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Contribution from the Department of Chemistry, Kent State University, Kent, Ohio 44242

Electron Transfer through Organic Structures. 21. Reductions of Ortho-Substituted Benzoatocobalt(III) Derivatives[1]

A. H. MARTIN, A. LIANG, and E. S. GOULD*

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The reductions, by Cr^{2+}, of a series of 2-hydroxybenzoato derivatives of $(NH_3)_5Co^{III}$ are compared with those of the 2-aminobenzoato analogues. Nearly all complexes in both series exhibit the rate law: rate = $[Cr^{2+}][Co^{III}](k_0 + k_{-1}[H^+]^{-1})$, in the range $[H^+] = 0.01$–1.0 M. Comparison of the distribution of Cr(III) products between chelate (VIII) and nonchelate (IX) with partition of the reduction into acid-independent and inverse-acid kinetic components extends to the 2-hydroxy complexes the three-path (chelated basic, chelated acidic, and nonchelated acidic) mechanism proposed earlier for the parent salicylato complex. Individual specific rates and the distribution between paths are quite insensitive to incorporation of ring substituents, but the inverse-acid path is seriously retarded for reactions proceeding through a seven- rather than a six-membered chelate. With 2-amino derivatives, all chelated product appears to be formed in the inverse-acid path; here, chelation cannot occur with the protonated reactant. Specific rates for the nonprotonated forms of the complexes (k_B's) lie between 2 and 64 M^{-1} s^{-1}. Values of k_B increase with basicity but are less intense functions of structure than are pK_A's. Comparison of such k_B's with analogous "rate constants" greater than 10^6 M^{-1} s^{-1} in the 2-hydroxy series provides further evidence that the latter values, which have been presumed to apply to direct reduction of the conjugate base (the o-O^- form of the Co^{III} complex) are fictitiously high.

Shortly after the establishment of the inner-sphere mechanism for electron-transfer reactions between appropriately substituted metal centers,[2] indications appeared that reactions of this type could sometimes be markedly accelerated by development of chelation in the transition state.[3] The early reactions proceeding through chelated activated complexes utilized Cr^{2+} as the reductant,[4] and evidence is now at hand for chelation in inner-sphere reductions by Cu^+,[5] V^{2+},[6] Eu^{2+},[7] and Ti^{3+}.[8] Nevertheless, Cr^{2+} must be regarded as the most versatile of the known reducing centers in this respect, for it appears, under favorable conditions, to form chelates involving –COOH,[4b,9a] $-COO^-$,[4c] alcoholic –OH,[9b] phenolic –OH and $-O^-$,[9c] –SR,[9a] –SeR,[7a] and donor nitrogen from pyridine,[4c] pyrazine,[9d] pyrrole,[4c] and pyrazole[9e] rings.

The present study compares the reductions, by Cr^{2+}, of a series of 2-hydroxybenzoatocobalt(III) complexes with those of the 2-aminobenzoato analogues. Parallelism between the action of these structurally similar mediating groups is, in part, masked, by the much greater ease with which the amino substituents are protonated in our reaction media, and even after this difference is taken into account, dissimilarities between the two groups remain.

Experimental Section

Materials. Those cobalt(III) complexes not available from previous studies[8,9c] were prepared from aquopentaamminecobalt(III) perchlorate in water[4c] or the corresponding carbonato nitrate[4c] in diethylene glycol[5] as described. Crystallization of aminobenzoato derivatives from dilute $HClO_4$ gave tris(perchlorates), whereas crystallization from water generally gave bis(perchlorates). Aside from 8-hydroxy-1-naphthoic acid, which was prepared by the method of Birch and co-workers,[10] carboxylic acid ligands were Aldrich products and were used as received. Elemental analysis of complexes prepared here for the first time or those for which a check in purity was desired appear in Table I. Lithium perchlorate[5] and Cr(II) solutions[9e] were prepared as described. The cation-exchange resin (Bio-Rad AG 50W-X2, 200–400 mesh) used in separations of reaction products was pretreated as described[11] and stored in 0.02 M $HClO_4$.

Table I. Analyses of Pentaamminecobalt(III) Perchlorates, $RCo(NH_3)_5(ClO_4)_2$

R	% calcd C	% calcd H	% calcd Co	% found C	% found H	% found Co[a]
2-Hydroxy-3-methylbenzoato	19.44	4.50	11.9	19.54	4.25	12.1
2-Hydroxy-5-methylbenzoato	19.44	4.50	11.9	19.75	4.28	11.8
2-Aminobenzoato[b]	14.55	3.84	10.2	14.56	3.81	10.0
2-Amino-3-methylbenzoato[b]	16.23	4.06	10.0	16.50	4.20	10.1
2-Amino-4-chlorobenzoato	16.2	3.9		16.36	4.0	
2-Amino-4-chlorobenzoato[b]	13.6	3.4		13.4	3.4	
2-Amino-5-chlorobenzoato[b]	13.6	3.4		13.2	3.5	
4-Aminobenzoato[b]	14.55	3.84	10.2	14.29	3.79	10.4

[a] See ref 4. [b] Tris(perchlorates), obtained from recrystallization from dilute $HClO_4$.

Table II. pK_A Values of Some 2-Aminobenzoatopentaamminecobalt(III) Complexes, $RCo(NH_3)_5^{2+}$

R	pK_A[a]
2-Aminobenzoato	3.74 ± 0.05
2-Amino-3-methylbenzoato	3.75 ± 0.10
2-Amino-4-methylbenzoato	3.85 ± 0.10
2-Amino-3,5-dichlorobenzoato	1.35 ± 0.10
2-Amino-4-chlorobenzoato	2.48 ± 0.05
2-Amino-5-chlorobenzoato	2.92 ± 0.10

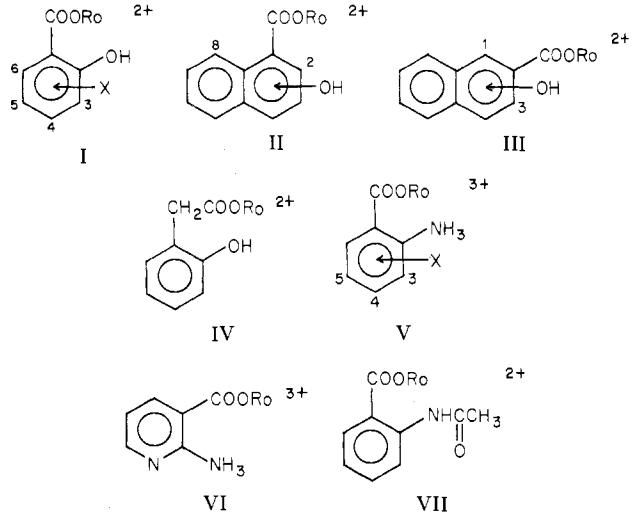
[a] Temperature was 25 °C; measurements were made in aqueous $NaClO_4$; $\mu = 1.0$.

Rate Measurements. Rates were estimated from measurements of absorbance decreases on the Cary 14 recording spectrophotometer as described.[6b,7a,9] Measurements were made at 502 nm. Reactions were first order each in Co(III) and in Cr(II), but rate measurements were generally carried out under pseudo-first-order conditions with

at least a tenfold excess of Cr(II). Rates were followed at three or more acidities in the range 0.01–1.0 M H^+. Ionic strengths were adjusted to near unity by addition of three times recrystallized $LiClO_4$. Reactions were followed for at least 5 half-lives. Rate constants evaluated from successive half-life values within a single run generally 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 6%. Temperatures were kept at 25.0 ± 0.2 °C during the entire series of experiments.

pK_A Determinations. pK_A values for six of the aminobenzoato complexes (Table II) were estimated by measuring the absorbance of solutions of these complexes in the region 310–315 nm in various solutions of known pH. Nonprotonated forms of these complexes exhibit a peak at 310–315 nm, whereas protonated forms absorb only weakly in this range.

Separation Experiments. Cation-exchange separations of Cr(III) reaction products were carried out as described.[9c] As in earlier work, recoveries of chelated Cr(III) products were nearly quantitative, whereas recoveries of nonchelated carboxylatochromium(III) products were erratic. Attempts to improve recovery of the latter by variation of column length, elution rate, pretreatment of the column, and substitution of a polycarboxylate resin for polystyrenesulfonate were of no avail. Extinction coefficients of the Cr(III) products were obtained as described.[9c] Chelated hydroxybenzoato products exhibited absorption maxima near 553 nm (ε 30–40) and shoulders at 425 nm (ε 40–50), whereas maxima for chelated aminobenzoato products lay at 540–545 nm (ε 50) and 400–405 nm (ε 30–40). Peaks for monodentate hydroxy derivatives were near 570 nm (ε 20–25) and 410 nm (ε 25–30), and those for monodentate amino derivatives were near 575 nm (ε 25–27) and 400–405 nm (ε 25–35).[12]



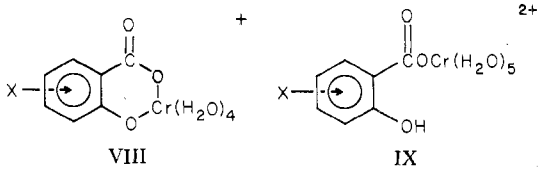
Ro = "roseo" = $(NH_3)_5Co^{III}$

Results and Discussion

All but two cobalt(III) complexes in the present study are reduced more rapidly at low acidity than at high. The adherence of all ortho hydroxy derivatives to the familiar two-term rate law for reduction

$$\text{rate} = [Cr^{2+}][Co^{III}](k_0 + k_{-1}/[H^+]) \quad (1)$$

the nearly quantitative formation of Cr(III) chelates of type VIII at low acidities (Table IV), and the partition of the



Cr(III) formed at high acidities between chelates (VIII) and monodentate products (IX) confirm and extend the three-path mechanism proposed earlier[9c] for reduction of the salicylato and 2,6-dihydroxybenzoato complexes. Acid-independent (k_0) and inverse acid (k_{-1}) specific rates, obtained by plotting values of k_{obsd} vs. $[H^+]^{-1}$ are collected in Table III. Chelated and nonchelated components of the acid-independent paths, evaluated from analysis of Cr(III) products obtained from reductions in 1.2 M H^+, are summarized in Table IV.

As with the Cr(II) reductions of other substituted benzoatocobalt(III) complexes,[4c] incorporation of ring substituents results in slight and almost random changes in specific rates. This striking insensitivity to structural alteration extends not only to the acid-independent component but also to the inverse-acid specific rates and to the distribution between the two acid-independent paths (Table IV). Although there is a hint of steric retardation in the values for those salicylato complexes having a substituent in the 3 or 6 position, sub-

Table III. Specific Rates for Chromium(II) Reduction of 2-Hydroxybenzoatopentaamminecobalt(III) and Related Derivatives, $R(NH_3)_5Co^{III}$ [a]

rate = $[Cr^{2+}][Co^{III}](k_0 + k_{-1}/[H^+])$ [b]

R	k_0,[c] M^{-1} s^{-1}	k_{-1},[c] s^{-1}
Salicylato Derivatives (I)		
2-Hydroxybenzoato (salicylato)	0.11	0.030
2,6-Dihydroxybenzoato	0.022	0.018
2,4-Dihydroxybenzoato	0.14	0.033
2-Hydroxy-3-methylbenzoato	0.047	0.0066
2-Hydroxy-4-methylbenzoato	0.14	0.027
2-Hydroxy-5-methylbenzoato	0.18	0.020
2-Hydroxy-5-chlorobenzoato	0.050	0.051
2-Hydroxy-4-thiomethylbenzoato	0.076	0.052
2-Hydroxy-3-phenylbenzoato	0.03	0.014
1-Naphthoato Derivatives (II)		
2-Hydroxy-1-naphthoato	0.097	0.048
8-Hydroxy-1-naphthoato	0.079	7×10^{-4}
2-Naphthoato Derivatives (III)		
1-Hydroxy-2-naphthoato	0.073	0.049
3-Hydroxy-2-naphthoato	0.089	0.013
o-Hydroxyphenylacetato (IV)	0.30	0.002

[a] 25 °C; $[Co^{III}]_0 = 0.000\ 13$–0.0013 M; $[Cr^{II}]/[Co^{III}] = 10$; $[H^+] = 0.01$–1.16 M; ionic strength 1.20; supporting electrolyte $LiClO_4$. [b] Individual values of k_{obsd} at various acidities are listed by Liang.[12] [c] Plots of observed specific rate vs. $1/[H^+]$ give k_0 as intercept and k_{-1} as slope (see ref 9c).

Table IV. Yields of Chromium(III) Chelate from Chromium(II) Reductions of 2-Hydroxybenzoatopentaamminecobalt(III) Complexes and Partition of the Acid-Independent Kinetic Components into Chelated and Nonchelated Paths

	$[H^+]$, M	% chelate	k_{chel}[a]	$k_{nonchel}$[a]
Salicylato	0.02	96	0.075	0.035
	1.20	74		
2,6-Dihydroxybenzoato	0.02	98	0.012	0.010
	1.20	74		
2-Hydroxy-3-methyl-benzoato	0.01	96	0.011	0.036
	1.20	32		
2-Hydroxy-4-methyl-benzoato	0.01	97	0.099	0.041
	1.20	76		
2-Hydroxy-5-methyl-benzoato	0.01	96	0.14	0.040
	0.02	92		
	1.20	78		
2-Hydroxy-5-chloro-benzoato	0.01	96	0.025	0.025
	1.20	73		

[a] Specific rates (in M^{-1} s^{-1}, 25 °C) for the chelated and nonchelated components of the acid-independent path, calculated from the yield of chelate obtained from reductions carried out in 1.2 M H^+. Correction has been made for that portion of chelate formed by the inverse-acid path at that acidity (see ref 9c).

Table V. Specific Rates for the Chromium(II) Reductions of 2-Aminobenzoatopentaamminecobalt(III) and Related Derivatives, $R(NH_3)_5Co^{III}$ [a]

rate = $[Cr^{2+}][Co^{III}](k_0 + k_{-1}/[H^+])$ [b]

R	k_0,[c] M^{-1} s^{-1}	k_{-1},[c] s^{-1}	k_B,[d] M^{-1} s^{-1}
Anthranilato Derivatives (V)			
2-Aminobenzoato (anthranilato)	0.0086	0.0080	45
2-Amino-3-methylbenzoato	0.0059	0.0035	19
2-Amino-4-methylbenzoato	0.0090	0.0081	64
2-Amino-4-chlorobenzoato	0.017	0.031	9.4
2-Amino-5-chlorobenzoato	0.004	0.014	12
2-Amino-3,5-dichlorobenzoato	[e]		2.0[e]
2-Aminonicotinato (VI)	0.045		
3-Aminobenzoato	0.15		
4-Aminobenzoato	0.17		
2-Acetamidobenzoato (VII)	0.047		

[a] 25 °C; $[Co^{III}]_0$ = 0.000 13–0.0013 M; $[Cr^{II}]/[Co^{III}]$ = 10; $[H^+]$ = 0.01–1.0 M; ionic strength 1.0; supporting electrolyte $LiClO_4$. [b] For individual values of k_{obsd} at various acidities, see ref 12. [c] Linear plots of observed specific rate vs. $1/[H^+]$ give k_0 as intercepts and k_{-1} as slopes (see ref 9c). [d] k_B values obtained by division of k_{-1} by measured K_A values (Table II). [e] Reduction exhibits rate law (2) in text; k_B is limiting specific rate at low acidity. Measured specific rates (at the indicated acidities) are 0.051 (1.17 M), 0.25 (0.20 M), 0.51 (0.10 M), 1.20 (0.035 M), 1.60 (0.015 M), and 1.85 (0.010 M H^+).

stantial attenuation of the inverse-acid path is encountered only with the 8-hydroxy-1-naphthoato (II, X = 8-OH) and o-hydroxyphenylacetato (IV) derivatives, both of which form a seven- rather than a six-membered chelate.

Kinetic results for reduction of the aminobenzoato derivatives are presented in Table V. A number of these reductions conform to the two-term rate law, (1), but the inverse-acid term, k_{-1}, is not observed for the acetamido complex (VII) (the nitrogen of which is virtually nonbasic in the medium employed) nor for the 3- and 4-amino complexes (which cannot partake in chelation). Specific rates for reduction of the 3,5-dichloro derivative fall sharply at high acidities but rise to a limiting value at low acidities. Rates for this complex follow eq 2, an expression consistent with partition of the

$$\text{rate} = \frac{k_{lim}[Cr^{II}][Co^{III}]}{1 + [H^+]/K_A} \qquad (2)$$

oxidant into an unreactive protonated form (having acidity constant K_A) and a reactive protonated form, reduced at specific rate k_{lim}, with the two forms existing in comparable concentrations in the acidity range studied. Reduction with a specific rate equal to half the limiting value occurs at pH 1.5, in reasonable agreement with the spectrophotometrically determined pK_A of this oxidant (Table II).[13] The other amino compounds exist predominantly in the $-NH_3^+$ form at the acidities employed.

An obvious functional difference between the o-OH and the o-NH_3^+ oxidants is that chelation in the latter series requires prior deprotonation. This condition rules out chelation in the protonated reduction path for the amino derivatives, although the other two paths observed with the hydroxy derivatives should persist. This means that the distribution of the Cr(III) product between chelate and nonchelate in the amino reductions should correspond closely to the partition of the reaction between the k_0 and k_{-1} paths.[14] Although product separation in this series is more difficult than is the case in the hydroxy series, those reactions for which product analyses could be carried out (Table VI) fit this pattern.

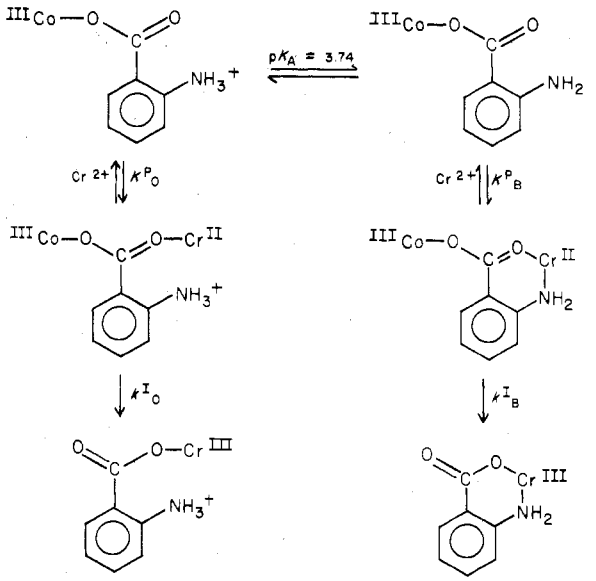
A closely related point is that the kinetic ambiguity associated with the inverse-acid path in the o-OH series, where H^+ may be lost either from the oxidant or from the chelated precursor complex, does not extend to the o-NH_3^+ derivatives.

Table VI. Yields of Chromium(III) Chelates from Chromium(II) Reductions of 2-Aminobenzoatopentaamminecobalt(III) Complexes

	H^+	% chelate
Anthranilato	0.02	100
	1.00	49 (48[a])
2-Amino-3-methylbenzoato	0.02	100
	1.00	51 (37[a])
2-Amino-5-chlorobenzoato	0.02	94
	1.00	85 (78[a])

[a] Calculated percentages, assuming that all chelated product arises from the inverse-acid path.

Scheme I



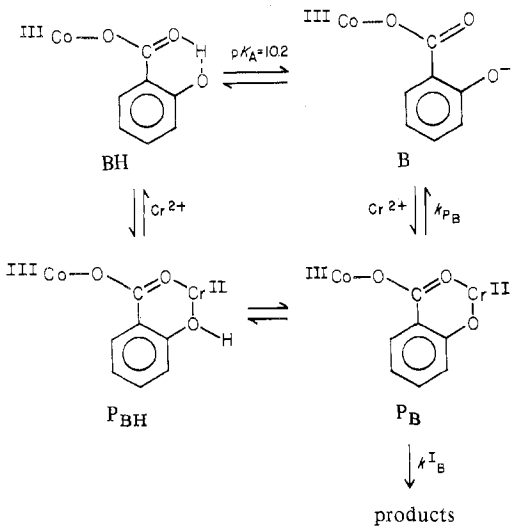
$k_0 = K^P_0 k^I_0 = 0.0086\ M^{-1}\ s^{-1}$ $k_B = K^P_B k^I_B = 45\ M^{-1}\ s^{-1}$

Since deprotonation in the latter series must precede chelation, reservations[9c] associated with the specific rates for the basic forms (k_B values, obtained by dividing k_{-1} by K_A) in the hydroxy series do not apply here. Reaction paths for the anthranilato complex are shown in Scheme I, in which the K^P's are formation constants for the precursors and k^I's are specific rates for internal electron transfer within the precursors.

Values of k_B are included in Table V. Rate enhancement by neighboring $-NH_2$, although generally more pronounced than that by neighboring –SR or alcoholic –OH, is seen to fall far short of that by pyridine nitrogen or –SH.[15,16] Note that k_B decreases as the ring is progressively chlorinated, doubtless reflecting changes in the association constant of the precursor complex attending the incorporation of electron-withdrawing chloro substituents. At the same time, electron withdrawal increases the acidity constant K_A (Table II), with K_A being rather more sensitive than k_B to ligand modification. A result of this combination of offsetting effects is that differences in the observed inverse-acid specific rates (values of $k_{-1} = k_B K_A$) stem, in large part, from relative availabilities of the deprotonated oxidants rather than their reactivities. Thus although the basic form of the 2-aminonicotinato complex, VI, would be expected to be at least as reactive as that of the anthranilato derivative, this complex does not exhibit an inverse-acid term in the range 0.05–1.0 M H^+ since it is too weakly acidic to supply an adequate quantity of the deprotonated form.[17]

Our interest in the k_B values for the aminobenzoato derivatives arises principally from comparison with the corresponding quantities in the o-OH series. For example, division of k_{-1} for the salicylato complex by K_A (5×10^{-11} M)[9c] yields the quotient $6 \times 10^8\ M^{-1}\ s^{-1}$. It has been our view[9c] that this is an unreasonably high bimolecular rate constant for a re-

Scheme II



action in which a 2+ and a 1+ species come together to form a ring, and we have suggested that in this case the precursor complex P_B (Scheme II) is formed mainly from deprotonation of its conjugate acid, P_{BH}, rather than from the basic form of the oxidant. Although this interpretation has been questioned,[18] we believe that the present results add support to it. Since the route of internal electron transfer in both the hydroxy and amino series is through the carboxyl group, the apparent 10^7-fold difference in calculated k_B values, if real, would have to be attributed almost completely to differences in the stabilities of the precursor complexes. Although stability constants for only a few Cr(II) complexes have been reported,[21] values for the salicylato (K_{sal}) and anthranilato (K_{an}) complexes of several dipositive transition metal ions similar to Cr(II) in size and acceptor properties are known.[22] In the absence of coordinated Co(III), K_{sal}/K_{an} ratios lie close to 8×10^4 for Mn(II), 2×10^5 for Fe(II), and 1×10^5 for Co(II). These are well below 1.3×10^7, the kinetically implied ratio for the Cr(II)–Co(III) precursors under consideration, and would be expected to decrease further when $-Co^{III}(NH_3)_5$ is attached to the carboxyls, for such ligation will greatly reduce the basicities of the ligands and should thus compress the range of pK values.[23]

Note also that the K_A's for the salicylato and anthranilato complexes differ by a factor of 3×10^6. This again is less than the factor by which the k_B's for the Cr^{2+} reductions would differ if k_B for the salicylato reduction were taken as 6×10^8 M^{-1} s^{-1}. Acceptance of the latter value thus implies that structural alteration (o-O^- for o-NH_2) in the bridging ligand has affected k_B proportionately more then K_A, whereas in instances in which unequivocal k_B's can be obtained (Tables II and V) sensitivities of the two quantities are seen to lie in the reverse order.

In short, although none of the arguments presented against the very high values suggested for k_B in the salicylato series can be considered conclusive, it would be well to regard with skepticism any specific rate greater than 10^6 M^{-1} s^{-1} for an inner-sphere reduction of Cr^{2+} mediated by an organic ligand unless such a value is measured rather than calculated.

Acknowledgment. The authors are indebted to Professor William Movius for valuable discussions.

Registry No. 2-Hydroxy-3-methylbenzoatoCo$(NH_3)_5(ClO_4)_2$, 59389-05-8; 2-hydroxy-5-methylbenzoatoCo$(NH_3)_5(ClO_4)_2$, 59389-06-9; 2-aminobenzoatoCo$(NH_3)_5(ClO_4)_3$H, 59389-09-2; 2-amino-3-methylbenzoatoCo$(NH_3)_5(ClO_4)_3$H, 59389-12-7; 2-amino-4-chlorobenzoatoCo$(NH_3)_5(ClO_4)_2$, 59389-14-9; 2-amino-4-chlorobenzoatoCo$(NH_3)_5(ClO_4)_3$H, 59389-15-0; 2-amino-5-chlorobenzoatoCo$(NH_3)_5(ClO_4)_3$H, 59389-18-3; 4-aminobenzoatoCo$(NH_3)_5(ClO_4)_3$H, 59460-71-8; I (X = H), 30931-74-9; I (X = 6-OH), 30931-76-1; I (X = 4-OH), 59388-95-3; I (X = 4-Me), 59388-93-1; I (X = 5-Cl), 59389-19-4; I (X = 4-SMe), 59389-20-7; I (X = 3-Ph), 54063-06-8; II(2-OH), 54063-08-0; II(8-OH), 59389-21-8; III(1-OH), 59389-22-9; III(3-OH), 59389-23-0; IV, 46826-87-3; V (X = 4-Me), 59389-24-1; V (X = 3,5-Cl), 59389-25-2; VI, 30472-65-2; 3-aminobenzoato$(NH_3)_5Co^{III}$, 59389-26-3; VII, 59389-27-4; VIII (X = H), 59389-28-5; VIII (X = 6-OH), 59389-29-6; VIII (X = 3-Me), 59389-30-9; VIII (X = 4-Me), 59389-31-0; VIII (X = 5-Me), 59389-32-1; VIII (X = 5-Cl), 59389-33-2; IX (X = H), 59389-34-3; IX (X = 6-OH), 59389-35-4; IX (X = 3-Me), 59389-36-5; IX (X = 4-Me), 59389-37-6; IX (X = 5-Me), 59389-38-7; IX (X = 5-Cl), 59389-39-8; anthranilatoCr$(H_2O)_4^{2+}$, 59389-40-1; 2-amino-3-methylbenzoatoCr$(H_2O)_4^{2+}$, 59389-41-2; 2-amino-5-chlorobenzoatoCr$(H_2O)_4^{2+}$, 59389-42-3; Cr^{2+}, 22541-79-3.

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(9) (a) E. S. Gould, *J. Am. Chem. Soc.*, **88**, 2983 (1966); (b) R. D. Butler and H. Taube, *ibid.*, **87**, 5597 (1965); (c) A. Liang and E. S. Gould, *ibid.*, **92**, 6791 (1970); (d) E. S. Gould, *ibid.*, **94**, 4360 (1972); (e) E. S. Gould, *ibid.*, **87**, 4370 (1965).
(10) A. J. Birch, M. Salahud-Din, and D. C. C. Smith, *J. Chem. Soc. C*, 523 (1966).
(11) E. S. Gould, *J. Am. Chem. Soc.*, **89**, 5792 (1967).
(12) For detailed spectra of Cr(III) products in this study, see the Ph.D. dissertations of A. Liang (Kent State University, 1973) and A. H. Martin (Kent State University, 1975).
(13) A kinetically derived pK_A value, 1.52, may be conveniently obtained by plotting the ratio k_{lim}/k_{obsd} vs. $[H^+]$. The slope of the resulting least-squares line[12] is $1/K_A$.
(14) In principle, a nonchelated inverse-acid path also contributes. Its specific rate should be less than 0.2 M^{-1} s^{-1}.[4c] It would therefore constitute 0.3–2% of the inverse-acid component in the amino series and far less than this in the hydroxy series and would not be detected in our analyses.
(15) Aliphatic carboxylato derivatives of $(NH_3)_5Co^{III}$ having an –OH or –SR group in the α position are reduced by Cr(II) at specific rates in the range 2–20 M^{-1} s^{-1}.[9a,b] Specific rates for reductions of complexes of 2-pyridinecarboxylic acids fall between 10^3 and 10^5 M^{-1} s^{-1}.[16] Preliminary measurements (E.S.G., Kent State University, 1975) indicate that the $(NH_3)_5Co^{III}$ derivative of $HSCH_2COOH$, prepared in situ by reduction of the mononuclear Co(III) complex of $(HOOC-CH_2-S-)_2$ with 0.68 mol of $NaBH_4$, is itself reduced by Cr(II) at an acid-independent specific rate near 5×10^3 M^{-1} s^{-1} (25 °C, μ = 1.0).
(16) E. S. Gould, *J. Am. Chem. Soc.*, **96**, 2373 (1974).
(17) 2-Aminopyridine derivatives have been found to be over 2 pK units more basic than the correspondingly substituted anilines (see, for example, A. Albert, R. Goldacre, and J. Phillips, *J. Chem. Soc.*, 2240 (1948)). If pK_A for complex VI is assumed to be almost 6.0 and k_B is estimated at 100 M^{-1} s^{-1}, k_{-1} will lie near 10^{-4} s^{-1}. At $[H^+]$ = 0.05 M, the lowest acidity used in the study of this complex, the inverse-acid path would constitute less than 5% of the reduction and would easily be overlooked. It would presumably become substantial at much lower acidities.
(18) A. Haim, *Acc. Chem. Res.*, **8**, 264 (1975), has pointed out that our distinction between paths (Scheme II) becomes meaningless if all preliminary steps (proton transfers and substitutions at Cr^{II}) are rapid compared to internal electron transfer within the precursor. Since every act of internal electron transfer leads to products, the rate of internal electron transfer for the inverse-acid path is simply $0.030[Cr^{2+}]\cdot[Co^{III}][H^+]^{-1}$. At the same time, the rate of formation of P_B from conjugate base B is $k_{P_B}[B][Cr^{2+}] = k_{P_B}[Co^{III}][Cr^{2+}]10^{-10.2}[H^+]^{-1}$. The value of k_{P_B} cannot exceed the diffusion-controlled limit of $10^{9.8}$ M^{-1} s^{-1},[19] and there is further an entropy term, conservatively about –17 eu,[9b] associated with the combination of two positive species in water and formation of the chelate ring. Hence, a realistic upper limit for k_{P_B} is 10^6 M^{-1} s^{-1}. The rate of formation of P_B from B is then less than $10^{-4.2}[Co^{III}][Cr^{2+}][H^+]^{-1}$, i.e., considerably less than the rate of internal electron transfer. Thus, although the specific rate for substitution of B in the coordination sphere of Cr(II) is large, the concentration of B is so low that any reaction proceeding mainly through this intermediate is slow.[20]

(19) See, for example, E. F. Caldin, "Fast Reactions in Solution", Wiley, New York, N.Y., 1964, p 12.
(20) For a view more closely corresponding to our own, see R. G. Linck, *MPT Int. Rev. Sci.: Inorg. Chem., Ser. One*, 9, 903 (1971).
(21) See, for example, R. L. Pecsok and N. Bjerrum, *Acta Chem. Scand.*, **11**, 1419 (1957).
(22) L. G. Sillen and A. E. Martell, *Chem. Soc., Spec. Publ.*, No. **17**, 533, 550 (1964).
(23) There is some evidence[22] that Jahn–Teller distortion, to which octahedral complexes of Cu^{II} (and Cr^{II}) are subject, raises selectivity toward salicylate. This effect (approximately 1 pK unit) appears to be too small to alter the argument presented.

Contribution from the Department of Chemistry, Kent State University, Kent, Ohio 44242

Electron Transfer through Organic Structures. 22. Mediation by Acylpyridines[1]

EDWIN S. GOULD,* NELSON A. JOHNSON, and ROBERT B. MORLAND

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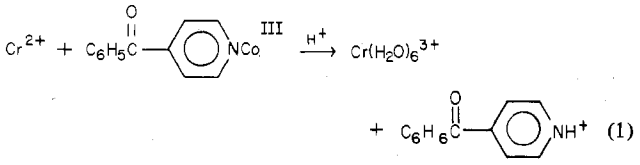
The reductions of eight 3- and 4-acylpyridine derivatives of $(NH_3)_5Co^{III}$ (IV, V) with Cr^{2+}, Eu^{2+}, and V^{2+} are compared. These complexes were prepared through the respective 1,3-dioxolanes (III). The acetyl, benzoyl, and butyryl derivatives exist in aqueous solution in the nonhydrated (carbonyl) forms, whereas the 3- and 4-CHO complexes are partially converted to hydrates ($-CH(OH)_2$). The ratios of specific rates for Cr^{2+} and V^{2+} reductions of the keto complexes lie in the range 10^2–10^4, in contrast to k_{Cr}/k_V ratios near 0.02 for reductions which are unequivocally outer sphere. Observed k_{Eu}/k_V ratios (10^1–10^3) are likewise far greater than the characteristic outer-sphere ratios (0.3) for this pair of reductants. Arguments are presented that reductions of the keto complexes by Cr^{2+} and Eu^{2+} are predominantly inner sphere but that the two possible paths are of comparable magnitude with V^{2+}. A plot of log k_{Cr} vs. log k_{Eu}, which includes values both for the keto complexes and for carboxylato complexes, approaches linearity, with the least-squares line corresponding to the equation $\log k_{Eu} = 0.61 \log k_{Cr} + 0.36$. This appears to be the first application of a linear free energy relationship to an inner-sphere series in which substantial structural variation occurs in the path of electron transfer. In the Cr^{2+} reactions with the –CHO complexes, a major fraction of each reduction occurs by a path independent of Cr^{2+} but first order in H^+. For this component, the rate is determined by slow generation of the more reactive keto form of the oxidant from the less active hydrate. Reductions by V^{2+} exhibit only one kinetic component, for the interconversion between forms is rapid in comparison with the reduction of either form. Reduction of the 4-CHO complex by Cr^{2+} is further complicated by the very rapid secondary reaction of Cr^{2+} with 4-pyridinecarboxaldehyde, liberated in the primary reaction, to form a strongly absorbing species, the properties of which correspond to a Cr(III)-bound radical cation, VII. The latter undergoes aquation (k = 63 s^{-1} at 25 °C) to a radical which, in turn, dimerizes to glycol IX, which can be isolated. The delay in formation of VII from the cobalt(III)–aldehyde complex points to a rate which is determined by aquation (k = 470 s^{-1} at 25 °C) of the carbonyl-bound chromium(III) product, X, formed initially by the very rapid electron transfer between metal centers.

The reductions of cobalt(III) complexes of substituted pyridines have furnished several of the more instructive examples of dramatic rate changes resulting from minor structural alteration.[2] For instance, incorporation of a 4-benzoyl group in pyridinepentaamminecobalt(III) increases, by a factor of 10^7, the specific rate of its reduction (eq 1) with

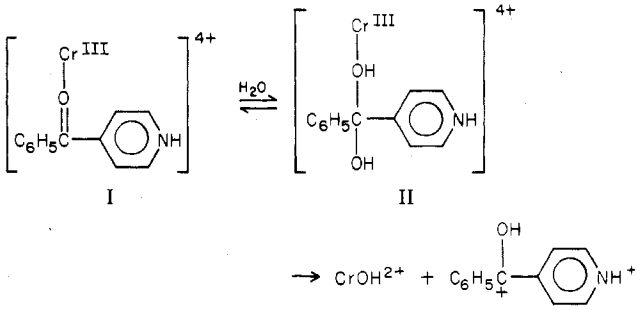


(1)

$k = 5 \times 10^4\ M^{-1}\ s^{-1}$ (25 °C, $\mu = 1.2$)[3]

Cr^{2+}.[2b,c,3] The magnitude of this rate enhancement has been attributed to a change in mechanism; i.e., it has been proposed that in contrast to the pyridine complex, which must be reduced via an outer-sphere path, the benzoylpyridine derivative is reduced by attack of Cr^{2+} at the keto group. The latter bridged path should yield the Cr(III)-bound ketone, I, as a primary product, but spectral profiles of this reaction[3] gave no indication of the intervention of such a species, although analogous intermediates of the type $^{III}Cr—O{=}CHAr$ have been detected in less strikingly accelerated reactions of a related type in which the aldehyde group assumes a "lead-in" role.[3–5]

Note that the proposed inner-sphere intermediate, I, features two aryl groups bound to the carbonyl carbon, whereas the aldehyde-bound intermediates have but one. It has long been recognized that the unimolecular heterolysis of C–O or C–X bonds in alkyl arenesulfonates or halides may be accelerated by several orders of magnitude in polar solvents upon incorporation of an aromatic ring α to the reaction center.[6] In somewhat the same way, heterolysis of the C–OCr bond in II, which is in mobile equilibrium with I,[7] would be expected



I II

to proceed much more rapidly than the corresponding conversion for the hydrates of the aldehyde intermediates, which exhibit decay constants near 10^1 s^{-1} in water at 25 °C.[3,4] A rate enhancement of 10^3 is not unreasonable,[6] leading to an estimated decay constant near 10^4 s^{-1} for the benzoyl intermediate I. Since the maximum degree of conversion to I under typical stop–flow experimental conditions would then be only a few percent and would occur before less than 10^{-3}-s reaction time,[8] it would almost certainly be missed.

The present work deals principally with carbonyl-substituted pyridinecobalt(III) derivatives having no second aryl group, several of which are reduced very nearly as rapidly as the 4-benzoyl complex. Although evidence for intervention of a carbonylchromium(III) intermediate is still not as clear-cut as desired, we have encountered some entertaining points. Moreover, there has been further development of synthetic procedures.