Electron Transfer through Organic Structural Units. VII. Reduction of Salicylatopentaamminecobalt(III)[1]

Anthony Liang and Edwin S. Gould[2]

Contribution from the Departments of Chemistry, San Francisco State College, San Francisco, California, and Kent State University, Kent, Ohio 44240.
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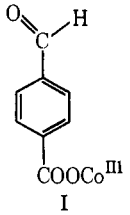
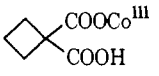
Abstract: The Cr^{2+} reductions of salicylatopentaamminecobalt(III) and of the related 2,6-dihydroxybenzoato complex conform to the rate law: rate = $[Cr^{2+}][Co^{III}](k_A + k_{-1})/[H^+]$, in the range $[H^+] = 0.004$–$1.2\ M$. Reductions at acidities below 0.02 M yield only chelated tetraaquochromium(III) derivatives (*e.g.*, VIII); reductions at 1.2 M H^+ yield mixtures of chelated and nonchelated products (*e.g.*, IX), with the chelate predominating. No significant interconversion between chelate and nonchelate was observed during reduction nor during separation of products. There are thus three separate paths for reductions of both Co(III) complexes. Chelated and monodentate Cr(III) products are formed from the salicylatocobalt(III) complex at acid-independent specific rates 0.075 and 0.035 M^{-1} sec^{-1} (25°, $\mu = 1.26$), and it is proposed that these arise from competing reductions of the hydrogen-bonded *cis* rotamer of the cobalt(III) derivative (Chart I). The inverse acid path almost certainly arises from deprotonation of the precursor complex, P_C, which intervenes also in one of the acid-independent paths; it is unlikely that direct Cr^{2+} reduction of the conjugate base (VI) of the cobalt(III) complex is kinetically significant. The pK_A for the protonated form, X, of the salicylatochromium(III) chelate is 0.5.

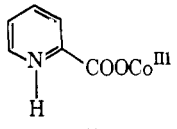
Although the reductions, with Cr(II), of carboxylatopentaamminecobalt(III) complexes most usually occur at rates independent of acidity, a variety of patterns for acid dependence may occasionally appear, and these point to the operation of several interesting effects.[3] A first-order acid term is sometimes observed for the reductions of complexes in which the Co(III)-bound carboxyl is separated from a carbonyl or unbound carboxyl group by a conjugated series of double bonds (I); this kinetic behavior is thought to be indicative of reduction *via* remote attack of Cr(II) at the noncoordinated substituent. In contrast, the reduction of complexes having an acidic center (*e.g.*, II) in addition to the bound Co(III) may



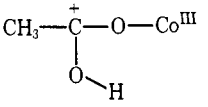
I



II



III



IV

exhibit a rate law having an inverse acid term. Such a term, which is associated with reduction of a deprotonated form of the complex, appears almost always in cases where a strain-free molecular model may be made of a chelated species containing Cr(III) and both functional groups, and has therefore been presumed to stem from reduction through a chelated transition state. When such a chelate is unusually stable (*e.g.*, the reduction of III), the inverse acid term may dominate the rate law to the exclusion of the usual acid-independent term.[3a]

Still another apparent variation in behavior has been observed by Taube and Deutsch,[4] who found, for example, that the rate of reduction of the acetato complex, although nearly independent of acidity in the range 0.04–1.0 M H^+, decreases markedly at very high acidities, owing probably to partial conversion of the complex to a much less reactive protonated form (IV).[5]

In the present study, the reduction of the salicylato complex (V) is reexamined. Earlier experiments[3a] showed that this reduction is retarded by increasing acidity, and on the basis of a few measurements in the range 0.3–2.8 M H^+, a rate law having an inverse acid term was assigned.[6] The magnitude of this term,

(1) From the M.Sc. thesis of A. Liang, Kent State University, 1969. This work was supported in part by the Petroleum Research Fund, administered by the American Chemical Society, under Grant No. 2868-A3.

(2) Address correspondence to author at Kent State University.

(3) (a) E. S. Gould and H. Taube, *J. Amer. Chem. Soc.*, **86**, 1318 (1964); (b) E. S. Gould, *ibid.*, **87**, 4730 (1965); **88**, 2983 (1966).

(4) E. Deutsch and H. Taube, unpublished experiments, Stanford University, 1965–1966. Similar rate behavior has been reported for the reduction of the levulinato complex,[3a] but here retardation at high acidities may reflect protonation of the γ-keto, rather than the carboxyl group.

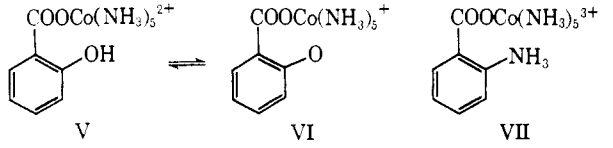
(5) A generalized description, which, however, tends to mask mechanistic differences, may be applied to the reductions of systems I–IV. In each case, the cobalt(III) complex exists in both a protonated and deprotonated form which are reduced at different specific rates. The rate law corresponding to this situation (assuming interconversion between forms to be rapid) may be shown to be

$$\text{rate} = [Cr^{II}][Co^{III}]\frac{\dfrac{k}{K_B[H^+]} + k'}{\dfrac{1}{K_B[H^+]} + 1} \qquad \text{(i)}$$

where k and k' are specific reduction rates of the deprotonated and protonated forms and K_B is the equilibrium constant for the protonation. In the reduction of complex I, the first term in the denominator is much greater than unity (a consequence of the low basicity of I), and $k' \gg k$. In the reduction of complex II, the first term in the denominator is much less than unity at acidities used for studies of this type, and the rate law closely approaches the familiar binomial form which includes the inverse acid term. In the reduction of III, the very large value of k results in further simplification, as the first term in the numerator of (i) greatly exceeds k'. Finally, in the reduction of the acetato complex, k' may be assumed to be very small; at low acidities the first term in the denominator is again much greater than one, corresponding to a reduction rate which is acid independent. At higher acidities, the terms in the denominator may become more nearly comparable, and retardation is observed.

(6) A similar rate law for reduction of the salicylato complex was suggested by R. T. M. Fraser [*J. Amer. Chem. Soc.*, **84**, 3440 (1962)],

when combined with the measured pK_A value of 9.77 for V, led to an estimated specific rate of 2×10^8 l. mol^{-1} sec^{-1} at 25° for reduction of the deprotonated form



V VI VII

VI. Because this value is higher, by several powers of ten, than that for reduction of any other type of carboxylato complex in the $Co(NH_3)_5$ series (approaching the limit for diffusion control), and because a corresponding inverse acid term was not observed for reduction of the nitrogen analog, VII,[3b] a confirmation of the proposed rate law was of interest, with extension of measurements to acidities as low as practicable. Moreover, the suggestion that the inverse acid path involves intervention of a chelated transition state, leading to a chelated Cr(III) product, prompted an examination of the products obtained at different acidities. We find that the sole Cr(III) product resulting from the inverse acid path is, as predicted, a chelate, but that two Cr(III) products, one of them a chelate, result from the acid-independent path. Evidence is here presented for three, rather than two, paths for reductions of both the salicylato and the related 2,6-dihydroxybenzoato complexes.

Experimental Section

Materials. Salicylatopentaamminecobalt(III) perchlorate and the corresponding benzoato, *p*-hydroxybenzoato, 2,6-dihydroxybenzoato, *o*-methoxybenzoato, and *o*-methylbenzoato perchlorates were prepared was described.[3a] Contamination with the parent acid was troublesome in the case of the 2,6-dihydroxy complex; this acid could be removed by continuous ether extraction. Chromous solutions were prepared by reduction of $Cr(ClO_4)_3$ with zinc amalgam,[3a] and sodium and lithium perchlorates (for kinetic experiments) were prepared from the carbonates and recrystallized before use. Concentrations of the Cr(II) solutions were determined from absorbances of the parent $Cr(ClO_4)_3$ solutions; 1 *M* Cr(II) solutions were used within 1 week after their preparation, whereas more dilute solutions were used within 3 days. The cation exchange resin (Bio-Rad AG 50W-X2, 200–400 mesh) used in separations of reaction products was pretreated as described[7] and stored in 0.02 *M* $HClO_4$.

Kinetic Experiments. Reductions were carried out under pseudo-first-order conditions with the ratio Cr(II)/Cr(III) $\sim$ 10 and were monitored by following the decrease in absorbance at 502–503 nm. Acidities ranged from 0.002 to 1.2 *M*; ionic strength was adjusted to 1.20–1.26 *M* (unless otherwise noted) by addition of $LiClO_4$ or $NaClO_4$. Temperatures were 25.0 ± 0.2°. Reactions at high acidities were run using approximately 10 mg of Co(III) complex in 2.0 ml of solution in a 1.0-cm cell; experiments at low acidities were carried out using about 2.0 mg of Co(III) complex in 25.0 ml of solution in a 10-cm cell to minimize the decrease in $[H^+]$ resulting from release of ammonia during the course of a run. For runs with smaller quantities of oxidant, absorbances were measured using the 0–0.2-range spectrophotometer slide wire. Transfers of Cr(II) through rubber serum caps were carried out using small syringes.[8] Reactions were allowed to proceed for at least five half-life periods, and good first-order plots were generally obtained. Rate constants evaluated from different runs at high acidities agreed to about 8%. For runs at acidities below 0.05 *M*, scatter became more severe, and rate constants obtained at the lowest acidities may be considered reliable to 10–15%.

A few experiments were run with SO_4^{2-}–HSO_4^- and $H_2PO_4^-$–H_3PO_4 buffers; good first-order plots were observed, but the Cr(III) products were green rather than the blue typical of pentaaquocarboxylatochromium(III) complexes, indicating that the reductions were carried out, at least in part, by sulfato- or phosphatochromium(II) species.

Separation Experiments. Cation exchange separations were run at 1–2°, using 7–8 in. of resin in a jacketed 25-ml buret. Cobalt(III) complexes were treated with a tenfold excess of Cr(II) at the appropriate acidity, and the reaction was allowed to proceed six to eight half-life periods. Oxygen was bubbled through the mixture to oxidize unreacted Cr(II) to dimeric Cr(III) products, and the solution was then diluted, if necessary, to 0.1 *M* in H^+ and absorbed onto the column. Initial stages of elution employed a solution 0.3 *M* in $NaClO_4$ or $LiClO_4$ and 0.02 *M* in $HClO_4$, but as the elution proceeded the salt concentration was gradually raised to 3.0 *M*. In the Cr(II) reduction of the salicylato complex, an initial dull green fraction was eluted with 0.3 *M* perchlorate, well before the pink Co^{2+} fraction, which was carried out by 0.8–1.0 *M* perchlorate. This was followed by a more diffuse blue fraction, which was eluted with 2.0–2.5 *M* perchlorate Whereas with care, recovery of the more easily eluted green fraction was satisfactorily reproducible (at a given acidity), recovery of the blue fraction was extremely erratic; typically, in four seemingly identical runs in 1.2 *M* $HClO_4$, the chromium contents of this fraction correspond to, 20, 24, 16, and <10% of the Co(III) taken Attempts to improve reproducibility here by variation in column length, elution rate, pretreatment of the column, and substitution of a chelating resin for the polystryenesulfonate were of no avail. Separations of the components in solutions resulting from reductions of the 2,6-dihydroxy complex followed essentially the same pattern. Reduction of the *p*-hydroxybenzoato and *o*-methoxybenzoato complexes gave no dull green fraction preceding Co^{2+}, but a similar blue fraction followed Co^{2+}. In a number of separations, $Cr(H_2O)_6^{3+}$ was introduced as a marker; this was eluted along with the blue fractions, although it exhibited a lower absorbance than the material from the reaction mixtures. Some runs were carried out with excess Co(III), but separations were completely unsatisfactory, with the blue Cr(III) fraction generally contaminated with unreacted Co(III) complex.

Extinction coefficients of the Cr(III) products were obtained by dividing observed absorbancies by total chromium content; the latter was estimated by oxidizing an aliquot with alkaline peroxide to chromate (ϵ_{370} 4940).[9]

Preparation of Salicylatochromium(III) Derivatives. The chelate tetraaquosalicylatochromium(III) was obtained by a modification of the method used by Hamm and coworkers[10] to prepare monodentate pentaaquocarboxylato complexes Sodium salicylate (2 mmol), 2 mmol of salicylic acid, and 4 mol of $Cr(ClO_4)_3$ in 50 ml of water were heated on the steam bath for periods up to 2 hr. The solution was cooled and filtered, and the filtrate was adsorbed onto a cation exchange column. Only two fractions were observed—a dull green fraction, which was eluted with 0.3 *M* $NaClO_4$, and a blue band, which was divided into four approximately equal fractions as it was eluted with 2.5 *M* perchlorate. All four of these blue fractions were $Cr(H_2O)_6^{3+}$. Under our conditions, the only isolable product was the chelate; this was the case for heating periods ranging from 10 min to 2 hr.

Attempted preparations of the pure nonchelated pentaaquosalicylatochromium(III) complex were not successful. However, the procedure of Huchital and Taube[11] yielded a mixture of the nonchelate and $Cr(H_2O)_6^{3+}$. To a deaerated solution 0.12 *M* in salicylic acid, 0.5 *M* in $HClO_4$, and 0.12 *M* in $Cr(ClO_4)_2$ (in 60% methanol) was added an oxygen-free solution of lead perchlorate until the resulting solution was 0.09 *M* in Pb^{2+}. The mixture was allowed to stand 10 min and diluted sixfold with distilled water; then air was bubbled through to convert unreacted Cr(II) to dimeric Cr(III). The mixture was filtered to remove precipitated lead, and the components were separated on cation exchange resin. A faint dull green forerun and a more substantial blue fraction were ob-

based on four measurements at 17.0°, two of which are recorded to only a single significant figure. The plot of these data *vs.* $1/[H^+]$ scatters badly.

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

(8) For injection of Cr(II) solutions, needles with plastic hubs are recommended. The use of needles with chrome-plated copper hubs, unless new, often resulted in formation of a red-brown precipitate (probably metallic copper) after injection of reductant. The time of appearance of this precipitate varied from a few minutes to an hour after the initiation of a run.

(9) "IUPAC Spectrophotometric Data," Butterworths, London, 1963, p 128.

(10) R. E. Hamm, R. L. Johnson, R. H. Perkins, and R. E. Davis, *J. Amer. Chem. Soc.*, 80, 4469 (1958).

(11) D. H. Huchital and H. Taube, *Inorg. Chem.*, 4, 1660 (1965).

served. The later, eluted with 2.5 M $NaClO_4$, exhibited molar extinction coefficients of 21 at 570 nm and 21 at 425 nm; these values lie nearly midway between the corresponding absorbancies for $Cr(H_2O)_6^{3+}$ [12] and known substituted benzoatochromium(III) complexes.[3a] When this fraction was allowed to stand overnight, or was treated with excess Cr(II), absorption in the region 370–400 nm increased and the spectrum slowly approached that observed for the salicylato chelate. A similar oxidation procedure, using $(NH_3)_5Co(H_2O)^{3+}$ instead of Pb^{2+} as an oxidizing agent, yielded significantly less of the desired nonchelated salicylato complex, whereas an attempted preparation *via* diazotization of the $Cr(H_2O)_5$ derivative of anthranilic acid yielded an intractable mixture.

The chelated tetraaquosalicylato complex is much less substitution labile on a polysulfonate resin than are many nonchelated carboxylatochromium(III) derivatives.[13] When a solution of the chelate in 0.02M $HClO_4$ was absorbed onto the resin at 35°, elution with 0.3 M $NaClO_4$ yielded over 95% of the chelate initially taken. Similarly, when the chelated 2,6-dihydroxybenzoatochromium(III) complex in 1.2 M $HClO_4$ was allowed to stand for 1 hr, absorbed onto the resin, and reeluted, over 94% of this chelate was recovered. The equilibrium between the chelated and nonchelated forms of the salicylatochromium(III) complex appears to favor the chelate strongly; when 0.006 mmol of the chelate in 1.2 M $HClO_4$ was treated with 0.03 mmol of Cr^{2+} under nitrogen, no spectral changes were observed, even after a waiting period of 45 min.

Results and Discussion

Kinetic Results. Rate data are summarized in Table I. The few entries for reactions at low ionic strengths indicate a positive kinetic salt effect, as expected for a reaction between two positive ions. This effect is less pronounced than that observed for the pyridinepentaamminecobalt(III) series,[7] in which the oxidant is tripositive. Considering the values for reductions of the salicylato and 2,6-dihydroxybenzoato complexes at high ionic strengths, it is clear that the rates do not level off at low acidities (as is the case for the acetato complex), but instead increase with decreasing acidity to the highest pH values employed.[14] Plots of the observed specific rates *vs.* $1/(H^+)$ (*e.g.*, Figure 1) closely approximate straight lines. For the salicylato complex, the slope is 0.030 sec^{-1}, in reasonable agreement with the earlier value of 0.034 at $\mu = 3$.[3a] Again, in accordance with earlier work, there is no indication of an inverse acid path in reduction of the benzoato or the *p*-hydroxybenzoato complexes.

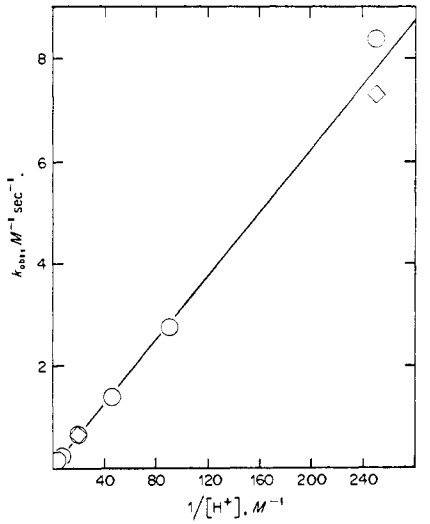


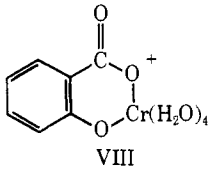
Figure 1. Inverse acid dependence of the observed specific rate for Cr^{2+} reduction of salicylatopentaamminecobalt(III), 25°, μ = 1.23 ± 0.03: ◇, reactions run in aqueous $NaClO_4$; ○, reactions run in aqueous $LiClO_4$. The limiting specific rate at high acidity is 0.11, the acid-independent contribution. The slope of the straight line shown, 0.030 sec^{-1}, is the specific rate for the inverse acid contribution.

Table I. Kinetic Data for Chromous Reduction of Carboxylatopentaamminecobalt(III) Complexes

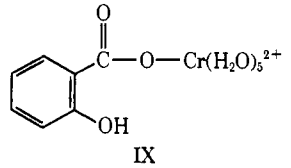
Organic ligand	$[H^+]$, M	μ	k^a
Salicylato[c]	0.0040	0.010	5.5
		1.21	7.3
		1.21[b]	8.4
	0.011	0.017	2.2
		1.21	2.7
	0.021	0.027	1.18
		1.21	1.40
	0.049	0.055	0.46
		1.21	0.69
		1.21[b]	0.69
	0.21	1.26	0.20
		1.26[b]	0.20
	0.402	1.26	0.17
	0.415	1.26[b]	0.16
	1.20	1.26	0.15
	1.19	4.06	0.20
	4.00	4.06	0.17
p-Hydroxybenzoato	0.011	1.21	0.20
	0.019	1.21	0.18
	0.21	0.27	0.10
		1.21	0.17
	1.20	1.26	0.16
2,6-Dihydroxybenzoato[c]	0.010	1.21	1.86
	0.015		1.12
	0.050		0.35
	0.10	1.23	0.23
	0.50	1.26	0.070
	1.20	1.26	0.056
Benzoato	0.020	1.21	0.15
	1.20	1.26	0.15
o-Methylbenzoato	1.20	1.26	0.087

[a] Specific rates in M^{-1} sec^{-1} at 25°; $[Co^{III}]_0$ = 0.00013–0.0013 M; $[Cr^{II}]/[Co^{III}]$ = 10; supporting electrolyte $LiClO_4$. [b] Supporting electrolyte $NaClO_4$. [c] Plots of k *vs.* $1/[H^+]$ give the intercept (limiting specific rate at high acidity) 0.11 M^{-1} sec^{-1} and slope 0.030 sec^{-1} for the salicylato complex (Figure 1), and an intercept of 0.022 M^{-1} sec^{-1} and slope 0.018 sec^{-1} for the 2,6-dihydroxybenzoato complex (μ = 1.23 ± 0.03).

Spectra of Cr(III) Products. Spectral properties of a number of Cr(III) products obtained by reduction of $Co(NH_3)_5$ derivatives are summarized in Table II. The more strongly absorbing of the two salicylato products is taken to be the chelated tetraaquosalicylato complex, VIII, on the basis of its elution behavior



VIII



IX

(characteristic of a unipositive cation) and its unusually low rate of aquation. Moreover, on treatment with

(12) J. A. Laswick and R. A. Plane, *J. Amer. Chem. Soc.*, **81**, 3564 (1959).

(13) E. S. Gould, *ibid.*, **90**, 1740 (1968).

(14) Rates of reactions in solutions where (H^+) was comparable to or less than $(Co^{III})_0$ could not be measured, for each $Co(NH_3)_5$ reduced releases five ammonia molecules; in such cases, acid becomes depleted during the reaction, and metal hydroxides precipitate. Reactions may be run at higher pH in buffered solutions (*e.g.*, the phosphate and sulfate buffers mentioned in the Experimental Section), but the basic component of the buffer coordinates with Cr^{2+}. Under such conditions, acceleration is noted, but the interpretation of kinetic results is complicated by the presence of a new reducing species.

Table II. Spectra of Cr(III) Products Obtained from Cr(II) Reduction of Carboxylatopentaamminecobalt(III) Complexes[a]

Ligand	λ_{max}, nm	ϵ_1	λ_{max}, nm	ϵ_2
Aquo[b]	408	15.6	574	13.4
p-Hydroxybenzoato[c]	411	26	572	26
o-Methoxybenzoato	409	30.0	568	27.5
	410[d]	31.2	568[d]	26.4
	411	25[e]	571	27[e]
Salicylato (chelate)[c]	425[e]	34	557	33
Salicylato (monodentate)[c,f]	410	20	570	18
2,6-Dihydroxybenzoato (chelate)[c]			558	33.1

[a] Spectra taken in 0.02 *M* $HClO_4$. [b] See ref 12. [c] Separated on cation exchange resin. [d] See ref 3a. [e] Shoulder. [f] Some $Cr(H_2O)_6^{3+}$ present.

strong acid it undergoes a rapid and reversible spectral change, whereas the *o*-methoxy and *p*-hydroxy complexes, which cannot form chelates, do not. In particular, the shoulder at 425 nm (ϵ 34) becomes obscured as the ultraviolet maximum at 325 nm (ϵ 1670) in dilute acid becomes more intense and shifts toward the visible (λ_{max} 335 nm; ϵ 1960) in 1.2 *M* $HClO_4$.[15] This chelate is the sole Cr(III) product from reductions of the salicylato complex at low acidities and remains the predominant product in 1.2 *M* acid.

The more difficultly eluted band from reduction of the salicylato complex appears to contain the monodentate Cr(III) product, IX, for if this product is heated or treated with Cr(II), it is slowly converted in part to chelate VIII. The monodentate product is contaminated with $Cr(H_2O)_6^{3+}$, from which, despite the charge difference, it cannot be satisfactorily separated. Absorbancies for this product lie between those of the pure aquo complex and those of other monodentate benzoatochromium(III) complexes listed in Table II. The aquochromium(III) contaminant does not arise from chelate VIII, for this has been shown to be stable under reaction and separation conditions, but almost certainly results from hydrolysis of the monodentate product on the sulfonate resin column, a process which has been shown to occur, to varying degrees, with many carboxylatochromium(III) complexes.[13] Moreover, some aquation of the *o*-methoxybenzoato complex apparently occurs when this Cr(III) derivative is subjected to cation exchange separation, for the absorbancies of column-treated material are slightly below those of the complex prior to such separation.

Spectra of mixtures of the salicylatocobalt(III) complex and Cr(II), taken as the reactions progress, exhibit isosbestic points (Table III), as do spectra from reactions of the benzoato and *o*-methoxybenzoato complexes. Their position depends, as expected, on acidity, but is independent of whether Cr(II) or Co(III) is taken in excess. The existence of these points, while consistent with the formation of only a single significantly absorbing reaction product, does not demand this. What is essential is that the ratio of products arising from the reaction must not change as the reaction progresses. In particular, the conversion of a primary product to another material, while the individual spectra are being observed, is ruled out.

(15) As a result of this shift, solutions of VIII, which are blue-purple in dilute acid, become green in strong acid; moreover, the chelate assumes a green color when absorbed on a polysulfonic acid resin, the surface of which is strongly acidic. This reversible change doubtless reflects conversion of the chelate to its conjugate acid; this conversion is half complete in 0.4 *M* $HClO_4$. Both forms of the chelate exhibit maxima at 245 (ϵ 6500) and 210 nm (ϵ 19,400). It is emphasized that when this chelate is produced by Cr(II) reduction of the salicylatocobalt(III) complex, its distribution between the green and purple forms is a function only of the final acidity of the solution and in no way depends upon the distribution of the reduction between its various kinetic paths. Both distributions are functions of pH, but one depends upon the acidity of the chelated product, whereas the other depends upon the acidity of a reacting species.

Table III. Isosbestic Points Observed during Chromous Reductions of Carboxylatopentaamminecobalt(III) Complexes[a]

Ligand	$[H^+]$	$[Cr^{2+}]_0$	Isosbestic points, nm
Benzoato	1.2	0.0080	561, 435, 388
o-Methoxybenzoato	1.2	0.0120	559, 435, 395
Salicylato	0.1	0.0120	554, 446
	1.2	0.0080	559, 448
		0.0012	559, 448

[a] $[Co^{III}]_{orig}$ = 0.010 *M*; reactions run in $HClO_4$ at 25°; Cr(II) added to Co(III).

Product Distribution and Reaction Paths. The yields of chelated chromium products from reduction of the salicylato- and 2,6-dihydroxybenzoatocobalt(III) complexes at high and low acidities are summarized in Table IV. Since the recovery of the chelate under our separation conditions is nearly quantitative, whereas that of the nonchelate is erratic, the yield of chelate has been taken as a measure of the distribution of product between complexes VIII and IX.[16] Independent estimates of this distribution in the more acidic reaction mixtures, not in contact with ion exchange resin, have been made from the observed optical densities at 410 nm (Table IV). Agreement is seen to be satisfactory, thus ruling out, as does the appearance of isosbestic points in the salicylato reductions, the Cr(II)-catalyzed conversion of one Cr(III) species to another (*i.e.*, ring closure of IX to chelate VIII) on a time scale similar to that of the reduction.

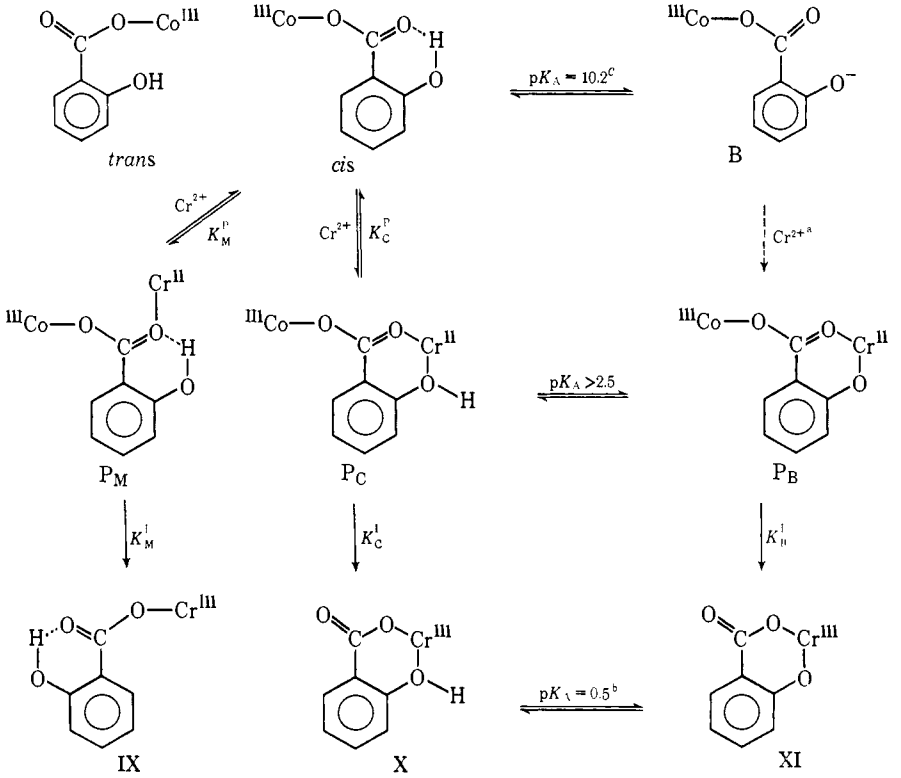
Table IV. Yields of Chelate from Chromium(II) Reductions of Salicylato- and 2,6-Dihydroxybenzoatopentaamminecobalt(III)[a]

	$[H^+]$	$[Co^{III}]_0$	$[Cr^{II}]_0$	Reaction time, min	Chelate, %
Sal	0.02	0.001[b]	0.005	18	95[c]
				20	96[c]
	1.2	0.01	0.05	15	72[c]
				10	74[c]
				20	73[d]
				20	78[d]
2,6	0.02	0.001[b]	0.005	30	98[c]
	1.2	0.01	0.05	40	74[c]
				40	72.5[d]

[a] $HClO_4$ solutions, 25°, Cr(II) added to Co(III). [b] Reactions at low acidity run with more dilute reagents so that NH_3 released during reduction will not deplete H^+ present in solution (see ref 14). [c] Separated on cation exchange column. [d] Estimated from optical density at 410 nm, taking ϵ_{410} for the salicylato chelate as 90.5, for the 2,6-dihydroxy chelate as 125, and for the monodentate complex as 31.2 (the observed value for the *o*-MeO complex; see Table II). Ion exchange separation was not carried out.

(16) Implicit in this expedient is the assumption that the only significant products from these reductions are benzoatochromium(III) complexes; in particular, outer-sphere reduction, which would lead to $Cr(H_2O)_6^{3+}$, is negligible.

Chart I. Proposed Paths for Cr(II) Reduction of Salicylatopentaamminecobalt(III)



[a] Cannot comprise a major pathway for formation of P_B (see text). [b] Approximate pK_A value from variation in spectrum with $[H^+]$ (see ref 15). [c] pK_A calculated for $\mu = 1.0$ (see ref 3a).

At the same time, the possibility of a *very fast* conversion of this type is eliminated by our finding that substantial quantities of IX may be separated from the reductions, with excess Cr(II), of the salicylatocobalt(III) complex, V (in 1.2 *M* $HClO_4$), or of $Pb(ClO_4)_2$ (in 0.12 *M* salicylic acid). Rapid Cr(II)-catalyzed equilibration in these cases would result in nearly complete conversion to chelate VIII, which has here been shown to be considerably more stable than the monodentate complex, IX.[17]

When the reduction of the salicylatocobalt(III) derivative is carried out in 0.02 *M* $HClO_4$, 90% of the reaction proceeds by the inverse acid path. At this acidity, very nearly all of the Cr(III) product is chelate VIII, in accord with the earlier suggestion[3a] of a chelated activated complex for this path. In 1.2 *M* $HClO_4$, only about 18% of the reduction proceeds *via* the inverse acid path. Assuming again that this path leads exclusively to chelate, the remainder of the 74% yield of chelate obtained at this acidity must have been formed *via* the acid-independent route. This corresponds to about 56% of the Cr(III) formed in the reduction, whereas the nonchelate comprises approximately 26%. *There are thus two components to the acid-independent term*, for which an overall specific rate of 0.11 M^{-1} sec^{-1} is evaluated from the intercept in Figure 1; chelate VIII is formed at specific rate 0.075, whereas nonchelate IX is formed at specific rate 0.035 M^{-1} sec^{-1}. An analogous treatment of the rate and product data for the 2,6-dihydroxy complex yields the two acid-independent specific rates 0.0117 M^{-1} sec^{-1} (chelate) and 0.0103 M^{-1} sec^{-1} (nonchelate).

Our interpretation of the kinetic and distribution data for the salicylato complex is summarized in Chart I. The three paths are represented as proceding through different binuclear intermediates or precursor complexes,[18] indicated as P_C, P_M, and P_B. The transition state leading to the chelate *via* the acid-independent path necessarily has one proton more than that intervening in the inverse acid path (P_B), but the distribution between the two chelated products is, as shown, a function of the final pH of the solution.

The possibility that the chelated and nonchelated products arise, respectively, from the *cis* and *trans* rotamers of the salicylatocobalt(III) complex appears to be ruled out by our observation that the 2,6-dihydroxy derivative (for which the two rotamers are identical) also yields, by an acid-independent path, two different Cr(III) products. It is considerably more likely that both products arise from the hydrogen-bonded *cis* rotamer, which would be expected to be much the predominant form of the Co(III) complex in solution. On this basis, the observed product distribution between the monodentate Cr(III) product, IX, and the chelate arising from the acid-independent path reflects both the competition between H^+ and Cr^{2+} for the chelated site in the precursor and the relative rates of internal electron transfer for the two possible precursors, P_C and P_M.[19]

(17) Cr(II)-catalyzed conversion of the primary Cr(III) product to another species, although not of importance in interpretation of the present work, has been found to be a complication in other Cr(II) reductions of Co(III) complexes. See, for example, H. Taube and J. K. Hurst, *J. Amer. Chem. Soc.*, 90, 1178 (1968); H. Taube and F. Nordmeyer, *ibid.*, 90, 1162 (1968); D. Huchital, *Inorg. Chem.*, 9, 486 (1970).

(18) See, for example: (a) N. Sutin, *Accounts Chem. Res.*, 1, 225 (1968); (b) H. Taube and E. S. Gould, *ibid.*, 2, 321 (1969).

(19) Assuming only small steady-state concentrations for precursors P_C and P_M, the ratio of observed specific rates for formation of chelate and monodentate products from the acid independent path is

$$k_C/k_M = K_C^P k_C^1 / K_M^P k_M^1 \qquad \text{(ii)}$$

Although reduction *via* the inverse acid path leads, as expected, only to a chelated Cr(III) product, the early view[3a] that this path represents reaction of conjugate base VI with Cr^{2+}, proceeding at a specific rate greater than 10^8 M^{-1} sec^{-1}, is almost certainly incorrect. The maximum rate for a diffusion-controlled bimolecular reaction between noncharged particles in water at 25° is approximately 7×10^9,[20] but this figure, in the present case, must be corrected for ionic charge and entropy of activation. The charge correction is difficult to estimate, for although a reaction between VI and Cr^{2+} involves two positive ions, the electrostatic interaction would be principally between Cr^{2+} and the negative phenoxy group; in any event, the correction factor here should not vary greatly from unity. The entropy of activation should resemble that for other Cr(II) reductions of carboxylatocobalt(III) complexes which proceed through chelated activated complexes. A reasonable value, −20 eu,[21] corresponds to 4.4 powers of ten in rate; hence the specific rate for direct reaction of VI cannot be much greater than 3×10^5. The reduction of complex V with $CrOH^+$, which is kinetically equivalent, can likewise be excluded, principally because of the very low acidity[22] of Cr_{aq}^{2+}; moreover, such a mechanism allows no role for the *o*-OH group, without which the inverse acid path is not observed.

It is suggested, therefore, that the activated complex for the principal inverse acid path is formed by loss of a proton from binuclear complex P_C, the precursor complex leading to chelate **X**. Although the acidity of P_C cannot be readily evaluated, this species may be assumed to be a much stronger acid than either Cr_{aq}^{2+} or the salicylatocobalt(III) complex, for there are two acid-strengthening groups, rather than one, bound to the hydroxyl; an analogous enhancement of acidity occurs with **X** ($pK_A = 0.5$), the conjugate acid of VIII, which is here observed to be a stronger acid than either salicylic acid or $Cr(H_2O)_6^{3+}$. At the same time, pK_A for precursor P_C must be significantly greater than 2.5, since reduction rates have been found to be inversely proportional to $[H^+]$ at pH values near this.

If the proposed inverse acid path for reduction is correct, this work adds to the growing body of evidence[23] that the dinuclear species intervening in such electron transfer reactions are true intermediates, rather than activated complexes, for an intermediate may undergo partition into two products, whereas a transition state may not.

Finally, it appears that internal electron transfer through precursor P_C is much slower than through its conjugate base P_B, although neither specific rate can, as yet, be measured. If the two chelated paths proceed through a common intermediate P_C under conditions where the rate of the conjugate base path varies as $1/[H^+]$, the ratio of rate constants, here found to be 0.030/0.075, is

$$k_B/k_C = K_A^C k_B^I / k_C^I \qquad (1)$$

where the k^I terms refer to the specific rates of internal electron transfer through the two precursors and K_A^C is the acidity constant for P_C. Since the latter value is less than 0.003, the ratio of the k^I values should exceed 130 and may be many times this figure.

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where the K^P values represent association constants for the precursors and the k^I values represent specific rates of internal electron transfer. It has been shown[3] that benzoato complexes of $Co(NH_3)_5$ having substituents with widely different electronic character, but with similar steric requirements, are reduced, in the absence of remote attack or chelation, at very nearly the same specific rates. The relatively low figure for formation of the monodentate product IX may then reasonably be taken to arise mainly from a low concentration of its precursor, P_M.

(20) See, for example, E. F. Caldin, "Fast Reactions in Solution," Wiley, New York, N. Y., 1964, p 12.

(21) R. D. Butler and H. Taube, *J. Amer. Chem. Soc.*, 87, 5597 (1965). The value selected is about 5 eu less negative than the $\Delta S^{\neq}$ values reported for Cr(II) reductions of the glycolato and benzilato complexes, since the latter two reactions involve Co(III) complexes having net charge of 2+.

(22) The acidity of Cr_{aq}^{2+} should lie between that of Mn_{aq}^{2+} (pK = 10.6) and that of Ca_{aq}^{2+} (pK_a = 12.6), being perhaps nearer to the former value. See, for example, F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967, p 32.

(23) See, for example: (a) M. P. Liteplo and J. F. Endicott, *J. Amer. Chem. Soc.*, **91**, 6977 (1969); (b) R. C. Patel, R. E. Ball, J. F. Endicott, and R. G. Hughes, *Inorg. Chem.*, **9**, 23 (1970).