Reactions of aquatitanium(II) with hypervalent chromium species†‡

Basab Bijayi Dhar,* Ritam Mukherjee and Edwin S. Gould*

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Titanium(II) solutions, prepared by dissolving titanium metal in triflic acid and HF, react readily with derivatives of Cr(VI), Cr(V) and Cr(IV). Reductions of Cr(VI) and Cr(IV), carried out with $[Co(NH_3)_5Br]^{2+}$ as a scavenger for Cr(II), yield no detectable Co^{2+}, indicating that $2e^-$ steps, bypassing Cr(V) and Cr(III), are not operative. Catalysis by Ti(IV) is observed only for reduction of Cr(VI). Rates for reduction by Ti(III) are remarkably similar to those for the corresponding reductions by Ti(II). The addition of Ti(III) to triflic acid and HF results in rapid and quantitative disproportionation to Ti(II) and Ti(IV).

Introduction

The first d-block of transition metals is of unusual interest to redox chemists, for it features several members having three or more accessible mononuclear oxidation states separated by single units. In instances where a di- or multi-valence change results from the reaction with a $2e^-$ co-reagent, it may be asked whether the overall transformation involves a series of single electron steps, whether $2e^-$ transfers are at work, or whether a combination of the two modes is occurring.

As early as 1949, Watanable and Westheimer[2] recorded rate experiments, which suggested the intervention of the less usual Cr(IV) and Cr(V) states in the reduction of Cr(VI) with 2-propanol, and in 1990–1992, Ghosh and co-workers[3–6] reported that reductions of $HCrO_4^-$ with As(III) or Sn(II) in aqueous media buffered by 2-ethyl-2-hydroxybutanoic acid (HLig) and its anion (Lig^-) yielded pink solutions of Cr(IV) chelates of this buffer ($\varepsilon_{511\,max} = 2.3 \times 10^3$ M^{-1} cm^{-1}) without major intervention of Cr(V).

Shortly afterwards, Scott, Bakac and Espenson[7] described reactions of a short-lived oxidizing species (half-life near 30 s in 1 M H^+) the behaviour of which corresponded to an oxochromium(IV) cation, $[Cr^{V}O]^{2+}$, which reacts with a series of primary and secondary alcohols in two-unit events, bypassing Cr(III). Moreover, Chandra has reported reductions of Cr(VI) to Cr(IV), and thence to Cr(II), using hypophosphite[8] and formate,[9] without intervention of Cr(V) or Cr(III).

In contrast, the reactions of hypervalent manganese species featuring Mn(III), Mn(IV), and Mn(III,IV) centers with the $2e^-$ reductants Sn(II), Ge(II), and In(I)[10] exhibit no transients or kinetic features attributable to $2e^-$ transactions.

The report, in 2003, of convenient generation and handling of aqueous solutions of aquatitatnium(II)[11] added an additional species to the roster of available strong reductants, which in principle, may reaction either by one- and two-unit paths. The present study deals with the reactions of this novel bifunctional donor with several acceptors derived from the higher oxidation states of chromium.

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 a further 2 h to remove dissolved oxygen. Titanium(II) solutions (0.10 M in Ti^{II} in 2.0 M triflic acid) were prepared under argon by the method of Kolle and Kolle.[11] These green solutions were kept in sealed containers and were used within 10 h of preparation. The Ti(II) concentration was determined by adding a measured volume to an excess of $[Co(NH_3)_5F](ClO_4)_2$ under argon, waiting 20 min, diluting tenfold with conc. HCl, and determining $[CoCl_4]^{2-}$ at 692 nm ($\varepsilon = 560$ M^{-1}cm^{-1}); as stated by Kolle,[11] these solutions contained equimolar quantities of Ti(IV). Titanium(IV) solutions were also prepared by air oxidation of Ti(II); after conversion to Ti(IV) was complete (as indicated by total loss of colour), argon was passed through the solution for 2 h more to remove traces of oxygen. Sodium triflate was prepared by the method of Stanbury.[12]

Potassium dichromate and 2-ethyl-2-hydroxybutanoic acid (the "ligand acid" used to stabilize Cr^{V} and Cr^{IV}) were Aldrich products and were used as received. Sodium bis(2-ethyl-2-hydroxybutanoato)oxochromate(V) was prepared as described by Krumpolc[13] and was kept in the dark at 0 °C; $\varepsilon_{510} = 165$ M^{-1} cm^{-1}). Chromium(IV) solutions were generated by treating known deficiencies of Cr(VI) with excess (0.01 M) As^{III} in 1 : 1 HLig–Lig^- "ligand buffer" as described by Ghosh.[5]

Spectrophotometric examinations of mixtures of the ligand buffer and Ti(II) solutions yielded no evidence for interaction in the absence of chromium species.

Stoichiometric and trapping studies. Stoichiometric determinations were carried out under argon, most generally with the oxidant in excess, and were monitored at or near the absorbance maximum of that oxidant. Measured deficient quantities of the reductant were added, and the quantity of oxidant consumed was estimated from the observed decrease in absorbance. Results are summarized in Table 1.

Department of Chemistry, Kent State University, Kent, Ohio 44242, USA

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Table 1 Reductions of hypervalent chromium species with Ti^{II}(aqua). Stoichiometry[a]

Oxidant	λ/nm	$[Ti^{II}]$/mM	[HLig + NaLig]/ mM[b]	$[H^+]$/M	Δ[ox]/Δ[Ti(II)]
Cr(VI)	350	0.40–1.50	0	0.50	0.64 ± 0.06
Cr(VI)	350	0.40–1.50	10	0.0041	0.68 ± 0.06
Cr(V)	510	0.50–1.00	0	0.50	0.96 ± 0.05
Cr(V)	510	0.50–1.00	20	0.0038	1.06 ± 0.06
Cr(IV)	510	0.25–1.00	20	0.010	1.92 ± 0.12

[a] [Cr] = 1.00 mM in all cases; $\mu = 0.50$ M ($HClO_4 + NaClO_4 + CF_3SO_3H$). [b] Solution buffered with 2-ethyl-2-hydroxybutanoic acid and its salt.

Trapping experiments to detect Cr(II) were carried out under argon in systems using excess Ti(II) along with Cr(VI) or Cr(IV) in deficiency. The trapping reagent was $[Co(NH_3)_5Br]^{2+}$, which reacts very rapidly with Cr^{2+} ($k = 1.4 \times 10^6$ $M^{-1}s^{-1}$ at 25 °C).[14] The resulting solutions were diluted tenfold with conc. HCl. No selective absorbance was observed near 692 nm (λ_{max} for $[CoCl_4]^{2-}$) in these solutions.

Kinetic studies. Reactions were carried out under argon. Rates were obtained from measurements of absorbance decreases associated with the oxidants using a Durrum–Gibson stopped-flow spectrophotometer connected with an OLIS computer system or using a Shimadzu 1601 UV-vis spectrophotometer. Reagent concentrations were most often adjusted so that no more than 10% of the reagent in excess was consumed during a single run (pseudo-first order conditions). Temperatures were maintained at 22.0 ± 0.5 °C during all experiments.

Results

Stoichiometric experiments (Table 1) with Cr^{VI}, Cr^{V}, and Cr^{IV} in excess indicate very nearly complete conversion to Cr(III) from all three oxidants (eqn (1–3)):

$$2Cr^{VI} + 3Ti^{II} \rightarrow 2Cr^{III} + 3Ti^{IV} \quad (1)$$

$$Cr^{V} + Ti^{II} \rightarrow Cr^{III} + Ti^{IV} \quad (2)$$

$$2Cr^{IV} + Ti^{II} \rightarrow 2Cr^{III} + Ti^{IV} \quad (3)$$

Kinetic runs with Ti(II) in excess were carried out in the presence of the chelator 2-ethyl-2-hydroxybutanoate, which is known to stabilize solutions of both Cr(V) and Cr(IV).[15] Data on reduction of Cr(IV) (Table S1†) generate a monomial expression, rate = $k[Ti^{II}][Cr^{IV}]$, with $k = (5.5 \pm 0.1) \times 10^5$ $M^{-1}s^{-1}$ at 22 °C and $\mu = 0.50$ M; (there is no significant $[H^+]$-dependence). Note that this value falls appreciably below the earlier estimated[16] lower limit, 7×10^6 $M^{-1}s^{-1}$, for the Ti(III)–Cr(IV) reaction in a similar medium.

The Ti(II)–Cr(V) reaction ($k = (5.1 \pm 0.4) \times 10^4$ $M^{-1}s^{-1}$, Table S2†) likewise exhibits no Ti(IV) catalysis, nor is it affected by variations in the concentration of the ligating anion.

Our trapping experiments with $[Co(NH_3)_5Br]^{2+}$ detect no participation of Cr(II). We may then conclude that the Cr^{IV}–Ti^{II} reaction proceeds by a single electron step leading to Cr^{III}, which is known to be inert to Ti^{II}. However, two possibilities remain for the Cr^{V}–Ti^{II} system. We may be dealing with a pair of single electron steps ($Cr^{V} \rightarrow Cr^{IV} \rightarrow Cr^{III}$), with the loss of Cr^{IV} much more rapid than reduction of Cr^{V}, (hence kinetically silent). Alternatively, a two-unit transaction may be operating, and this would presumably utilize an inner-sphere path involving an oxo bridge (Cr^{V}–O–Ti^{II}) since the Franck–Condon barrier to outer-sphere $2e^-$ transfers is generally taken to be prohibitively high.[17]

The Cr(VI)–Ti(II) reaction, when carried out in 2-ethyl-2-hydroxybutanoate buffer, generates biphasic profiles, a rapid rise in absorbance, followed by a more gradual decrease (Fig. 1). Maximal absorbance generally occurs within the first 100 ms after mixing. With Ti(II) in excess, curves were analyzed by treating the system as consecutive pseudo-first order processes (eqn 4),

$$Cr(VI) \xrightarrow{Ti^{II},k_1} Cr(V) \xrightarrow{Ti^{II},k_2} Cr(III) \quad (4)$$

then using the method of Bose[18] to evaluate the contributing rate constants (k_1 and k_2). One of these arises from the growth of an intermediate species, the other from its loss. Neither of these involves Cr(IV), which is shown to be reduced much more rapidly ($k = 5.5 \times 10^5$ $M^{-1}s^{-1}$) than is either component, but the calculated k_2 values fall near the Cr(V)–Ti(II) rates determined independently (Table S2†). We then may assign the k_1 component to the conversion of Cr(VI) to Cr(V).

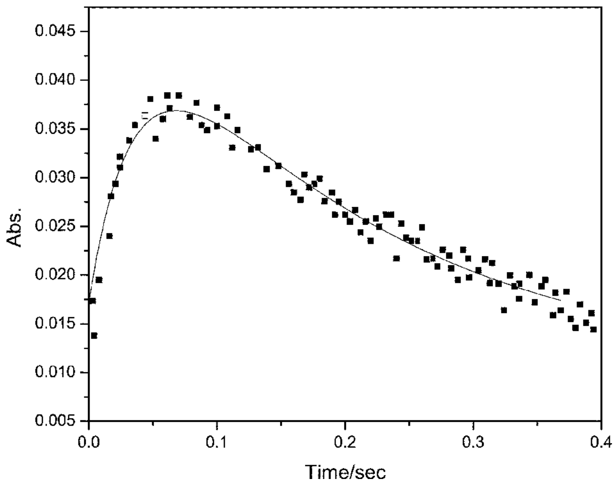

Fig. 1 Kinetic profile for the reaction of Cr^{VI} with Ti^{II}_{aq}. Reaction carried out at 22.0 °C, monitored at 510 nm. $[Cr^{VI}] = 5.0 \times 10^{-5}$ M; $[Ti^{II}] = 5.0 \times 10^{-4}$ M; $\mu = 0.50$ M ($NaClO_4/Lig^-$); pH 3.08; [HLig] + [NaLig] = 0.285 M. Small squares denote experimental data; the solid line was calculated using the procedure of Bose (ref. 18*a*), taking contributing rate constants as 28 and 6.2 s^{-1}.

Note that the Cr(VI)–Ti(II) reaction, if carried out at higher acidities in the absence of chelating ligands (Table S3†) generates single-component exponential curves. Under these conditions, the overall rate is determined by the initiation step, and destruction of intervening states, which are no longer stabilized, become kinetically silent. Our experiments do not indicate whether such initiation is a $1e^-$ or a $2e^-$ act (or a combination of both).

Of the reactions in this series, only the reduction of Cr(VI) to stabilized Cr(V) exhibits catalysis by Ti(IV). Catalyst dependence exhibits kinetic saturation (eqn (5))

$$(k)_{obsd} = k_{cat} K \frac{[Ti^{II}][Ti^{IV}]}{1 + K[Ti^{IV}]} \quad (5)$$

Table 2 Reductions of hypervalent chromium with Ti(II) and Ti(III). Rate laws and kinetic parameters

Oxidant	λ/nm	Rate laws	Parameters
A. Reductions with Ti(II)			
Cr(VI)[a]	350	$[Cr^{IV}][Ti^{II}](k_o + k_H[H^+])$	$k_o = (2.3 \pm 0.1) \times 10^3$ $M^{-1}s^{-1}$, $k_H = (18.0 \pm 0.1) \times 10^3$ $M^{-2}s^{-1}$
Cr(VI)[b]	510	$k_{cat}K\left[Cr^{VI}\right]\frac{\left[Ti^{II}\right]\left[Ti^{IV}\right]}{1+K\left[Ti^{IV}\right]}$	$k_{cat} = (15.8 \pm 0.7) \times 10^4$ $M^{-1}s^{-1}$, $K = (1.8 \pm 0.1) \times 10^2$ M^{-1}
Cr(V)[b,c]	510	$k[Cr^V][Ti^{II}]$	$k = (5.9 \pm 0.2) \times 10^4$ $M^{-1}s^{-1}$
Cr(V)[b]	510	$k[Cr^V][Ti^{II}]$	$k = (5.1 \pm 0.4) \times 10^4$ $M^{-1}s^{-1}$
Cr(IV)[b]	510	$k[Cr^{IV}][Ti^{II}]$	$k = (5.6 \pm 0.1) \times 10^5$ $M^{-1}s^{-1}$
B. Reductions with Ti(III)			
Cr(VI)[a]	350	$k[Cr^{IV}][Ti^{III}]$	$k = (4.1 \pm 0.1) \times 10^3$ $M^{-1}s^{-1}$
Cr(VI)[b]	510	$k[Cr^{VI}][Ti^{III}]$	$k = (1.02 \pm 0.03) \times 10^3$ $M^{-1}s^{-1}$
Cr(V)[b,d]	510	$[Cr^V][Ti^{III}](k_o + k_2$ [HLig]$)$[f]	$k_o = 1.2\times 10^4$ M^{-1} s^{-1}, $k_2 = 3.2 \times 10^5$ M^{-2} s^{-1}
Cr(IV)[e]	510	$k[Cr^{IV}][Ti^{III}]$	$k = (1.3 \pm 0.1) \times 10^5$ M^{-1} s^{-1}

[a] $[H^+] = 0.05–0.50$ M ($HClO_4/CF_3SO_3H$), $\mu = 0.50$ M; no chelating ligand added. [b] pH = 3.08; [HLig] + [NaLig] = 0.28 M. [c] Lower portion of Cr(VI)–Ti(II) decay curve. [d] Ref. 16. [e] pH = 3.50; [HLig] + [NaLig] = 0.01 M; $\mu = 0.10$ M. [f] HLig = 2-ethyl-2-hydroxybutanoic acid.

with $k_{cat} = (16 \pm 1) \times 10^4$ $M^{-2}s^{-1}$, and $K = (1.8 \pm 0.1) \times 10^2$ M^{-1}. Note that the Ti(IV) association constant is substantially different from the analogous value (4×10^2) derived for the Ti(IV)-catalyzed Ti(II)–quinone reactions,[19] which were carried out in strongly acid solutions in the absence of the chelating agent. In the case at hand chelation of the Ti(IV) center would not be unexpected.

Discussion

The most notable feature of this study is the absence of evidence of $2e^-$ paths for Ti(II) reductions of both Cr(VI) and Cr(IV). Attempted trapping experiments, using $[Co(NH_3)_5Br]^{2+}$, have ruled out significant intervention of Cr(II) in these systems. A similar conclusion applied to the reduction of Cr(V) is not possible from our experiments but must be considered very unlikely in view of the earlier demonstrated $1e^-$ paths for its reactions with bisulfite,[20] ascorbate,[21] and nitrite.[22]

The most straightforward (and least informative) exponential profiles are obtained for the Cr(VI)–Ti(II) reaction in the absence of chelating ligands which stabilize Cr(IV) and Cr(V). The two-term rate law, (eqn (6)), points to competing protonated (k_H) and deprotonated (k_o) paths,

$$\text{rate} = [Ti^{II}][Cr^{VI}](k_o + k_H[H^+]) \qquad (6)$$

and is in accord with a sequence in which rates are determined by the initial steps. These precede rapid (kinetically silent) acts leading to Cr(III). The site of protonation may be taken to be a Cr(VI)-bound oxo function, as has been proposed for other oxidations by Cr(VI).[23]

When this reaction is carried out in solution buffered by the chelating ligand, 2-ethyl-2-hydroxybutanoate, both the generation of chelated Cr(V) and its consumption may be observed. Rates for its loss agree with those independently measured using the pre-purified Cr(V) chelate (Table S2†). The transformation of Cr(V) to Cr(III) (Table 1) may be taken to proceed *via* two steps ($Cr^V \rightarrow Cr^{IV} \rightarrow Cr^{III}$) with the overall rate determined by the Cr(V)–Cr(IV) conversion. The $Cr^{IV} \rightarrow Cr^{III}$ step, as demonstrated using independently prepared Cr(IV), is the more rapid (5.5×10^5 $M^{-1}s^{-1}$).

Rate laws and kinetic parameters appear in Table 2, which also lists, for comparison, data for the corresponding reductions by Ti(III). Catalysis by Ti(IV), which is here detected only for the Cr(VI)–Ti(II) reaction in the presence of stabilizing chelators, has been reported for Ti(II) reductions of quinones[19] and substitution-inert metal center oxidants.[1] Arguments have been presented that such enhancement is significant only for single electron outer-sphere processes and that catalysis becomes negligible when a rapid bridged route is available.[19] This distinction suggests, but does not establish, a non-bridged path for Ti(II) reduction of hexavalent chromium.

Despite the minor differences in rate laws, the overall picture noted earlier[24] is applicable here as well; rate constants pertaining to reductions by Ti(II) and by Ti(III) are remarkably similar.

This similarity may be considered in conjunction with a recent report[11] that Ti(III) solutions undergo rapid and quantitative disproportionation to Ti(II) and Ti(IV) when treated with concentrated HF (eqn (7)):

$$2\,Ti^{III} \xrightarrow{HF} Ti^{II} + Ti^{IV} \qquad (7)$$

The transformation (eqn (7)) reflects, in part, the conversion of Ti(IV) to its very stable hexafluoro complex ($K_f = 10^{11}$),[25] corresponding to a drop of 0.66 V in potential for $Ti^{III,IV}$ (for which $E°$ is listed as 0.10 V).[26] If the reaction (eqn (7)) is assumed to proceed with an equilibrium constant greater than 10^2, corresponding to a net positive potential ≥ 0.12 V, a lower limit for $Ti^{II,III}$ may be estimated as –0.4 V, which is consistent with the value –0.37 V reported[27] over eighty years ago.

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