Kinetics of the Reaction between Titanium(III) and Vanadium(V)

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The kinetics of the one-equivalent reaction between titanium(III) and vanadium(V), $Ti^{III} + V^{V} \longrightarrow Ti^{IV} + V^{IV}$, have been studied by stopped-flow spectrophotometry. The rate is independent of chloride-ion concentration over the range up to 0·5M investigated (replacement of perchlorate by chloride). Subsequently hydrochloric acid reactant solutions adjusted to I = 0·5M with NaCl were used, thereby avoiding the use of titanium(III) in perchlorate solutions. At temperatures 2·6—35° and with hydrogen-ion concentrations in the range 0·04—0·49M the rate law (i) gives a satisfactory fit to the experimental data. At 25°, $k_0 = (7{\cdot}8 \pm 0{\cdot}5) \times 10^3$ l mol^{-1} s^{-1} and

$$\frac{-d[V^{V}]}{dt} = (k_0 + k_{-1}[H^+]^{-1})\,[Ti^{III}][V^{V}] \qquad (i)$$

$k_{-1} = (8{\cdot}3 \pm 0{\cdot}4) \times 10^2$ s^{-1}, and activation parameters are $\Delta H^‡_0 = 7{\cdot}2 \pm 0{\cdot}2$ kcal mol^{-1}, $\Delta S^‡_0 = -16{\cdot}6 \pm 0{\cdot}8$ cal K^{-1} mol^{-1}, $\Delta H^‡_{-1} = 14{\cdot}7 \pm 0{\cdot}3$ kcal mol^{-1}, and $\Delta S^‡_{-1} = 4{\cdot}1 \pm 1{\cdot}1$ cal K^{-1} mol^{-1}. With the titanium(III) reactant in an excess a much slower second stage involving titanium(III) reduction of vanadium(IV) is observed. Use of stainless-steel syringe needles resulted in serious contamination of reactant solutions, and it was necessary to use Teflon needles at all times.

THE aim of this and a number of related investigations is to obtain more extensive information on the redox aqueous solution chemistry of titanium ions. Details of the kinetics of the vanadium(II) reduction of titanium(IV) and the titanium(III) reduction of vanadium(IV) have been reported previously.[1] The third reaction between vanadium and titanium ions which it is possible to study provides the subject of this paper.

Procedure.—Titanium(III) reacts with oxygen and anaerobic techniques as described previously [2] were necessary. Stopped-flow experiments using aqueous perchloric acid solutions of titanium(III) perchlorate and vanadium(V) perchlorate, $[H^+] = 0{\cdot}3$M, indicated a single-stage reaction, $\lambda = 310$ nm. With titanium(III) in excess the reduction of vanadium(IV) [1] can also be observed; this reaction is considerably slower however and is not effective on the same time scale. The storage of titanium(III)/perchloric acid solutions is difficult owing to the titanium(III) reduction of perchlorate ions, half-life of 2 h at 25 °C in 1M-perchloric acid.[3] The possibility of replacing perchloric acid by hydrochloric acid was therefore investigated. The use of stainless-steel syringe needles was not possible under these conditions for the following reasons. For experiments in which the titanium(III) reactant was in excess stopped-flow traces gave a second stage (prior to the Ti^{III}–V^{IV} reaction), and for experiments in which the vanadium(V) reactant was in excess, the dominant spectrophotometric change at 310 nm corresponded to yet another reaction. Neither of these additional reactions was observed when Teflon needles were used. The effects are attributed to the presence of iron(III) in the vanadium(V) reactant solution, and iron(II) in the titanium(III) solution following dissolution of stainless-steel needles in the HCl media. Depending which reactant is in excess the titanium(III)–iron(III) [4] or iron(II)–vanadium(V) [5] reaction is observed. The complexing of iron(III) with chloride [6a] may also contribute.† All subsequent transferences, and the deoxygenation of reactant solutions in the presence of HCl, were carried out using Teflon needles.‡

Preliminary Observations.—With metal-ion concentrations in the range (1—5) × 10^{-3}M spectra of vanadium(IV), vanadium(V), and titanium(IV) in the region 250—400 nm were found to be identical with $[ClO_4^-] = 0{\cdot}5$M and $[Cl^-] = 0{\cdot}5$M, $[H^+] = 0{\cdot}3$M in both cases. It is concluded that there is no spectrophotometric evidence for extensive complexing of chloride to these metal ions.§ Titanium(III) does not complex extensively with chloride.¶ Since titanium(IV) has a tendency to associate with other metal ions, *e.g.* vanadium(IV) [7] and iron(II),[8] in the presence of complexing anions, evidence

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† Coll *et al.* give the absorption spectrum of $FeCl^{2+}$.[6b] Independent measurements at $[H^+] = 0{\cdot}3$M were found to be in satisfactory agreement.

‡ The complicated behaviour apparent in the early stages of this work was similar to that described in a recent paper (on the same reaction) by Birk and Logan, *Inorg. Chem.*, 1973, **12**, 580. Our studies simplified considerably when Teflon needles were used, and we must conclude that two of the stages reported by Birk and Logan are in fact spurious. Our results and interpretation differ from theirs in two other respects. We have at no time had to make allowances for titanium(III) dimer formation, and the acid dissociation constants for Ti^{3+} required by Birk and Logan are far in excess of the values which our data demand, and which have been reported elsewhere in the literature (see discussion in ref. 1).

§ W. S. Melvin and G. Gordon, *Inorg. Chem.*, 1972, **11**, 1912 report an equilibrium constant of 0·23 l mol^{-1} for the complexing of chloride with VO^{2+} at 25°, $I = 2{\cdot}0$M. A value 0·42 l mol^{-1} has been reported by A. A. Ivakin *Zhur. priklad. Khim.*, 1966, **39**, 277 for the complexing of chloride with VO_2^+ at 19°, $I = 1{\cdot}0$M. No data is available for titanium(IV).

¶ The equilibrium constant for the complexing of chloride to titanium(III) is reported to be 0·07—0·2 l mol^{-1} at 25° by H. J. Gardner, *Austral. J. Chem.*, 1967, **20**, 2357.

[1] J. D. Ellis and A. G. Sykes, *J.C.S. Dalton*, 1973, 537.

[2] See for example A. Adin and A. G. Sykes, *J. Chem. Soc.* (*A*), 1966, 1230, and subsequent papers from these laboratories.

[3] F. R. Duke and P. R. Quinney, *J. Amer. Chem. Soc.*, 1954, **76**, 3800.

[4] R. Critchley, Ph.D. Thesis, University of Manchester, 1965; R. Critchley and W. C. E. Higginson, unpublished work, quoted in A. G. Sykes 'Kinetics of Inorganic Reactions,' Pergamon Press, 1970, p. 166.

[5] N. A. Daugherty and T. W. Newton, *J. Phys. Chem.*, 1963, **67**, 1090.

[6] (*a*) J. K. Rowley and N. Sutin, *J. Phys. Chem.*, 1970, **74**, 2043; (*b*) H. Coll, R. V. Nauman, and P. M. West, *J. Amer. Chem. Soc.*, 1959, **81**, 1284.

[7] M. L. Reynolds, *J. Chem. Soc.*, 1965, 2991.

[8] M. L. Reynolds, *J. Chem. Soc.*, 1965, 2993.

for such interactions was looked for in the present study. No interactions between titanium(IV) and vanadium(IV) or vanadium(V) were detected (250—800 nm) with $[Cl^-] = 0·5$M, $[H^+] = 0·3$M, and spectra were in all cases additive and as expected. A study of the stability of vanadium(V) with hydrogen-ion concentration was also made. The spectrum of a 2×10^{-4}M solution of the vanadium(V) was unaffected by concentrations of perchloric acid in the range 0·02—2·00M. Spectra remained unchanged over a period of 7 days.

Stoicheiometry.—Solutions of titanium(III) and vanadium(V) were mixed and the resulting spectra measured in the region 300—850 nm. Metal-ion concentrations were of the order of 10^{-2}M and the concentration of HCl in the range 0·3—0·5M. Resultant spectra were analysed using the following absorption coefficients: $\varepsilon_{max.} = 8·3$ l mol^{-1} cm^{-1} at 395 nm and $\varepsilon_{max.} = 5·5$ l mol^{-1} cm^{-1} at 585 nm for vanadium(III), $\varepsilon_{max.} = 17·2$ l mol^{-1} cm^{-1} at 760 nm for vanadium(IV), $\varepsilon = 140$ l mol^{-1} cm^{-1} at 350 nm for vanadium(V), and $\varepsilon = 24·9$ l mol^{-1} cm^{-1} at 300 nm for titanium(IV). Corrections were made for absorption by titanium(III). With an excess of titanium(III) there was a consumption of 2 mol of titanium(III) per mol of vanadium(V), and the vanadium(V) was reduced to vanadium(III). With an excess of vanadium(V) there was a consumption of 1 mol of titanium(III) per mol of vanadium(V), and the vanadium(V) was reduced to vanadium(IV). The titanium(III) reduction of vanadium(IV) [1] is *ca.* 10^4 times slower than the reduction of vanadium(V), and does not interfere with the present study. Kinetic studies described below are consistent with the consumption of 1 mol of titanium(III) per mol of vanadium(V), as in equation (1), in an initial

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

fast step. For the range of hydrogen-ion concentrations investigated the various species are present predominantly as Ti^{3+}, VO_2^{+}, TiO^{2+} [or $Ti(OH)_2^{2+}$, see ref. 1] and VO^{2+}.

The Effect of Chloride.—Rate constants (see next section for details of evaluation) for runs in which the chloride-ion concentration was varied are listed in Table 1. Perchloric acid and lithium perchlorate were introduced in the vanadium(V) reactant solution. Since rate constants are independent of chloride there are no complications in this study from chloride dependent paths. Rate constants with $I = 0·5$M ($LiClO_4$) were in good agreement with those obtained with $I = 0·5$M (NaCl). Thus at 25° values obtained with $[H^+] = 0·05$M are $2·65 \times 10^4$ l mol^{-1} s^{-1} (average from Table 1) and $2·47 \times 10^4$ l mol^{-1} s^{-1} respectively; and with $[H^+] = 0·30$M are $1·07 \times 10^4$ l mol^{-1} s^{-1} (average from Table 1) and $1·08 \times 10^4$ l mol^{-1} s^{-1} respectively. All subsequent work was with $I = 0·5$M (NaCl).

TABLE 1

Rate constants (25°) for the reaction of titanium(III) ($1·1 \times 10^{-3}$M) and vanadium(V) ($1·1 \times 10^{-4}$M) in the presence of varying amounts of chloride, $I = 0·5$M ($LiClO_4$)

$[H^+]$ [a] / M	$[Cl^-]$ [b] / M	$10^{-4}k$ / l mol^{-1} s^{-1}
0·05	0·05	2·69
0·05	0·10	2·64
0·05	0·15	2·80
0·05	0·20	2·64
0·05	0·25	2·51
0·05	0·30	2·71
0·30	0·05	1·07
0·30	0·10	1·08
0·30	0·15	1·06
0·30	0·20	1·05
0·30	0·30	1·10

[a] $[H^+]$ adjusted as required with HCl and $HClO_4$. [b] HCl and NaCl used.

TABLE 2

The dependence of first-order rate constants k_{obs} on the concentration of titanium(III). Second-order rate constants k have also been evaluated, and determined directly with the vanadium(V) reactant in excess. Temperature 25°, [HCl] = 0·3M, and $I = 0·5$M (NaCl)

$10^3[Ti^{III}]$ / M	$10^4[V^{V}]$ [a] / M	k_{obs} / s^{-1}	$10^{-4}k$ / l mol^{-1} s^{-1}
0·5	0·5	5·06	1·01
0·6	0·5	6·34	1·06
0·9	0·5	10·1	1·12
1·0	0·5	10·0	1·00
1·2	0·5	13·9	1·15
1·5	0·5	15·9	1·06
1·5	0·5	15·9	1·06
2·0	0·5	21·1	1·05
2·4	1·2	27·0	1·12
2·4	1·8	27·4	1·14
2·4	2·4	27·0	1·12
2·5	0·5	26·5	1·06
2·5	1·0	27·1	1·08
2·5	1·5	26·6	1·06
2·5	2·0	27·2	1·09
2·5	2·5	26·2	1·05
2·5	2·5	27·1	1·08
2·5	2·5	26·9	1·07 [b]
2·5	2·5	28·2	1·13 [c]
2·5	2·5	27·1	1·08 [d]
2·5	2·5	27·2	1·09 [e]
3·0	0·5	32·2	1·07
0·05	3·0		1·02
0·05	6·0		1·06
1·0	1·0	24·7	2·47 [f,g]
0·05	6·0		2·57 [f]

[a] Small amounts of ClO_4^- <0·018M introduced with vanadium(V) reactant. [b] $[V^{IV}] = 2·5 \times 10^{-4}$M initially. [c] $[V^{IV}] = 2·5 \times 10^{-3}$M initially. [d] $[V^{IV}] = [Ti^{IV}] = 2·5 \times 10^{-4}$M initially. [e] $[V^{IV}] = [Ti^{IV}] = 2·5 \times 10^{-3}$M initially. [f] [HCl] = 0·05M. [g] From data in Table 3.

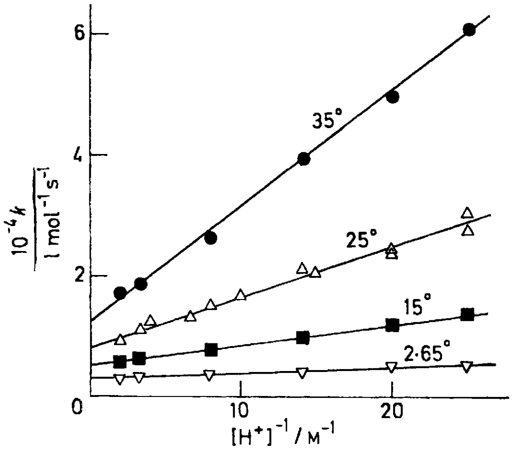
Kinetic Studies.—Absorbance (OD) changes were monitored at 310 nm, at which wavelength absorption coefficients ε (l mol^{-1} cm^{-1}) for vanadium(V), vanadium(IV), titanium(IV), and titanium(III) are 425, 11·1, 15·2, and 0·3 respectively. For runs in which the titanium(III) reactant was in at least ten-fold excess, pseudo-first-order rate constants, k_{obs}, were obtained from the gradient ($k_{obs}/2·303$) of plots of log ($OD_t - OD_\infty$) against time. Such plots were linear to 85—90% completion. A strictly first-order dependence on the concentration of titanium(III) was observed, hence the rate law is as in equation (2), and second-order rate constants k, Table 2,

$$-d[V^{V}]/dt = k[Ti^{III}][V^{V}] \qquad (2)$$

could be evaluated from k_{obs}. Rate constants k evaluated at five other wavelengths in the range 310—410 nm were in good agreement ($\pm 4\%$). With the vanadium(v) reactant in excess k was obtained from second-order plots (linearity 85%) of log ([$\mathrm{V^V}$]/[$\mathrm{Ti^{III}}$]) against time, Table 2. The agreement of k values obtained using the two procedures is satisfactory. Rate constants (and the linearity of plots) were also found to be independent of quantities of titanium(IV) and vanadium(IV) added initially, concentrations equal to that of titanium(III). Six runs using a titanium(III) solution prepared from titanium metal also gave a linear dependence on titanium(III), with $k = 1{\cdot}08 \times 10^4$ l mol^{-1} s^{-1} at 25°, [$\mathrm{H^+}$] = 0·3M, I = 0·50M, in good agreement with data in Table 2. Rate constants obtained for runs in which NaCl was replaced by LiCl were also in satisfactory agreement. On varying the hydrogen-ion concentration in the range 0·04—0·49M k values, Table 3, gave a good fit to equation (3). Linear plots were observed at four

$$k = k_0 + k_{-1}[\mathrm{H^+}]^{-1} \qquad (3)$$

temperatures (Figure). From the data in Table 3, and using a non-linear least-squares programme,[9] with each data point given equal weighting, activation parameters corresponding to k_0 and k_{-1} were evaluated. These are $\Delta H^{\ddagger}_0 = 7{\cdot}2 \pm 0{\cdot}2$ kcal mol^{-1}, $\Delta S^{\ddagger}_0 = -16{\cdot}6 \pm 0{\cdot}8$ cal K^{-1} mol^{-1}, $\Delta H^{\ddagger}_{-1} = 14{\cdot}7 \pm 0{\cdot}3$ kcal mol^{-1}, and $\Delta S^{\ddagger}_{-1} = 4{\cdot}1 \pm 1{\cdot}1$ cal K^{-1} mol^{-1}, and are as obtained by plotting log (k/T) against $1/T$. Rate constants k_0 and k_{-1} at each temperature and corresponding errors, Table 4, were obtained from these activation parameters.



The inverse hydrogen-ion dependence of rate constants k for the reaction of titanium(III) with vanadium(v), I = 0·5M (NaCl)

DISCUSSION

The hydrogen-ion dependence of the titanium(III) reduction of vanadium(v), [$\mathrm{H^+}$] = 0·04—0·49M, is adequately described by equation (3). The acid dissociation constant of the $\mathrm{Ti^{3+}}$ ion is believed to be *ca.* 2×10^{-3} mol l^{-1} at 25°,* and inclusion of a $(1 + K_a[\mathrm{H^+}]^{-1})$ term in equation (3) would be expected to contribute only *ca.* 5%. We would not expect such an effect to be apparent in the Figure, and in any case there may be small contributions from an [$\mathrm{H^+}$]$^{-2}$ dependent pathway, as observed in the vanadium(III) reduction of vanadium(v), which if effective would give curvature at low [$\mathrm{H^+}$] in the opposite direction. Since no curvature is detected in Figure 1 this would suggest that for such an [$\mathrm{H^+}$]$^{-2}$ path k_{-2} is $<2{\cdot}4$ mol l^{-1} s^{-1} at 25°.

TABLE 3

The variation of k with hydrogen-ion concentration and temperature, for the reaction of titanium(III) (0·8—1·0) $\times$ 10^{-3}M, with vanadium(v), (0·8—1·0) $\times$ 10^{-4}M,[a] I = 0·5M (NaCl)

Temp./°C	[H$^+$] / M	$10^{-4}k$ / l mol^{-1} s^{-1}
2·65	0·040	0·53
	0·050	0·51
	0·071	0·40
	0·125	0·37
	0·30	0·32
	0·49	0·30
15·0	0·040	1·36
	0·050	1·18
	0·071	0·97
	0·125	0·76
	0·30	0·61
	0·49	0·59
25·0	0·040	3·02
	0·040	2·75
	0·050	2·43
	0·050	2·39
	0·067	2·06
	0·071	2·10
	0·100	1·66
	0·125	1·50
	0·150	1·32
	0·250	1·22
	0·30	1·11
	0·49	0·92
35·0	0·040	6·10
	0·050	4·98
	0·071	3·95
	0·125	2·63
	0·30	1·88
	0·49	1·70

[a] Small amounts of $\mathrm{ClO_4^-}$ $<0{\cdot}003$M introduced with vanadium(v) reactant.

TABLE 4

Variation of k_0 and k_{-1} with temperature, I = 0·5M (NaCl)

Temp./°C	$10^{-3}k_0$ / l mol^{-1} s^{-1}	$10^{-2}k_{-1}$ / s^{-1}
2·65	2·76 ± 0·17	1·04 ± 0·05
15·0	5·11 ± 0·33	3·38 ± 0·16
25·0	7·83 ± 0·51	8·32 ± 0·38
35·0	12·1 ± 0·8	19·4 ± 0·9

A comparison is made of data obtained in this investigation, with that for the reaction of vanadium(III) with vanadium(v)[10] (Table 5). We note that rate constants for the titanium(III) reduction at 25° are $k_0 > k_{-1} \gg k_{-2}$, whereas for the vanadium(III) reduction $k_{-1} > k_0 > k_{-2}$. This is consistent with the point we have made earlier[1] that (at 25°) titanium(III) reactions tend to be less dependent on inverse hydrogen-ion dependent paths. A possible implication is that the

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* See discussion of available data in ref. 1.

[9] Los Alamos Report LA 2367, 1959, and Addenda by R. H. Moore and R. K. Ziegler.

[10] N. A. Daugherty and T. W. Newton, *J. Phys. Chem.*, 1964, **68**, 612.

titanium(IV) ion is less extensively hydrolysed than the vanadium(IV) ion. By this we mean that either the Ti–O bond is less stable than the V–O bond, or that hydrolysis of titanium(IV) is fundamentally different and possibly gives rise to $Ti(OH)_2^{2+}$ ions.

The titanium(III) reduction of vanadium(V) does not exhibit a chloride dependence with $[Cl^-]$ as high as 0·30M, Table 1. This reflects the inability of titanium(III) and vanadium(V) to complex extensively with chloride; the chloro-complexes which are formed in small amounts do not appear to have any enhanced redox activity. The titanium(III) reduction of iron(III) shows a significant chloride dependence (stopped-flow runs at 25°, $[H^+] = 0{\cdot}05$ and 0·30M, $I = 0{\cdot}5$M adjusted with NaCl), and in this instance complexing of iron(III) with chloride is much more extensive.

Finally some comment as to whether the reaction is of the inner- or outer-sphere type is pertinent. Contributions from $[H^+]^{-1}$ paths do not necessarily imply an inner-sphere mechanism with hydroxide functioning as a bridging ligand. Thus the vanadium(III) reduction of hexachloroiridate(IV)[11] proceeds solely by an $[H^+]^{-1}$ path, in spite of the fact that hydroxide bridging is not a possibility in view of the inertness of the $IrCl_6^{2-}$ reactant. Rather in such instances is the $[H^+]^{-1}$ dependence indicative of the need of one of the reactants to change its degree of hydrolysis, which it does in part prior to formation of the activated complex. Since titanium(IV) is much more extensively hydrolysed than the corresponding (III)-state ions, we do not consider the detection of $[H^+]^{-1}$ paths in the present study to be indicative of an inner-sphere activated complex with hydroxide bridging. Moreover a decrease in the extent of hydrolysis of vanadium(V) would be expected to favour conversion into vanadium(IV), whereas an activated complex $[TiOHVO_2]^{3+}$ formed from $TiOH^{2+}$ and VO_2^+ most probably represents an increase in extent of hydrolysis of the vanadium(V) centre. No examples of inner-sphere activated complexes in which H_2O functions as a bridging ligand are known,[12] and we are therefore inclined to exclude an activated complex $[TiH_2OVO_2]^{4+}$ as a possibility for k_0. Activated complexes for k_0 and k_{-1} respectively having the structures $[TiOVO]^{4+}$ and $[OHTiOVO]^{3+}$ seem more likely if the mechanism is in fact of the inner-sphere type. The first of these might be formed in some part in a substitution-controlled process. Information regarding substitution reactions of Ti^{3+} is at present somewhat limited. The complexing with thiocyanate (rate constants for the outer- to inner-sphere step are *ca.* 8×10^3 s^{-1} at 25°)[13] and water-exchange reaction (*ca.* 10^5 s^{-1} by n.m.r.)[14] have been studied, and indications are that the reactions have associative (S_N2) character. Activation parameters have been obtained for the latter study, $\Delta H^\ddagger = 6{\cdot}1$ kcal mol^{-1} and $\Delta S^\ddagger = -15$ cal K^{-1} mol^{-1}. Those for k_0 in Table 5 would certainly be acceptable for a titanium(III) substitution-controlled process. A similar assignment seems less likely in the case of the k_{-1} path because an enhancement in rate of substitution (k_{-1}/K_a = *ca.* 4×10^7 l mol^{-1} s^{-1} at 25°) is not expected with $TiOH^{2+}$ as reactant by analogy with the thiocyanate complexing to titanium(III), which shows no such dependence on $[H^+]$. If oxo-bridging occurs in the activated complex it would be reasonable to expect the successor complex $[Ti^{IV}OV^{IV}O]^{4+}$ following electron transfer, to exhibit substitution inert properties.* No such intermediate was detected in this study. Electron transfer *via* outer-sphere activated complexes must therefore remain a possibility.

TABLE 5

A comparison of kinetic data (25°) for the titanium(III) and vanadium(III) reductions of vanadium(V)

	$Ti^{III} + V^{V}$ [a]	$V^{III} + V^{V}$ [b]
$k_{-2}/l^{-1}\ mol\ s^{-1}$	<2·4	4·9
$\Delta H^\ddagger$/kcal mol^{-1}		18·9
$\Delta S^\ddagger$/cal K^{-1} mol^{-1}		8·0
k_{-1}/s^{-1}	830	180
$\Delta H^\ddagger$/kcal mol^{-1}	14·7	16·5
$\Delta S^\ddagger$/cal K^{-1} mol^{-1}	4·1	7·1
$k_0/l\ mol^{-1}\ s^{-1}$	7800	25
$\Delta H^\ddagger$/kcal mol^{-1}	7·2	8·3
$\Delta S^\ddagger$/cal K^{-1} mol^{-1}	−16·6	−24·3
$k_1/l^2\ mol^{-2}\ s^{-1}$		46
$\Delta H^\ddagger$/kcal mol^{-1}		12·6
$\Delta S^\ddagger$/cal K^{-1} mol^{-1}		−8·7

[a] This work, $I = 0{\cdot}5$M (NaCl); replacement of chloride by perchlorate has no effect (Table 1). [b] Data in ref. 10 obtained at $I = 2{\cdot}0$M ($LiClO_4$); ionic strength variations 0·06—2·50M have little effect on overall rate constants.

To summarize an inner-sphere mechanism with oxo-bridging is perhaps most likely. However since a binuclear titanium(IV)–vanadium(IV) successor complex was not detected, the possibility that outer-sphere paths are effective cannot be excluded. A substitution-controlled process for k_0 is not ruled out.

EXPERIMENTAL

Preparation of Titanium Solutions.—The preparation and standardization of titanium(III) chloride (in HCl) and titanium(IV) perchlorate (in $HClO_4$) were as described previously.[1] By appropriate modification of the above procedure a solution of titanium(IV) sulphate ($TiOSO_4,2H_2O$) in HCl was obtained, the small amount of sulphate having negligible effect on spectra. A solution of titanium(III) perchlorate in perchloric acid was prepared from a solution of titanium(III) sulphate by addition of barium perchlorate. The precipitate of $BaSO_4$ was filtered off. A solution of titanium(III) in HCl was also prepared from titanium metal. Titanium sponge (0·5 g, Johnson Matthey Chemicals, Specpure grade) was dissolved in concentrated HCl (3 h) under air-free conditions at 50—70°. Excess of metal was filtered off rapidly (in air), and the filtrate diluted six-fold with dilute HCl which had been de-oxygenated. The

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* The oxo-ligand of VO^{2+} exhibits substitution inert properties, K. Wüthrich and R. E. Connick, *Inorg. Chem.*, 1967, **6**, 583; 1968, **7**, 1377.

[11] R. N. F. Thorneley and A. G. Sykes, *J. Chem. Soc.* (*A*), 1970, 1036.

[12] D. L. Toppen and R. G. Linck, *Inorg. Chem.*, 1971, **10**, 2635.

[13] H. Diebler, *Z. phys. Chem.*, 1969, **68**, 64.

[14] A. M. Chmelnick and D. Fiat, unpublished work, quoted in D. Fiat and R. E. Connick, *J. Amer. Chem. Soc.*, 1968, **90**, 608.

titanium(III) was then de-oxygenated by bubbling argon gas through the solution. The transferences in air resulted in a <2% titanium(IV) contamination. The titanium(III) was standardized spectrophotometrically, $\varepsilon_{max.} = 3{\cdot}97$ l mol^{-1} cm^{-1} at 502 nm, and the hydrogen-ion concentration determined by first exchanging the titanium(III) onto an Amberlite IR-120(H) resin, and then titrating with 0·1M-NaOH.

Preparation of Vanadium Solutions.—Ammonium vanadate, NH_4VO_3 (B.D.H. AnalaR Grade Reagent) was dissolved with stirring in perchloric acid to give a 0·1M-solution of vanadium(V), VO_2^+, in 3·0M-perchloric acid. The vanadium(V) was determined by titration with freshly prepared ferrous ammonium sulphate in 5M-H_2SO_4 using ferroin as indicator. The ferrous solution was standardized by titration with standard B.D.H. cerium(IV) solution. The difference between this value and the concentration as determined from the weight of ammonium vanadate dissolved was <0·5%. Stock solutions of *ca.* 0·1M-vanadium(V) in 3·0M-$HClO_4$ were stored at 0°. Subsequent dilutions for kinetic runs were with HCl. Thus 10^{-4}M-vanadium(V) reactant solutions contain 0·003M-$HClO_4$. The preparation of vanadium(IV) perchlorate solutions (in aqueous $HClO_4$) was as described previously.

Preparation of Iron Solutions.—Solutions of iron(II) and iron(III) were prepared by weighing out samples of $FeCl_2,4H_2O$ (Fisons Standard Laboratory Reagent, 99·0%) or $FeCl_3,6H_2O$ (Hopkin and Williams, AnalaR) into HCl and $HClO_4$ solutions as required. Iron(II) solutions were deoxygenated immediately after preparation, and were stored under nitrogen.

Reagents NaCl, HCl, and $HClO_4$ were of AnalaR Grade Purity. Lithium chloride (G.P.R. Hopkin and Williams) was crystallized twice from hot water, and a *ca.* 7M-stock solution prepared. Lithium perchlorate was prepared by addition of perchloric acid to lithium carbonate. The product was recrystallized until free from trace anion impurities. Solutions of NaCl, LiCl, and $LiClO_4$ were standardized by exchanging onto a column of Amberlite IR-120(H) cation exchange resin in the hydrogen-ion form. The eluant solutions (and also HCl and $HClO_4$ stock solutions) were standardized by titration with 0·1M-NaOH to the phenolphthalein end-point.

Kinetic runs were using a Durrum–Gibson stopped-flow spectrophotometer with an optical path length of 1·91 cm. Standard anaerobic techniques were employed for the transference and storage of reactant solutions using Suba-Seal serum caps and Atlas nylon syringes.

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