

Reductions of oxo species by aquatitanium(II) as catalyzed by titanium(IV)†‡

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Titanium(II) solutions, prepared by dissolving titanium wire in triflic acid + HF, contain equimolar quantities of Ti(IV). These preparations react readily with oxidizing species such as VO_2^+ , substituted benzoquinones, and the biguanide complex of Mn(IV). Reactions with excess Ti(II) yield Ti(III). Reductions of 1,4-benzoquinones and the Mn(IV) complex are catalyzed by added Ti(IV) but stoichiometry is unaffected. Rate laws for the Ti(IV)-catalyzed reactions are consistent with formation of a $\text{Ti}^{\text{II}}\text{--Ti}^{\text{IV}}$ complex ($K_{\text{formation}} 4 \times 10^2 \text{ M}^{-1}$), which, in some cases, also partakes in contributing deprotonated and halogen-catalyzed paths.

Introduction

In 2003, Kolle and Kolle reported the preparation of solutions of aquatitanium(II) in $\text{HF--CF}_3\text{SO}_3\text{H}$, stabilized by equimolar concentrations of Ti(IV).² Such solutions may be handled under nitrogen or argon without unusual difficulty and may be kept unchanged for 12 h at room temperature, in contrast to more sensitive preparations described earlier by Forbes and Hall³ and Olver and Ross.⁴

Preliminary examinations^{5,6} of the oxidations of these Ti(II) solutions with metal centers revealed two unexpected facets: (A) Reductions by such Ti(II) preparations are sluggish (despite the highly negative formal potential of this state),^{3,4} sometimes lagging well behind those by Ti(III); and (B) some, but not all, of such reductions are markedly catalyzed by Ti(IV). The present study, which deals mainly with oxo-species, pursues these points.

Experimental

Materials

Solutions were prepared from Millipore-Q-system deionized water that had been boiled for 2 h and then purged with argon for a further 2 h to remove dissolved oxygen. 1,4-Benzoquinone and substituted quinones (Aldrich products) were used as received, as were ammonium vanadate (NH_4VO_3) and triflic acid ($\text{CF}_3\text{SO}_3\text{H}$). Thorium nitrate ($\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$, Baker) and sodium perrhenate (NaReO_4 , Alfa) were used as received. Potassium nitrosodisulfonate dimer (Fremy's salt) was prepared as orange microcrystals as described by Yamada and Tsuchida⁷ and kept at -18°C . The water-stable manganese(IV) complex of biguanide, $[\text{Mn}(\text{bigH})_3]_2\text{SO}_4(\text{NO}_3)_6 \cdot 3\text{H}_2\text{O}$, was prepared by the procedure of Banerjee *et al.*⁸

Titanium(II) solutions (0.10 M in 2.0 M triflic acid) were prepared under argon by the method of Kolle.² These green solutions were kept in sealed containers and used within 10 h of preparation. The Ti(II) concentration was determined by adding

a known volume to a solution of excess $[\text{Co}(\text{NH}_3)_5\text{F}](\text{ClO}_4)_2$ under argon, waiting 20 min, diluting tenfold with conc. HCl, and determining $[\text{CoCl}_4]^{2-}$ at 692 nm ($\epsilon = 560 \text{ M}^{-1}\text{cm}^{-1}$). Ti(IV) solutions were prepared by air oxidation of Ti(II) solutions; after the oxidation to Ti(IV) was complete (indicated by the loss of color), Ar was passed through the solution for 2 h to remove all dissolved oxygen. Sodium triflate, $\text{CF}_3\text{SO}_3\text{Na}$, was prepared as described by Saha and Stanbury.¹⁰

Zirconium(IV)–triflic acid solutions were prepared by stirring 1.77 g $\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ in 25 ml of 1.0 M HClO_4 and heating to 50°C . Barium triflate (4.4 g in water) was added and stirred for 15 min. The precipitated BaSO_4 was then removed by centrifugation, and the clear filtrate was used in kinetic studies.

Stoichiometric studies

Stoichiometric determinations were carried out under argon, 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 oxidant consumed was calculated from the decrease in absorbance. For the very slow reactions, stoichiometries could not be determined precisely in this manner since a portion of the added reductant was consumed by adventitious traces of air.

Kinetic studies

Reactions were performed under argon and were monitored at λ_{max} associated with the oxidant, using either a Shimadzu 1601 UV-visible spectrophotometer or a Durrum–Gibson stopped-flow spectrophotometer interfaced with an OLIS computer system. Temperatures were kept at $22.0 \pm 0.3^\circ\text{C}$. Ionic strength was generally maintained with $\text{HClO}_4\text{--NaClO}_4$ or $\text{CF}_3\text{SO}_3\text{H--CF}_3\text{SO}_3\text{Na}$. Reactions were most often carried out under pseudo-first order conditions with Ti(II) present in greater than tenfold excess and yielded exponential decay curves.

Results

Stoichiometric experiments (Table 1) with oxidants in excess indicate consumption of very nearly equimolar quantities of VO_2^+ , Mn(IV), and the quinones, but a 2 : 1 mole ratio for the 1-equivalent

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† Electron transfer. Part 164.¹

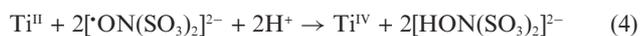
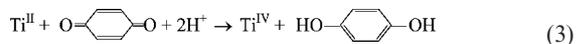
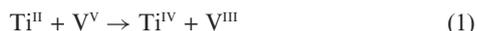
‡ Electronic supplementary information (ESI) available: Detailed kinetic data for redox reactions (Tables S1–S6). See DOI: 10.1039/b616438b

Table 1 Reductions of oxo species by Ti(II). Stoichiometries^a

Oxidant	λ/nm	[ox]/mM	[Ti ^{II}]/mM	[Ti ^{IV}]/mM	$\Delta[\text{ox}]/\Delta[\text{Ti(II)}]$
1,4-Benzoquinone	260	0.05	0.005–0.025	0.005–0.025	1.00 ± 0.09
Chloranilic acid ^b	315	0.05	0.005–0.025	0.005–0.13	0.91 ± 0.04^c
[VO ₂] ⁺	330	1.0	0.20–0.80	0.20–4.5	0.96 ± 0.03
[Mn ^{IV} (bigH) ₃] ⁴⁺	433	0.20	0.03–0.08	0.03–0.18	0.90 ± 0.05
[[•] ON(SO ₃) ₂] ²⁻	540 ^c	12.0	2.0–5.0	2.0–8.5	1.98 ± 0.04

^a [H⁺] = 0.50 M (HClO₄); μ = 0.50 M unless otherwise noted. ^b 2,5-Dichloro-3,6-dihydroxy-1,4-benzoquinone. ^c Reactions in acetic acid/acetate buffer, pH 4.7.

oxidant, nitrosodisulfonate [[•]ON(SO₃)₂]²⁻, which is included for comparison:



Kinetic profiles carried out with Ti(II) in excess exhibit no irregularities pointing to intervention of an intermediate formed or destroyed on a time scale comparable to that of the principal conversion.

Although each of the oxo species reacts readily with Ti(II), kinetic responses to changes in medium are varied. 1,2-Naphthoquinone (alone among the quinones) and vanadium(V) (VO₂⁺) obey straightforward second order rate laws,

$$\begin{aligned} \text{Rate} &= k[\text{Ti}^{\text{II}}][\text{ox}] & k_{1,2\text{-NO}} &= (2.4 \pm 0.1) \times 10^2 \text{ M}^{-1} \text{ s}^{-1} \\ & & k_{\text{V(V)}} &= (9.6 \pm 0.1) \times 10^3 \text{ M}^{-1} \text{ s}^{-1} \end{aligned} \quad (5)$$

whereas the remaining oxidants are subject to marked catalysis by added Ti(IV). Kinetic data for these catalyzed reactions (Tables S1–S6 of the ESI†) lead to rate laws and parameters summarized in Table 2.

Each of the 1,4-quinones exhibits a [Ti^{IV}]-dependence which includes a quotient of type (6) (kinetic saturation), consistent with

Table 2 Catalyzed reductions by titanium(II): rate laws and kinetic parameters^a

Oxidant	Rate laws	Parameters
1,4-Benzoquinone	$k_o = \frac{kK[\text{Ti}^{\text{II}}][\text{Ti}^{\text{IV}}]}{1 + K[\text{Ti}^{\text{IV}}]}$	$k = (1.06 \pm 0.04) \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ $K = (4.1 \pm 0.3) \times 10^2 \text{ M}^{-1}$
Tetrahydroxy-1,4-benzoquinone	$k_o = \frac{kK[\text{Ti}^{\text{II}}][\text{Ti}^{\text{IV}}]}{1 + K[\text{Ti}^{\text{IV}}]}$	$k = 70 \pm 1 \text{ M}^{-1} \text{ s}^{-1}$ $K = (4.0 \pm 0.4) \times 10^2 \text{ M}^{-1}$
2,5-Dichloro-3,6-dihydroxybenzoquinone	$k_o = \left(k_1 + k_2[\text{H}^+]^{-1}\right) \frac{K[\text{Ti}^{\text{II}}][\text{Ti}^{\text{IV}}]}{1 + K[\text{Ti}^{\text{IV}}]}$	$k_1 = (8.8 \pm 0.3) \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$, $k_2 = 35 \pm 4 \text{ s}^{-1}$, $K = (3.7 \pm 0.3) \times 10^2 \text{ M}^{-1}$
2,5-Dihydroxy-1,4-benzoquinone	$k_o = \left(k_1 + k_2[\text{H}^+]^{-1}\right) \frac{K[\text{Ti}^{\text{II}}][\text{Ti}^{\text{IV}}]}{1 + K[\text{Ti}^{\text{IV}}]}$	$k_1 = (4.6 \pm 0.2) \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$, $k_2 = 58 \pm 6 \text{ s}^{-1}$, $K = (3.5 \pm 0.3) \times 10^2 \text{ M}^{-1}$
1,2-Naphthoquinone Nitrosodisulfonate ^b [VO ₂] ⁺ [Mn ^{IV} (bigH) ₃] ⁴⁺	$k_o = k[\text{Ti}^{\text{II}}]$ $k_o = k[\text{Ti}^{\text{II}}][\text{Ti}^{\text{IV}}]$ $k_o = k[\text{Ti}^{\text{II}}]$ $k_o = \left(k_1 + k_2[\text{Hal}^-]^{-1}\right) \frac{K[\text{Ti}^{\text{II}}][\text{Ti}^{\text{IV}}]}{1 + K[\text{Ti}^{\text{IV}}]}$	$k = (2.4 \pm 0.01) \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$ $k = (3.0 \pm 0.1) \times 10^5 \text{ M}^{-2} \text{ s}^{-1}$ $k = (9.6 \pm 0.1) \times 10^3 \text{ M}^{-2} \text{ s}^{-1}$ $k_1 = (1.09 \pm 0.02) \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$, $K = (3.5 \pm 0.3) \times 10^2 \text{ M}^{-1}$ $k_2 = (5.0 \pm 0.3) \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ (Hal ⁻ = F ⁻), $(1.00 \pm 0.13) \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ (Hal ⁻ = Cl ⁻)

^a Reactions at 22.0 ± 0.5 °C; μ = 0.5 M (HClO₄–NaClO₄–CF₃SO₃H). ^b Reactions in LiCl–HCl–CF₃SO₃H.

formation of a complex of Ti(IV) (association constant K) and a limiting specific rate, k .

$$\frac{kK[\text{Ti}^{\text{IV}}]}{1+K[\text{Ti}^{\text{IV}}]} \quad (6)$$

The reductions of benzoquinone and its tetrahydroxy derivative proceed by a single path of this type, whereas rate laws for the two dihydroxyquinones contain terms reflecting the operation of competing protonated (k_1) and deprotonated ($k_2/[\text{H}^+]$) paths. Reduction of the manganese(IV) complex is subject to additional catalysis by added chloride and fluoride.

With the nitrosodisulfonate radical anion, $[\text{ON}(\text{SO}_3)_2]^{2-}$, (the sole $1e^-$ oxidant included), Ti(IV) catalysis operates, but kinetic saturation is no longer evident.

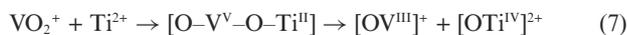
Kinetic runs carried out with $\text{Al}(\text{ClO}_4)_3$, $\text{ZrO}(\text{triflate})_2$, NaReO_4 or $\text{Th}(\text{NO}_3)_4$ added (rather than Ti^{IV}), showed no significant catalytic action.

Discussion

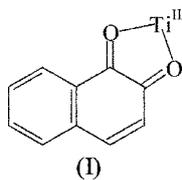
Rate laws for five of the oxidants in Table 2 feature proportionalities to quotient (6), pointing, in each case, to the intervention of a Ti(IV) complex. Refinements of data pertaining to all five lead to virtually the same formation constant ($K = 4 \times 10^2 \text{ M}^{-1}$) for this adduct, indicating that we are dealing with the same complex in each system, *i.e.*, that Ti(IV) has become attached to the Ti(II) center rather than to each of the various oxidants. The persistence of quotient (6) in the rate laws for the two dihydroxyquinones suggests that the active Ti(II)–Ti(IV) species attacks both the uncharged quinone and its deprotonated form, whereas its appearance in both the halide-free and halide-proportional terms in the Mn(IV) reduction indicates that it is involved in both the chloride- and fluoride-catalyzed components, as well as in the halide-free path.

The simpler (monomial) rate law for reduction of the nitrosodisulfonate anion suggest that Ti(IV) operates principally in a different manner here, probably by ion-pairing with the negatively charged periphery of the substrate. Some interaction with Ti(II) may be occurring as well, but it is overshadowed by coulombic effects.

Two of the oxidants in this study are consumed without catalysis by Ti(IV). The very rapid reduction of VO_2^+ may reflect, at least in part, the high formal potential (+1.00 V) of this oxidant and, in addition, the possibility that reaction may occur *via* oxo transfer:



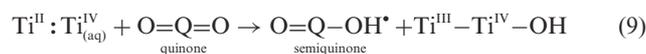
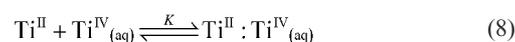
The 1,2-dicarbonyl function of 1,2-naphthoquinone allows a two-sided approach to the Ti(II) coreagent (I), and the combined action of the two electron-withdrawing sites may disfavor attachment of the Ti(IV) center.



As pointed out by Yang *et al.*,⁶ the catalytic action of Ti(IV) in these reactions cannot be attributed to a preliminary comproportionation ($\text{Ti}^{\text{II}} + \text{Ti}^{\text{IV}} \rightarrow 2 \text{Ti}^{\text{III}}$), yielding a more reactive Ti(III) donor, since our Ti(II) solutions are not perceptibly changed when treated with Ti(IV) in excess. For an alternate rationalization, recall that Ti(II) must be regarded as a singularly sluggish reagent when its strongly negative potential is considered.⁵ Both octahedral cations, $\text{Ti}(\text{H}_2\text{O})_6^{2+}$ ($3d^2$) and $\text{Ti}(\text{H}_2\text{O})_6^{3+}$ ($3d^1$), are expected to show minor Jahn–Teller distortions and the occupancy of the non-degenerate orbitals may not match, thus retarding self-exchange for the hexaaqua Ti(II,III) system. The loss of symmetry when the Ti(II) octahedra is converted to $\text{Ti}^{\text{II}}-\text{Ti}^{\text{IV}}$ may minimize structural differences between the Ti(IV)-bound states, thus lowering the barrier to the redox process.

The mechanistic picture applying to these systems is complicated by the capacity of our oxidants and reductant to undergo both one- and two-electron changes. Beyond that, if single-electron paths are preferred, are outer-sphere or bridged paths utilized?¹¹ Aside from the $\text{VO}_2^+ + \text{Ti}(\text{II})$ reaction, for which we favor an oxo-transfer path (7), the pervasiveness of Ti(IV)-catalysis suggests initiation by single-electron transfer from Ti(II). Since we find no spectral evidence for the accumulation of an odd-electron intermediate in any of our quinone reactions, we infer that further reduction of the semiquinone transient must be rapid and hence kinetically silent.

Our proposed sequence for the catalyzed reactions is eqn (8)–(10):



For those systems exhibiting an inverse- $[\text{H}^+]$ term in the rate law, this sequence is supplemented by an analogous route probably featuring Ti(IV) in its deprotonated form, whereas the Mn(IV) reductions may be presumed to utilize paths involving halo complexes.

Does the suggested electron-transfer step, (9), require preliminary formation of a Ti(II)–oxo bridge? We think not. Such a bridge should be favored by 2-hydroxy substituents in positions allowing chelation at the reducing center, which would then be expected to enhance reaction rates significantly. However, the several 2-hydroxy-substituted oxidants (Table 2) exhibit rate constants very similar to that for 1,4-benzoquinone itself which offers no chelation paths. The evidence at hand therefore indicates that the rate-determining steps in the catalyzed conversions are $1e^-$ outer-sphere acts.

One point remains. If, as we believe, the catalytic action of Ti(IV) stems mainly from its strongly electrophilic character, why are not analogous catalyses observed with such centers as Al(III), Zr(IV), Re(VII) and Th(IV)? Resolution of this puzzling question probably awaits more complete characterization of such positive metal-center species in concentrated triflate media.

Acknowledgements

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- 11 Note that outer-sphere routes for 2e transfers are generally taken to be prohibitively slow, reflecting exceptionally high Franck–Condon barriers. See, for example: G. Lippin, *Redox Mechanisms in Inorganic Chemistry*, Ellis Harwood, New York, 1994, ch. 5.