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Electron Transfer. 73. Reduction of Carboxylato-Bound Chromium(V) with Titanium(III)[1]

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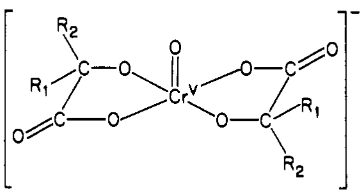
The chelated chromium(V) complex sodium bis(2-ethyl-2-hydroxybutyrato)oxochromate(V) (I) reacts smoothly and rapidly with Ti(III) at pH 1–2 in aqueous chloride. The spectral and ion-exchange properties of the chromium product correspond to those of a bis-chelated hydroxycarboxylato derivative of $(H_2O)_2Cr^{III}$. Reactions are accelerated by α-hydroxy acids (including the ligand acid, HLig, related to the oxidant) and by ethylenediaminetetraacetic acid but are generally inverse first order in $[H^+]$. Reactive reducing species are taken as $Ti^{III}(OH)$, $Ti^{III}(Lig)(OH)$, and $Ti^{III}(edta)(H_2O)$. Unlike reductions by N_2H_4 and NH_2OH, reactions of Ti(III) do not require loss of a ligand from Cr(V) prior to electron transfer. The modest rate enhancements resulting from replacement of $Ti^{III}(OH)$ by $Ti^{III}(edta)(H_2O)$ as the reductant are consistent with outer-sphere, rather than inner-sphere, kinetic patterns, an inference supported by the very high (5×10^5 M^{-1} s^{-1}) bimolecular rate constant for reduction by $Ti^{III}(OH)$. Although reduction of Cr(V) to Cr(III) must pass through a Cr(IV) intermediate, detectable quantities of a Cr(IV) transient, which have been observed in reductions by Fe^{2+} and VO^{2+}, do not intervene here, suggesting that Cr(IV) is reduced by $Ti^{III}(OH)$ at least 20 times as rapidly as is Cr(V), again by an outer-sphere process. It further appears that the composite electron-transfer sequence ($Cr^V \rightarrow Cr^{IV} \rightarrow Cr^{III}$) proceeds with conservation of the ligand environment about chromium, indicating that ligand substitution at the Cr(IV) center is slow in relation to its reaction with the Ti(III) species in these systems.

Shortly after the reported preparation of air-stable water-soluble carboxylato complexes of chromium(V),[2] mechanistic investigations of the reactions of this unusual oxidation state with inorganic reductants were initiated. Studies dealing with the reductions of Cr(V) chelates I and II using hydrazine[3] and hydroxylamine[4] and with the disproportionation of Cr(V) as catalyzed by Ce(III)[5] suggested that each of these reactions proceeds by preliminary loss of a hydroxycarboxylato ligand, followed by the formation of a precursor complex between redox partners and then by an act of internal electron transfer (2e for N_2H_4, 4e for NH_2OH, and 1e for Ce^{III}) to Cr(V).



I, $R_1 = R_2 = C_2H_5$
II, $R_1 = CH_3$, $R_2 = C_2H_5$

We here describe the reduction of Cr(V) complex I with Ti(III), a single-electron reductant, which appears to utilize quite a different path.

Experimental Section

Materials. Stock solutions of Ti(III) were prepared by dissolving $TiCl_3$ (Alfa) in 1.0 M HCl and were standardized by titration[6] against $Cr_2O_7^{2-}$ or by spectrophotometry ($\epsilon_{502} = 3.97$ M^{-1} cm^{-1});[7] all manipulations with this reductant were carried out under N_2. Acidities were determined by titration with NaOH.[8a] Titanium(III)–edta solutions were prepared as described by Thompson and Sykes.[8b] Sodium bis(2-ethyl-2-hydroxybutyrato)oxochromate(V) (complex I) was prepared as its monohydrate as described by Krumpolc[2] and was kept in the dark[9] at 0 °C; $\epsilon_{510} = 165$ M^{-1} cm^{-1} (lit.[2] 168 M^{-1} cm^{-1}). Organic hydroxy acids (Aldrich products) were used as received; purities were checked by titration with NaOH. Cation-exchange resin (Bio-Rad 50W-X2; 200–400 mesh), used in separation of reaction products, was pretreated as described.[10]

Stoichiometric Studies. The stoichiometries of the Cr^V–Ti^{III}_{aq} and Cr^V–$Ti^{III}(edta)$ reactions were determined by spectrophotometric titrations. In a typical experiment, a series of solutions 0.005 M in Cr^V (each 10.0 mL) were mixed with Ti(III) solutions of known varying concentrations, with the total volume kept constant. The spectrum of each mixture (400–700 nm) was recorded immediately after mixing. Plots of absorbance (at 450 and 510 nm) vs. the molar ratio Ti(III)/Cr(V) showed "break points" at the ratio 2.00 ± 0.05 for both Ti^{III}_{aq} and $Ti^{III}(edta)$.

Examination of the Chromium(III) Reaction Products. A reaction mixture that was 0.005 M in the Cr(V) complex (I), 0.010 M in $TiCl_3$, 0.1 M in HCl, and 0.050 M in the ligand 2-ethyl-2-hydroxybutyric acid exhibited, immediately after mixing, absorption maxima at 583 ($\epsilon = 48$) and 413 nm ($\epsilon = 62$ M^{-1} cm^{-1}). This spectrum was indistinguishable from that observed when the same Cr(V) complex was reduced, in the presence of excess ligand acid, with $Eu(ClO_4)_2$ or $VO(ClO_4)_2$. It remained unchanged for over 30 min at pH 1, but if the pH were increased to 3.0, maxima gradually shifted to 572 ($\epsilon = 24$) and 410 nm ($\epsilon = 32$ M^{-1} cm^{-1}). When the Cr(V)–Ti(III) reaction was carried out in the absence of excess ligand, a shifting spectrum was obtained; just 3 min after mixing, maxima were at 575 ($\epsilon = 37$) and 418 nm ($\epsilon = 43$ M^{-1} cm^{-1}), whereas after 2.5 h, these maxima had moved to 570 ($\epsilon = 17$) and 408 nm ($\epsilon = 19$ M^{-1} cm^{-1}).[11] When the mixture having excess ligand was subjected to cation-exchange chromatography at 2 °C,[12] about half of the dissolved chromium was eluted as a light green solution showing maxima near 585 and 414 nm. These shifted on 5-h standing to 570 ($\epsilon = 22$) and 410 nm ($\epsilon = 29$ M^{-1} cm^{-1}). The trailing band, containing the remainder of the dissolved chromium, was rapidly eluted with 0.5 M $HClO_4$ and exhibited maxima at 570 ($\epsilon = 25$) and 410 nm ($\epsilon = 33$ M^{-1} cm^{-1}).

The corresponding reaction between Cr(V) and $Ti^{III}(edta)$ (at pH 2.0) in the presence of excess 2-ethyl-2-hydroxybutyric acid yielded, immediately after mixing, a solution having absorption maxima at 580 ($\epsilon = 49$) and 415 nm ($\epsilon = 62$ M^{-1} s^{-1}). This spectrum shifted, slowly at pH 2, but more rapidly at pH 3, to that characteristic of $Cr^{III}(edta)$.[13]

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[1] Joint sponsorship of this work by the donors of the Petroleum Research Fund, administered by the American Chemical Society, and by the National Science Foundation (Grant 8313253) is gratefully acknowledged.

[2] Krumpolc, M.; Roček, J. *J. Am. Chem. Soc.* **1979**, *101*, 3206.

[3] Srinivasan, V. S.; Gould, E. S. *Inorg. Chem.* **1981**, *20*, 3176.

[4] Rajasekar, N.; Subramaniam, R.; Gould, E. S. *Inorg. Chem.* **1983**, *22*, 971.

[5] Rajasekar, N.; Gould, E. S. *Inorg. Chem.* **1983**, *22*, 3798.

[6] Pierson, R. H.; Gantz, E. S.-C. *Anal. Chem.* **1954**, *26*, 1809.

[7] Birk, J. P.; Logan, T. P. *Inorg. Chem.* **1973**, *12*, 580. For Kinetic experiments with $[Ti(III)] \leq 10^{-3}$ M, concentrations were determined both before and after the kinetic runs. Loss of Ti(III) was less than 5% in 1 h.

[8] (a) Davies, K. M.; Earley, J. E. *Inorg. Chem.* **1978**, *17*, 3350. (b) Thompson, G. A. K.; Sykes, A. G. *Ibid.* **1979**, *18*, 2025.

[9] Aqueous solutions of the chromium(V) chelate I were found to undergo rapid decomposition to Cr(III) species in direct sunlight.

[10] Gould, E. S. *J. Am. Chem. Soc.* **1967**, *89*, 5792.

[11] The kinetic characteristics of this slow spectral change were not straightforward. Preliminary examination indicated it to result from the superposition of at least two first-order processes.

[12] Separations were carried out with use of Bio-Rad 50W-X2 sulfonate resin, H^+ form, 200–400 mesh, column length 5 cm, column capacity 2.0 mequiv. Use of a larger column led to more serious decomposition of the eluted Cr(III) complexes. For estimation of extinction coefficients of Cr(III) species, aliquots of each eluted fraction were oxidized with basic H_2O_2, and the total chromium content was determined as CrO_4^{2-}. See, for example: Haupt, G. W. *J. Res. Natl. Bur. Stand.* (*U.S.*) **1952**, *48*, 414.

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Table I. Representative Kinetic Data for Reduction of Carboxylato-Bound Chromium(V) with Titanium(III)[a]

10^4[Cr(V)], M	10^3[Ti(III)], M	[RCOOH], M	[H$^+$], M	$10^{-4}k_2$,[b] M^{-1} s^{-1}
A. Added Carboxylic Acid (RCOOH) 2-Hydroxy-2-ethylbutyric Acid				
2.0	3.0	0	0.10	1.17
3.0	3.0	0.010	0.10	1.43
2.0	3.1	0.025	0.10	2.3
2.0	6.2	0.025	0.10	2.2
2.0	3.1	0.025	0.050	4.5
5.0	6.0	0.025	0.020	8.5
3.0	3.0	0.020	0.10	1.93
3.0	3.0	0.040	0.10	3.1
3.0	3.0	0.075	0.10	3.5
3.0	3.0	0.075	0.15	2.9
3.0	3.0	0.075	0.20	1.67
3.0	3.0	0.100	0.10	4.2
3.0	3.0	0.150	0.10	5.6
B. Added Carboxylic Acid (RCOOH) Lactic Acid				
2.0	3.0	0.030	0.10	1.93
2.0	3.0	0.060	0.10	2.3
2.0	3.0	0.100	0.10	3.3
C. Added Carboxylic Acid (RCOOH) Glycolic Acid				
3.0	3.0	0.030	0.10	1.17
3.0	3.0	0.060	0.10	1.40
3.0	3.0	0.100	0.10	1.97

[a] Reactions were carried out at 23 °C; μ = 0.5 M (HCl + LiCl). Chromium(V) was added as sodium bis(2-ethyl-2-hydroxybutyrato)oxochromate(V) (I). [b] Second order rate constants, $=(d(\ln [\mathrm{Cr^V}])/dt)[\mathrm{Ti^{III}}]$.

Kinetic Studies. Rates were estimated from measurements of decreases in absorbance at 475 nm, with a Durrum-Gibson stopped-flow spectrophotometer. Total ionic strength was maintained at 0.50 M by addition of LiCl. Reactions were first order each in Cr(V) and Ti(III), but most runs were carried out under pseudo-first-order conditions with the reductant in greater than 10-fold excess. Replicate reactions, with the same pair of master solutions, were carried out until decay curves from three successive runs superimposed. Rate constants, obtained from logarithmic plots of absorbance differences against reaction time, agreed to better than 5% for runs with different master solutions. For the (more rapid) reductions by Ti$^{\mathrm{III}}$(edta), reactions were carried out under second-order conditions with use of a slight excess of reductant. Rate constants in such cases were estimated with use of an iterative nonlinear least-squares[14] fit of eq 1,[15] where B and A are the initial concentrations of the reactants, and D_0, D, and D_∞ are the absorbances at time zero, at time t and at infinite time, respectively.

$$D = \frac{D_0(B-A) + D_\infty B[e^{(B-A)kt} - 1]}{Be^{(B-A)kt} - A} \qquad (1)$$

Kinetic profiles gave no indication of intermediates formed or destroyed on a time scale comparable to that for the measured disappearance of Cr(V).

Results and Discussion

The observed "break point" near mole ratio 2.0 in the spectrophotometric titration of Cr(V) with Ti(III) allows us to represent the net reaction schematically as (2).

$$\mathrm{Cr^V} + 2\mathrm{Ti^{III}} \rightarrow \mathrm{Cr^{III}} + 2\mathrm{Ti^{IV}} \qquad (2)$$

The spectral properties of the Cr(III) product formed in the reaction of Ti(III) with the Cr(V) complex in the presence of an excess of the carboxylato ligand (λ_{max} 585 (ϵ 48), 413 nm (ϵ 62 M^{-1} cm^{-1})) do not correspond to those of a nonchelated carboxylato complex of $(H_2O)_5Cr^{III}$ (which should exhibit ϵ values of 20–30),[16] to a nonchelated dicarboxylato complex of $(H_2O)_4Cr^{III}$ (for which ϵ values lie in the same range),[16e] nor to a chelated complex of $(H_2O)_4Cr^{III}$ (for which molar absorptivities between 30 and 40 M^{-1} cm^{-1} would be expected).[3,16c] They are instead indicative of a bis chelate of $(H_2O)_2Cr^{III}$, and the observed ion-exchange elution behavior is consistent with this assignment. This product is seen to decay slowly in two stages,[11] a process that is retarded, but not arrested, by addition of excess ligand. This decay is presumed to reflect aquation with successive loss of the two bound carboxyl groups. Decay in contact with sulfonic acid resin is found to be still more marked, in agreement with the known column sensitivity of (carboxylato)chromium(III) species.[17]

Table II. Kinetic Data for Reduction of Carboxylato-Bound Chromium(V) with Ti$^{\mathrm{III}}$(edta)[a]

[RCOOH], M[b]	[RCOO$^-$], M[c]	pH	$10^{-6}k_2$,[d] M^{-1} s^{-1}
0.024	0.0012	2.0	1.0
0.022	0.0034	2.5	1.4
0.025	0.025	3.3	1.5
0.075	0.075	3.3	1.6
0.100	0.100	3.3	1.6

[a] Reactions were carried out at 23 °C; μ = 0.5 M (HCl + LiCl). Chromium(V) was added as sodium bis(2-ethyl-2-hydroxybutyrato)oxochromate(V) (I). $[\mathrm{Cr(V)}]_0 = 2.0 \times 10^{-4}$ M; $[\mathrm{Ti(III)}]_0 = 5.0 \times 10^{-4}$ M. [b] 2-Ethyl-2-hydroxybutyric acid. [c] 2-Ethyl-2-hydroxybutyrate. [d] Second order rate constants, evaluated from nonlinear least-squares treatment of absorbance data in accord with eq 1 (see Experimental Section).

Representative kinetic data appear in Tables I and II. Specific rates (k_2 values) for reductions with Ti$^{\mathrm{III}}$(aq) (Table I) are seen to be very nearly inversely proportional to [H$^+$] within the (relatively narrow) range 0.02–0.20 M H$^+$, indicating a preequilibrium involving loss of a proton from one of the redox partners. The deprotonated active species is almost certainly $\mathrm{Ti(OH)^{2+}}$, in accord with the behavior reported for many (although not all) reductions by Ti$^{\mathrm{III}}$ in acidic media.[18,19] The acid dependence is found to disappear, however, when Ti$^{\mathrm{III}}$(edta) is substituted for $\mathrm{Ti^{III}_{aq}}$ as a reductant (Table II). No evidence for kinetic saturation in the acidity pattern for $\mathrm{Ti^{III}_{aq}}$ appears at acidities as low as 0.05 M, in keeping with the reported p*Ka* value 2.64 for $\mathrm{Ti^{III}_{aq}}$ in aqueous chloride.[20]

Unlike the redox reactions of Cr(V) investigated previously,[3-5] reductions by Ti(III) are not retarded by addition of the parent carboxylato ligand. Such inhibition, when occurring, was taken to reflect a preliminary equilibrium involving loss of one unit of ligand ($\mathrm{Cr^VO(Lig)_2} \rightleftharpoons \mathrm{Cr^VO(Lig)} + \mathrm{Lig^-}$) prior to formation of a precursor complex with the reductant. Although it thus appears that the initial dissociation is not required for the reactions at hand, we cannot be certain as to whether attack by Ti$^{\mathrm{III}}$ utilizes, as a bridge, a Cr(V)-bound ligand (the oxo group or one of the two carboxyls), whether it takes place without bridging (an outer-sphere route), or whether a combination of processes is involved. At present, we favor the second of these alternatives.

The acceleration of the Cr(V)–Ti(III) reaction by added ligand acid is evidently not associated with alteration of the oxidant but rather with partial ligation of Ti(III). It is observed also, albeit to a lesser degree, when lactic or glycolic acid (both of them α-hydroxy acids) is substituted for the parent ligand. Kinetic

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(13) The low-energy maximum for Cr$^{\mathrm{III}}$(edta) at pH 2–5 is recorded at 545 nm (ϵ = 176 M^{-1} cm^{-1}) (Hamm, R. E. *J. Am. Chem. Soc.* **1953**, *75*, 5670). Conversion of the initial Cr$^{\mathrm{V}}$–Ti$^{\mathrm{III}}$(edta) produt to Cr$^{\mathrm{III}}$(edta) is found to proceed with a half-life period near 1.5 h at pH 3.

(14) A nonlinear least-squares program, NLLSQ, written in BASIC for the Apple II + computer, was kindly provided by Professor J. H. Espenson of Iowa State University.

(15) See, for example: Braddock, J. N.; Meyer, T. J. *J. Am. Chem. Soc.* **1973**, *95*, 3158.

(16) For comparisons of spectra of chelated and nonchelated monocarboxylato derivatives of Cr(III), see: (a) Hamm, R. E.; Johnson, R. L.; Perkins, R. H.; Davis, R. E. *J. Am. Chem. Soc.* **1958**, *80*, 4469. (b) Gould, E. S.; Taube, H. *Ibid.* **1964**, *86*, 1318. (c) Butler, R. D.; Taube, H. *Ibid.* **1965**, *87*, 5597. (d) Schlafer, H. L.Z. *Phys. Chem.* (*Munich*) **1957**, *11*, 65. (e) Ward, J. R.; Haim, A. *J. Am. Chem. Soc.* **1970**, *92*, 475.

(17) See, for example, ref 10 in: Gould, E. S. *J. Am. Chem. Soc.* **1968**, *90*, 1740.

(18) (a) Orhanovic, M.; Earley, J. E. *Inorg. Chem.* **1975**, *14*, 1478. (b) Earley, J. E.; Bose, R. N.; Berrie, B. H. *Ibid.* **1983**, *22*, 1836. (c) Hery, M.; Wieghardt, K. *Ibid.* **1978**, *17*, 1130. (d) Thompson, G. A. K.; Sykes, A. G. *Ibid.* **1976**, *15*, 638.

(19) Ram, M. S.; Martin, A. H.; Gould, E. S. *Inorg. Chem.* **1983**, *22*, 1103.

(20) Brunschwig, B. S.; Sutin, N. *Inorg. Chem.* **1979**, *18*, 1731.

dependencies in each case correspond to eq 3, where $a = 7.3 \times 10^4$ $M^{-2}\ s^{-1}$ for glycolic acid, 2.1×10^5 for lactic acid, and 3.2×10^5 for 2-hydroxy-2-ethylbutyric acid (23 °C, pH 1). Each carboxylato derivative of $Ti^{III}(OH)$ is a more facile reductant than $Ti(OH)^{2+}$ itself, but since the observed accelerations are proportional to the added carboxylic acid, our kinetic data do not allow us to estimate the association constants for these complexes or the specific rates at which they undergo oxidation.[21] Further rate enhancement resulting from ligation of Ti(III) is exemplified by the very rapid ($>10^6\ M^{-1}\ s^{-1}$) reductions by Ti^{III}(edta) (Table II).

$$k_{obsd} = 1.2 \times 10^4\ M^{-1}\ s^{-1} + a[RCOOH] \qquad (3)$$

Significant increases in redox reaction rates resulting from incorporation of a carboxylato species at a Ti(III) center have been reported.[8b,22] In the case of inner-sphere reactions, these have been attributed to labilization of metal-bound water molecules (by carboxyl coligands) prior to formation of a precursor complex, an effect for which there is independent evidence.[23] More particularly, the specific rate of water substitution on $Ti^{III}(edta)(H_2O)$[24] may be estimated[25] to be 10^3 as great as that for $Ti(H_2O)_5(OH)^{2+}$. For outer-sphere reactions, enhancements are more modest and their origins less obvious. Thompson and Sykes[8b] have shown that outer-sphere reductions of Co(III) species by Ti^{III}(edta) proceed about 10 times as rapidly as those by $Ti(H_2O)_5(OH)^{2+}$.

The bimolecular specific rate for reduction of the Cr(V) chelate I by $Ti(OH)^{2+}$ (obtained by dividing k_{obsd} at pH 1 by the fraction of Ti^{III} existing as $Ti(OH)^{2+}$ at this pH) is $5 \times 10^5\ M^{-1}\ s^{-1}$, about one-third the observed specific rate for the edta-bound reductant. This reactivity ratio thus falls close to that expected for an outer-sphere process. Note further that the specific rate calculated for reduction by $Ti(OH)^{2+}$ is considerably greater than $10^4\ M^{-1}\ s^{-1}$, the estimated[26] value for substitution of NCS^- at Ti^{III}_{aq}, a difference further supporting the assignment of an outer-sphere mechanism to the Cr(V)–Ti(III) reaction.

Since Ti(III) can part with only one electron, reduction of Cr(V) to Cr(III) must pass through a Cr(IV) intermediate. A strongly absorbing brown transient species having kinetic characteristics corresponding to such an intermediate has been observed[27] when the same Cr(V) chelate is treated with the 1e reductants Fe^{2+} and VO^{2+} in the presence of excess carboxylate ligand, but kinetic profiles for Ti(III)–Cr(V) systems indicate that detectable quantities of such a transient do not intervene here, even when Cr(V) is in large excess. The implication is that each of the Ti(III) species in this study reacts with Cr(IV) significantly more rapidly than with Cr(V). We estimate the ratio of rates to exceed 20;[28,29] the specific rate for reaction of $Ti(OH)^{2+}$ with Cr(IV) is then greater than $7 \times 10^6\ M^{-1}\ s^{-1}$, clearly too rapid for an inner-sphere process involving this reductant.

The primary Cr(III) species from each of these reactions, which appears to be a bis chelate, is not the thermodynamically favored product, for it is found to undergo slow aquation, even in the presence of excess ligand. Although five stereoisomers (excluding enantiomorphs) may be envisaged, we suspect that its structure is related to that of the initial Cr(V) chelate, with the two carboxyl functions lying trans to each other and two coordinated H_2O groups also trans. If so, the composite electron-transfer sequence ($Cr^V \rightarrow Cr^{IV} \rightarrow Cr^{III}$) has proceeded with preservation of the ligand environment about the chromium center. This point is of particular interest with respect to Cr(IV), for there is scattered evidence[5,30] that this oxidation state is substitution-labile. Our reactions, however, involve Ti(III) centers, which would be expected to react much more rapidly with Cr(IV) than would the less strongly reducing cations (Mn^{II} and Ce^{III}) featured in earlier studies addressed to this question. It is not inconceivable that ligand substitution at Cr(IV) is rapid in relation to Cr(IV) reduction in the latter instances but slow in relation to Cr(IV) reactions with the Ti(III) species in the present systems.[31] Further work with additional reductants is in progress.[32]

Acknowledgment. The authors are grateful to Dr. Y.-T. Fanchiang for valuable discussions concerning the nature of the chromium(III) product in these reactions.

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(21) Spectrophotometric examinations of solutions of Ti(III) (0.035 M) and 2-hydroxy-2-ethylbutyric acid (0.005–0.80 M) at pH 1–2 indicated that at least two Ti(III)–carboxylate complexes are formed within this range of ligand acid concentrations. The position of λ_{max} for Ti(III) shifted from 502 to 550 nm on addition of successive portions of carboxylic acid, but a limiting spectrum could not be obtained. Calculation of individual extinction coefficients and association constants did not appear to be feasible with the data at hand.

(22) (a) Lee, R. A.; Earley, J. E. *Inorg. Chem.* **1981**, *20*, 1739. (b) Earley, J. E.; Berrie, B.; Barone, P.; Bose, R. N.; Lee, R. A. "Coordination Chemistry-20"; Banerjea, D., Ed.; Pergamon Press: Oxford, 1980; p 65.

(23) See, for example: (a) Chaudhuri, P.; Diebler, H. *J. Chem. Soc., Dalton Trans.* **1977**, 596. (b) Matsubara, T.; Creutz, C. *Inorg. Chem.* **1979**, *18*, 1956.

(24) For evidence that the tetracarboxylate ligand in the edta complex of Ti(III) is five-coordinate, with the sixth position occupied by H_2O, see, for example: Podlahova, J.; Podlaha, J. *J. Inorg. Nucl. Chem.* **1966**, *28*, 2267.

(25) Lee and Earley[22a] have estimated that H_2O substitution in $Ti^{III}(edta)(H_2O)$ is 10^4 times as rapid as that in $Ti(H_2O)_6{}^{3+}$ under similar conditions, whereas the data of Ram[19] and that of Chaudhuri and Diebler[23a] indicate that such substitution in $Ti(H_2O)_5(OH)^{2+}$ is no more than 10 times as rapid as that in $Ti(H_2O)_6{}^{3+}$.

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

(27) Fanchiang, Y.-T.; Bose, R. N., unpublished experiments, Kent State University, 1984. This intermediate, which exhibits λ_{max} at 500 nm ($\epsilon = 1.5 \times 10^3\ M^{-1}\ s^{-1}$), is quickly consumed by addition of excess Fe^{2+} or VO^{2+}.

(28) If rate constants for reaction of Ti(III) with Cr(V) and Cr(IV) are taken as 1.2×10^4 and $1.8 \times 10^5\ M^{-1}\ s^{-1}$, respectively, maximal conversion to Cr(IV) at pH 1 and [Ti(III)] = 0.0030 M may be calculated[29] to occur 4.4 ms after mixing, a time interval slightly less than the mixing time of the Durrum instrument. Maximal conversion to Cr(IV) would correspond to only 5.0% of the Cr(V) used. If extinction coefficients at 500 nm are 150 $M^{-1}\ cm^{-1}$ for Cr(V) and 1500 $M^{-1}\ cm^{-1}$ for Cr(V),[27] the kinetic profile of the biphasic reaction at 500 nm would show no maximum; departures from strict exponential behavior during the initial portions of the reaction would be marginally perceptible.

(29) See, for example: Frost, A. A.; Pearson, R. G. "Kinetics and Mechanism", 2nd ed.; Wiley: New York, 1962; p 35.

(30) (a) Plane, R. A.; Taube, H. *J. Phys. Chem.* **1952**, *56*, 33. (b) Ogard, A. E.; Taube, H. *Ibid.* **1958**, *62*, 357.

(31) It may also be that the high concentrations of ligand acid in a number of our reaction mixtures substantially retard solvolytic disruption of the bis chelated Cr(IV) intermediate, just as they are found here to retard aquation of the Cr(III) product. Such an effect is presumed to reflect mass-law reversal of ligand loss from the metal ion center. It would allow, but not require, some alteration of configuration of the chelate.

(32) A reviewer asks us to suggest a basis for the difference between the behavior of $Ti(OH)^{2+}$, which, according to the arguments presented here, reduces the Cr(V) chelate I much more slowly than its Cr(IV) analogue, and Fe(II) and VO^{2+}, which appear to reduce the two oxidation states of chromium at more nearly comparable specific rates. We suspect that, with the last two reductants, inner-sphere reductions of Cr(V) have assumed importance and that this reflects a combination of rapid ligand substitution at these reducing centers and relatively low outer-sphere rates for these weakly reducing species. With the more strongly reducing $Ti(OH)^{2+}$, the outer-sphere reduction is much more rapid, whereas the importance of an inner-sphere route is limited by the relatively slow substitution at the Ti(III) center.