

Hypovalent titanium and Ti(II)–Ti(III) interconversions†‡

Basab Bijayi Dhar* and Edwin S. Gould*

Received 24th July 2009, Accepted 6th November 2009

First published as an Advance Article on the web 14th December 2009

DOI: 10.1039/b914989a

Treatment of pink titanium(III) triflate (0.045 M) with HF in triflic acid (CH₃SO₃H) converts Ti(III) rapidly to a 1 : 1 mixture of Ti^{IV} and green Ti^{II}: (2 Ti^{III} + 4 HF → TiF₄ + Ti^{II} + 4 H⁺). This disproportionation is half complete when [HF] added is 0.027 M. Substituted 1,4-benzoquinones are reduced rapidly by Ti(III) in the absence of fluoride, yielding straightforward logarithmic curves, but reactions of the same quinones with Ti(II) in fluoride media exhibit more complex profiles, the major portions of which are zero order in oxidant. These reactions are strongly catalyzed by added Ti(IV). Analyses of complex curves are consistent with a reaction sequence initiated by Ti(II)–Ti(IV) disproportionation, forming Ti(III), which reacts with the quinone, yielding the quinhydrone, QH[•]. The latter is rapidly reduced by Ti(II). Values of rate constants obtained from these analyses are in agreement with those for reductions of quinones by Ti(III), in the absence of fluoride.

Introduction

For over 160 years after the discovery of titanium in 1791, the chemistry of that element was concerned mainly with the metal itself and its 3+ and 4+ states. The report, in 1955,² of titanium-based Ziegler catalysts for the polymerization of alkenes triggered a remarkable growth of low-valent titanium chemistry, and an impressive array of organotitanium compounds have been reported during the intervening half century,³ many of these derived from the dipositive state. In addition, titanium(II) cyclopentadienyls and alkoxides have exhibited versatility in organic conversions.⁴

Nevertheless, relatively little attention has been devoted to the “parent” Ti(II) entity, the aquatitanium(II) cation, Ti²⁺(aq). Reports by Forbes and Hall⁵ and Olver and Ross⁶ indicated that this cation readily reduces aqueous solutions to H₂ at low pH, thus complicating study using conventional methods of handling. Among the 3d-block dipositive ions, Ti(II) is undoubtedly the most elusive.

However, facile preparations of this state in HF-triflic acid mixtures were reported in 2003 by Kolle and Kolle,⁷ and Yang has noted that 0.1 M Ti(II) solutions so generated survive for 12 h at room temperature under argon.⁸

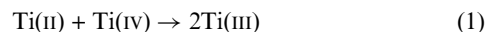
Titanium(II) solutions prepared in this manner contain equivalent concentrations of Ti(IV) and a HF/Ti(II) ratio approximately 6 : 1. Although such preparations are strongly acidic, it is likely that Ti(IV) is present in part as TiF₆²⁻ and/or TiF₅⁻. Conversion of Ti(II) (a d² cation) to a fluoro complex is slight.⁹ Yang's solutions absorb preferentially at 430 and 660 nm, but extinction coefficients (6.0 and 3.5 M⁻¹ cm⁻¹) are greater than those reported by Kolle and Kolle.⁷

Dipositive titanium presents features which are seldom observed among the other elements. The occurrence of two adjacent oxidation states exhibiting similar reducing reactivities (similar patterns of rate constants) despite substantial differences in formal

potentials is rare and stands in contrast to other cation pairs such as V(II)/V(III) (with the lower state much more active) and s-centers such as In(I)/In(II) (with the higher state much more reactive).¹⁰

An unusually wide variety of catalyses has been reported for reductions by Ti(II). Reductions of iron(III) and ruthenium(III) complexes are accelerated by halide, with the effects of added fluoride much more marked than those by the heavier halides.¹¹ Dramatic catalysis by added Ti(IV) has been reported for reductions of quinones,¹² and Ti(II) reductions of triiodide and pentapositive vanadium are accelerated by added molybdic acid.¹³

Ti(II) is of particular interest because it can be induced to undergo oxidations at rates independent of oxidant. This unusual kinetic picture, first observed with very reactive Co(III) oxidants,¹⁴ implies the slow generation of an activated reducing species. We here present evidence that this behavior reflects the initial formation of Ti(III) by comproportionation (1):



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 removed traces of dissolved O₂. Titanium(II) solutions (ca 0.10 M in reductant in 2.0 M triflic acid) were prepared under argon by a modification of the method of Kolle and Kolle.^{7,8} Those 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 [Co(NH₃)₅F](ClO₄)₂ under argon, waiting 20 min, diluting ten-fold with con HCl, and determining [CoCl₄]²⁻ at 692 nm (ε = 560 M⁻¹ cm⁻¹). Titanium(III) chloride (10% in 25% HCl) (Aldrich) was used as received. Titanium(IV) solutions were prepared by air oxidation of Ti(II) solutions; after oxidation to Ti(IV) was complete (total loss of color), argon was passed through the solution for 2 h to remove dissolved O₂. Sodium triflate was prepared by the method of Stanbury.¹⁵ Solutions of Ti(III) free

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

† Electron transfer part 168. For part 167, see ref. 1.

‡ Electronic supplementary information (ESI) available: Detailed kinetic data for redox reactions (Tables S1–S3). See DOI: 10.1039/b914989a

from Cl^- in 1 M triflic acid were prepared by a modification of the method of Martin.¹⁶

Spectroscopic studies

Spectral studies with Ti^{II} and Ti^{III} solutions were carried out under argon using a Shimadzu 1601 UV-visible spectrophotometer. The single λ_{max} for Ti^{III} in 0.5 M triflic acid is at 502 nm, whereas Ti^{II} exhibits peaks at 540 and 650 nm. When treated with a five-fold excess of fluoride in 0.5 M triflic acid, Ti^{III} is converted rapidly and very nearly completely to a 1 : 1 mixture of Ti^{II} and Ti^{IV} .

Kinetic studies

Reactions were run under argon. Rates of reduction of quinones were obtained from absorbance decreases at λ_{max} values of the oxidant, using a Durrum-Gibson stopped-flow spectrophotometer. Concentrations of reagents were generally adjusted so that no more than 10% of the reagent in excess was consumed in a single run. Temperatures were maintained at 22.0 ± 0.5 °C during all experiments. All reductions by Ti^{III} exhibited straightforward exponential decay curves which yielded pseudo-first order rate constants proportional to the concentrations of excess reductant. Reductions by excess Ti^{II} , on the other hand, gave more complex patterns (e.g. Fig. 3) from which several contributing rate constants could be obtained by computerized procedures.

Results and discussion

Ti^{III} – Ti^{II} interconversions

Treatment of pink Ti^{III} solutions in 0.5 M triflic acid with successive portions of HF results in fading of the peak at 500 nm and the growth of peaks at 430 and 650 nm typifying Ti^{II} .^{7,8} Isosbestic points appear at 490 and 600 nm (Fig. 1). The reaction is a disproportionation which is favored by the strong affinity of fluoride for tetrapositive titanium.¹⁷

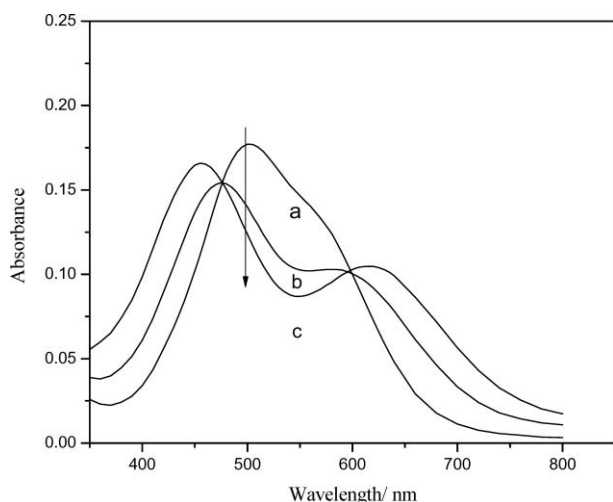
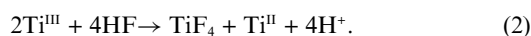


Fig. 1 Conversion of 0.045 M Ti^{III} to Ti^{II} + Ti^{IV} in 0.50 M $\text{CF}_3\text{SO}_3\text{H}$ by addition of HF. Curve a—no HF; curve b—0.0375 M HF; curve c—0.0675 M HF. Vertical line denotes the change in absorbance at 500 nm as HF is added.

For the system at hand, a simplified equilibrium quotient (3) applies since $[\text{H}^+]$ is kept at 0.50 M

$$K_{3,2} = \frac{[\text{Ti}^{\text{II}}]^2}{[\text{Ti}^{\text{III}}]^2[\text{HF}]^4} \quad (3)$$

and $[\text{Ti}^{\text{II}}] = [\text{Ti}^{\text{IV}}]$.

Ti^{IV} does not contribute to visible absorbance. Hence, the absorbance of these solutions reflects only the two lower states:

$$\text{Abs} = [\text{Ti}^{\text{III}}]\epsilon_3 + [\text{Ti}^{\text{II}}]\epsilon_2 \quad (4)$$

Treatment of absorbances at different $[\text{HF}]$ values, in conjunction with the summation relationship (4), generates (Appendix) a series of simultaneous equations, one for each portion of added HF. Least squares refinement of data at 500 nm yields

$$\epsilon_3 = 4.1 \text{ M}^{-1} \text{ cm}^{-1}, \quad \epsilon_2 = 4.5 \text{ M}^{-1} \text{ cm}^{-1} \quad \text{and} \quad K_{3,2} = (2.4 \pm 0.2) \times 10^5 \text{ M}^{-4}$$

Calculated and observed absorbances are compared in Fig. 2 and Table S-1.† Alternate treatments using 3 HF and 5 HF in (2) gave much poorer fittings. Analogous treatment of absorbance data, at 430 and 650 nm, yields $K_{3,2}$ values of $(2.3 \pm 0.1) \times 10^5$ and $(2.3 \pm 0.2) \times 10^5 \text{ M}^{-4}$.

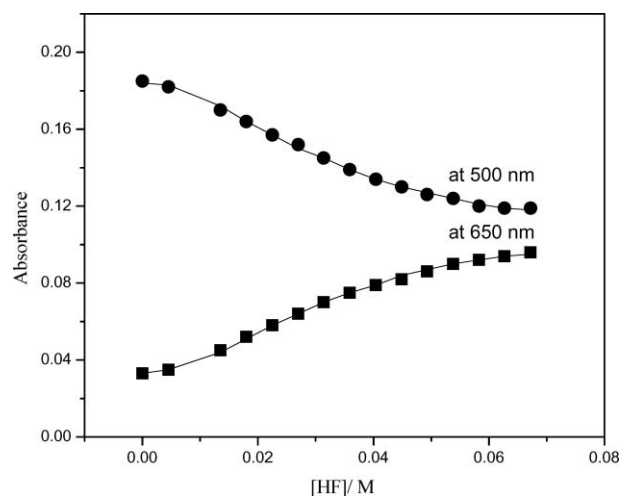


Fig. 2 Observed and calculated absorbance changes at 500 and 650 nm as HF is added to Ti^{III} . Solid lines were obtained from eqn (4) in text and eqn (g) in Appendix. Extinction coefficients (in $\text{M}^{-1} \text{ cm}^{-1}$) for Ti^{III} (ϵ_3) and Ti^{II} (ϵ_2) are tabulated below. Reaction quotient $K_{3,2}$ (eqn (3) in text) is taken as $2.4 \times 10^5 \text{ M}^{-4}$

	500 nm	650 nm
ϵ_3	4.10	0.74
ϵ_2	4.50	4.9

Reduction of quinones

An earlier study⁸ showed that reductions of 1,4-benzoquinone in aqueous acid, both by Ti^{II} and Ti^{III} , yield the corresponding hydroquinones (1,4-dihydroxybenzenes). It is reasonable to suspect that action by both reductants is initiated by single electron

Table 1 Titanium(III) reductions of 1,4-benzoquinones. Kinetic parameters^{a,b}

$k_{\text{obs}} = k_o + k_{-1}/[\text{H}^+]$		
Quinone	$k_o, \text{M}^{-1}\text{s}^{-1}$	k_{-1}, s^{-1}
1,4-Benzoquinone	$(1.07 \pm 0.01) \times 10^2$	23 ± 1
Chloranilic acid ^c		$(7.0 \pm 0.1) \times 10^3$
Tetrahydroxy-1,4-benzoquinone		$(1.0 \pm 0.1) \times 10^2$

^a Reactions at 22.0 ± 0.5 °C. Acidity was maintained using triflic acid, $\mu = 0.5 \text{ M}$ ($\text{CF}_3\text{SO}_3\text{H} + \text{CF}_3\text{SO}_3\text{Na}$). ^b Parameters were obtained by refinement of data in Table S-3. ^c 2,5-Dichloro-3,6-dihydroxy-1,4-benzoquinone.

steps, but distortion of decay curves reflecting semiquinone intervention is not generally observed, indicating that reduction of this intermediate is rapid in this medium and, hence, kinetically silent.

Reductions by Ti(III) are retarded by boosts in acidity (Table S-3).[‡] The observed dependency for the benzoquinone reduction follows rate-law (5), whereas with the ring-substituted quinones, the acid-independent component, k_o , is negligible (Table 1).

$$k_{\text{obs}} = (k_o + k_{-1}/[\text{H}^+])[\text{Ti}^{\text{III}}] \quad (5)$$

The inverse-acid dependence, $k_{-1}/[\text{H}^+]$, often appears in Ti(III) reductions in aqueous media^{16,18} and is commonly attributed to participation of the conjugate base, $[\text{Ti}^{\text{III}}(\text{OH})]^{2+}$.

Kinetic profiles for the reductions of these quinones by Ti(II) are much more complex than the exponential patterns obtained with Ti(III). As shown in Fig. 3, which is typical, a major portion of the curve is linear, during which the rate of reaction is nearly independent of the concentration of the quinone. The slope of this section is nearly proportional to the concentration of Ti(II) taken, and also to the concentration of Ti(IV) present. In addition, slight acceleration occurs during the first few percent of reaction, and

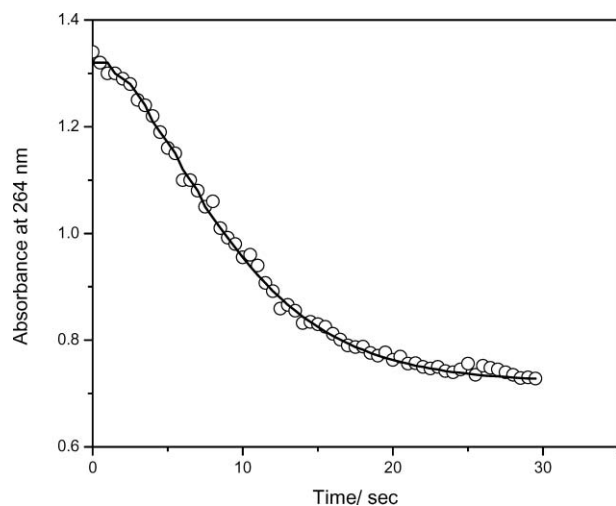
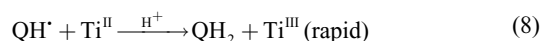
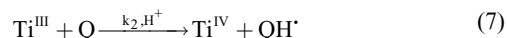
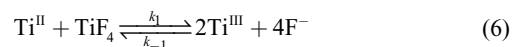


Fig. 3 Kinetic profile at 246 nm for reaction of 1,4-benzoquinone with Ti(II) in 0.50 M $\text{CF}_3\text{SO}_3\text{H}$. $[\text{Ti}^{\text{II}}] = 1.0 \text{ mM}$; $[\text{HF}] = 0.25 \text{ mM}$, $[\text{quinone}] = 0.05 \text{ mM}$. Circles represent the experimental data, whereas the solid line was obtained by KINSIM simulation (ref. 19) of the proposed mechanism (6)–(8), taking k_1 as $120 \text{ M}^{-1} \text{ s}^{-1}$, k_{-1} as $5.0 \text{ M}^{-1} \text{ s}^{-1}$, and k_2 as $150 \text{ M}^{-1} \text{ s}^{-1}$. $[\text{Ti}^{\text{IV}}] = 1.00 \text{ mM}$; molar absorptances (ϵ values) were $2.60 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ for this oxidant and $1.40 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ for the product. Path length = 1.00 cm .

curvature becomes important during the final stages as the oxidant becomes nearly consumed.

The striking kinetic behavior, in conjunction with the recognized ease of the Ti(II)/Ti(III) interconversion in fluoride-containing media, points strongly to sequence (6)–(8) for the Ti(II)-quinone reactions.



Incorporation of sequence (6)–(8) into a variant of the KINSIM treatment¹⁹ yielded calculated absorbance curves which were compared with the observed kinetic profiles. Kinetic parameters giving optimal agreement with the run pictured in Fig. 3 are $k_1 = 1.2 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$, $k_{-1} = 5.0 \text{ M}^{-1} \text{ s}^{-1}$, and $k_2 = 150 \text{ M}^{-1} \text{ s}^{-1}$. Parallel treatments of runs at different acidities indicate that k_1 and k_{-1} do not vary significantly with $[\text{H}^+]$, whereas k_2 falls from 150 to $90 \text{ M}^{-1} \text{ s}^{-1}$ between 0.250 mM and 7.5 mM HF. Note that the value of k_2 is in reasonable agreement with the second order rate constant ($0.15/0.0010 = 150 \text{ M}^{-1} \text{ s}^{-1}$) obtained by direct kinetic measurement of the Ti(III)-quinone system (Table S-2).[‡]

Kinetic parameters contributing to the Ti(II) reductions of several quinones under similar conditions are summarized in Table 2. As expected, values of k_1 and k_{-1} are independent of the oxidant, which is waiting to enter the picture. A conditional equilibrium quotient for the comproportionation²⁰ step may be estimated as $k_1/k_{-1} = 110/5.0 = 22$. The modest value of this

Table 2 Titanium(II) reductions of 1,4-benzoquinones. Kinetic parameters^a

$\text{Ti}^{\text{II}} + \text{Ti}^{\text{IV}} \xrightleftharpoons[k_{-1}]{k_1} 2\text{Ti}^{\text{III}}$				
$\text{Ti}^{\text{III}} + \text{Q} \xrightarrow{k_2, \text{H}^+} \text{Ti}^{\text{IV}} + \text{QH}^*$				
Quinone	[HF], mM	k_1^b	k_{-1}^b	k_2^b
Chloranilic acid ^c	0.25	110	5.0	2300
	2.5	115	5.0	1400
	5.0	105	3.9	640
	7.5	105	5.0	360
	7.5	110	5.0	370 ^e
	7.5	120	5.0	380 ^d
1,4-Benzoquinone	0.25	120	5.0	150
	2.5	104	4.0	120
	5.0	110	5.0	95
	7.5	106	4.4	90
Tetrahydroxy-1,4-benzoquinone	0.25	100	5.0	280
	2.5	104	5.0	200
	5.0	110	5.0	180
	7.5	106	4.4	180

^a Component rate constants (22 °C) obtained by KINSIM treatment (ref. 19) of kinetic data for Ti(II) reductions of benzoquinones in 0.50 M $\text{CF}_3\text{SO}_3\text{H}$ in the presence of 2.0 mM Ti(IV) and added HF. $[\text{Ox}] = 0.01 \text{ mM}$; $[\text{Ti}^{\text{II}}] = 1.0 \text{ mM}$ unless otherwise indicated. ^b Second order rate constants giving optimal fit of calculated and observed kinetic curves. ^c $[\text{Ti}^{\text{II}}] = 0.25 \text{ mM}$. ^d $[\text{Ti}^{\text{II}}] = 0.50 \text{ mM}$. ^e 2,5-Dichloro-3,6-dihydroxybenzoquinone.

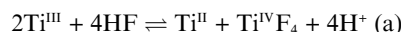
quotient reminds us that in fluoride-rich media the effective oxidation potentials of Ti(II) and Ti(III) approach each other and that this trend arises not from complexation of Ti(II), but rather from ligation of Ti(IV), the product from Ti(III).

Rates for the Ti^{III}-quinone step (k_2) are seen to diminish perceptibly with increases of (HF), presumably due to the partial loss of the more active reducing species, [Ti^{III}OH]²⁺ (eqn (5)).

In short, at high concentrations of HF, direct electron transfer from Ti(II) to quinone is so slow that virtually all loss of oxidant is triggered instead by reaction with Ti(III). We suspect that the sluggish action of Ti(II), may reflect, at least in part, an unusually low Ti(II,III) self-exchange rate. Both Ti^{II} (3d²) and Ti^{III} (3d¹) should be 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) need not match. The two states may have quite different geometries, and this mismatch would be expected to result in a higher Franck–Condon barrier to exchange.²¹ Beyond this, there is the possibility of reversible donor–acceptor interaction between the d² center and the highly conjugated quinone molecule, yielding a complex which geometrically disfavors internal electron transfer. Such intervention need not persist when we are dealing with Ti^{III} (a d¹ center), or with a less markedly conjugated semiquinone (QH[•]) transient.

Appendix

Treatment of absorbance data for Ti(II), Ti(III), Ti(IV) systems



$$[\text{Ti}^{\text{III}}] + [\text{Ti}^{\text{II}}] + [\text{Ti}^{\text{IV}}] = [\text{Ti}]_{\text{tot}} \quad (\text{b})$$

In these systems, [Ti^{II}] = [Ti^{IV}]; hence [Ti^{III}] + 2[Ti^{II}] = [Ti]_{tot} (c)

For our measurements [H⁺] is very nearly constant (0.50 M

$$\text{CF}_3\text{SO}_3\text{H}) K_{3,2} = \frac{[\text{Ti}(\text{II})]^2}{[\text{Ti}(\text{III})]^2[\text{HF}]^4}, \quad (\text{d})$$

$$\text{Whence } [\text{Ti}^{\text{II}}] = (K_{3,2})^{1/2}[\text{Ti}^{\text{III}}][\text{HF}]^2 \quad (\text{e})$$

Substituting (e) into (c):

$$[\text{Ti}^{\text{III}}] + 2(K_{3,2})^{1/2}[\text{Ti}^{\text{III}}][\text{HF}]^2 = [\text{Ti}]_{\text{tot}} \quad (\text{f})$$

$$\text{Solving for } [\text{Ti}^{\text{III}}], [\text{Ti}^{\text{III}}] = \frac{[\text{Ti}]_{\text{tot}}}{1+2(K_{3,2})^{1/2}[\text{HF}]^2} \quad (\text{g})$$

$$\text{OD} = \varepsilon_3[\text{Ti}^{\text{III}}] + \varepsilon_2[\text{Ti}^{\text{II}}] \quad (\text{Beer's law}) \quad (\text{h})$$

$$\frac{\varepsilon_3[\text{Ti}]_{\text{tot}}}{1+2(K_{3,2})^{1/2}[\text{HF}]^2} + \frac{\varepsilon_2(K_{3,2})^{1/2}[\text{HF}]^2[\text{Ti}]_{\text{tot}}}{1+2(K_{3,2})^{1/2}[\text{HF}]^2} \quad (\text{i})$$

$$\text{OD} = \frac{(\varepsilon_3 + \varepsilon_2(K_{3,2})^{1/2}[\text{HF}]^2)[\text{Ti}]_{\text{tot}}}{1+2(K_{3,2})^{1/2}[\text{HF}]^2} \quad (\text{j})$$

Acknowledgements

We are grateful to Dr Yuriy Tolmachev, Dr Paul Sampson, and Mr Robert Hoover for helpful discussions and to Mrs Arla Dee McPherson for technical assistance.

References

- 1 Part 167.B. B. Dhar, R. Mukherjee and E. S. Gould, *Dalton Trans.*, 2009, 868.
- 2 K. Ziegler, E. Holzkamp, H. Breil and H. Martin, *Angew. Chem.*, 1955, **67**, 541.
- 3 (a) Reviews: E. A. Mints, in *Encyclopedia of Inorganic Chemistry*, R. B. King, ed. Vol. 8, Wiley, New York, 1994, 4206–4224.; (b) S. B. Smith and D. W. Stephan, in *Comprehensive Coordination Chemistry*, J. A. McCleverty and T. J. Meyer, Ed., v. 4, Elsevier, Amsterdam, 2004, Chapt. 4.2.
- 4 Reviews: F. Sato and H. Urabe, *Titanium and Zirconium in Organic Synthesis*, I. Marek, ed., Wiley, New York, 2002, pp. 281–329.
- 5 G. S. Forbes and L. P. Hall, *J. Am. Chem. Soc.*, 1924, **46**, 385.
- 6 J. W. Olver and J. W. Ross, Jr., *J. Am. Chem. Soc.*, 1963, **85**, 2565.
- 7 U. Kolle and P. Kolle, *Angew. Chem., Int. Ed.*, 2003, **42**, 4540.
- 8 Z. Yang and E. S. Gould, *Dalton Trans.*, 2005, 1781.
- 9 R. M. Smith and A. E. Martell, *Critical Stability Constants*, v. 4, Plenum, New York, 1971, p. 99.
- 10 S. K. Chandra and E. S. Gould, *Inorg. Chem.*, 1996, **35**, 3381.
- 11 R. Mukherjee, V. Mannivanan and E. S. Gould, *Inorg. Chim. Acta*, 2007, **360**, 3633.
- 12 B. B. Dhar and E. S. Gould, *Dalton Trans.*, 2007, 1416.
- 13 Z. Yang and E. S. Gould, *Dalton Trans.*, 2006, 396.
- 14 R. Mukherjee, Z. Yang and E. S. Gould, *Dalton Trans.*, 2006, 772.
- 15 B. Saha and D. Stanbury, *Inorg. Chem.*, 2000, **39**, 1294.
- 16 A. H. Martin and E. S. Gould, *Inorg. Chem.*, 1975, **14**, 873.
- 17 L. Ciavatta and A. Pirozzi, *Polyhedron*, 1983, **2**, 769.
- 18 J. P. Birk, *Inorg. Chem.*, 1975, **14**, 1724.
- 19 B. A. Barshop, R. F. Wrenn and C. Frieden, *Anal. Biochem.*, 1983, **130**, 134.
- 20 This quotient differs from $K_{3,2}$ derived from spectral studies under a much wider range of (HF) and (F⁻). During the kinetic runs treated with KINSIM, these parameters are held nearly constant.
- 21 Note that an unusually low self-exchange rate has been calculated for the analogous d¹, d² pair, [V^{IV}O(H₂O)₄]²⁺, [V^{III}(OH)₂(H₂O)₃]⁺. See: M. C. Ghosh and E. S. Gould, *J. Am. Chem. Soc.*, 1993, **115**, 3167.