Cu$^+$, of carboxylato derivatives of (NH$_3$)$_5$Co^{III} are rapid only if the organic ligand features a basic site which, together with the coordinated carboxyl, can partake in chelation with the incoming reducing center. Since Cu$^+$ reductions of the complexes of 2,3-, 2,4-, and 2,5-pyridinedicarboxylic acids were observed to be more than 10^3 as fast as reductions of ordinary aliphatic and aromatic derivatives, it was inferred that the conversions of these pyridine acids to mononuclear cobalt(III) complexes yielded predominantly the 2-COOCo^{III} products, VI, VII, and VIII. Only one such complex, IX, can arise from the 2,6 acid. The Cr(II) reductions of the members of this series are here found to be exceedingly rapid and strongly acid dependent. Earlier studies[2] have shown that the Cr(III) products are chelates. For all four of these complexes, the acid dependencies are too steep to be attributed solely to partial protonation to their tripositive forms, for which pK_A values lie between 0.7 and −0.6 (Table III). In each case an additional protonation equilibrium, presumably involving an inverse acid contribution to the reduction, must enter the picture. If reduction of the diprotonated oxidant is considered to be negligibly slow, and if the extent of the second ionization is small in the acid range studied, the rate law for reductions of these complexes assumes the form shown as eq 2, where K_{H_2A} is the acidity

(22) G. Svatos and H. Taube, J. Amer. Chem. Soc., 83, 4172 (1961).
(23) R. D. Butler and H. Taube, J. Amer. Chem. Soc., 87, 5597 (1965).
(24) A. R. Katritzky and A. J. Waring, J. Chem. Soc., 1540 (1962).
(25) A. Liang and E. S. Gould, Inorg. Chem., 12, 12 (1973).

**Table III.** Kinetic Parameters for Chromium(II) Reduction of Pyridinedicarboxylatopentaamminecobalt(III) Complexes[a]

Complex	pK_{H_2A}[b]	pK_{HA}[c]	k_{HA}[d]	k_{-1}[d]
2,3 (VII)	0.28		1.9×10^3	6.7×10^2
2,4 (VIII)	0.70		7.3×10^4	2.6×10^4
2,5 (VI)	−0.15	3.80	2.0×10^3	1.3×10^3
2,6 (IX)	−0.6	3.45		1.5×10^4

[a] Reactions at 25°, $\mu = 1.2$. [b] See ref 5. [c] See ref 2a. [d] Values of k_{H_2A} in $M^{-1} sec^{-1}$; values of k_{-1} in sec^{-1}. See eq 2 and text.

$$k_{obsd} = \frac{rate}{[Co^{III}][Cr^{II}]} = \frac{k_{HA} + (k_{-1}/[H^+])}{1 + ([H^+]/K_{H_2A})} \quad (2)$$

constant for the tripositive (diprotonated form), k_{HA} the specific rate for reduction of the dipositive oxidant, and k_{-1} the specific rate associated with the inverse-acid component. Plots of $k_{obsd}(1 + ([H^+]/K_{H_2A}))$ vs. $1/[H^+]$ approach linearity and yield, as slopes and intercepts, the values for k_{HA} and k_{-1} given in Table III. For the 2,6 complex, the low precision of values of k_{obsd} at low acidities, in conjunction with the uncertainty in K_{H_2A}, appears to prevent a decision as to the reality of k_{HA}.

The specific rates for the inverse-acid terms (k_{-1} values) for reduction of the 2,4 and 2,6 acid are by far the largest rate constants of this sort recorded to date. If the inverse-acid contributions are attributed to direct reduction of the nonprotonated (unipositive) forms of these oxidants, the resulting bimolecular rate constants (obtained by dividing k_{-1} by K_{HA}) would fall in the range 10^6 to 10^8 M^{-1} sec^{-1}. Liang,[12b] however, has presented arguments that specific rates for Cr(II) reductions of carboxylatocobalt(III) complexes of this sort proceeding through chelated transition states cannot be much greater than 3×10^5 M^{-1} sec^{-1}. It is therefore suggested that the inverse-acid terms in these reductions reflect proton loss from the chelated monoprotonated precursor complex (e.g., XXIV in Scheme I). As indicated in this scheme, the monoprotonated

Scheme I
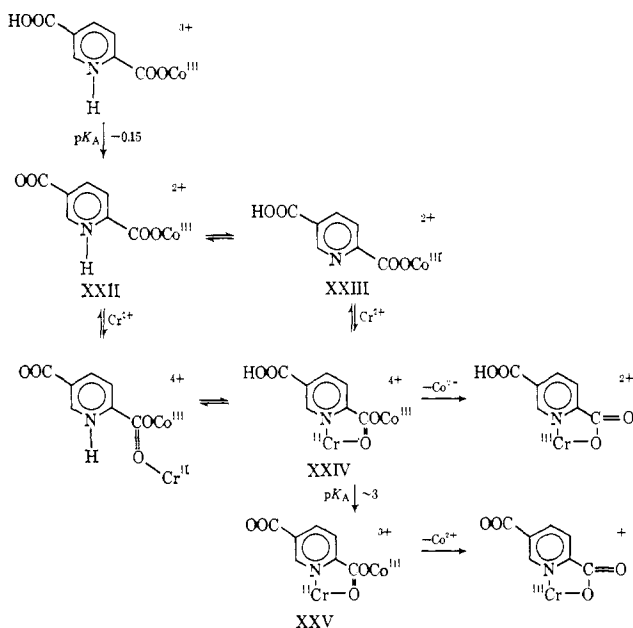
oxidant exists as a mixture of microspecies XXII and XXIII, of which only the latter can participate in

chelate formation with the reducing center. Two fates are possible for the dinuclear intermediate XXIV; it may lose a proton to yield conjugate base XXV, which then undergoes internal electron transfer, or it may undergo electron transfer directly.

Note that the values of k_{-1} for the 2,4 and 2,6 complexes, as well as k_{HA} for the 2,4 complex, substantially exceed the corresponding specific rates for the 2,3 and 2,5 derivatives. It is probable that the differences here arise principally not from preequilibria involving the formation and protonation of the precursor but rather from higher rates of internal electron transfer in the 2,4 and 2,6 systems, which in turn may be taken to reflect the relative ease in reducing pyridine derivatives in which two carboxyl groups lie in direct conjugation with nitrogen.[2,26]

The magnitudes of the inverse-acid contributions in the pyridinedicarboxylato reductions are especially noteworthy in view of the general absence of such terms in other instances where remote nonparticipating carboxyl groups undergo ionization.[27] The present interpretation implies that the inverse-acid terms arise not because deprotonation increases the association constant for the precursor or eases the path for electron transfer but rather because the monoprotonated oxidant exists as a mixture of two tautomers (e.g., XXII and XXIII) whereas the nonprotonated oxidant is a single reactive species. The calculated values of k_{HA} necessarily represent the weighted average of specific rates associated with each of the two monoprotonated microspecies. Since the zwitterion-like form XXII, which cannot chelate, is much less reactive than its tautomer XXIII, a specific rate for the latter alone would be much larger than the k_{HA}'s listed and would perhaps be expected to approach 4×10^5 M^{-1} sec^{-1}, the value applicable to the monodeprotonated $(NH_3)_5Co^{III}$ complex of 2-pyridinemonocarboxylic acid[28] for which partial diversion to a less active tautomer is not possible. The present data on the dicarboxylato complexes confirm earlier evidence, derived from studies of reductions by Cu(I)[5] and V(II),[19] that equilibria of the type XXII ⇌ XXIII favor the less reactive zwitterion-like species. Moreover, with the 2,6 derivative (IX), the inverse-H$^+$ contribution, as represented by k_{-1}, is seen to overshadow k_{HA}; here, because of the proximity of the unbound carboxyl to the ring nitrogen, the tautomeric equilibrium at the monoprotonated level would be expected to be the most one-sided.

(26) J. Volke in "Physical Methods in Heterocyclic Chemistry," Vol. I, A. R. Katritzky, Ed., Academic Press, New York, N. Y., 1963, p 296.

(27) Typically, the reductions of the terephthalato, 3,5-pyrazole-dicarboxylato, and 4,4′-thiodibenzoato derivatives of $(NH_3)_5Co^{III}$ exhibit negligible hydrogen ion dependence.[2] Ionization of the remote carboxyl is of importance, however, in reductions of ring-coordinated pyridinecarboxylato complexes [C. Norris and F. Nordmeyer, *Inorg. Chem.*, 10, 1235 (1971)]; here, the carboxyl offers the sole entry into the conjugated ligand.

(28) The rate constant for the Cr(II) reduction of the 2-pyridine-carboxylato complex has been reported as $36/(H^+)$ sec^{-1} at 25° and $\mu = 1.1$; the specific rate for the deprotonated form is obtained by division by 10^{-4} M, the K_A value for this complex.[5]