Kinetic Studies on the Vanadium(II)–Titanium(IV) and Titanium(III)–Vanadium(IV) Redox Reactions in Aqueous Solutions

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The one-equivalent reduction of titanium(IV) by vanadium(II) ions has been studied at temperatures in the range 20—40 °C by the stopped-flow method and shown to be independent of hydrogen-ion concentration $[H^+] = 0{\cdot}35$—$1{\cdot}85$M, $I = 2{\cdot}0$M ($LiClO_4$). The rate law is as in (i). At 25 °C, $k_{24} = 1{\cdot}95$ l mol^{-1} s^{-1} and activation parameters,

$$-d[V^{II}]/dt = d[Ti^{III}]/dt = k_{24}[V^{II}][Ti^{IV}] \quad \text{(i)}$$

$\Delta H^\ddagger = 12{\cdot}7 \pm 0{\cdot}4$ kcal mol^{-1} and $\Delta S^\ddagger = -14{\cdot}6 \pm 1{\cdot}3$ cal K^{-1} mol^{-1}, are consistent with a process which is vanadium(II)-substitution controlled. The one-equivalent reduction of vanadium(IV) by titanium(III) ions has also been studied by the stopped-flow method at temperatures 15—45 °C. Since titanium(III) stock solutions were made up in aqueous HCl, it was necessary to investigate the effect of chloride ions on the rate of the reaction. Data obtained at ionic strength $I = 0{\cdot}5$M ($LiClO_4$) fit the rate law (ii), where, at 25 °C, $k_a = 0{\cdot}34$ l mol^{-1} s^{-1},

$$-d[V^{IV}]/dt = k_{34}[Ti^{III}][V^{IV}] = (k_a + k_b[H^+]^{-1} + k_c[Cl^-])[Ti^{III}][V^{IV}] \quad \text{(ii)}$$

$k_b = 0{\cdot}037$ s^{-1}, and $k_c = 0{\cdot}72$ l^2 mol^{-2} s^{-1}. Activation parameters for all the three paths in equation (ii) have been determined.

FEW redox reactions involving the titanium(III)–titanium(IV) couple have been investigated. This is partly because it is not known with certainty whether titanium(IV) is present in solution as the $Ti(OH)_2^{2+}$

(ref. 1) or the TiO^{2+} (ref. 2) aquo-ion and because, at low hydrogen-ion concentrations $[H^+] < 0{\cdot}1M$, polymerization is known to occur.[3] At $[H^+] < 0{\cdot}1M$, it has been suggested that there is an equilibrium between titanium(IV) species of charge 1+ and 2+.[1] Furthermore hexa-aquotitanium(III) ion is known to be oxidized by perchlorate ions.[4] Despite these difficulties titanium(III) reductions of plutonium(IV),[5] plutonium(VI),[6] mercury(II),[7] iron(III),[7,8] iodine,[9] and some penta-amminecobalt(III) complexes [10] have been studied. As yet no kinetic study has been reported on redox reactions between titanium and vanadium metal ions. Standard reduction potentials for the relevant couples are summarized in Table 1. From these it is concluded that the one-equivalent reactions (1)—(3) are thermodynamically

TABLE 1

Standard reduction potentials [a] for titanium and vanadium ions in acidic solution

Reaction	Potential [b,c] / V
$TiO^{2+} + 2H^+ + e^- \longrightarrow Ti^{3+} + H_2O$ [c]	+0·1
$V^{3+} + e^- \longrightarrow V^{2+}$	−0·26
$VO^{2+} + 2H^+ + e^- \longrightarrow V^{3+} + H_2O$	+0·36
$VO_2^+ + 2H^+ + e^- \longrightarrow VO^{2+} + H_2O$	+1·00

[a] Taken from W. M. Latimer, 'Oxidation Potentials,' 2nd edn., Prentice–Hall, Inc. New York, 1952. [b] The sign is the same as the potential of the actual electrode (I.U.P.A.C. convention). [c] Titanium(IV) may be present as the ion $Ti(OH)_2^{2+}$ and not TiO^{2+} (ref. 1).

$$V^{II} + Ti^{IV} \longrightarrow V^{III} + Ti^{III} \qquad (1)$$

$$Ti^{III} + V^{IV} \longrightarrow Ti^{IV} + V^{III} \qquad (2)$$

$$Ti^{III} + V^{V} \longrightarrow Ti^{IV} + V^{IV} \qquad (3)$$

favourable. The kinetics of all three reactions have now been studied by the stopped-flow technique and details of (1) and (2) are reported in this paper. The reaction of titanium(III) with vanadium(V) ions will be reported elsewhere.[11]

RESULTS

Titanium(IV) *Solutions*.—Solutions of titanium(IV) perchlorate in perchloric acid do not absorb significantly in the visible region (ε *ca.* 0·6 at 350 nm, $<0{\cdot}6$ l mol^{-1} cm^{-1} throughout the visible region). The u.v. spectrum 200—350 nm (ε 104 at 250 and 24·9 l mol^{-1} cm^{-1} at 300 nm) is not affected by variations in hydrogen-ion concentration from 0·1 to 2·0M and spectra of such solutions with $[Ti^{IV}] = 10^{-3}M$ showed no change over 7 days at 25 °C. However with solutions of $[H^+] = 0{\cdot}02M$ the absorbance increased slowly and after 2 days a fine precipitate was observed. Stock solutions, *ca.* 0·05M in titanium(IV) and 2·0M in $HClO_4$, were frozen and stored at *ca.* −5 °C. No changes in their spectra were observed over 6 weeks. Ion-exchange experiments were consistent with the presence of monomeric 2+ ions [and not higher polymeric titanium(IV) ions] in solutions where $[H^+] > 0{\cdot}1M$. The position of the equilibrium in either (4) or (5), whichever is applicable, is uncertain. It

$$TiO^{2+} + H_2O \rightleftharpoons TiO(OH)^+ + H^+ \qquad (4)$$

$$Ti(OH)_2^{2+} + H_2O \rightleftharpoons Ti(OH)_3^+ + H^+ \qquad (5)$$

has been suggested that, at $[H^+] = 0{\cdot}1M$, the equilibrium is predominantly to the left-hand side.[2] However other evidence has suggested that significant amounts of the 1+ ion are present at this $[H^+]$.[1]

Titanium(III) *Solutions*.—Titanium(III) ions react with perchlorate ions, (6), with a half-life of *ca.* 2 h at 25 °C in

$$8Ti^{III} + ClO_4^- + 8H^+ \longrightarrow 8Ti^{IV} + Cl^- + 4H_2O \qquad (6)$$

1·0M-perchloric acid.[4] This presents considerable difficulties in the preparation and storage of titanium(III) perchlorate solutions and stock solutions in aqueous hydrochloric acid were therefore used. Typical concentrations were $[Ti^{III}] = 0{\cdot}15$ and $[Cl^-] = 1{\cdot}0M$. Solutions of vanadium(IV) in aqueous perchloric acid were used and the chloride-ion concentration of the mixed reactant solutions was varied so that rate constants at $[Cl^-] = 0$ could be obtained. To minimize possible mixing effects in the stopped-flow, the ionic strength was limited to $I = 0{\cdot}5M$.

The Vanadium(II) *Reduction of Titanium*(IV).—The formation of titanium(III) was monitored at 485 nm (ε 3·62 l mol^{-1} cm^{-1}), a vanadium(II)–vanadium(III) isosbestic point (ε 1·50 l mol^{-1} cm^{-1}). The vanadium(II) was in most cases present in an eight-fold excess over titanium(IV). Absorbance (OD) changes were obtained from oscilloscope traces and first-order plots of log $(OD_\infty - OD_t)$ against time were linear to *ca.* 80% completion. Second-order rate constants, k_{24}, were evaluated assuming the rate law (7) to apply.

$$d[Ti^{III}]/dt = k_{24}[V^{II}][Ti^{IV}] \qquad (7)$$

Additional runs under second-order conditions, with the titanium(IV) reactant present in a two-fold excess over vanadium(II), gave k_{24} values in good agreement with those above (Table 2), thus confirming the form of (7). It was also possible to monitor the decrease in concentration of vanadium(II) at 850 nm (ε 3·22 l mol^{-1} cm^{-1}), when k_{24} values were again in satisfactory agreement. The linearity of these plots was to 75—80% completion.

All spectrophotometric measurements were consistent with a 1 : 1 stoicheiometry as in equation (1). There was no observable dependence of k_{24} on hydrogen-ion concentration over the range 0·35—1·85M. Activation parameters, $\Delta H^{\ddagger}_{24} = 12{\cdot}7 \pm 0{\cdot}4$ kcal mol^{-1} and $\Delta S^{\ddagger}_{24} = -14{\cdot}6 \pm 1{\cdot}3$ cal K^{-1} mol^{-1}, were computed from runs obtained under pseudo-first-order conditions using a least-squares program; each data point was given equal weight-

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TABLE 2

Second-order rate constants, k_{24}, for the vanadium(II) reduction of titanium(IV) ions. $I = 2{\cdot}0$M (LiClO$_4$) and $\lambda = 485$ nm

Temp. / °C	[H$^+$] / M	10^2[V^{II}] / M	10^3[Ti^{IV}] / M	k_{24} / l mol^{-1} s^{-1}
20	0·35	2·45	3·09	1·23
	0·85	2·58	3·09	1·22
	1·35	2·59	3·09	1·25
	1·84	2·58	3·09	1·25
25	1·0	2·41	3·11	1·99
	1·45	2·47	3·11	1·80
	1·85	2·45	3·11	2·07
	1·40	0·674	14·0	2·11
	1·40	0·651	14·0	2·19
	1·40	0·634	14·0	2·44
	1·40	0·494	14·0	1·90 [a]
	1·40	0·530	14·0	1·79 [a]
30	0·55	2·59	3·09	2·77
	1·20	2·45	3·09	2·57
	1·85	2·45	3·09	2·88
35	0·55	2·46	3·09	3·81
	1·20	2·48	3·09	3·85
	1·85	2·66	3·09	4·23
40	0·55	2·46	3·09	5·08
	1·20	2·48	3·09	5·75
	1·85	2·56	3·09	5·55

[a] $\lambda = 800$ nm.

ing. From this treatment values of k_{24}/l mol^{-1} s^{-1} are: 1·31 (20), 1·95 (25), 2·83 (30), 4·03 (35), and 5·71 (40 °C). The variation of k_{24} with ionic strength was also investigated briefly (Table 3).

TABLE 3

Variation of second-order rate constants (25 °C) with ionic strength (LiClO$_4$) for the vanadium(II) reduction of titanium(IV) ions. [H$^+$] = 0·35M, [V^{II}] = 0·025M, [Ti^{IV}] = 0·0031M, and $\lambda = 485$ nm

I / M	k_{24} / l mol^{-1} s^{-1}
0·5	0·876
1·0	1·18
1·5	1·45
2·0	1·95

On mixing 10^{-3}—10^{-2}M solutions of titanium(IV) and vanadium(III) ions at [H$^+$] = 0·1—2·0M, [Cl$^-$] = 0—1·5M, and $I = 2{\cdot}0$M (LiClO$_4$), spectra in the 300—850 nm region were additive and there was no evidence for any association of the two metal ions.

The Titanium(III) *Reduction of Vanadium*(IV).—Spectrophotometric changes were consistent with a 1 : 1 reaction as in equation (2). The reaction was followed at 760 nm where vanadium(IV) (ε 17·2 l mol^{-1} cm^{-1}) is the only absorbing species. Titanium(III) was generally in a ten-fold excess over vanadium(IV), and first-order plots were linear

$$-\mathrm{d}[\mathrm{V^{IV}}]/\mathrm{d}t = k_{34}[\mathrm{Ti^{III}}][\mathrm{V^{IV}}] \qquad (8)$$

to 80—90% completion. Second-order rate constants, k_{34} as defined in (8), were evaluated and were in satisfactory agreement for six-fold variations in the metal-ion concentrations (Table 4). Adjustment of the ionic strength to $I = 0{\cdot}5$M with LiClO$_4$ or NaClO$_4$ gave no observable difference in the rate constants. The reaction shows a linear dependence on chloride-ion (Figure 1) and inverse hydrogen-ion concentrations (Figure 2). For [Cl$^-$] = 0·10–0·43M and [H$^+$] = 0·075—0·40M, the results (Table 4) gave a good fit to equation (9).

$$k_{34} = k_a + k_b[\mathrm{H^+}]^{-1} + k_c[\mathrm{Cl^-}] \qquad (9)$$

TABLE 4

Second-order rate constants, k_{34}, for the titanium(III) reduction of vanadium(IV) ions. $I = 0{\cdot}5$M (LiClO$_4$)

Temp / °C	[H$^+$] / M	[Cl$^-$] / M	10^2[Ti^{III}] / M	10^3[V^{IV}] / M	k_{34} / l mol^{-1} s^{-1}
15	0·072	0·10	1·43	1·43	0·396
		0·21	1·43	1·43	0·426
		0·32	1·43	1·43	0·442
		0·43	1·43	1 43	0·491
	0·121	0·10	1·43	1·43	0·318
		0·21	1·43	1·43	0·347
		0·32	1·43	1·43	0·380
		0·43	1·43	1·43	0·427
	0·40	0·10	1·43	1·43	0·266
		0·21	1·43	1·43	0·297
		0·32	1·43	1·43	0·329
		0·43	1·43	1·43	0·360
25	0·072	0·10	1·73	1·73	0·928
		0·21	1·73	1·73	1·05
		0·32	1·73	1·73	1·14
		0·43	1·73	1·73	1·18
	0·09	0·10	1·46	1·50	0·814
		0·10	1·46	1·50	0·828 [a]
		0·21	1·46	1·50	0·917
		0·21	1·46	1·50	0·909 [a]
		0·32	1·46	1·50	0·990
		0·32	1·46	1·50	1·02 [a]
		0·43	1·46	1·50	1·10
	0·121	0·10	1·73	1·73	0·725
		0·21	1·73	1·73	0·812
		0·21	1·40	1·35	0·808 [b]
		0·21	1·40	1·35	0·768 [b]
		0·26	4·70	4·70	0·812
		0·26	4·70	2·74	0·804
		0·26	4·70	0·78	0·836
		0·26	2·74	0·78	0·851
		0·26	0·78	0·78	0·855
		0·32	1·73	1·73	0·905
		0·43	1·73	1·73	0·976
	0·186	0·10	1·73	1·73	0·624
		0·21	1·73	1·73	0·705
		0·32	1·73	1·73	0·769
		0·43	1·73	1·73	0·886
	0·40	0·10	1·56	1·59	0·531
		0·21	1·56	1·59	0·585
		0·32	1·56	1·59	0·686
		0·43	1·56	1·59	0·741
35	0·072	0·10	1·49	1·49	2·25
		0·21	1·49	1·49	2·45
		0·32	1·49	1·49	2·47
		0·43	1·49	1·49	2·81
	0·121	0·10	1·49	1·49	1·58
		0·21	1·49	1·49	1·79
		0·32	1·49	1·49	1·89
		0·43	1·49	1·49	2·15
	0·40	0·10	1·49	1·49	1·00
		0·21	1·49	1·49	1·15
		0·32	1·49	1·49	1·30
		0·43	1·49	1·49	1·53
45	0·072	0·10	1·49	1·49	5·51
		0·21	1·49	1·49	5·63
		0·32	1·49	1·49	6·36
		0·43	1·49	1·49	6·80
	0·121	0·10	1·49	1·49	3·70
		0·21	1·49	1·49	4·07
		0·32	1·49	1·49	4·19
		0·43	1·49	1·49	4·91
	0·40	0·10	1·49	1·49	1·94
		0·21	1·49	1·49	2·24
		0·32	1·49	1·49	2·52
		0·43	1·49	1·49	3·03

[a] Ionic strength adjusted with NaClO$_4$. [b] [Fe^{II}] = 1·5 × 10^{-3}M.

Assuming that the acid dissociation constant for water is in the range $K_W = 10^{-14}$—$10^{-13\cdot7}$ mol^2 l^{-2} (in a variety of media $I = 0 \longrightarrow 3{\cdot}0\text{M}$),[12] data obtained by Pecsok and Fletcher [13] give acid dissociation constants for Ti^{3+} in the range $12{\cdot}6 \times 10^{-3}$—$6 \times 10^{-3}$ mol l^{-1} at 25 °C and $I = 0{\cdot}5\text{M}$. However, Paris and Gregoire [14] report a value $K_a = 2{\cdot}8 \times 10^{-3}$ mol l^{-1} at 25 °C and $I = 3{\cdot}0\text{M}$ (KBr), while Krentzien and Brio [15] find $K_a = 1{\cdot}68 \times 10^{-3}$ mol l^{-1} at 25 °C and $I = 3\text{M}$ (KCl), in good agreement with values reported for V^{3+}.[16] A decrease in ionic strength $I = 3{\cdot}0 \longrightarrow 0{\cdot}5\text{M}$ is not expected to increase K_a by more than a factor of two. Hexa-aquotitanium(III) ion is therefore more extensively hydrolysed than is VO^{2+} (K_a *ca.* 10^{-6} mol l^{-1}).[17] The data obtained here do not appear to require inclusion of a term in $(1 + K_a[H^+]^{-1})$, which is consistent with $K_a = ca.\ 2 \times 10^{-3}$ mol l^{-1} at 25 °C as determined by Paris and Gregoire [14] and Krentzien and Brio.[15] The temperature dependence of K_a is uncertain and it seems inappropriate to make any corrections for the term $(1 + K_a[H^+]^{-1})$, which in any case (at 25 °C) has <4% effect on k_{34}. From the experimental k_{34} values, activation parameters were obtained using a non-linear least-squares program [18] with a weighting factor of $1/k_{34}^2$. The rate constants k_a, k_b, and k_c and their corresponding activation parameters are listed in Table 5.

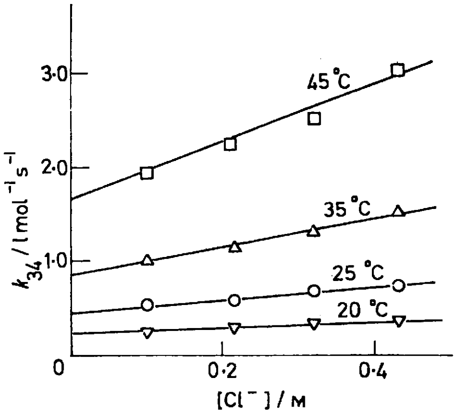

FIGURE 1 Dependence of rate constants, k_{34}, on chloride-ion concentration for the titanium(III) reduction of vanadium(IV) ions at $[H^+] = 0{\cdot}4\text{M}$ and $I = 0{\cdot}5\text{M}$ ($LiClO_4$)

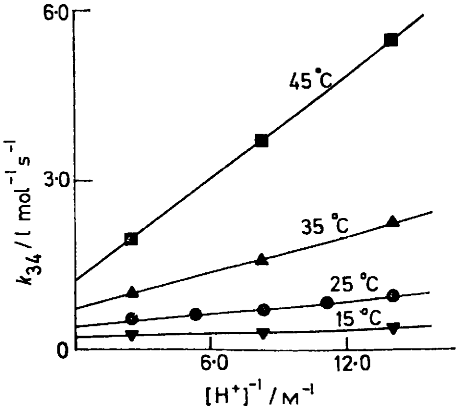

FIGURE 2 Dependence of rate constants, k_{34}, on hydrogen-ion concentration for the titanium(III) reduction of vanadium(IV) ions at $[Cl^-] = 0{\cdot}1\text{M}$ and $I = 0{\cdot}5\text{M}$ ($LiClO_4$)

TABLE 5

Summary of kinetic data for reactions between titanium and vanadium metal ions in aqueous solution

Reaction		Rate constant [a]	$\Delta H^\ddagger$ / kcal mol^{-1}	$\Delta S^\ddagger$ / cal K^{-1} mol^{-1}
$V^{II} + Ti^{IV}$	(k_{24}) [b]	$1{\cdot}95 \pm 0{\cdot}04$ l mol^{-1} s^{-1}	$12{\cdot}7 \pm 0{\cdot}4$	$-14{\cdot}6 \pm 1{\cdot}3$
$Ti^{III} + V^{IV}$	(k_a) [c]	$0{\cdot}34 \pm 0{\cdot}01$ l mol^{-1} s^{-1}	$8{\cdot}7 \pm 0{\cdot}4$	$-31{\cdot}6 \pm 1{\cdot}3$
	(k_b) [c]	$0{\cdot}037 \pm 0{\cdot}002$ s^{-1}	$19{\cdot}1 \pm 0{\cdot}3$	$-0{\cdot}9 \pm 0{\cdot}8$
	(k_c) [c]	$0{\cdot}72 \pm 0{\cdot}02$ l^2 mol^{-2} s^{-1}	$13{\cdot}1 \pm 0{\cdot}6$	$-15{\cdot}2 \pm 1{\cdot}9$

[a] 25 °C. [b] $I = 2{\cdot}0\text{M}$ ($LiClO_4$). [c] $I = 0{\cdot}5\text{M}$ ($LiClO_4$).

If k_b is the true rate constant for the reaction of the ions $TiOH^{2+}$ and VO^{2+} (*i.e.* $k_b = k_b'K_a$), then assuming ΔH_0 *ca.* 10 kcal mol^{-1} and ΔS_0 *ca.* 20 cal K^{-1} mol^{-1} for the formation of the ion $TiOH^{2+}$,* activation parameters for k_b' are $\Delta H^\ddagger = 9{\cdot}1$ kcal mol^{-1} and $\Delta S^\ddagger = -20{\cdot}9$ cal K^{-1} mol^{-1}.

Spectra in the region 300—850 nm were found to be additive on mixing 10^{-3}—10^{-2}M titanium(IV) and vanadium(IV) solutions at $[H^+] = 0{\cdot}1$—$2{\cdot}0\text{M}$ and $[Cl^-] = 0$—$1{\cdot}5\text{M}$.

DISCUSSION

Titanium(IV) has a strong tendency to associate with other metal ions in solution. Thus charge-transfer bands in the visible region are observed on mixing titanium(IV) with iron(II) (in aqueous HCl, H_2SO_4, and $HClO_4$) and with vanadium(IV) ions (in aqueous H_2SO_4).[19] With iron(II) ions 2 : 1 as well as 1 : 1 (Fe^{II} : Ti^{IV}) species have been identified.[20] The formation of a 1 : 1 titanium(III)–titanium(IV) adduct has also been observed in aqueous HCl [21] and H_2SO_4 [22] solutions. Possible interactions of titanium(IV) ions, which are a reactant in (1) and a product in (2), have been considered in the present studies. However, visible spectra in the region 300—850 nm were found to be additive on mixing titanium(IV) with first vanadium(III) and then vanadium(IV) ions (10^{-3}—10^{-2}M) at $[H^+] = 0{\cdot}1$—$2{\cdot}0\text{M}$, $[Cl^-] = 0$—$1{\cdot}5\text{M}$, and $I = 2{\cdot}0\text{M}$ ($LiClO_4$). Also kinetic plots for both (1) and (2) showed satisfactory linearity under a variety of conditions and there was no evidence for the formation of binuclear species.

The labilities of the various metal ions involved is relevant in considering whether the reactions proceed by an inner- or outer-sphere mechanism. From studies

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* Thermodynamic quantities ΔH_0 and ΔS_0 for the formation of $TiOH^{2+}$ have not been measured and those obtained for VOH^{2+} (S. C. Furman and C. S. Garner, *J. Amer. Chem. Soc.*, 1950, **72**, 1785) are assumed to be applicable.

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on the complexing of hexa-aquotitanium(III) with thiocyanate ions (rate constants for the outer- to inner-sphere step are *ca.* 8×10^3 s^{-1} at 25 °C)[23] and the exchange of an inner-sphere water ligand for solvent water (rate constant *ca.* 10^5 s^{-1} by n.m.r. line broadening),[24] the ion $Ti(H_2O)_6{}^{3+}$ is known to be labile, as would be expected for an ion having a d^1 electronic configuration. Whereas most substitution reactions of octahedral complexes exhibit S_N1 character, those of titanium(III) are believed to proceed by an S_N2 mechanism.[24,25] The complexing of hydrogen peroxide with titanium(IV) has been studied (*k ca.* $1{\cdot}8 \times 10^2$ l mol^{-1} s^{-1} at 25 °C, 1M-$HClO_4$, and $I = 3{\cdot}0$M),[26] and titanium(IV) also exhibits the properties of a labile metal ion. Although vanadium(II) is the most inert of the 2+ ions in the first transition series, the hexa-aquo-ion is in fact labile and at 25 °C the rate constant for water exchange is *ca.* 90 s^{-1}.[27,28] Water ligands bonded to vanadium(III) (*k ca.* 10^2 s^{-1})[23] and vanadium(IV) ions ($k = 500$ s^{-1})[29] are also labile. The oxo-ligand of vanadium(IV) is known to be inert.[29]

A comparison of kinetic data for the reactions of vanadium(II) with the ions titanium(IV) and vanadium(IV)[30] is notable for the similarities exhibited. The rate law is in both cases as in (7), with small contributions from a term first order in $[H^+]$ in the reaction of vanadium(II) with vanadium(IV) ions. Rate constants, as defined in (7), are 1·95 l mol^{-1} s^{-1} for titanium(IV) and 1·58 l mol^{-1} s^{-1} for vanadium(IV), at 25 °C and $I = 2{\cdot}0$M ($LiClO_4$); activation parameters are also very similar, $\Delta H^{\ddagger} = 12{\cdot}7$ kcal mol^{-1} and $\Delta S^{\ddagger} = -14{\cdot}6$ cal K^{-1} mol^{-1} for titanium(IV) and $\Delta H^{\ddagger} = 12{\cdot}3$ kcal mol^{-1} and $\Delta S^{\ddagger} = -16{\cdot}5$ cal K^{-1} mol^{-1} for vanadium(IV). Since vanadium(IV) is a stronger oxidant (Table 1), this suggests that the reactions proceed by a common mechanism which is vanadium(II)-substitution controlled. However only about 65% of the vanadium(II) reduction of vanadium(IV) proceeds *via* a binuclear intermediate VOV^{4+} and is demonstrably inner sphere.[30] The remainder of the reaction goes direct to final products, probably by way of an outer-sphere activated complex. It is now generally accepted that the rate-determining step for the reaction proceeding *via* VOV^{4+} is substitution into the V^{2+} co-ordination sphere, where this type of reaction generally exhibits rate constants 1—50 l mol^{-1} s^{-1} (at 25 °C) and activation parameters $\Delta H^{\ddagger} = 11$—13 kcal mol^{-1} and $\Delta S^{\ddagger} = -7$ to -17 cal K^{-1} mol^{-1}.[31] Although no binuclear intermediate was identified in the reaction of vanadium(II) with titanium(IV) ions, the kinetic data are consistent with the reaction proceeding, at least in part and possibly predominantly, by an inner-sphere mechanism which is vanadium(II)-substitution controlled. However, in common with the vanadium(II) reductions of the ions copper(II)[32] and mercury(II)[33] which also have kinetic parameters in the range required for a vanadium(II)-substitution controlled process, it is not clear why these reactions should be of this type when the oxidant is in each case sufficiently labile to form an inner-sphere activated complex by an alternative route. A possible explanation in the case of titanium(IV) is that the oxo- or hydroxo-group is functioning as the bridging ligand and that, unlike the water ligand, this group is not labile.

The similarity of the dependence of the rate constants on ionic strength for the vanadium(II) reductions of the titanium(IV) and vanadium(IV) ions is noted (Figure 3).

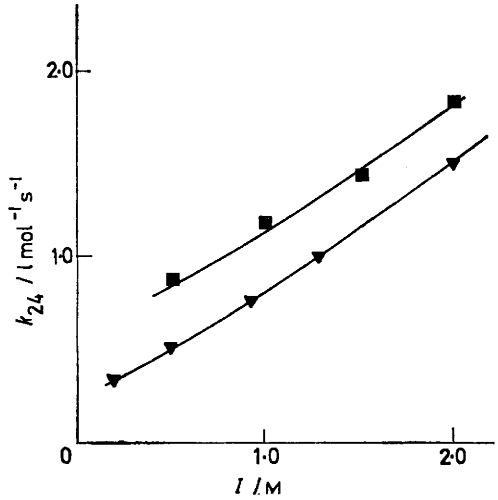

FIGURE 3 Variation of rate constants, k_{24}, with ionic strength, I ($LiClO_4$), for the vanadium(II) reduction of titanium(IV) (■) and of vanadium(IV) (▼) (data from ref. 6)

Newton and Baker[30] have observed that the variation in the case of the vanadium(II) reduction of vanadium(IV) gives a good fit to an extended form of the Debye–Hückel equation. The data in Figure 3 clearly indicate that the titanium(IV) reactant must be a 2+ species. We do not however consider this similarity in behaviour to be necessarily indicative of a structure TiO^{2+} rather than $Ti(OH)_2{}^{2+}$ for the titanium(IV) reactant.

Details of the rate laws observed for some titanium and vanadium reactions are summarized in Table 6. A comparison of dependences on hydrogen-ion concentration for different pairs of reactions (with a common oxidant or reductant) suggests that the titanium(III) ⟶ titanium(IV) conversion is less dependent on inverse hydrogen-ion dependent terms than is the vanadium(III) ⟶ vanadium(IV) conversion. Also, in the one case where a comparison is possible, the vanadium(IV) ⟶ vanadium(III) conversion shows a greater

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[31] H. J. Price and H. Taube, *Inorg. Chem.*, 1968, **7**, 1; N. Sutin, *Accounts Chem. Res.*, 1968, **1**, 225.

[32] O. J. Parker and J. H. Espenson, *Inorg. Chem.*, 1969, **8**, 185.

[33] M. Green and A. G. Sykes, *J. Chem. Soc.* (*A*), 1970, 3221; 1971, 3067.

dependence on first-order hydrogen-ion concentration terms than does the titanium(IV) ⟶ titanium(III) change. The extent of the variation in hydrogen-ion concentration for each pair of titanium and vanadium reactions is comparable, except perhaps in the case of the titanium(III) and vanadium(III) reductions of vanadium(V) ions. The smaller ionic strength used for the reaction of titanium(III) with vanadium(V) ions does not permit values $[H^+] > 0{\cdot}5$M and we cannot therefore exclude contributions from a k_1 path at higher $[H^+]$ values. The effectiveness of different $[H^+]$ paths suggests that hydrolysis of titanium(IV) is less extensive than that of vanadium(IV) ions, and that the titanium–oxygen bond in TiO^{2+} is weaker or that hydrolysis of titanium(IV) is different in kind from that of vanadium(IV). An explanation consistent with these observations is that titanium(IV) is present as the ion $Ti(OH)_2^{2+}$.

TABLE 6

Comparison of rate laws for pairs of reactions involving titanium(IV) and vanadium(IV) ions. The second column specifies which terms in the rate law, $k_{obs} = k_1[H^+] + k_0 + k_{-1}[H^+]^{-1} + k_{-2}[H^+]^{-2}$, are effective

Reaction	Effective terms	Range of $[H^+]$ studied M	Other comments	Ref.
$V^{II} + Ti^{IV}$	k_0	0·35—1·85		This work
$V^{II} + V^{IV}$	k_0, k_1 (small)	0·20—2·00	Cl^- catalysis [a]	31
$Ti^{III} + V^{IV}$	k_0, k_{-1}	0·07—0·40	Cl^- catalysis studied [a]	This work
$V^{III} + V^{IV}$	k_{-1}	0·50—2·00		*b*
$Ti^{III} + Pu^{IV}$	k_{-1}	0·27—2·02	0·05M-Cl^- small effect [a]	5
$V^{III} + Pu^{IV}$	k_{-1}, k_{-2}	0·25—2·00	0·23M-Cl^- no effect	*c*
$Ti^{III} + V^{V}$	k_0, k_{-1}	0·04—0·49	0·3M-Cl^- no effect	11
$V^{III} + V^{V}$	k_1, k_0, k_{-1}, k_{-2}	0·02—2·00	0·15M-Cl^- no effect	*d*
$Ti^{III} + Pu^{VI}$	k_{-1}	0·25—2·00	0·02M-Cl^- no effect	6
$V^{III} + Pu^{VI}$	k_{-1}, k_{-2}	0·10—1·00		*e*
$Ti^{III} + Fe^{III}$	k_0 (small), k_{-1}	0·50—2·50	Cl^- catalysis studied	7
$V^{III} + Fe^{III}$	k_0 (small, k_{-1}, k_{-2}	0·70—2·7	10^{-3}M-Cl^- no effect	*f*
$Ti^{III} + Hg^{II}$	k_{-1}, k_{-2}	0·50—2·00	Cl^- inhibits	7
$V^{III} + Hg^{II}$	k_{-2} (dominant)	0·25—1·00	10^{-3}M-Cl^- no effect	*g*

[a] Catalytic effect is mild. [b] S. C. Furman and C. S. Garner, *J. Amer. Chem. Soc.*, 1952, **74**, 2333. [c] S. W. Rabideau and R. J. Kline, *J. Inorg. Nuclear Chem.*, 1960, **14**, 91. [d] N. A. Daugherty and T. W. Newton, *J. Phys. Chem.*, 1964, **68**, 612. [e] S. W. Rabideau, *J. Phys. Chem.*, 1958, **62**, 414. [f] W. C. E. Higginson and A. G. Sykes, *J. Chem. Soc.*, 1962, 2841; O. J. Parker and J. H. Espenson, *J. Amer. Chem. Soc.*, 1969, **91**, 1313. [g] M. Green, W. C. E. Higginson, J. B. Stead, and A. G. Sykes, *J. Chem. Soc. (A)*, 1971, 3068.

The chloride-ion catalysis of the titanium(III) reduction of vanadium(IV) ions is mild and similar to that observed for the corresponding reduction of plutonium(IV) ions.[5] It is only clearly defined in the present study by using high chloride-ion concentrations up to 0·43M. No catalysis of the reaction of titanium(III) with plutonium(VI) ions is observed with $[Cl^-] = 0{\cdot}02$M.[6] These observations are consistent with weak complexing of chloride ions to titanium(III) ($K = 0{\cdot}07$—$0{\cdot}2$ l mol^{-1} at 25 °C).[34] Since at 25 °C complexing of chloride ions to VO^{2+} is of the same magnitude ($K = 0{\cdot}24 \pm 0{\cdot}10$ l mol^{-1}),[35] it is possible that for the k_c path chloride ion is brought into the activated complex by the 2+ vanadium(IV) reactant as $VOCl^+$. At the highest chloride-ion concentration used, *ca.* 10% of the VO^{2+} ion is in the form $VOCl^{2+}$ and <10% of the Ti^{3+} ion is present as $TiCl^{2+}$. This is not expected to give rise to significant curvature in Figure 1. The titanium(III) reduction of mercury(II) ions is inhibited by chloride ions [7] and here, in view of the extensive complexing of chloride to mercury(II) ions (log K 6·48),[36] it can presumably be concluded that $HgCl^+$ and/or $HgCl_2$ is much less reactive than the ion Hg^{2+}.

EXPERIMENTAL

Preparations.—*Titanium*(IV). Solutions of titanium(IV) (*ca.* 0·05M) were prepared by dissolving the sulphate $TiOSO_4,2H_2O$ (high purity sample, trace metals <0·06%; British Titan Products) in 2M-perchloric acid at 60 °C. To remove the sulphate ions an equivalent amount of 0·8M-barium perchlorate was added and, after leaving for 12 h, the barium sulphate was filtered off using a No. 4 sinter. Solutions of titanium(IV) were frozen and stored at *ca.* −5 °C. The titanium(IV) concentration was determined spectrophotometrically as the peroxo-complex (ε 717 ± 2 l mol^{-1} cm^{-1} at the 408 nm peak) by addition of H_2O_2 (0·14M) and H_2SO_4 (1·8M). Solutions of titanium(IV) made up by weight from $TiOSO_4,2H_2O$ and TiH_2 were used to standardize the procedure and determine the absorption coefficient.

It was concluded that titanium(IV) solutions, $[H^+] > 0{\cdot}1$M, contained monomeric 2+ (and not polymeric) titanium(IV) ions by comparing the behaviour of the ions vanadium(IV) and titanium(IV) in ion-exchange experiments using Dowex 1-X8 20—50 mesh resin. The resin was washed successively with 1M-$HClO_4$, distilled water, acetone–water (1 : 1), ethanol and distilled water and a 1 × 7·5 cm column prepared. The vanadium(IV) or titanium(IV) ions (10^{-4} mole in 50 ml of 0·5M-$HClO_4$) were exchanged on the column and then eluted with 0·5M-$HClO_4$. The vanadium(IV) ions passed down the column in a *ca.* 2 cm band and were collected in a fraction (150—250 ml). The titanium(IV) ions were collected similarly (175—275 ml fraction). Analyses for titanium(IV) were carried out spectrophotometrically (ε 104 l mol^{-1} cm^{-1} at 250 nm) and were checked at 408 nm after addition of hydrogen peroxide to form the peroxo-complex (details as above). The amount of titanium(IV) retrieved was >98%.

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Titanium(III). Titanium hydride (Fluka, AnalaR, >99·5% purity; 0·5 g) was dissolved in concentrated hydrochloric acid (10 ml) maintained at 35—40 °C (*ca.* 6 h) under oxygen-free conditions. The excess of solid was removed using a No. 4 filter and the solution diluted sixfold with nitrogen-degassed water. Small amounts of titanium(IV) were removed by electrolytic reduction at a mercury-pool cathode (5·3 V, 0·3 A) for 2—3 h. The extent of electrolysis was checked by monitoring the absorption of the titanium(III) ions at 502 nm until it was constant; low absorption at 300 nm [ε 24·9 for titanium(IV) and ε < 1·0 l mol^{-1} cm^{-1} for titanium(III)] was also consistent with removal of titanium(IV) ions. The titanium(III) solution was standardized by addition of an excess of cerium(IV) and back-titrating with iron(II) in 1M-H_2SO_4 using ferroin as indicator. The absorption coefficient, $\varepsilon_{max.}$ = 3·97 l mol^{-1} cm^{-1}, at 502 nm was used for subsequent standardizations ($[H^+]$ = 0·5—1·0M).

Vanadium(IV). Vanadium(IV) sulphate (B.D.H. Reagent Grade, 100 g) was dissolved in 0·1M-$HClO_4$ (250 ml) at 40 °C. The solution was passed down a 3 × 16 cm column of Amberlite IR 120(H) cation-exchange resin initially in the acid form. The column was washed free from sulphate ions and the vanadium(IV) ions were eluted with 1·0M-$HClO_4$. The vanadium(IV) concentration was determined spectrophotometrically at 760 nm (ε 17·2 l mol^{-1} cm^{-1}).

Vanadium(II). A solution of vanadium(IV) (0·14M) in 0·6M-$HClO_4$ was reduced under oxygen-free conditions at a mercury-pool cathode (5·2 V, 0·3 A, *ca.* 4 h). The extent of the electrolysis in its final stages was followed spectrophotometrically by measuring the absorbance due to the vanadium(II) and vanadium(III) ions at 850 and 400 nm. Vanadium(II) is the only absorbent at 850 nm (ε 3·22 l mol^{-1} cm^{-1}), whereas at 400 nm both vanadium(II) (ε 1·1 l mol^{-1} cm^{-1}) and vanadium(III) (ε 8·35 l mol^{-1} cm^{-1}) absorb. Solutions of vanadium(II) prepared in this way contained <2% vanadium(III). Solutions were stored at 0 °C in air-free conditions for periods of up to 10 days.

The hydrogen-ion concentrations of titanium(IV), titanium(III), vanadium(IV), and vanadium(II) solutions were determined by passing aliquot portions down a column of Amberlite IR 120(H) cation-exchange resin. The hydrogen-ion concentration of the eluent solution was determined by titration with 0·1M-NaOH.

Kinetic experiments were carried out on a Durrum–Gibson stopped-flow spectrophotometer. All reactant solutions were deoxygenated by bubbling argon through them for *ca.* 30 min. Solutions were transferred using Atlas nylon syringes fitted with stainless-steel needles.

We wish to thank British Titan Products for an S.R.C. postgraduate C.A.P.S. award (to J. D. E.) and for numerous discussions with members of the Research Division, in particular Mr. T. Wiseman.

[2/1410 *Received*, 19*th June*, 1972]