Reductions by titanium(II) as catalyzed by titanium(IV)†‡

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The cobalt(III) complexes, $[(NH_3)_5COBr]^{2+}$ and $[(NH_3)_5CoI]^{2+}$ are reduced by Ti(II) solutions containing Ti(IV), generating nearly linear (zero-order) profiles that become curved only during the last few percent of reaction. Other Co(III)–Ti(II) systems exhibit the usual exponential traces with rates proportional to [Co(III)]. Observed kinetics of the biphasic catalyzed Ti(II)–Co(III)Br and Ti(II)–Co(III)I reactions support the reaction sequence:

$$\begin{split} [\text{Ti}(\text{II})(\text{H}_2\text{O})_n]^{2+} + [\text{Ti}(\text{IV})\text{F}_5]^- & \stackrel{k_1}{\underset{k_{-1}}{\longrightarrow}} [\text{Ti}(\text{II})(\text{H}_2\text{O})_{n-1}]^{2+} + [(\text{H}_2\text{O})\text{Ti}(\text{IV})\text{F}_5]^- \\ & [\text{Ti}(\text{II})(\text{H}_2\text{O})_{n-1}]^{2+} + \text{Co}(\text{III}) \stackrel{k_2}{\longrightarrow} \text{Ti}(\text{III}) + \text{Co}(\text{II}) \end{split}$$

with rates determined mainly by the slow Ti(IV)–Ti(II) ligand exchange ($k_1 = 9 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ at 22 °C). Computer simulations of the catalyzed Ti(II)–Co(III) reaction in perchlorate–triflate media yield relative rates for reduction by the proposed active [Ti(II)(H₂O)_{n-1}]²⁺ intermediate; $k_{\text{Br}}/k_{\text{I}} = 8$.

Introduction

Kinetic examinations of the reactions of two-electron reductants have disclosed instances in which rates are independent of the concentration of oxidant, even when the latter is in deficiency. The oxidations of Ge(II) by I_3^{-} ,² by [W(CN)₈]³⁻,³ and by Cr(VI) in HCl,⁴ as well as oxidation of In(I) by vitamin B_{12a} in HCl,⁵ behave in this manner, indicating that, in each case, the reaction is initiated by a slow step not involving the oxidant. Kinetic profiles are consistent with a rate-determining heterolysis of the reductants (*e.g.*, Ge(II)–OH₂) to a more reactive form (Ge(II):) which then reacts rapidly with the oxidant:

$$Ge(II)-OH_2 \rightarrow Ge(II): + H_2O \text{ (slow)}$$
(1)

$$Ge(II): + I_3^- \to Ge(IV) - I + 2I^- (rapid)$$
(2)

If sequence (1)–(2) is correct, it represents one of the rare cases where a sluggish bond breaking at a simple metal complex in aqueous solution occurs without a substantial loss in ligand field stabilization.⁶

It has recently been reported that $[Br(NH_3)_5Co]^{2+}$ and its iodo analog are reduced by $Ti(II)_{aq}$ at rates independent of oxidant.¹ Since this reductant, as prepared by the method of Kolle,⁷ contains equivalent quantities of Ti(IV), it appeared that the possibility of catalysis by that tetrapositive state should be considered.

Experimental

Materials

All solutions were prepared from Millipore-Q system deionized water that had been boiled for 2 h and then purged with pure argon

for two more hours to remove dissolved oxygen. Trifluoromethanesulfonic acid (triflic acid), as well as inorganic reagents (Aldrich or Fisher products) were used as received. Pentaamminecobalt(III) complexes, bromopentaamminecobalt(III) perchlorate,⁸ and its iodo,⁹ binoxalato,¹⁰ and azido¹¹ complexes were prepared as described. Titanium(II) solutions in 1.0–2.0 M triflic acid were prepared under argon by a modification of the method of Kolle.⁷ These green solutions were kept in sealed containers and used within 10 h of preparation. Titanium(IV) solutions were prepared by air oxidation of titanium(II) solutions; after oxidation was complete, as indicated by complete loss of color, argon was bubbled through the solution for 2 h to remove traces of dissolved oxygen. Sodium triflate was prepared by neutralization of concentrated triflic acid, boiled to remove carbon dioxide, and the salt obtained by cooling.¹²

Kinetic studies

Reactions were performed under argon. Rates were obtained from measurements of absorbance decreases associated with the oxidants using a Shimadzu 1601 UV-visible spectrophotometer. Temperatures were kept at 22.0 ± 0.5 °C. Ionic strengths were maintained with NaClO₄/HClO₄/CF₃SO₃H or CF₃SO₃H/CF₃SO₃Na. In most cases, the bromo- and iodo-substituted oxidants gave very nearly linear traces (rates independent of oxidant) with perceptible appearance of curvature during the last few percent reaction. The oxalate and azido complexes, included here for comparison, yielded exponential absorbance traces, with rate constants proportional to [Ti(II)].

Results and discussion

A previous study¹ emphasized differences between the kinetic behavior of the reductants Ti(II) and Ti(III). Dissimilarities are particularly marked for the familiar homologous series of oxidants, fluoro-, chloro-, bromo- and iodo-pentaamminecobalt(III).

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Reductions, using Ti(III), of each halogen-substituted complex yields the expected exponential profiles, as were observed also for the Ti(II)–fluoro and Ti(II)–chloro systems. Curves for the Ti(II)–bromo and Ti(II)–iodo reactions were, however, clearly biphasic, featuring a predominant linear (zero order) component and a small curved portion in the late stages (Fig. 1(A), (B)). Moreover, initial rates in these biphasic conversions appeared to be second order in Ti(II).



Fig. 1 Kinetic profiles for the reduction of $[Co(NH_3)_5Br]^{2+}$ (A, 551 nm) and $[Co(NH_3)_5I]^{2+}$ (B, 580 nm) with $Ti(II)_{aq}$ (12.0 mM) in the presence of added Ti(IV) (72 mM); $[H^+] = 0.7 \text{ M}$ (CF₃SO₃H/HClO₄); $\mu = 1.0 \text{ M}$. Circles represent the experimental data, whereas the solid line was obtained by KINSIM simulation of the proposed mechanism, (6)–(7), using parameters from Tables 1 and 2 (bromo: $k_1 = 10.0 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$, $k_2/k_{-1} = 160$; iodo: $k_1 = 9.5 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$, $k_2/k_{-1} = 22$). $\varepsilon_{Co(m)}$ was taken as 53 M⁻¹ cm⁻¹ for bromo and 79 M⁻¹ cm⁻¹ for iodo. Optical path length = 1.00 cm.

No other Co(III) complex examined here mimics the bromo and iodo reduction patterns. The azido derivative, $[(NH_3)_5CoN_3]^{2+}$ follows a straightforward monomial rate law (3) whereas the oxalato complex (Table S1, ESI⁺) exhibits a $1/[H^+]^2$ -dependence (4) reminiscent of the analogous

Rate =
$$k$$
[CoN₃][Ti(II)]; $k = (6.9 \pm 0.2) \text{ M}^{-1} \text{ s}^{-1}$ (3)

Rate = $k[Co(C_2O_4)][Ti(II)][H^+]^{-2}; k = (0.45 \pm 0.01) \text{ M s}^{-1}$ (4)

reduction of [(NH₃)₅Co(C₂O₄)]⁺ by Ti(III).¹³

$$rate = -d[Co(III)]/dt = k[Ti(II)][Ti(IV)][Co(III)]^{0}$$
(5)

Examination of the action of Ti(IV), which is present in our

Treatment of data for initial rates yields $k = (8.4 \pm 0.4) \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ for the bromo oxidant and $(9.0 \pm 0.6) \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ for the iodo. Observed and calculated rates (in parentheses) are compared at the right of these tables.¹⁴ Note that [Ti(II)] and [Ti(IV)] are very nearly the same in the Ti(II) master solutions used,⁷ thus accounting for the apparent [Ti(II)]² dependence erroneously assigned when no additional Ti(IV) was added.

The biphasic profiles observed, in conjunction with the dependence on Ti(IV) and the observed increase in absorbance at 502 nm (a Ti(III) maximum), are consistent with mechanistic sequence (6)–(7) for the bromo- and iodo-substituted Co(III) oxidants.

$$[\text{Ti}(\text{III})(\text{H}_{2}\text{O})_{n}]^{2+} + [\text{Ti}(\text{IV})\text{F}_{5}]^{-} \frac{k_{1}}{k_{-1}} [\text{Ti}(\text{II})(\text{H}_{2}\text{O})_{n-1}]^{2+} + [(\text{H}_{2}\text{O})\text{Ti}(\text{IV})\text{F}_{5}]^{-}$$
(6)

$$[\mathrm{Ti}(\mathrm{II})(\mathrm{H}_{2}\mathrm{O})_{n-1}]^{2+} + \mathrm{Co}(\mathrm{III}) \xrightarrow{k_{2}} \mathrm{Ti}(\mathrm{III}) + \mathrm{Co}(\mathrm{II})$$
(7)

Here the active reducing species is taken as the coordinatively unsaturated Ti(II) center (probably $[Ti(II)(H_2O)_3]^{2+}$), designated $[Ti(II)(H_2O)_{n-1}]^{2+}$. Incorporation of sequence (6)–(7) into the KINSIM treatment¹⁵ yielded calculated absorbance curves which were compared to the observed kinetic profiles. Values of k_1 and the ratio k_2/k_{-1} giving optimal agreement with runs in which the reactants are varied are listed in Tables 1 and 2. Note that this treatment does not yield individual values of k_{-1} and k_2 but only their ratio. The k_1 values for the two systems, designating the aqua transfer from Ti(II) to Ti(IV), are in agreement (0.008–0.010 M⁻¹ s⁻¹ at 22 °C). This rate is very nearly independent of acidity.

Table 1 Rate constants pertaining to the reduction of $[(NH_3)_5CoBr]^{2+}$ byTi(II) as catalyzed by Ti(IV)^a

[Ti(II)]/mM	[Ti(IV)]/mM	[H ⁺]/M	$10^{3}k_{1}/M^{-1} \mathrm{s}^{-1}$	$10^{-2}k_2/k_{-1}$
40	40	0.70	8.0	1.6
25	25	0.70	9.0	1.4
20	20	0.70	10.0	1.6
12	12	0.70	11.0	1.4
12	24	0.70	9.5	1.5
12	48	0.70	9.0	1.6
12	72	0.70	10.0	1.6
25	25	0.40	9.8	3.0
25	25	0.50	9.5	2.4
25	25	0.60	8.2	2.1
25	25	0.90	8.6	1.3
25	25	0.70^{b}	8.6	1.3
25	25	0.70^{c}	8.2	1.6
25	25	0.70^{d}	8.2	2.0

^{*a*} Parameters pertain to sequence (6)–(7) in text. T = 22 °C; [Co(III)] = 1.1–1.8 mM; $\mu = 1.0$ M (NaClO₄/HClO₄/CF₃SO₃H) unless otherwise indicated; $\lambda = 551$ nm. Values of k_1 listed are those giving optimal agreement between observed and calculated absorbances. Extinction coefficient of [(NH₃)₅CoBr]²⁺ was taken as 53 M⁻¹ cm⁻¹. Optical path length = 1.0 cm. ^{*b*} $\mu = 0.80$ M. ^{*c*} $\mu = 1.40$ M. ^{*d*} $\mu = 1.80$ M.

[Ti(II)]/mM	[Ti(IV)]/mM	[H ⁺]/M	$10^{3}k_{1}/M^{-1} s^{-1}$	k_2/k_{-1}
32	32	0.70	9.5	20
25	25	0.70	10.0	20
16	16	0.70	10.0	18
12	24	0.70	11.6	22
12	48	0.70	9.5	20
12	72	0.70	9.5	22
32	32	0.20	9.7	60
32	32	0.30	9.5	42
32	32	0.40	8.4	35
32	32	0.50	8.5	27

^{*a*} Parameters pertain to sequence (6)–(7) in text. T = 22 °C; [Co(III)] = 0.7–2.5 mM; $\mu = 1.0$ M (NaClO₄/HClO₄/CF₃SO₃H). Values listed are those giving optimal agreement between observed and calculated absorbances; $\lambda = 580$ nm. Extinction coefficient of [(NH₃)₅CoI]²⁺ was taken as 79 M⁻¹ cm⁻¹. Optical path length = 1.00 cm.

An alternative sequence, (8)–(9), features electron transfer from Ti(III) to Co(III) and initiation by a Ti(IV)–Ti(II) comproportionation:

$$Ti(II) + Ti(IV) \frac{k_8}{k_{-8}} 2Ti(III)$$
(8)

$$2\text{Ti}(\text{III}) + 2\text{Co}(\text{III}) \xrightarrow{k_0} 2\text{Ti}(\text{IV}) + 2\text{Co}(\text{II})$$
(9)

Although (8) + (9) appears to be very nearly consistent with our profiles, this alternative is ruled out by the reported¹⁶ very slow Ti(III) reductions (in 0.44 M H⁺) of both the bromo ($k = 4 \times 10^{-3}$ M⁻¹ s⁻¹) and the iodo ($k = 5.4 \times 10^{-2}$ M⁻¹ s⁻¹) complexes. The final curved portions of the profiles in Fig. 1 indicate half-life periods approximately 25 s for the iodo and <10 s for the bromo, whereas the reported $k_{\text{Ti(III)}}$ values correspond to $t_{1/2} = 3.9$ h (bromo) and 0.28 h (iodo) when the reductant is 12 mM. Neither of these Ti(III) reactions is catalyzed by Ti(IV).

The ratio k_2/k_{-1} is seen to vary as $1/[H^+]$ for both oxidants. Since measured rates for faster Ti(II)–Co(III) reactions have been shown to be independent of acidity,¹ values of k_{-1} must be proportional to [H⁺]. It is reasonable that protonation of Ti(IV)-bound water in (6) eases its departure from the Ti(IV) center.

Comparison of k_2/k_{-1} ratios indicates that the activated Ti(II) center reduces the bromo oxidant about eight times as rapidly as the iodo. The order of reactivity corresponds to that for reductions by Eu(II),¹⁷ but is the reverse of that for reductions by Fe(II),¹⁸ and In(I),¹⁹ suggesting that the present reducing species, like Eu(II), is a hard acid in the Pearson sense.¹⁷ This conclusion

matches that pertaining to Ti(II) in the absence of catalysis by Ti(IV), but the selectivities of the two centers is likely to be quantitatively different.

In sum, our thinking ascribes the zero order disappearance of these Co(III) oxidants to a preliminary rate-determining transfer of a Ti(II)-bound aqua ligand to an electrophilic Ti(IV) center. As such, it is closely related to the zero-order disappearance of I_3^- in the Ge(II)– I_3^- reaction.² In both instances initiation involves slow heterolysis of a cation–OH₂ linkage of the reductant, and both systems feature electrophilic catalysis, in the present case by Ti(IV), in the Ge(II) reaction, by H⁺.

One puzzling point emerges. Why is the preliminary heterolysis at the Ti(II) center (which involves no appreciable alteration of crystal field stabilization energy) so slow? In the absence of further evidence, we suspect that this sluggishness simply reflects the relative reluctance of the fluorophilic Ti(IV) center to take on an additional (softer and O-donor) ligand.

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