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

(5) Carbonyl-bound Cr(III) intermediates have also been characterized in the reductions of ring-coordinated Co(III) derivatives of 3- and 4-pyridinecarboxamide.[2b] The carbonyl groups in such species are part of amide systems and are therefore much more strongly basic than those in the present study.

(6) See, for example, A. Streitwieser, Jr., "Solvolytic Displacement Reactions", McGraw-Hill, New York, N.Y., 1962, p 35.

(7) D. Samuel and B. L. Silver, *Adv. Phys. Org. Chem.*, **3**, 149 (1965).

(8) See, for example, A. A. Frost and R. G. Pearson, "Kinetics and Mechanism", 2d ed, Wiley, New York, N.Y., 1961, p 167.

(9) (a) F.-R. F. Fan and E. S. Gould, *Inorg. Chem.*, **13**, 2639, 2647 (1974); (b) E. R. Dockal and E. S. Gould, *J. Am. Chem. Soc.*, **94**, 6673 (1972).

(10) (a) J. C. Chen and E. S. Gould, *J. Am. Chem. Soc.*, **95**, 5539 (1973); (b) P. R. Guenther and R. G. Linck, *ibid.*, **91**, 3767 (1969); (c) G. Telep and D. F. Boltz, *Anal. Chem.*, **23**, 901 (1951).

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

(12) S. Sugasawa and M. Kirisawa, *Chem. Pharm. Bull.*, **6**, 615 (1958); *Chem. Abstr.*, **54**, 14243*i* (1960).

(13) C. K. Bradsher and J. C. Parham, *J. Org. Chem.*, **28**, 84 (1963).

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

(15) H. J. Price and H. Taube, *J. Am. Chem. Soc.*, **89**, 269 (1967).

(16) The extinction coefficient is estimated from absorbance at maximum conversion to the intermediate (calculated[8] to be 73%). This estimate also takes into account the partition of oxidant into the active carbonyl and inactive hydrated forms (Table III).

(17) An additional kinetic component, a first-order decrease in absorbance, was observed for many Cr(II) reductions in this series when the mixtures were observed in the spectral range 300–330 nm. The decay constant, 3.5×10^2 s^{-1}, was independent of $[Cr^{2+}]$, $[H^+]$, and $[Co^{III}]_0$. The magnitude of the spectral change could be minimized by taking special precautions to remove oxygen, but vestiges of the curve (with decay constant unchanged) persisted. The characteristics of this reaction are consistent with unimolecular decay of a complex formed very rapidly from the reaction of Cr(II) with traces of oxygen in the system (see, for example, M. Ardon and R. A. Plane, *J. Am. Chem. Soc.*, **81**, 3197 (1959)).

(18) W. Mathes, W. Sauermilch, and T. Klein, *Chem. Ber.*, **87**, 1870 (1954). In our hands, high yields of this glycol were obtained only when the reaction mixture was stirred at 100 °C for 2 h rather than at room temperature for 5 h as recommended by these workers.

(19) See, for example: (a) R. P. Bell, *Adv. Phys. Org. Chem.*, **4**, 1 (1966); (b) Y. Ogata and A. Kawasaki, "Chemistry of the Carbonyl Group", Vol. 2, J. Zabicky, Ed., Interscience, New York, N.Y., 1970, p 1.

(20) Y. Pocker, J. E. Meany, and B. J. Nist, *J. Phys. Chem.*, **71**, 4509 (1967).

(21) See, for example, Y. Wang and E. S. Gould, *J. Am. Chem. Soc.*, **91**, 4998 (1969).

(22) A portion of the bound ligand may also be reduced rapidly *before* reduction of Co(III) (as is the case in reductions of nitrobenzoatocobalt(III) complexes[23]). Such reduction should yield a second, less conjugated, Co(III) complex, leading to a two-component kinetic curve when the disappearance of Co(III) is monitored in the presence of excess reductant. A second, very slow, component is indeed observed for some of the reductions by Eu(II) and V(II) but not for reductions of the keto-substituted complexes by Cr(II). Although this component, when present, did not seriously complicate evaluation of the specific rates for the primary reactions, further examination of these systems is desirable.

(23) E. S. Gould, *J. Am. Chem. Soc.*, **88**, 2983 (1966).

(24) D. P. Rillema, J. F. Endicott, and R. C. Patel, *J. Am. Chem. Soc.*, **94**, 394 (1972).

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

(26) R. G. Linck, *Inorg. Chem.*, **9**, 2529 (1970).

(27) A. H. Martin and E. S. Gould, *Inorg. Chem.*, **14**, 873 (1975).

(28) The following specific rates (M^{-1} s^{-1}, 25 °C) for Cr^{2+} reductions of carbonyl-substituted benzoato derivatives of $(NH_3)_5Co^{III}$ have been reported: 2-C_6H_5CO, 5.4 (μ = 3.0);[2a] 2-CHO, 94 (μ = 1.2);[3] 4-C_6H_5CO, 0.32 + 1.5$[H^+]$ (μ = 3.0);[2a] 4-CHO, 53 + 380$[H^+]$ (μ = 1.0).[4] Note that the greater bridging effectiveness of the CHO group extends to the first-order $[H^+]$ term, as well as to the acid-independent term.

(29) H. Strehlow, *Z. Elektrochem.*, **66**, 392 (1962).

(30) Y. Pocker and J. E. Meany, *J. Phys. Chem.*, **72**, 655 (1968), reported a specific rate 1400$[H^+]$ s^{-1} for the H^+-catalyzed hydration of uncomplexed 4-pyridinecarboxaldehyde. If the reverse reaction, the dehydration, is taken to proceed at specific rate near 1$[H^+]$ s^{-1}, the carbonyl:hydrate ratio at equilibrium may be approximated as 0.007, in agreement with the upper limit for this ratio estimated by NMR (Table III).

(31) It is likely that the V^{2+} reduction of the 4-CHO derivative is predominantly outer sphere. The k_V value for this complex lies very close to that for the $(NH_3)_5Co^{III}$ complex of *N,N*-dimethylnicotinamide (1.38 s^{-1}),[10a] an outer-sphere oxidant.[32]

(32) E. S. Gould, *J. Am. Chem. Soc.*, **90**, 1740 (1968).

(33) The lower limit 10^6 M^{-1} s^{-1} for Cr^{2+} reduction of the 4-CHO complex was estimated by assuming the specific rate for this reduction (a pseudo-first-order reaction under the conditions used) to be at least 5 times that for aquation of X at the lowest concentration of Cr^{2+} taken (0.0025 M) to accommodate the observed nondependence on $[Cr^{2+}]$.

(34) See, for example, J. K. Hurst and H. Taube, *J. Am. Chem. Soc.*, **90**, 1174 (1968).

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

Electron Transfer through Organic Structures. 23. Titanium(III) Reductions of Salicylatocobalt(III) Derivatives[1]

ALBERT H. MARTIN and EDWIN S. GOULD*

Received January 13, 1976 AIC600325

Rates of reduction, with Ti(III), of the salicylato (I) and several substituted salicylato derivatives of $(NH_3)_5Co^{III}$ have been measured at 25 °C and 0.025–1.0 M H^+ in *p*-toluenesulfonate media. These reactions follow a rate law of the type: rate = $[Ti^{III}][Co^{III}]k_{lim}(1 + [H^+]/K)^{-1}$ where values of k_{lim}, the limiting specific rate at low acidities, lie near 100 M^{-1} s^{-1} and K is approximately 1 M. Neither the oxidant (pK_A = 8–10) nor the reductant (pK_A = 2–3) is substantially deprotonated in the region where $[H^+]$ dependence is steepest. Rate behavior is consistent with the intervention of a chelated precursor complex (II) formed (k_1) from the two metal centers with loss of H^+, after which internal electron transfer (k_2) competes with nonproductive dissociation of the precursor (k_{-1}). Values of k_1, which reflect substitution at the Ti(III) center, are comparable to reported estimates for $(NH_3)_5CoF^{2+}$ and $(NH_3)_5CoN_3^{2+}$ but about 10^2 lower than the specific rate for substitution of NCS^- at $Ti(H_2O)_6^{3+}$, which is electrostatically more favorable. The ratios k_2/k_{-1} for the salicylato oxidants are 20–100 times as great as for the fluoro and azido complexes, mirroring the enhanced stability of the salicylato precursor arising from chelation.

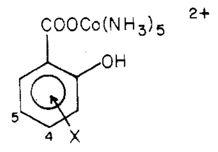
Since 1973 there has been a quickening of interest in the electron-transfer reactions of Ti(III).[2,3] Various difficulties reported by earlier workers[4] to be associated with choice of reaction media have been sidestepped, and specific rates for reduction of over two dozen Co(III) complexes by this d^1 center have been measured. Strong, although indirect, evidence is at hand that such reactions proceed by inner-sphere paths if the oxidant features a sufficiently hard bridging ligand. It has further been shown[3d] that chelating substituents having O donors may strongly influence reaction rates and that reaction paths featuring the loss of H^+ from the Ti(III) center are unusually prominent. Moreover, it now appears that

Table I. Kinetic Data for Titanium(III) Reductions of Substituted Salicylatopentaamminecobalt(III) Complexes, $R(NH_3)_5Co^{III}$

Organic ligand, R	$[H^+]$, M	k,[a] M^{-1} s^{-1}
Salicylato	0.98	43
	0.72	49
	0.47	56
	0.24	66
	0.095	88
	0.050	88
	0.026	88
4-Methylsalicylato	0.99	55
	0.72	65
	0.45	79
	0.23	92
5-Methylsalicylato	0.98	70
	0.72	82
	0.57	88
	0.47	90
	0.24	105
	0.095	118
2,4-Dihydroxybenzoato	0.99	65
	0.72	74
	0.45	87
	0.36	94
	0.14	114
	0.070	128
Salicylato[b]	1.00	27
	0.50	41
	0.10	77
	0.050	84
	0.0375	87

[a] Specific rates at 25 °C, $\mu = 1.0$; supporting electrolyte HOTs–NaOTs unless otherwise indicated. k defined as $(-d[Co^{III}]/dt)\cdot[Co^{III}]^{-1}[Ti^{III}]^{-1}$. $[Co^{III}] = 3 \times 10^{-4}$–$10^{-3}$ M and $[Ti^{III}]_0/[Co^{III}] = 0.1$–$0.2$. Values are averages of two to five replicate runs; agreement between runs was better than 6%. [b] Supporting electrolyte $HClO_4$–$LiClO_4$.

substitution at Ti(III), which must occur in the formation of a binuclear precursor complex, need not be much more rapid than electron transfer within the precursor. The latter point is of particular interest in the present work, which deals with reduction, by Ti(III), of substituted salicylatopentaamminecobalt(III) derivatives (I) in *p*-toluenesulfonate (OTs⁻) media.



I

Experimental Section

Materials. Titanium(III) solutions,[3d] solutions of *p*-toluenesulfonic acid (HOTs) and its sodium salt (NaOTs),[3d] and lithium perchlorate[5] were prepared as described. Cobalt(III) complexes were available from previous studies[6] or were prepared by published procedures.[7]

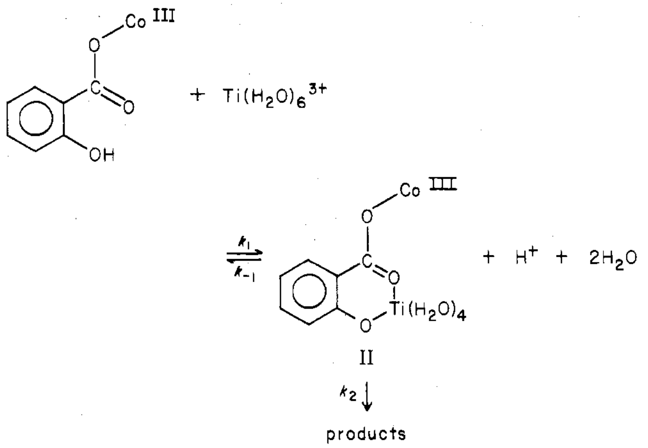
Rate Measurements. Reactions were followed by measuring absorbance differences on a Cary spectrophotometer as described.[3d] Measurements were carried out under pseudo-first-order conditions using at least a fivefold excess of Co(III). The temperature was maintained at 25.0 ± 0.2 °C for all runs. The ionic strength was kept near 1.0 using HOTs–NaOTs or, in a few cases, $HClO_4$–$LiClO_4$. All reactions were first order each in Co(III) and Ti(III). Reactions were followed for at least 5 half-lives. Rate constants obtained from successive half-life values within a single run agreed to within 4%. No trends indicative of systematic errors were noted, and average values did not differ significantly from those obtained from least-squares treatment of logarithmic plots of absorbance differences against reaction time. Specific rates obtained from replicate runs checked to within 6%. No evidence for autocatalysis, as reported for related systems,[8] was obtained.

Results and Discussion

Kinetic data appear in Table I. Reductions of each of the salicylato complexes in the present study are retarded at high acidities. However, we are not dealing with a simple $[H^+]^{-1}$ proportionality, for specific rates approach limiting values at $[H^+]$ near 0.05–0.10 M. This acidity dependence is by no means general for Ti(III)–Co(III) reactions. Reductions inverse first order in $[H^+]$ are more usual, particularly for oxidants having no acidic hydrogen.[3d,e] Several other substituted salicylatocobalt(III) complexes are reduced at rates independent of $[H^+]$,[3d] and rate laws with terms proportional to $[H^+]^{-2}$ have also been found.[3d] The observed variations of rate with acidity are too steep to be attributed reasonably to medium effects associated with substitution of Na^+ for H^+ in the supporting electrolyte,[9] nor can they be linked to peculiarities of toluenesulfonate systems, for they persist when reductions are carried out in $HClO_4$–$LiClO_4$.

The observed acidity patterns are of the type appropriate for systems in which one of the reacting species is partitioned into an inactive acidic form and a kinetically active basic form, with the two forms existing in nearly equal concentrations in 1 M HOTs. However, both the reductant (which exhibits a medium-dependent pK_A value between 1.9 and 2.8)[10-12] and the oxidants (for which pK_A's lie between 8 and 10)[7] exist very nearly completely in their protonated forms at this high acidity.

The same difficulty has been encountered by Birk[3c] in the study of the Ti(III) reduction of $Co(NH_3)_5N_3^{2+}$ and by Thompson and Sykes[13] in the Ti^{III}–$Co(NH_3)_5F^{2+}$ system. Observed rate laws in both cases are consistent with the intervention of a precursor complex, formed from the two metal centers with loss of H^+, after which the act of internal electron transfer occurs:



Applying the steady-state approximation to the precursor (here represented as II) leads to rate law (1)[14,15]

$$\text{rate} = \frac{[Ti^{III}][Co^{III}]k_1k_2}{k_{-1}[H^+] + k_2} \tag{1}$$

where $[Ti^{III}]$ represents total tripositive titanium in solution. This simplifies to the more familiar inverse-acid form contributing to a number of reductions by Cr(II),[7] Cu(I),[5] and Eu(II)[16] when the formation of the precursor and its reversal become very rapid in relation to internal electron transfer.

Experiments under steady-state conditions do not allow evaluation of all three rate constants in (1). However, plots of $(\text{rate}/[Ti^{III}][Co^{III}])^{-1}$ vs. $[H^+]$, which are closely linear, give $1/k_1$ as intercept and k_{-1}/k_1k_2 as slope, thus allowing calculation of k_1 and the ratio k_2/k_{-1}. These parameters are assembled and compared with the corresponding quantities reported for reductions of the fluoro and azido complexes in Table II.

Table II. Calculated Kinetic Parameters for Titanium(III) Reductions of Pentaamminecobalt(III) Complexes, $R(NH_3)_5Co^{III}$ [a]

Ligand, R	k_1,[b] M^{-1} s^{-1}	k_2/k_{-1},[b] M
Salicylato	94	0.79
4-Methylsalicylato	117	0.89
5-Methylsalicylato	124	1.33
4-Hydroxysalicylato	137	0.93
Azido[c]	47	0.045
Fluoro[d]	562	0.112

[a] Reactions at 25 °C, $\mu = 1.0$; supporting electrolyte HOTs–NaOTs unless otherwise indicated. [b] k_1, k_{-1}, and k_2 are specific rates in eq 1. Values were calculated from plots of $1/k_{obsd}$ vs. $[H^+]$ (see text). [c] $\mu = 0.50$; supporting electrolyte LiCl–LiClO$_4$ (see ref 3c). [d] $\mu = 0.50$; supporting electrolyte LiCl (see ref 13).

In the mechanism proposed, k_1 is the specific rate for a substitution at the Ti(III) center. Values of k_1 for the dipositive salicylato complexes in this study fall between those for the fluoro and azido complexes (also dipositive) and, on this basis, may be considered reasonable. All k_1's lie well below 10^4 M^{-1} s^{-1}, the estimated[17] bimolecular specific rate for substitution of NCS^- at Ti^{3+}, but this retardation may be presumed to stem, in large part, from the marked dissimilarity in charge type (to which reactions of this sort have been shown to be sensitive[18]). The ratio k_2/k_{-1} is 20–100 times as great for the salicylato complexes as for the fluoro and azido oxidants. We attribute the greater salicylato ratios not to differences in k_2, the specific rates of internal electron transfer, but mainly to lower values of k_{-1}, the rate constant for dissociation of the precursor. Hence, the extra stability in the precursor arising from chelation, which results in enhanced overall rates of reductions with Cu(I) and Cr(II),[5-7] is reflected specifically in this term in the present series.

When k_2 greatly exceeds $k_{-1}[H^+]$, the initial step becomes essentially irreversible, rate law (1) assumes a simple monomial form with no H^+ dependence, and the rate of reaction is determined by substitution about Ti(III). This appears to be the case in the reductions of the 3-methylsalicylato, 3-phenylsalicylato, and 1-hydroxy-2-naphthoato[19] derivatives of $(NH_3)_5Co^{III}$, which, although closely related to the oxidants in this study, are reduced at acid-independent specific rates near 3 M s^{-1} (25 °C, 0.04–1.0 M H^+).[3d] We are astonished, however, that incorporation of a nonreacting substituent at a site well removed from the reaction center has so profoundly influenced the kinetic character of the oxidation. Not only has it markedly altered the relative values of k_{-1} and k_2 but (if our interpretation is correct) it also has retarded substitution at Ti(III) by a factor of 30–40. We can, at present, offer no convincing rationale for the intensity of this effect.

Acknowledgment. The authors are indebted to Professor A. G. Sykes for making known his kinetic results prior to publication.

Registry No. I (X = H), 30931-74-9; I (X = 4-Me), 59388-93-1; I (X = 5-Me), 59388-94-2; I (X = 4-OH), 59388-95-3; Ti^{III}, 22541-75-9.

References and Notes

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

(2) For references to early studies, see J. D. Ellis and A. G. Sykes, *J. Chem. Soc., Dalton Trans.*, 573 (1973).

(3) (a) J. P. Birk and T. P. Logan, *Inorg. Chem.*, **12**, 580 (1973); (b) T. P. Logan and J. P. Birk, *ibid.*, **12**, 2464 (1973); (c) J. P. Birk, *ibid.*, **14**, 1724 (1975); (d) A. H. Martin and E. S. Gould, *ibid.*, **14**, 873 (1975); (e) M. Orhanovic and J. E. Earley, *ibid.*, **14**, 1478 (1975).

(4) See, for example, V. W. Cope, R. G. Miller, and R. T. M. Fraser, *J. Chem. Soc. A*, 301 (1967).

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

(6) (a) A. Liang and E. S. Gould, *J. Am. Chem. Soc.*, **92**, 6791 (1970); (b) A. H. Martin, A. Liang, and E. S. Gould, *Inorg. Chem.*, **15**, 1925 (1976).

(7) E. S. Gould and H. Taube, *J. Am. Chem. Soc.*, **86**, 1318 (1964).

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

(9) For examples of such medium effects in inner-sphere reductions of Co(III), see: (a) D. L. Toppen and R. G. Linck, *Inorg. Chem.*, **10**, 2635 (1971); (b) C. Lavallee and E. Deutsch, *ibid.*, **11**, 3133 (1972); (c) P. K. Thamburaj and E. S. Gould, *ibid.*, **14**, 15 (1975).

(10) Reported pK_A's for $Ti^{III}(aq)$ are 2.8 (in aqueous chloride[11]), 2.0 (in aqueous bromide and iodide[12]), and 1.9 (in aqueous perchlorate[3c]).

(11) H. Krentzien and F. Brio, *Ion (Madrid)*, **30**, 14 (1970); *Chem. Abstr.*, **73**, 7865 (1970).

(12) R. L. Pecsok and A. N. Fletcher, *Inorg. Chem.*, **1**, 155 (1962).

(13) G. A. K. Thompson and A. G. Sykes, *Inorg. Chem.*, **15**, 638 (1976).

(14) Birk[3c] has pointed out that the alternate path

$$Co^{III} + TiOH^{2+} \rightleftharpoons CoTiOH \xrightarrow{H^+} \text{products}$$

is also consistent with a rate law having the form (1). This sequence, however, features an act of electron transfer which is triggered by protonation. Such a step appears to be without precedent for oxidants of the present type, although protonation is known to facilitate the inner-sphere reduction of certain carboxylatocobalt(III) complexes having an aldehyde or keto group in conjugation with the bound carboxyl.[15]

(15) (a) A. Zanella and H. Taube, *J. Am. Chem. Soc.*, **94**, 6403 (1972); (b) E. S. Gould, *ibid.*, **96**, 2373 (1974).

(16) F. R.-F. Fan and E. S. Gould, *Inorg. Chem.*, **13**, 2639 (1974).

(17) H. Diebler, *Z. Phys. Chem. (Frankfurt am Main)*, **68**, 64 (1969), reported a unimolecular rate constant 8×10^3 s^{-1} (9 °C, $\mu = 1.5$) for substitution of NCS^- for H_2O in the ion pair $Ti(H_2O)_6{}^{3+}$,NCS^-. This value, in conjunction with the estimated formation constant of this ion pair (ca. 1 M^{-1}), leads to a bimolecular specific rate near 8×10^3 M^{-1} s^{-1} for the composite process at 9 °C.

(18) See, for example, D. J. Hewkin and R. H. Prince, *Coord. Chem. Rev.*, **5**, 45 (1973).

(19) Note that this complex was incorrectly designated a 2-hydroxy-1-naphthoato derivative in an earlier report.[3d]