FULL PAPER

Reactions of tris(oxalato)cobaltate(III) with two-electron reductants[†]‡

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The tris(oxalato)cobaltate(III) complex $[Co(C_2O_4)_3]^{3-}$, $E^{o}_{Co}^{III/II} = +0.57$ V) is readily reduced by the 2e⁻ reagents, Sn(II) and Ge(II), in contrast to $(NH_3)_5CoCl^{2+}$ and $(NH_3)_5CoBr^{2+}$, which are unreactive toward these donors. Rates for the oxalato oxidant are only 10^{-3} – 10^{-2} as great as those for vitamin B_{12a} (aquacob(III)alamin, E^{o} +0.35 V at pH 1), in accord with the suggestion that reductions of corrin-bound cobalt(III) by Sn(II) and Ge(II) occur predominantly through an additional path involving Co(I). Reductions of the oxalato complex by 2e⁻ donors are taken to proceed by initial formation of odd-electron intermediates (*e.g.*, Sn^{III} and Ge^{III}) which react rapidly with Co^{III}. Such a two-step sequence is in keeping with the observed behavior of the rare reductant, Ti^{II}, which is found to be oxidized by $[Co(C_2O_4)_3]^{3-}$ more slowly than (independently prepared) Ti(III) under comparable conditions.

Introduction

Procedures for preparation of workable concentrations of the hydrated $p^{0}s^{2}$ -ions, indium(I),² germanium(II),³ and gallium(I)⁴ have been recently described, allowing us to compare the individual peculiarities of these strongly reducing species in solution.

Striking differences are observed, for example, in reactions with bound cobalt(III) . In contrast to In(1), which readily reduces halo and oxalato derivatives of (NH₃)₅Co(III), both Ge(II)_{aq} and Ga(I)_{aq} react immeasurably slowly with such oxidants, but cleanly reduce corrin-bound Co(III) (vitamin B_{12a} related species).⁵

The reductions of B_{12} have been attributed to intervention of a Co(1) transient:

 $(\text{corrin})\text{Co}^{\text{III}} + \text{Ge}^{\text{II}} \rightarrow (\text{corrin})\text{Co}^{\text{I}} + \text{Ge}^{\text{IV}}$ (1)

 $(corrin)Co^{I} + (corrin)Co^{III} \rightarrow 2(corrin)Co^{II} (rapid)$ (2)

but may reflect, at least in part; the more positive potential associated with the corrin-derived system.^{6,7} Since, however, Hin-Fat and Higginson⁷ have noted that replacement of ligating ammonias in $\text{Co}(\text{NH}_3)_6^{3+}$ by three chelating oxalato groups boosts its potential markedly (by approximately 500 mV), we anticipated that examination of the reactions of the readily prepared $\text{Co}(\text{C}_2\text{O}_4)_3^{3-}$ complex with Ge(II), Ga(I) and other 2e⁻ reductants might be instructive.

This report includes, we believe for the first time, kinetic data pertaining to electron transfer reactions of the unusual state, titanium(II) in aqueous media.

Experimental

Materials

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All solutions were prepared from Millipore-Q system deionized water that had been boiled for 2 h and then sparged with pure argon for a further 2 h to remove dissolved oxygen. Inorganic reagents, including indium metal, germanium dioxide, "gallium dichloride" (Ga^IGa^{III}Cl₄), titanium trichloride (in HCl), silver trifluoromethanesulfonate (silver triflate), barium triflate, and ammonium iron(II) sulfate hexahydrate (all Aldrich products) were used as received.

Stock solutions of indium(I) triflate in anhydrous CH₃CN,² Sn(II) solutions in HCl–NaCl,⁸ Ge(II) solutions in HCl,³ and Ga(I) solutions in H₂O–CH₃CN were prepared and analyzed as described. Vanadyl triflate solutions were made by treatment of VOSO₄ with barium triflate, were reduced to V(II) using zinc amalgam in triflic acid, and the V(II) converted to V(III) by mixing with a 10% excess of VO²⁺ in acid.⁹ Uranium(IV) solutions were prepared as described by Bose¹⁰ and potassium tris(oxalato)cobaltate(III), K₃Co(C₂O₄)₃, was synthesized by the procedure of Bailar and Jones.¹¹

Titanium(II) solutions were prepared under argon by a modification of the method of Kolle and Kolle.¹² 100 mg of titanium wire was dissolved in a mixture of 2 ml of neat triflic acid, 8 ml of water, and 0.4 ml of 48% HF at room temperature. The green solution was kept in a sealed container and used within 10 h of preparation. In our hands, such solutions exhibited $\varepsilon_{660} = 3.5 \pm 0.2 \text{ M}^{-1} \text{ cm}^{-1}$ and $\varepsilon_{430} = 6.0 \pm 0.5 \text{ M}^{-1} \text{ cm}^{-1}$.¹³ These preparations became discolored on standing for 24 h.

Stoichiometric studies. Stoichiometric determinations were carried out under argon, most often with the oxidant in excess, and were monitored at the absorbance maximum of that oxidant. Measured deficient quantities of the reductant were added, and the decreases in absorbance were compared to those resulting from addition of an excess of the reductant.

Kinetic studies. Reactions were performed under argon in a darkened room since $Co(C_2O_4)_3^{3-}$ is light-sensitive. Freshly prepared Co(III) was used for each series of runs. Rates were obtained from measurements of absorbance decreases of the oxidant, using a Durrum-Gibson stopped-flow spectrophotometer interfaced with an OLIS computer system or a Shimadzu 1601 UV-visible spectrophotometer. Temperatures were kept at 22.0 \pm 0.5 °C. Ionic strength was maintained with NaCl-HCl or HCl-HClO₄. Concentrations were most often adjusted so that no more than 10% of the reagent in excess was consumed in a given run (pseudo-first order conditions). The resulting exponential curves were followed for at least five halflife periods, and rate constants were evaluated by nonlinear least-squares fittings to the relationship corresponding to first-order decay. The very rapid reaction of Ga(I) could not be monitored via stopped-flow, due to interference by H_2 bubble formation; when the reaction was examined using conventional mixing, only a lower limit, $k_2 > 2 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$ (22 °C) could be obtained.

[†] Electronic supplementary information (ESI) available: Tables S1–S4; detailed kinetic data for redox reactions. See http://www.rsc.org/ suppdata/dt/b4/b408758p/

[‡] Electron Transfer. Part 159. For Part 158, see ref. 1.

Table 1 Stoichiometry of the reactions of $[Co(C_2O_4)_3]^{3-}$ with single-electron and two-electron reductants^{*a*}

Reductant (red)	Δ [Co ^{III}] ^b / Δ [red]
1e ⁻ reagents	
Fe(II) ^c	1.01
$Ti(III)^{c}$	1.02
2e ⁻ reagents	
In(I) ^d	1.93
Ge(II) ^c	1.94
Sn(II) ^c	1.84
Ti(II) ^e	1.91

^{*a*}Reactions at 22 °C in a darkened room. ^{*b*}Determined spectrophotometrically at 603 nm. ^{*c*}In 0.50 M HCl. ^{*d*}In 0.20 M HAc–Ac⁻ buffer (pH 4.7). ^{*c*}In 0.4 M NaCl–0.2 M HCl.

Results

In addition to the $2e^-$ reductants (Sn^{II}, Ge^{II}, In^I and Ti^{II}) some experiments with the single-electron reagents Fe^{II}, Ti^{III}, and V^{III} are included for comparison. The le⁻ donors are seen (Table 1) to exhibit very nearly 1:1 stoichiometry, whereas the $2e^-$ reagents (including Ti^{II}) approach the expected 1:2. Slight deviations with the slower reductants probably reflect loss from traces of O₂ during the longer waiting periods. Monophasic kinetic profiles obtained in all instances rule out the intervention of transients formed or consumed on a time scale comparable to that of the principal redox transformation.

One-electron reductions

Reductions of $[Co(C_2O_4)_3]^{3-}$ by our le⁻ reagents are relatively straightforward. Data for the Fe^{II}–Co^{III} reaction generate the simple monomial rate law: rate = k[Ox][Red]with $k = 35 \pm 1$ M⁻¹ s⁻¹, under our conditions. Reductions by Ti(III) and V(III) (Tables S1 and S2, ESI†) exhibit inverse acid terms, a type of dependence which has long been recognized for these reductants.^{9,14} The relatively high Fe(II) rate ($E^\circ = 0.77$ V for Fe^{III/II}), in contrast to that for the more strongly reducing V(III) ($E^\circ = 0.36$ V for V³⁺/VO²⁺) points to an important innersphere component for the d⁶ center, but Grossman and Haim¹⁵ have pointed out that the very rapid consumption of the same oxidant by V^{II} ($k_{25 \circ C} = 2 \times 10^4$ M⁻¹ s⁻¹) must be predominantly outer sphere since it proceeds much more quickly than ligand attachment to the V(II) center.

Two-electron reductions

The facile reduction ($k = 10.4 \text{ M}^{-1} \text{ s}^{-1}$) by In(I), nominally a 2e⁻ donor, brings to mind the versatility of its action toward (NH₃)₅Co^{III} oxidants.² Initiation of reaction in such cases, is taken to proceed through short-lived In(II):

$$Co^{III} + In^{I} \rightarrow Co^{II} + In^{II}$$
 (rate determining) (3)

$$Co^{III} + In^{II} \rightarrow Co^{II} + In^{III}$$
(rapid) (4)

Both Sn(II) and Ge(II) are likewise found to react readily. These are, to our knowledge, the first reported reductions of non-corrin-bound Co(III) by these $2e^{-}$ donors. Sequences analogous to eqns. (3) and (4) may be involved here.

However, consideration of the Sn(II) reduction in Clcontaining media (Table S3, ESI[†]) must take into account the partial conversion of this reaction into four ligation levels:¹⁶

$$\operatorname{Sn}^{2+} + \operatorname{Cl}^{-} \to \operatorname{Sn}\operatorname{Cl}^{+} (K_1 = 11.2)$$
(5)

 $\operatorname{Sn}^{2+} + 2\operatorname{Cl} \to \operatorname{Sn}\operatorname{Cl}_2 \ (K_2 = 32) \tag{6}$

$$Sn^{2+} + 3Cl^{-} \to SnCl_{3}^{-} (K_{3} = 14)$$
 (7)

Sn(II)–Co(III) rates (Table S3A, ESI†) conform to expression (8)

$$-d[Co^{III}]/dt = \frac{[Co^{III}][Sn^{II}](k_3K_3[Cl^-]^3)}{1 + K_1[Cl^-] + K_2[Cl^-]^2 + K_3[Cl^-]^3}$$
(8)

where the denominator indicates the partition of Sn(II) into three chloro complexes. The numerator points to a preponderant path, $k_3K_3[Cl^-]^3$, involving $SnCl_3^-$. Refinement of data in terms of eqn. (8) yields rate constants in Table 2. Alternate sequences, involving the lower chloro complexes as well, did not improve the fit. Calculated and observed rates are compared at the right of this table.

Reductions by Ge(II) (Table S3B, ESI[†]) are less sensitive to changes in the medium than those by Sn(II) eqn. (8). The resulting rate law is given by eqn. (9); refinement of data yields $k_1 = (2.01 \pm 0.03) \text{ M}^{-1} \text{ s}^{-1}$.

$$-d[Co^{III}]/dt = \frac{[Co^{III}][Ge^{II}](k_1K[CI^-])}{1 + K[CI^-]}$$
(9)

This reaction then utilizes a path requiring just one extra Cl⁻. The small anation constant, $K_{Cl} = 0.20 \text{ M}^{-1}$, associated with attachment of an additional Cl⁻ to the principal Ge(II) center, is consistent with that reported earlier.⁵

Somewhat unexpectedly, reductions by Ti(II) (Table S4, ESI[†]) are *slower* than those by Ti(III) under comparable conditions. Slight but perceptible inhibition, both by H⁺ and by Cl⁻, is observed. The rates are correlated by expression (10):

rate =
$$[Co^{III}][Ti^{II}](k_0 + a/[H^+] + b/[Cl^-])$$
 (10)

Refinement yields parameters $k_0 = 62 \pm 2$ M⁻¹ s⁻¹, $a = 6.1 \pm 0.5$ s⁻¹ and $b = 3.3 \pm 0.4$ s⁻¹. It is most unlikely that the *a* term in (10) is mechanistically meaningful. If it is attributed to reaction by the deprotonated form of the reductant, [Ti^{II}(OH)]⁺, a bimolecular rate constant, obtained by division by K_a for Ti^{II}(aq) (p K_A near 12.0),¹⁷ greatly exceeds the diffusion controlled limit. We therefore ascribe this term to a medium effect. Interpretation of the *b* term in eqn. (10) requires (as yet unavailable) knowledge of the anation quotients applicable to chloro complexes of Ti(II) in this medium.

Rate laws and kinetic parameters are summarized in Table 2.

Discussion

In our view, the most noteworthy aspects of this study are: (a) the facile reduction of the Co(III) oxidant by Sn(II) and Ge(II), and (b) the relatively sluggish redox action of the Ti(II) center.

The usual reluctance of Sn^{II} and Ge^{II} to utilize ligand bridging in reductions of $Co(III)^5$ implies that reductions by these s² centers use non-bridged paths, as has been demonstrated with V(II).¹⁵

If, as we suspect, these reductions are initiated by single electron transfers, our observations confirm the suggestion by Higginson¹⁷ that this oxidant, converts Sn(II) to short-lived Sn^{III} and we may extend this inference to the conversion of Ge^{III} to Ge^{III}:

$$Co^{III} + Ge^{II} \rightarrow Co^{II} + Ge^{III}$$
(11)

$$Co^{III} + Ge^{III} \rightarrow Co^{II} + Ge^{IV}$$
 (rapid) (12)

Since the increased reactivity of $[Co(C_2O_4)_3]^{3-}$ reflects, in large part, its favorable potential ($E^\circ = 0.57$ V),⁴ one may ask whether the remarkable reactivity of Sn(II) and Ge(II) toward corrin-bound Co(III) in B_{12a}⁵ is simply potential-related. We think not. Rates for Sn(II)–B_{12a} are about 3×10^2 as great as those for reduction of our tris-oxalato complex despite a 0.20 V potential gap favoring the latter. Similarly, rates for Ge(II)–B_{12a} are about 10³ as large as those for Ge(II) –Co(ox)₃³⁻. Even when potential differences are taken into account, evidence persists for reduction of B_{12a} *via* its Co(I) counterpart (sequence (1), (2)).

Table 2 Rate laws and kinetic parameters for reductions of $C_0(C_2O_4)^{3-a}$

	-		
	Red	Rate law	Parameters
	Fe(II)	<i>k</i> [Co ¹¹¹][Fe ¹¹]	$k = 35 \pm 1 \text{ M}^{-1} \text{ s}^{-1}$
	Ti(III)	$k[Co^{III}][Ti^{III}][(k_0 + k'/[H^+])$	$k_0 = (1.5 \pm 0.2) \times 10^2 \mathrm{M}^{-1} \mathrm{s}^{-1}$ $k' = (56 \pm 3) \mathrm{s}^{-1}$
	V(III)	$k[Co^{III}][V^{III}](k_0 + k'/[H^+])$	$k_0 = (1.3 \pm 0.1) \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$ $k' = (4.3 \pm 0.2) \times 10^{-3} \text{ s}^{-1}$
	In(I) ^c	<i>k</i> [Co ^{III}][In ^I]	$k = 10.4 \pm 1.3 \text{ M}^{-1} \text{ s}^{-1b}$
	V(II)	<i>k</i> [Co ^{III}][V ^{II}]	$k = 2 \times 10^4 \mathrm{M}^{-1}\mathrm{s}^{-1b}$
	Sn(II)	$\frac{[\text{Co}^{III}][\text{Sn}^{II}](k_3K_3[\text{Cl}^-]^3)}{1+K_1[\text{Cl}^-]+k_2[\text{Cl}^-]^2+K_3[\text{Cl}^-]^3}$	$k_3 = (0.41 \pm 0.01) \text{ M}^{-1} \text{ s}^{-1}$ $K_1 = 11.2; K_2 = 32; K_3 = 14$
	Ge(II)	$\frac{[\mathrm{Co}^{\mathrm{II}}][\mathrm{Ge}^{\mathrm{II}}]kK[\mathrm{Cl}^{-}]}{1+K[\mathrm{Cl}^{-}]}$	$k = (2.01 \pm 0.03) \text{ M}^{-1} \text{ s}^{-1}; K = 0.20$
	${\rm Ti}({\scriptstyle \rm II})^d$	$[Co^{III}][Ti^{II}](k_0 + a/[H^+] + b/[Cl^-])$	$k_0 = (62 \pm 2) \text{ M}^{-1} \text{ s}^{-1}$ $a = (6.1 \pm 0.5) \text{ s}^{-1}; b = (3.3 \pm 0.4) \text{ s}^{-1}$
	Ga(I)	<i>k</i> [Co ^{III}][Ga ^I]	$k > 200 \text{ M}^{-1} \text{ s}^{-1}$
^a Reactions were carried	l out at 22.0 \pm	0.5 °C; μ = 0.50 M (HCl/NaCl) unless otherwise	the indicated; $\lambda = 603$ nm. ^b Ref. 15. ^c $\mu = 0.050$ M. ^d $\mu = 1.0-1.2$ M.

Here and elsewhere2-4 those reductions of FeIII, CoIII, or IrIV by 2e⁻ donors which exhibit exponential profiles have been taken to proceed via two-step sequences such as (11) + (12), in which the rate constant associated with the odd electron transient (e.g., Ge^{III}) is much greater than that for the parent reductant. However, direct observation of such intermediates has proved elusive. In the present study, comparisons of reductions by Ti(II) with those by Ti(III) (prepared independently) confirm the reasonableness of this path. Once again, the odd-electron reductant is found to be the more rapid reactant.

Why is reduction by Ti(II) so slow? This cannot be attributed to an inadequate potential, but if considered on the basis of the model of Marcus for outer-sphere reactions,18 may instead imply a very low value for the Ti(III,II) self-exchange rate in our media. Both Ti^{II} (3d²) and Ti^{III} (3d¹) are, in principle, subject to minor Jahn-Teller distortions, but the degree of such distortion and the occupancy of the non-degenerate orbitals [(one short, two long) vs. (two short, one long)] would not necessarily match. The two states might then feature substantially different, geometries, and this mismatch would presumably be reflected in a higher Franck-Condon barrier to exchange. Alternatively, partial olation of Till centers to unreactive dimeric or higher associated species cannot be ruled out, although it would not be expected in the strongly acidic solutions used.

The ease with which Ti(II) can be prepared¹² bears upon the current uncertainty in the value of E°(TiIII/TiII).19 Of the two most frequently cited potentials, we favor -0.37 V forwarded by Forbes and Hall²⁰ over the much more negative figure -2.1 V suggested by Oliver and Ross.²¹ The latter is difficult to reconcile with the lack of redox activity of Ti(II) with H⁺ and Co²⁺ in our systems.

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