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Electron Transfer. 62. Keto Carboxylato Groups as Mediators in the Reactions of Titanium(III) with Bound Cobalt(III)[1]

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The reductions, using titanium(III), of $(NH_3)_5Co^{III}$ complexes of keto-substituted carboxylic acids conform to three distinct kinetic acidity patterns. Complexes of β- and γ-keto acids are reduced at rates comparable to those for complexes of acids that are devoid of carbonyl groups and, like the latter group, exhibit straightforward dependence on $[H^+]^{-1}$. Hence, no rate enhancement results from incorporation of remote keto groups. Six of the α-carbonyl-substituted oxidants, each of which is partially converted by hydration to a *gem*-diol species ($>C{=}O + H_2O \rightleftharpoons >C(OH)_2$), are reduced much more rapidly with rates proportional to an expression of the type $(a[H^+] + b[H^+]^2)^{-1}$. For this group, the proposed mechanism entails reversible attack by the deprotonated reductant, $Ti(OH)^{2+}$, on the *gem*-diol form of the oxidant (with specific rate 400–2000 $M^{-1}\ s^{-1}$), yielding a chelated precursor complex and expelling another proton, followed by the act of internal electron transfer. In such systems, reduction by Ti(III) differs from that by Cr(II) and Eu(II), for the latter centers react preferentially with the dehydrated (carbonyl) form of the oxidant. The complexes of substituted phenylglyoxylic acids (e.g., VII) are also reduced rapidly, but here rates are proportional to an expression of the type $(a + b[H^+])^{-1}$. The latter pattern is consistent with a two-step sequence in which a Co(III)–Ti(III) precursor is formed from $Ti(H_2O)_6^{3+}$ (with proton loss) prior to electron transfer. Ligands in this class display enhanced electron affinity and exist almost wholly in their dehydrated forms; rapid reductions of the complex are attributed to the existence of a low-lying acceptor orbital, which embraces the aromatic ring, the α-carbonyl group, and the $-COOCo^{III}$ function. Reduction of the oxamato complex is found to be complicated by formation of a 1:2 complex $(H_2NCOCOO)_2Ti^+$ (λ_{max} = 410 nm; $K_{dis} = 4 \times 10^{-7}\ M^2$) arising from ligation of Ti(III) by the carboxylic acid liberated in the primary reaction.

Past reports dealt in part with kinetic acidity patterns governing the inner-sphere reactions of metal ion reductants with carboxylato-bound cobalt(III).[2] Patterns associated with reductions by $Ti(H_2O)_6^{3+}$ have been found to be particularly diverse.[3] This cation (pK_A = 1.9–2.8)[4,5] undergoes significant partition between protonation levels, even at relatively low pHs; moreover, the sluggishness of substitution at the Ti(III) center[5c,6] leads to further kinetic variations that have not yet been encountered in the redox chemistry of Cr^{2+}, Eu^{2+}, and U^{3+}.

The present work, which constitutes an extension of our study[3] of inner-sphere Ti(III)–Co(III) reactions, is concerned principally with mediation by ligands of a single structural type, carbonyl-substituted carboxylate groups. Even within these confines, marked behavioral differences appear.

Experimental Section

Materials. Lithium chloride (Aldrich), used as a supporting electrolyte in kinetic studies, was recrystallized once and then dried at 130 °C. Solutions of $TiCl_3$ were made by dissolving the salt (an Alfa product) in deoxyganated 1 M HCl (glovebag) and then filtering. The stock solution, which was approximately 0.2 M in Ti(III), was stored under N_2 and was used within 3 days of preparation. It was standardized by spectrophotometric methods (ϵ_{502} 3.97 $M\ cm^{-1}$)[7] or by treatment with an excess of the binoxalato derivative of $(NH_3)_5Co^{III}$, diluting with a known volume of concentrated HCl, and measuring the quantity of Co(II) present at 692 nm.[8,9] Of the organic acids used as ligands, trimethylpyruvic acid[10] and (4-methoxyphenyl)- and (2,4,6-trimethoxyphenyl)glyoxylic acids[11] were prepared by using known oxidation procedures. The remaining ligands (Aldrich products) were used as received.

Cobalt(III) Complexes. (Carboxylato)pentaamminecobalt(III) perchlorates, used as oxidants, were prepared by treatment of the parent carboxylic acids with the corresponding aquopentaammine perchlorate in water[9] or with the (carbonato)pentaammine nitrate in methanol[12] or in diethylene glycol.[13,14] Modifications of literature procedures were introduced in several instances. Ligation of glyoxylic acid was carried out at 65 °C for 4 h (rather than at the suggested[15] 45 °C for 12 h). The unusually soluble complex of ketomalonic acid was prepared from the lithium salt (rather than the less soluble sodium salt) and was purified by passage through a column of Biogel P2 Resin.[16a] The usual final recrystallizations from water were omitted for the complexes of trichloropyruvic and γ-ketopimelic acids; the trichloro derivative was found to suffer partial hydrolysis to the oxalato complex, whereas the γ-keto derivative undergoes aquation with astonishing ease. Analyses of new complexes appear in Table I. Treatment of the complexes of α-keto acids in solution with 0.1 M

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[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) Taube, H.; Gould, E. S. *Acc. Chem. Res.* **1969**, *2*, 321. (b) Hurst, J. K.; Taube, H. *J. Am. Chem. Soc.* **1968**, *90*, 1178. (c) Zanella, A.; Taube, H. *Ibid.* **1972**, *94*, 6403. (d) Barrett, M. B.; Swinehart, J. H.; Taube, H. *Inorg. Chem.* **1971**, *10*, 1983. (e) Gould, E. S. *J. Am. Chem. Soc.* **1974**, *96*, 2373. (f) Thamburaj, P. K.; Loar, M.; Gould, E. S. *Inorg. Chem.* **1977**, *16*, 1946. (g) Thomas, J. C.; Reed, J. W.; Gould, E. S. *Ibid.* **1975**, *14*, 1696. (h) Loar, M.; Thomas, J. C.; Reed, J. W.; Gould, E. S. *Ibid.* **1977**, *16*, 2877.

[3] Martin, A. H.; Gould, E. S. *Inorg. Chem.* **1975**, *14*, 873; **1976**, *15*, 1934.

[4] Reported pK_A's for $Ti^{III}(aq)$ are 2.64 (in aqueous chloride[5a]), 2.0 (in aqueous bromide and iodide[5b]), and 1.9 (in aqueous perchlorate[5c]).

[5] (a) Brunschwig, B. S.; Sutin, N. *Inorg. Chem.* **1979**, *18*, 1731. (b) Pecsok, R. L.; Fletcher, A. N. *Ibid.* **1962**, *1*, 155. (c) Birk, J. P. *Ibid.* **1975**, *14*, 1724.

[6] (a) Thompson, G. A. K.; Sykes, A. G. *Inorg. Chem.* **1976**, *15*, 638. (b) Diebler, H. *Z. Phys. Chem. (Frankfurt am Main)* **1969**, *68*, 64.

[7] Birk, J. P.; Logan, T. P. *Inorg. Chem.* **1973**, *12*, 580.

[8] The standardization of Ti(III) solutions by electron transfer is a modification of that previously described,[3,9] but the more commonly used chloro complex of $(NH_3)_5Co^{III}$ has been replaced by the corresponding hydrogen oxalato derivative. This substitution avoids possible precipitation of $Cl(NH_3)_5CoCl_2$ in the added HCl if too large an excess of the oxidant is used. In our hands, treatment of the $TiCl_3$ stock solution with zinc amalgam, to reduce traces of Ti(IV), or work with concentrations of the reductant greater than 0.2 M often resulted in the development of turbidity.

[9] Gould, E. S.; Taube, H. *J. Am. Chem. Soc.* **1964**, *86*, 1318.

[10] (a) Glucksmann, C. *Monatsh. Chem.* **1889**, *10*, 770. (b) Price, H. J.; Taube, H. *Inorg. Chem.* **1968**, *7*, 1.

[11] (a) Businelli, M. Italian Patent 475 964, 1952; *Chem. Abstr.* **1955**, *49*, 12539*d*. (b) Fanchiang, Y.-T.; Thomas, J. C.; Neff, V. D.; Heh, J. C.-K.; Gould, E. S. *Inorg. Chem.* **1977**, *16*, 1942.

[12] Fan, F.-R. F.; Gould, E. S. *Inorg. Chem.* **1974**, *13*, 2639.

[13] Dockal, E. R.; Everhart, E. T.; Gould, E. S. *J. Am. Chem. Soc.* **1971**, *93*, 5661.

[14] Complexes of phenylglyoxylic, α-ketobutyric, glyoxylic, oxamic, levulinic, and ketomalonic acids were prepared in water,[9] that of trichloropyruvic acid was prepared in diethylene glycol,[13] and the remainder for this study were prepared in methanol.[12]

[15] Price, H. J.; Taube, H. *J. Am. Chem. Soc.* **1964**, *86*, 1686.

[16] (a) Harrowfield, J. MacB.; Sargeson, A. M. *J. Am. Chem. Soc.* **1979**, *101*, 1514. Similar difficulties in preparing the ketomalonato complex were reported by these workers, who instead isolated this derivative as the hydrated monoperchlorate of its conjugate base. (b) The same authors have shown that color changes of this type are due to condensation of the carbonyl group with a cis-NH_3 ligand, yielding chelated α-imino species.

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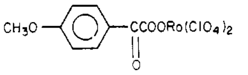
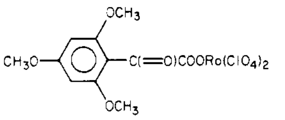
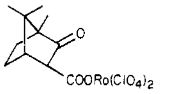
Table I. Analyses of Carbonyl-Substituted (Carboxylato)pentaamminecobalt(III) Perchlorates

complex[a]	% C calcd	% C found	% H calcd	% H found	% Co calcd	% Co found[b]
$Cl_3C(OH)_2COORo(ClO_4)_2$[c]	6.53	6.54	3.08	3.22	10.7	10.5
 $CH_3CH_2C(=O)COORo(ClO_4)_2$	10.8	10.8	4.50	4.65	13.3	13.1
$HOOCC(OH)_2COORo(ClO_4)_2$[d]	7.53	7.31	3.56	3.48	12.3	11.8
 $HOOC(CH_2)_2C(=O)(CH_2)_2COORo(ClO_4)_2$	16.3	14.1[e]	4.65	4.33	11.4	11.3
	20.7	20.8	4.21	4.31	11.3	11.4
	22.7	22.4	4.47	4.62	10.1	10.0
	24.5	24.2	5.57	5.54	11.0	11.1

[a] Ro = "roseo" = $(NH_3)_5Co^{III}$. [b] See ref 9. [c] Hydrated form of the trichloropyruvato complex. [d] Hydrated form of the ketomalonato (mesoxalato) complex. [e] Some contamination with the aquo perchlorate, reflecting unusually facile aquation of this complex (see Experimental Section).

NaOH turns them a dark red-brown,[16b] whereas the complex of camphor-3-carboxylic acid, which is derived from a β-keto acid, yields a bright yellow color.

Rate Measurements. Reactions were followed by monitoring decreases in absorbance at 502 nm and by using a Cary 14 or Beckman 5260 recording spectrophotometer.[3] In accordance with the results of Birk,[5c,7] which indicate that added Cl^- does not participate in inner-sphere Co(III)–Ti(III) reactions, LiCl–HCl was generally substituted for the more expensive NaOTs–HOTs as the supporting electrolyte. Ionic strength was kept near 1.0. Choice of cell size, reagent taken in excess, quantities of materials, and reaction conditions was as described.[17] All reactions were first order each in Co(III) and Ti(III). Except for the very slow reactions, where specific rates were obtained from initial rates, reactions were followed for at least 5 half-lives. Rate constants obtained from successive half-life values within a single run agreed to within 5%. No trends indicative of systematic errors were noted, and average values did not differ significantly from those obtained from logarithmic plots of absorbance differences against reaction time. Aside from the fastest systems, specific rates from replicate runs checked to within 10%.

(Oxamato)titanium(III) Complex. During the reduction of the (oxamato)cobalt(III) complex, an intense yellow color developed in solution. The absorbing species was taken to result from reaction of oxamic acid, released just after the primary redox reaction, with excess Ti(III). The same, or closely related,[18] complex was formed when a solution of unligated oxamic acid was added to $TiCl_3$ in the same chloride media as that used in the redox reactions. Experiments, using Job's method of continuous variation,[19] indicated that with the ligand in excess the predominant complex was of the form $TiLig_2$. A more detailed study of the variation of the absorbances of Ti(III) solutions in the presence of measured quantities of oxamic acid (Table VIII), in conjunction with the acidity constant of that acid, allowed determination of both the molar absorbance and the association constant for this complex.

Table II. Kinetic Data for Ti(III) Reductions of the $(NH_3)_5Co^{III}$ Complexes of Camphor-3-carboxylic and Oxamic Acids[a]

complex	$[H^+]$, M	10^2k_{obsd},[b] $M^{-1}\ s^{-1}$
camphor-3-carboxylato (I)	0.050	9.5
	0.10	4.5
	0.20	2.7
	0.80	0.57
oxamato (II)	0.10	45
	0.20	20
	0.50	10.8

[a] Reactions were carried out at 25.0 °C; $\mu = 1.0$ (LiCl–HCl). $[Ti^{III}] = 0.02–0.07$ M; $[Co^{III}] = 0.0025$ M. [b] $k_{obsd} = (d(\ln [Co^{III}])/dt)[Ti^{III}]^{-1}$.

The pK_A value for oxamic acid[20] in 1 M LiCl solution at 25 °C was estimated as 1.71 ± 0.05 by partial titration with NaOH. A second determination, yielding the value 1.77, utilized a partition method, described by Sherrill,[21] in which the sparingly soluble solid acid was allowed to equilibrate with a solution of the sodium salt of dichloroacetic acid ($pK_A = 0.88$) of known concentration, after which the total acidity in the supernatant solution was determined directly by titration.

Results and Discussion

The most usual acidity pattern observed[3] for reductions of (carboxylato)cobalt(III) complexes by $Ti^{III}(aq)$ is a monomial dependence on $[H^+]^{-1}$:

$$\text{rate} = \frac{k[Ti^{III}][Co^{III}]}{[H^+]} \qquad (1)$$

Rate law 1, which pertains to many oxidants having no acidic protons, implies reduction through a transition state of composition $Ti^{III}–OH–Co^{III}$ and indicates that $Ti(OH)^{2+}$, rather than Ti^{3+}, is the active reducing species.[22] Representative

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(17) Dockal, E. R.; Gould, E. S. *J. Am. Chem. Soc.* **1972**, *94*, 6673.

(18) The element of doubt here stems from the possibility that the complex predominating with Ti(III) in excess may not be that predominating with oxamic acid in excess, i.e., that the former may be a 1:1 complex. Our examination of Ti(III)–oxamate systems (Table VIII) indicates that, if such a complex is formed, it is substantially less stable than the 2:1 complex, with spectral features closely resembling those of the latter. We therefore did not attempt to characterize the less stable complex.

(19) See, for example: Vosburgh, W. C.; Cooper, G. R. *J. Am. Chem. Soc.* **1941**, *63*, 437. Woldbye, F. *Acta Chem. Scand.* **1955**, *9*, 299. The present determination utilized a series of solutions in which the sum $[Ti^{III}]$ + [oxamic acid] was kept at 0.025 M, but the mole ratio of the two components was allowed to vary. Absorbance measurements were made at 410 nm, where neither of the components absorbed appreciably when alone. The maximum absorbance was observed with the oxamic acid:Ti^{III} ratio near 2:1.

(20) Oxamic acid is sparingly soluble (0.35 M at 25 °C) in 1 M aqueous lithium chloride. The acidity constant for this acid, either in LiCl or in water, does not appear to have been reported. Note that in partial neutralization of an acid of this strength, the concentration of the anion significantly exceeds the concentration of added base.

(21) Sherrill, M. S. "A Course of Laboratory Experiments in Physico-Chemical Principles"; Macmillan: New York, 1924; p 64.

(22) A number of the very rapid reductions appear to utilize both Ti^{3+} and $Ti(OH)^{2+}$ as reductants. Rate laws for these feature both an acid-independent and inverse-acid term. See, for example: Orhanovich, M.; Earley, J. E. *Inorg. Chem.* **1975**, *14*, 1478.

Table III. Specific Rates for Ti(III) Reductions of (Carboxylato)pentaamminecobalt(III) Complexes, $R(NH_3)_5Co^{III}$, Exhibiting Monomial Inverse-Acid Dependencies[a]

ligand, R	10^3k, s^{-1}	ligand, R	10^3k, s^{-1}
camphor-3-carboxylato (I)	4.7	4-formylbenzoato	2.2[b,c]
levulinato (III)	7.3	acetato	4.9[b,c]
γ-ketopimelato (IV)	6.0	formato	7.0[c]
oxamato (II)	46	glycolato	310[c]
2-formylbenzoato	1.7[b,c]		

[a] Reactions were carried out at 25 °C; $\mu = 1.0$ (LiCl-HCl) unless otherwise indicated. Specific rates (k values) are defined in eq 1 of text. [b] $\mu = 1.7$. [c] Supporting electrolyte NaOTs-HOTs.[3]

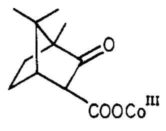
Table IV. Kinetic Data for Ti(III) Reductions of the $(NH_3)_5Co^{III}$ Complexes of Pyruvic and α-Ketobutyric Acids[a]

complex	$[H^+]$, M	k_{obsd},[b] $M^{-1}\,s^{-1}$	k_{calcd},[c] $M^{-1}\,s^{-1}$
pyruvato (V)[d]	0.98	0.42	0.41
	0.51	1.15	1.17
	0.22	3.6	3.9
	0.12	7.8	9.3
	0.076	15.6	14.4
	0.054	22	21
	0.039[f]	29	30
	0.035[f]	35	34
	0.030[f]	38	40
	0.021[f]	58	58
α-ketobutyrato (VI)[e]	0.90	0.38	0.38
	0.50	0.90	0.91
	0.20	2.9	3.0
	0.10	6.9	6.8
	0.050	13.8	14.4

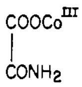
[a] Reactions were carried out at 25 °C; $\mu = 1.0$. $[Ti^{III}] = 0.002$–0.15 M; $[Ti^{III}]/[Co^{III}] = 10$ unless otherwise indicated. [b] $k_{obsd} = (d(\ln[Co^{III}])/dt)[Ti^{III}]^{-1}$. [c] Values calculated from eq 2 in text, by utilizing parameters a and b in Table IV. [d] Medium was NaOTos-HOTos. [e] Medium was LiCl-HCl. [f] Reactions were carried out with excess Co^{III}; $[Co^{III}] = 6 \times 10^{-4}$ M; $[Ti^{III}] = 1 \times 10^{-4}$ M.

kinetic data for the complexes of camphor-3-carboxylic acid (I) and oxamic acid (II), both of which conform to (1), appear in Table II. Specific rates for these complexes and for complexes of γ-keto acids, III and IV, are compared to those for several nonketonic oxidants exhibiting the same rate law in Table III.

Note that oxidant I, which is derived from a β-keto acid, and oxidants III and IV, which are derived from γ-keto acids, exhibit specific rates lying close to those reported for the acetato and formato complexes,[3] demonstrating that remotely located carbonyl groups are virtually without effect on reductions by Ti(III). This is the case even when the carbonyl lies in conjugation with the bound carboxyl, as shown by the law rates for reduction of the complexes of 2- and 4-formylbenzoic acids (aldehydobenzoic acids). The oxamato complex (II) enjoys a modest rate enhancement, due almost certainly to chelation by the $-CONH_2$ function in the activated complex, but the effect is not nearly as marked as that observed for the glycolato (2-hydroxyacetato) derivative.[3]

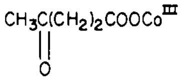


I



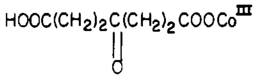
$$\begin{array}{c} COOCo^{III} \\ | \\ CONH_2 \end{array}$$

II



$$CH_3\underset{\underset{O}{\|}}{C}(CH_2)_2COOCo^{III}$$

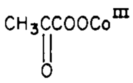
III



$$HOOC(CH_2)_2\underset{\underset{O}{\|}}{C}(CH_2)_2COOCo^{III}$$

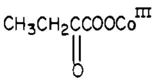
IV

Data for six of the α-carbonyl-substituted oxidants generate a pattern that appears to be unlike that for any electron-transfer reaction thus far described. Representative data for two of these, the pyruvato (V) and the α-ketobutyrato (VI) complexes are assembled in Table IV. At the lowest acidities examined, rates are seen to be very nearly inversely proportional to $[H^+]$, but at high acidities, the dependency is much steeper. The rate dependence conforms to expression 2. In



$$CH_3\underset{\underset{O}{\|}}{C}COOCo^{III}$$

V



$$CH_3CH_2\underset{\underset{O}{\|}}{C}COOCo^{III}$$

VI

$$\text{rate} = k_{obsd}[Co^{III}][Ti^{III}] = \frac{[Ti^{III}][Co^{III}]}{a[H^+] + b[H^+]^2} \qquad (2)$$

these instances, plots of $(k_{obsd}[H^+])^{-1}$ vs. $[H^+]$ are linear and yield the kinetic parameters a (as intercepts) and b (as slopes). Values of a and b appear in Table V; rates calculated from these parameters and eq 2 (k_{calcd}) are compared to the observed values, for the pyruvato and ketobutyrato complexes, in Table IV.

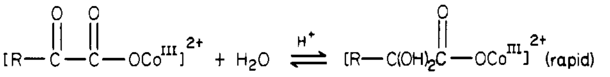
The $[H^+]^2$ term in the denominator of (2) implies the loss of two protons prior to electron transfer. The first of these is doubtless associated with deprotonation of $Ti(H_2O)_6^{3+}$ ($pK_A = 2.64$).[5a] The second, which exhibits kinetic saturation behavior near pH 2, can be attributed neither to rapid and reversible deprotonation of Co(III)-bound ammonia ($pK_A > 14$)[23] nor to rapid loss of a second proton from the reductant,

Table V. Calculated Kinetic Parameters for the Titanium(III) Reductions of Cobalt(III) Complexes, $R(NH_3)_5Co^{III}$, of Those α-Keto Acids That Are Partially Converted to *gem*-Diols in Aqueous Solution[a]

ligand, R	a,[a] s	b,[a] M^{-1} s	$10^{-2}k_1$,[b] $M^{-1}\,s^{-1}$	$f_{hydrate}$[c]	$10^{-2}k_{hydrate}$,[d] $M^{-1}\,s^{-1}$	k_2/k_{-1}[e]
$CH_3C(=O)COO$[f]	0.78 ± 0.03	1.73 ± 0.07	5.2	0.28[g]	19	0.45
$C_2H_5C(=O)COO$	1.34 ± 0.03	1.78 ± 0.06	3.5	0.23[h]	15	0.70
$CCl_3C(=O)COO$	1.16 ± 0.15	1.75 ± 0.34	3.8	0.99+[h]	4	0.64
$C(CH_3)_3C(=O)COO$	6.7 ± 0.1	4.2 ± 1.0	0.66	0.07[g]	9	1.31
$HOOCC(=O)COO$	1.10 ± 0.14	8.9 ± 0.6	4.0	0.99+[h]	4	0.12
$HC(=O)COO$	5.0 ± 0.6	6.3 ± 1.3	0.86	0.98+[i]	0.9	0.87

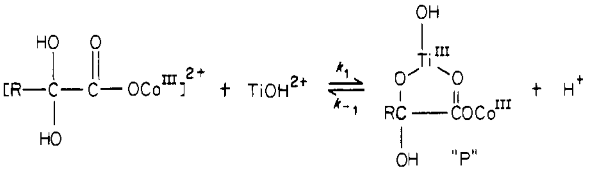
[a] Reactions were run at 25 °C; $\mu = 1.0$. The supporting electrolyte was HCl–LiCl unless otherwise indicated. Parameters a and b (eq 2 in text) were obtained from intercepts and slopes of plots of $(k_{obsd}[H^+])^{-1}$ vs. $[H^+]$ or by nonlinear least-squares refinement of values of k_{obsd} according to eq 2. [b] Values of k_1 (eq 5) calculated as $(K_A a)^{-1}$, where $K_A = 2.3 \times 10^{-3}$ M.[5a] [c] Fraction of the oxidant existing as its hydrated (*gem*-diol) form. [d] Specific rates for formation of precursor P (eq 5) from the *gem*-diol form of the oxidant and $TiOH^{2+}$, calculated as $k_1/f_{hydrate}$. The reactivity of the dehydrated (carbonyl) form of the oxidant is considered negligible. [e] Ratio k_2/k_{-1} (eq 5, 6) (M), calculated as a/b. [f] Reactions run in HOTos–NaOTos. [g] Reference 10b. [h] Estimated from the fraction hydrate of the parent acid (Strehlow, H. *Z. Elektrochem.* **1962**, *66*, 392). The equilibrium constant for hydration of the Co(III) complex is taken to be one-sixth that for hydration of the parent acid.[10b] [i] Reference 15.

for which pK_A greatly exceeds 3. Since expression 2 is found to apply only to carbonyl-substituted oxidants that are substantially converted, by hydration, to the *gem*-diol forms ($>C{=}O + H_2O \rightarrow >C(OH)_2$),[24] it is likely that these carbonyl hydrates have entered the picture. Again, however, deprotonation of the *gem*-diol cannot be taken as a rapid preequilibrium, for this would lead to a simple monomial dependence on $[H^+]^{-2}$, as has been observed[3] for reduction of the binoxalato complex.[25] We suspect instead that this deprotonation accompanies formation of a chelated precursor complex, "P", from $Ti(OH)^{2+}$ and the *gem*-diol. The proposed reaction sequence is then



$$[R{-}C(=O){-}C(=O){-}OCo^{III}]^{2+} + H_2O \underset{}{\overset{H^+}{\rightleftharpoons}} [R{-}C(OH)_2C(=O){-}OCo^{III}]^{2+} \text{ (rapid)} \quad (3)$$

$$Ti^{3+}(aq) \rightleftharpoons TiOH^{2+} + H^+ \quad (\text{rapid; } pK_A = 2.64) \quad (4)$$



(5)

$$P \xrightarrow{k_2} \text{products} \quad (6)$$

Application of the steady-state approximation to precursor P leads to the rate law

$$\text{rate} = \frac{[TiOH^{2+}][Co^{III}]k_1k_2}{k_{-1}[H^+] + k_2} \quad (7)$$

In the range of acidities examined ($[H^+] > K_A$ for $Ti^{3+}(aq)$), (7) may be rewritten as (8), which is algebraically equivalent

$$\text{rate} = \frac{[Ti^{III}][Co^{III}]K_Ak_1k_2}{[H^+](k_{-1}[H^+] + k_2)} \quad (8)$$

to the empirical rate law (2), where parameter *a* corresponds to $(k_1K_A)^{-1}$ and *b* equals $k_{-1}(k_1k_2K_A)^{-1}$. Calculated values of k_1 and the ratio k_2/k_{-1} are included in Table V. Note that the individual specific rates of k_2 and k_{-1} cannot be obtained by steady-state experiments alone.

The calculated specific rate (k_1) for formation of precursor P from $TiOH^{2+}$ is a weighted average of the specific rates associated with the carbonyl and *gem*-diol forms of the oxidant in solution. If the carbonyl is considered to be much the less reactive, the specific rate pertaining to the diol alone may be obtained by dividing k_1 by the estimated fraction of diol at equilibrium. The resulting quotients (k_{hydrate}) also appear in Table V. Aside from the glyoxylato complex, the ground state of which may be stabilized by unusually strong solvation, there is only slight variation in these specific rates. Their values, 400–2000 M^{-1} s^{-1}, fall somewhat above the corresponding rate constants (100–500 M^{-1} s^{-1})[26,27] for reaction of $TiOH^{2+}$ with the Co(III) complexes of α-hydroxy acids, $RCH(OH)COOCo^{III}$, and may lie near the limit imposed by the rate of substitution at the Ti(III) center.

Table VI. Kinetic Data for Ti(III) Reductions of the $(NH_3)_5Co^{III}$ Complexes of Phenylglyoxylic and (*p*-Methoxyphenyl)glyoxylic Acids[a]

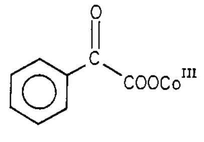
complex	$[H^+]$, M	k_{obsd},[b] M^{-1} s^{-1}	k_{calcd},[c] M^{-1} s^{-1}
phenylglyoxylato (VII)	0.99	18.0	18.4
	0.97	18.0	18.7
	0.70	23	25
	0.50	36	33
	0.40	43	39
	0.10	105	95
	0.050	116	124
(*p*-methoxyphenyl)glyoxylato	1.00	24	26
	0.50	52	42
	0.20	83	70
	0.10	92	89
	0.050	92	102

[a] Reactions were carried out at 25 °C; $\mu = 1.0$ (HCl–LiCl). $[Ti^{III}] = (4–13) \times 10^{-4}$ M; $[Co^{III}] = 1.0 \times 10^{-4}$ M. [b] $k_{\text{obsd}} = d(\ln [Co^{III}])/dt)[Ti^{III}]^{-1}$. [c] Values calculated from eq 9 in text, by using parameters *a* and *b* in Table VII.

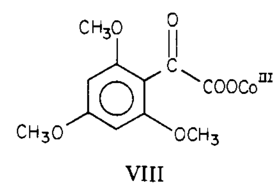
α-Carbonyl-substituted oxidants of this type are known also to react very rapidly with Cr(II)[10b,15] and with Eu(II),[12] but in these systems, as well as in closely related ones,[28] it is the carbonyl form, rather than the *gem*-diol, that is the reactive species. Recognition of the strongly reducing character of these dipositive centers ($E°_{Eu(II)} = -0.379$ V; $E°_{Cr(II)} = -0.41$ V)[29] has, in the past, led to the suggestion that the unsaturated carbonyl function in such ligands is involved in accommodation of the incoming electron, either by initial localized 1e reduction of the ligand (the "chemical mechanism")[20,30] or, more probably,[31] by extending the acceptor molecular orbital, which also includes $-COOCo^{III}$, and thereby lowering the energy of this orbital. In view of the less strongly negative potential of Ti(III) ($E° = -0.016$ V in 1.0 M HCl)[5a] it is not astonishing that such rate enhancement by the carbonyl group does not extend to this center, which instead appears to utilize the chelated path afforded by the *gem*-diol.

It may then be asked whether increasing the reducibility of the keto function in the mediating ligand will induce Ti(III) to utilize the carbonyl group in the manner of the more powerful reductants. Reduction of the complex of phenylglyoxylic acid, $C_6H_5C({=}O)COOH$, is instructive on this point, for this acid has been shown to be reduced significantly more easily than pyruvic acid[32] and exists very nearly completely in its (nonhydrated) keto form.[32]

Kinetic data for reductions of the phenylglyoxylato complex (VII) and its 4-methoxy derivative (Table VI) point to an



VII



VIII

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(24) Ahrens, M.-L. *Z. Elektrochem.* **1969**, *72*, 691.

(25) pK_A values for *gem*-diols fall in the range 10–13 except for those molecules featuring an α-CF_3 or -CCl_3 group. See, for example: Rochester, C. H. "Chemistry of the Hydroxyl Group"; Patai, S., Ed.; Wiley: New York, 1971; Part I, p 371.

(26) These values are obtained by dividing the acid-dependent specific rates for reductions of the glycolato and lactato complexes[3] by 2.3×10^{-3} M (K_A for $Ti(H_2O)_6^{3+}$).[5a] Reservations as to the utility of values of this sort have been described by Linck[27a] and by Liang.[27b]

(27) (a) Linck, R. G. *MTP Int. Rev. Sci.: Inorg. Chem., Ser. One* **1972**, *9*, 303. (b) Liang, A.; Gould, E. S. *J. Am. Chem. Soc.* **1970**, *92*, 6791.

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(30) Although it has been difficult to demonstrate the operation of the chemical mechanism in the 1e reductions of monomeric $(NH_3)_5Co^{III}$ derivatives of α-keto acids, evidence for this mechanism in reduction of carboxyl-bridged $(Co^{III})_2$ derivatives of such acids is substantial. See, for example: Srinivasan, V. S.; Singh, A. N.; Wieghardt, K.; Rajasekar, N.; Gould, E. S. *Inorg. Chem.* **1982**, *21*, 2531.

(31) See, for example: Liu, C.-L.; Fanchiang, Y.-T.; Gould, E. S. *Inorg. Chem.* **1978**, *17*, 1831.

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Table VII. Calculated Kinetic Parameters for the Titanium(III) Reductions of Cobalt(III) Complexes of Phenylglyoxylic Acids, $R(NH_3)_5Co^{III}$ [a]

			for sequence (10)-(11)		for sequence (12)	
ligand, R	10^3a,[b] M s	10^2b,[b] s	k_1,[c] M^{-1} s^{-1}	k_2/k_{-1},[d] M	$10^{-3}k_1'$,[e] M^{-1} s^{-1}	k_2'/k_{-1}',[f] M^{-1}
phenylglyoxylato (VII)	5.6 ± 0.6	4.9 ± 0.3	180	0.11	8.9	8.7
(4-methoxyphenyl)glyoxylato	8.2 ± 1.1	3.0 ± 0.4	122	0.27	14.5	3.7
(2,4,6-trimethoxyphenyl)glyoxylato (VIII)[g]	<3	104 ± 5	>320	<0.003	0.43	>300
salicylato[h]			94	0.79		
4-methylsalicylato[h]			117	0.89		
5-methylsalicylato[h]			124	1.33		
4-hydroxysalicylato[h]			137	0.93		

[a] Reactions were run at 25 °C; $\mu = 1.0$ (LiCl-HCl). [b] Parameters a and b (eq 9 in text) were obtained by nonlinear least-squares refinements of values of k_{obsd} according to eq 9. [c] Values of k_1 (eq 13) calculated as a^{-1}. [d] Ratio of k_2/k_{-1} (eq 13) calculated as a/b. [e] Values of k_1' (eq 14) calculated as $(K_Ab)^{-1}$, where $K_A = 0.0023$ M.[5a] [f] Ratio k_2'/k_{-1}' (eq 14) calculated as b/a. [g] Rate law for this complex experimentally indistinguishable from eq 1 with $k = 0.93\ s^{-1}$. [h] Reactions in NaOTos-HOTos.[3]

acidity dependence much less steep than that described by eq 2 but conform instead to rate law 9. Values of the parameters giving the closest agreement between observed and calculated specific rates are listed in Table VII.

$$\text{rate} = k_{obsd}[Co^{III}][Ti^{III}] = \frac{[Ti^{III}][Co^{III}]}{a + b[H^+]} \tag{9}$$

As in earlier instances,[5c,33] two mechanisms are consistent with a rate law of type 9. The first, sequence (10)-(11), is

$$Ti^{3+}(aq) + \text{Lig–}Co^{III} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [\text{HO–Ti–Lig–}Co^{III}]^{4+} + H^+ \tag{10}$$

$$P \xrightarrow{k_2} \text{products} \tag{11}$$

similar to that proposed for the nonphenylated oxidants collated in Table V, save that the precursor, P, is formed from $Ti^{3+}(aq)$, rather than from $Ti(OH)^{2+}$. The alternate path, sequence 12, features formation of the precursor directly from

$$Ti(OH)^{2+} + \text{Lig–}Co^{III} \underset{k_{-1}'}{\overset{k_1'}{\rightleftharpoons}} [\text{HO–Ti–Lig–}Co^{III}]^{4+} \xrightarrow[k_2']{H^+} \text{products} \tag{12}$$

$Ti(OH)^{2+}$ followed by slow electron transfer triggered by H^+. Application of the steady-state approximation to precursor P in the two sequences leads to rate laws 13 and 14, both of which are seen to be equivalent to (9). For sequence (10)-(11)

$$\text{rate} = \frac{[Ti^{III}][Co^{III}]k_1k_2}{k_{-1}[H^+] + k_2} \tag{13}$$

For sequence (12)

$$\text{rate} = \frac{[Ti^{III}][Co^{III}]K_Ak_1'k_2'}{k_{-1}' + k_2'[H^+]} \tag{14}$$

Values of rate constants pertaining to the two mechanisms are compared in Table VII. Consideration of the k_1' values (applying to sequence 12) for the phenylglyoxylato complex and its 4-methoxy derivative allows a choice between mechanisms. The initial (k_1') step in (12), conversion of $TiOH^{2+}$ to precursor P, is analogous to step 5 in the sequence already proposed for reduction of those complexes that are partially converted to *gem*-diols. Calculated k_1' values, however, are about 1 order of magnitude greater than the corresponding rate constants in Table V (which are taken to refer to chelate formation) and exceed what appears, from this and earlier[3] studies, to be the subsitution-controlled upper limit (about 2000 M^{-1} s^{-1}) for reactions of $TiOH^{2+}$ with oxidants of this charge type. In contrast, values of k_1, pertaining to reaction 10, are seen to lie close to those for several substituted salicylato derivatives that conform to the same rate law,[3] further supporting our choice of sequence (10)-(11).

Table VIII. Representative Absorbance Data for Mixtures of Titanium Trichloride and Oxamic Acid in Aqueous LiCl[a]

$[H^+]$, M	10^2[oxamic acid], M	Abs_{obsd}[b]	Abs_{calcd}[c]
0.165	0.186	0.140	0.117
	0.360	0.35	0.33
	0.53	0.53	0.53
	0.70	0.65	0.67
	0.86	0.77	0.77
	1.00	0.84	0.83
	1.15	0.87	0.87
	1.29	0.92	0.91
	1.42	0.95	0.93
0.50	0.67	0.146	0.154
	1.30	0.32	0.39
	2.50	0.69	0.74
	3.60	0.94	0.88
	4.61	1.07	0.95
	5.55	1.14	1.19
	6.43	1.18	1.26
	7.24	1.20	1.32

[a] Data were taken in 10.0-cm cell at 20 °C; $\mu = 1.0$ M (HCl-LiCl); $[TiCl_3] = 3.0 \times 10^{-4}$ M throughout. [b] Absorbance observed at 410 nm. [c] Values were calculated by using eq 15 in text; l was taken as 10.0 cm, ϵ_{410} as 350 M^{-1} cm^{-1}, K_{dis} as 3.7×10^{-7} M^2, and K_A for oxamic acid as 1.8×10^{-2} M.

The reduction of the 2,4,6-trimethoxy complex (VIII) in this series is much slower (0.92 M^{-1} s^{-1} in 1 M H^+) than its analogues in Table VII, and its rate is proportional to $[H^+]^{-1}$ (eq 1). If a common mechanism is assumed, the observed simplification in rate law implies that k_2 has fallen well below $k_{-1}[H^+]$. This appears to be an instance in which conjugation has been impaired (but not completely eliminated) by the 2- and 6-methoxy groups, which serve to hold the keto group out of the plane of the benzene ring, thus elevating the energy of the acceptor orbital.[34]

We are not certain as to the site of attack by Ti^{III} in the rapid reactions of these phenylglyoxylato derivatives. Initial attack by Cr^{2+} at a remote carbonyl function lying in conjugation with $-COOCo^{III}$ has been demonstrated,[2ce] but it appears that Cr(II) attack on α-keto oxidants, although very rapid, occurs at the ligated carboxylato group.[2e,10b,30] We therefore suspect that tripositive titanium, a harder center (in the Pearson sense[35]) than Cr^{2+}, likewise prefers the carboxylato

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(33) Heh, J. C.-K.; Gould, E. S. *Inorg. Chem.* **1978**, *17*, 3142.

(34) Note that kinetic saturation is observed for electron-transfer reactions of $Ti(H_2O)_6^{3+}$ only when specific rates approach 100 M^{-1} s^{-1}.

(35) See, for example: Pearson, R. G., Ed. "Hard and Soft Acids and Bases"; Dowden, Hutchison, and Ross: Stroudsburg, PA, 1973.

function to the more polarizable carbonyl group.

We note finally that reduction of the oxamato derivative of $(NH_3)_5Co^{III}$ is complicated by formation of a strongly absorbing yellow species (λ_{max} = 410 nm), which can be prepared also by adding oxamic acid to Ti(III) solutions. Absorbance data at a number of acidities (of which the entries in Table VIII are representative) conform to eq 15, where l is the optical

$$\mathrm{Abs} = \frac{l\epsilon[\mathrm{Ti^{III}}]_T}{1 + \dfrac{k_{dis}}{K_A{}^2}\left(\dfrac{[\mathrm{H^+}]}{[\mathrm{HOx}]}\right)^2} \qquad (15)$$

path length, ϵ the molal extinction coefficient of the absorbing species, $[Ti^{III}]_T$ the total concentration of added Ti^{III}, K_{dis} the dissociation constant of the absorbing species, K_A the acidity constant of oxamic acid (determined independently as 1.8×10^{-2} M in this medium), and [HOx] the concentration of added oxamic acid. Expression 15 corresponds to that applying to a system in which the principal absorbing species is a dioxamato complex of Ti^{III}, $(H_2NCOCOO)_2Ti^+$, a complex which, to our knowledge, has not yet been reported. A nonlinear least-squares refinement of the absorbance data (unweighted) leads to a value of 350 ± 40 M^{-1} cm^{-1} for the molal extinction coefficient and $(3.7 \pm 0.7) \times 10^{-7}$ M^2 for the dissociation constant ($TiOx_2^+ \rightleftharpoons Ti^{3+} + 2Ox^-$).

The extinction coefficient of the dioxamato complex lies close to that reported[36] for the analogous dioxalato complex (490 M^{-1} cm^{-1}) and suggests that both are chelates. However the oxalato complex ($K_{dis} = 3 \times 10^{-13}$ M^2 at 10 °C) is by far the more stable, a difference that is attributable to the additional unit of negative charge on the oxalato anion.

Registry No. I, 84731-51-1; II, 19306-89-9; III, 49861-86-1; IV, 84731-52-2; V, 19306-91-3; VI, 84731-53-3; $R(NH_3)_5Co^{III}$ (R = 2-formylbenzoato), 42532-71-8; $R(NH_3)_5Co^{III}$ (R = 4-formylbenzoato), 19743-65-8; $R(NH_3)_5Co^{III}$ (R = acetato), 16632-78-3; $R(NH_3)_5Co^{III}$ (R = formato), 19173-64-9; $R(NH_3)_5Co^{III}$ (R = glycolato), 31279-86-4; Ti, 7440-32-6.

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Electrochemistry of Mixed-Metal Bimetallic Complexes Containing the Pentacyanoferrate(II) or Pentaammineruthenium(II) Metal Center

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The electrochemistry of a series of mixed-metal bimetallic complexes of the type $B_5MLM'B'_5$, where $B_5M = (CN)_5Fe^{II}$ or $(NH_3)_5Ru^{II}$, L = pyrazine, 4,4′-bipyridine, or 4-cyanopyridine, $M'B'_5 = Rh^{III}(NH_3)_5$ or $Co^{III}(CN)_5$, is reported. The bimetallic complexes all have metal-to-ligand charge-transfer (MLCT) bands associated with the M–B unit ($d_\pi M \rightarrow p_\pi{}^*L$). The effect of the remote metal center, $M'B'_5$, is to function as a Lewis acid, shifting the MLCT maximum to lower energy and shifting the $M^{III/II}$ reduction potential more positive with respect to free B_5ML. The remote metal influence is attenuated by longer bridging ligands and by reduced π-overlap. A comparison of the electrochemical data of the mixed-valence Fe(II)/Fe(III) and Ru(II)/Ru(III) complexes to the mixed-metal Fe(II)/Co(III) and Ru(II)/Rh(III) complexes has enabled a quantitative measure of the stabilization due to electron delocalization in the mixed-valence complexes. The results show that electron delocalization is greater for the ruthenium complexes than for the iron complexes, is a small contributor to the total stabilization of the mixed-valence state, and even in ruthenium drops off rapidly as the length of the bridge increases.

Introduction

There have been numerous studies on the thermal[1-9] and photochemical[10-12] reactions of unsaturated, nitrogen, heterocyclic ligands (L) bound to pentacyanoferrate(II) and pentaammineruthenium(II) metal centers. The near-ultraviolet and visible spectra of these complexes are dominated by an intense metal-to-ligand charge-transfer (MLCT) band assigned as $d_\pi M \rightarrow p_\pi{}^*L$ in character.[2,13] The energy of the MLCT band maximum is very sensitive to substituent changes on L (i.e., the energy of the π^* orbitals of free L), with more electron-withdrawing substituents causing red shifts in the MLCT maximum as well as greater ground-state delocalization of d_π-electron density into L (π-back-bonding).[2]

Numerous types of instrumental methods have been used, in addition to electronic spectroscopy, to probe the extent of π-back-bonding from Fe(II) or Ru(II) into various L ligands. Electrochemical measurements are one such method that has been used for $Fe(CN)_5L^{2,14,15}$ and $Ru(NH_3)_5L^{16-18}$ complexes. In these previous studies, a positive increase in the reduction

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