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Mechanism of the Reduction of Vanadium(V) by Titanium(III) in Acidic Aqueous Solution

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The reduction of vanadium(V) by titanium(III) in acidic chloride or perchlorate solutions occurs in three distinct consecutive steps; the third was present only with V(V) in excess, while the first two were studied with excess Ti(III). The pseudo-first-order rate constant for the first step follows the equation $k_1 = k_r + k_f[\text{Ti(III)}]$, where $k_f = a/(K_a + [\text{H}^+])$ and K_a is the acid dissociation constant of Ti^{3+} . For the second step, $k_2 = b[\text{Ti(III)}]/(1 + K[\text{Ti(III)}])$, where the value of K as well as its $[\text{H}^+]$ dependence agrees identically with the ratio k_f/k_r from the first step, and $b = d/(e[\text{H}^+] + [\text{H}^+]^2)$. The third step which is identified as the formation of a Ti(IV)-V(V) binuclear complex follows the equation $-d \ln [\text{Ti(IV)}]/dt = (f + g[\text{H}^+] + h[\text{H}^+]^2)[\text{V(V)}]_{\text{XS}}$. Mechanisms for these reactions are presented and discussed. Evidence is also presented for the existence of a dimeric species in Ti(III) solutions.

Introduction

Kinetic studies of the reduction of chromium(VI)¹ and vanadium(V)^{2,3} by the iron(II) complexes $\text{Fe}(\text{CN})_6^{4-}$, $\text{Fe}(\text{bipy})(\text{CN})_4^{2-}$ (bipy = 2,2'-bipyridyl), $\text{Fe}(\text{bipy})_2(\text{CN})_2$, and $\text{Fe}(\text{bipy})_3^{2+}$ have indicated some very close similarities in the mechanisms for reduction of these two d^0 metal ions. This is not a surprising result, considering that these metal ions are isoelectronic and probably isostructural.⁴ These results suggest that the study of the reductions of V(V) should provide information relevant to the mechanisms of reductions of Cr(VI), which are potentially more complex because of the occurrence of unstable intermediate oxidation states, Cr(V) and Cr(IV). As part of a series of kinetic studies of reactions of d^0 oxidants, we have now studied the reduction of Cr(VI)⁵ and of V(V) by Ti(III), the latter reaction to be presented here.

These systems are of further interest in that the use of Ti(III) as a reducing agent has received relatively little attention. Kinetic studies of the Ti(III) reduction of inorganic molecules in acidic aqueous solution have been limited to I_2 ,^{6,7} Fe^{3+} ,⁸ Hg^{2+} ,⁹ PuO_2^{2+} ,¹⁰ Pu^{4+} ,¹¹ cobalt(III)-amine complexes,^{12,13} ClO_4^- ,^{12,14} VO_2^{2+} ,¹³ HCrO_4^- ,⁵ UO_2^{2+} ,¹⁵ and VO_2^+ .

Experimental Section

Materials. Solutions of titanium(III) were prepared by dissolution of spectrographically standardized Johnson Matthey Chemicals titanium metal in ca. 6 M HCl at 80–90°. Stable perchlorate solutions could not be prepared because of the Ti^{3+} reduction of ClO_4^- .^{12,14}

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Before addition of titanium, the HCl solution, contained in a bottle capped with a Buna-N self-sealing rubber disk, was purged with purified¹⁶ nitrogen to exclude oxygen, using polyethylene or platinum needles to avoid possible contamination by iron. The purging was continued throughout the dissolution process (ca. 5 hr to obtain a solution 0.05 M in Ti^{3+} after fivefold dilution). The solution was then filtered under N_2 pressure through a glass-wool plug in a system of tubing and inert needles into an appropriate volume of N_2 -purged distilled water. The solutions were stored under a positive pressure of N_2 in bottles capped with Buna-N rubber disks. A spectral check for the absence of Ti(IV) was made using a Cary 14 recording spectrophotometer. A maximum absorbance occurs at 504 nm (ϵ 3.94 $M^{-1} \text{cm}^{-1}$) for Ti^{3+} in 0.5–2 M HCl solution and essentially no absorbance is observed in the 300-nm region if Ti(IV) is absent. This spectral check was repeated periodically during the lifetime of a solution, which was discarded upon appearance of Ti(IV). Solutions were analyzed for Ti(III) by titration under N_2 with Ce(IV) in ca. 2 M H_2SO_4 to a ferroin end point and for Cl^- by titration of a Cr(VI)-oxidized aliquot with AgNO_3 to a chromate end point. The acid concentration was determined by difference, assuming the absence of Ti(IV).

Solutions of vanadium(V) perchlorate were prepared by dissolution of a weighed amount of V_2O_5 in a known excess of HClO_4 .² The solutions were analyzed by titration of an aliquot in 0.95 M H_2SO_4 with 0.1 M Fe^{2+} in 0.95 M H_2SO_4 (standardized with Ce(IV)) to a ferroin end point (which was not very sharp and was taken as the appearance of an orange color with no trace of brown).¹⁷ Results agreed well with the weight of V_2O_5 used. Acid concentration was obtained by difference.

Lithium chloride was obtained by neutralization of HCl with Li_2CO_3 or as Baker Analyzed reagent grade LiCl which was recrystallized repeatedly until concentrated solutions no longer deposited an unidentified brown material on standing. Solutions were analyzed both by ion-exchange titrations¹ and by titration with AgNO_3 . The preparation and analysis of solutions of HCl, HClO_4 , and LiClO_4 have been previously described.¹ Water used in all solutions was either laboratory distilled water or this water carefully redistilled from alkaline permanganate. No qualitative or quantitative difference in behavior was observed between the two sources of water.

Kinetics. Kinetic measurements were carried out with a Durrum stopped-flow spectrophotometer primarily at 340 nm, with no variation in rates being observed in the range 320–400 nm. Vanadium(V) reactant solutions were prepared in volumetric flasks closed with serum caps and were purged with N_2 for at least 15 min before use. Titanium(III) reactant solutions were prepared similarly except that the Ti(III) was not added until after purging since it is somewhat oxygen sensitive, and the final dilution was then made with N_2 -purged distilled water. The solutions were transferred into the stopped-flow reservoir syringes by purging and filling the syringes with nitrogen, followed by pumping small portions of the gas through a needle into the solution flask and allowing the solution to be driven back into the syringe by the resultant gas pressure.

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Results

Stoichiometry. The stoichiometry of the reaction of vanadium(V) with titanium(III) was determined by spectrophotometric titrations. The ratio of Ti(III) consumed to V(V) consumed is 1.04 ± 0.02 , consistent with eq 1. With



excess Ti^{3+} , further reduction of VO^{2+} to V^{3+} does occur, but this reaction should be negligible during the time periods involved here,¹³ although it might give rise to the slightly high value of the stoichiometric ratio. With excess VO_2^+ , a further reaction occurs and is identified as the formation of a V(V)-Ti(IV) binuclear complex, as discussed below.

Dimer Dissociation. Difficulty in the interpretation of absorbance-time traces in preliminary experiments led us to suspect the existence of an extraneous interfering absorbance change, probably arising during the dilution of Ti(III). Indeed, when a Ti^{3+} solution was mixed in the stopped-flow apparatus with a solution containing only HCl and LiCl, an absorbance decrease was observed. We believe this absorbance decrease to be due to the dissociation of a Ti(III) dimer, which must be present at only very low concentrations since it was not detected in some rather careful spectrophotometric examinations of Ti(III) solutions.¹⁸ The absorbance change did not occur when a Ti^{3+} solution containing $\sqrt{2X} M \text{H}^+$ was mixed with an equal volume of a $(2 - \sqrt{2})X M \text{H}^+$ solution (where X is the desired $[\text{H}^+]$ upon twofold dilution and mixing in the stopped-flow instrument), suggesting a dimer of formula $\text{Ti}(\text{OH})_2\text{Ti}^{4+}$ or TiOTi^{4+} , although other interpretations may be possible. The relative acid concentrations were calculated, assuming the above formula, as necessary to maintain the same dimer concentration before and after dilution. This species would be analogous to dimers known to exist for many trivalent aquometal ions (e.g., V,¹⁹ Cr,²⁰ Fe,²¹ Co,²² U²³). The kinetics of this absorbance change were determined at 25.0° , $0.50 M$ ionic strength (with LiCl), $(0.50-5.03) \times 10^{-4} M \text{Ti(III)}$, and $0.015-0.110 M \text{H}^+$. Good first-order kinetics were observed, with a rate constant of $2.16 \pm 0.09 \text{ sec}^{-1}$, independent of Ti(III) and H^+ concentrations. It is somewhat surprising that an additional term first order in H^+ does not occur in the rate law since dissociation of these dimers, as well as related binuclear oxo- or hydroxy-bridged species, usually follows such a rate law.²⁴ It is possible that thermodynamic effects are operating since the relative importance of the acid-independent and acid-dependent terms correlates reasonably well with the acid dissociation constant of the product aquometal ion. This correlation would predict only a small contribution from an acid-dependent term in the case of Ti(III).

Oxidation-Reduction Reaction. The reaction between Ti(III) and V(V) is accompanied, under various conditions, by three distinct absorbance changes when the acid concentrations were controlled as described above to eliminate any

interference from dimer dissociation. With excess Ti(III), the condition for most experiments, two distinct reaction steps (absorbance decreases) could be observed. The kinetics of these steps were determined at $0.500 M$ ionic strength (with LiCl or LiClO_4) and 25.0° over the concentration ranges $(1-15) \times 10^{-4} M \text{Ti(III)}$, $(1-15) \times 10^{-5} M \text{V(V)}$, $0.05-0.30 M \text{H}^+$, and $0.042-0.50 M \text{Cl}^-$. Each step followed good pseudo-first-order kinetics, plots of $\ln(D_t - D_\infty)$ vs. time (D = absorbance) or Guggenheim plots²⁵ being linear for at least 90% reaction. The rates of both steps were independent of $[\text{Cl}^-]$. The pseudo-first-order rate constant for the first step (k_1) followed the equation

$$k_1 = k_x + k_f[\text{Ti(III)}] \quad (2)$$

Plots of k_1 vs. $[\text{Ti(III)}]$ at various $[\text{H}^+]$ are shown in Figure 1. As indicated by Figure 1, the value of k_x was independent of $[\text{H}^+]$, while the value of k_f followed the equation

$$k_f = a/(K_a + [\text{H}^+]) \quad (3)$$

Values of k_1 were fit to eq 2 and 3 using a nonlinear least-squares computer program²⁶ with each point weighted as k_1^{-2} . The values of k_x and k_f at each $[\text{H}^+]$ are given in Table I. The best fit of all values of k_1 to the combined eq 2 and 3 (i.e., with the value of k_x restrained to have the same value at all $[\text{H}^+]$) was obtained with $k_x = 9.09 \pm 0.76 \text{ sec}^{-1}$, $a = 2130 \pm 340 \text{ sec}^{-1}$, and $K_a = 0.041 \pm 0.013 M$.

The second step obeyed the rate equation

$$k_2 = b[\text{Ti(III)}]/(1 + K[\text{Ti(III)}]) \quad (4)$$

Conformance to this equation is demonstrated by plots of k_2 vs. $[\text{Ti(III)}]$, shown in Figure 2, the downward curvature indicating the presence of the denominator term. Conformance to this equation is also shown by the agreement between observed and calculated values of k_2 given in Table II. The best values of the parameters obtained with a nonlinear least-squares computer program²⁶ are given in Table III. As indicated in Table III, the values of K at the various $[\text{H}^+]$ are identical within experimental error to the ratio $K = k_f/k_x = a/k_x(K_a + [\text{H}^+])$, obtained from the first step. Although there is a fair amount of scatter (Table III), the parameter b has a $[\text{H}^+]$ dependence given at least approximately by $b = c[\text{H}^+]^{-2}$ with $c = 100 \pm 23 M \text{sec}^{-1}$. An alternate treatment which is consistent with but not demanded by the data, considering the amount of scatter, would have $b = d(e[\text{H}^+] + [\text{H}^+]^2)^{-1}$. As will be seen in the Discussion, the mechanisms to be proposed will demand this form of $[\text{H}^+]$ dependence rather than the simpler form given above.

Binuclear Complex Formation. With V(V) in excess, an additional reaction step was observed in the form of an absorbance increase. The initial absorbance decreases were similar to those described above but could not be evaluated quantitatively. The absorbance increase, although slower, was of much greater magnitude so that only a small amount of reaction was sufficient to interfere with the initial steps. The absorbance increase, but not the decreases, also occurred at the same rate when a solution of V(V) was mixed with an equimolar mixture of Ti(IV) and V(IV) (generated from Ti(III) and V(V) immediately before use to eliminate possible irreversible hydrolysis or polymerization of Ti(IV)²⁷). Since such changes are not observed on mixing V(V) with

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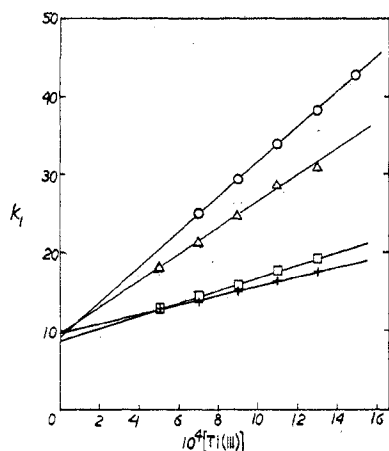


Figure 1. Plots of k_1 vs. $[Ti(III)]$ showing conformance to eq 2: \circ , 0.050 M H^+ ; Δ , 0.10 M H^+ ; \square , 0.20 M H^+ ; $+$, 0.30 M H^+ . Lines were calculated from the best computer fit to eq 2.

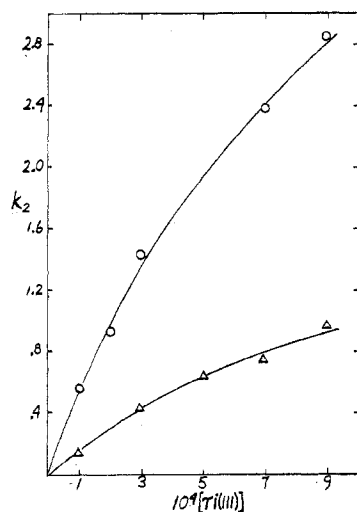


Figure 2. Plots of k_2 vs. $[Ti(III)]$, showing conformance to eq 4: \circ , 0.13 M H^+ ; Δ , 0.20 M H^+ . Lines were calculated from the best computer fit to eq 4.

V(IV), the absorbance increase was attributed to the formation of a V(V)-Ti(IV) binuclear complex whose exact composition with respect to oxo, hydroxo, or chloro groups is not known. Attempts to measure the formation constant were made with 5×10^{-4} M Ti(IV), 5×10^{-4} – 4×10^{-3} M V(V), 0.25 M H^+ , and 0.50 M Cl^- using a spectrophotometric technique. Under the conditions studied, complexation was essentially complete, yielding an estimate for the formation constant of $\geq 10^5$ M. The kinetics of this reaction were studied briefly at 25.0° and 0.500 M ionic strength over the concentration ranges 5×10^{-5} M Ti(IV) and V(IV), $(2-11) \times 10^{-4}$ M V(V), 0.040–0.40 M H^+ , and 0.050–0.50 M Cl^- . Each experiment followed good pseudo-first-order kinetics for $\geq 90\%$ reaction according to the equation

$$-d[Ti(IV)]/dt = k_3[Ti(IV)][V(V)] \quad (5)$$

At 0.050 M H^+ , with $10^4[V(V)] = 2, 4, 5, 7, 9$, and 11, $k_3 = 565, 552, 518, 544, 533$, and 555 (average 545 ± 13 $M^{-1} \text{sec}^{-1}$), in conformance with eq 5. The value of k_3 was found to vary only with $[H^+]$ (Table IV), according to the equation

$$k_3 = f + g[H^+] + h[H^+]^2 \quad (6)$$

A nonlinear least-squares computer fit²⁶ to this equation

Table I. Rate Constants for the First Step in the Reaction of V(V) with Ti(III) at 25.0° and 0.50 M Ionic Strength

$[H^+], M$	k_1, sec^{-1}		$10^{-3}k_1, M^{-1} \text{sec}^{-1}$	
	Eq 2 ^a	Eq 2, 3 ^b	Eq 2 ^a	Eq 2, 3 ^b
0.050	9.36 ± 0.17	9.09 ± 0.76	22.2 ± 0.2	23.4
0.100	9.80 ± 0.55	9.09 ± 0.76	16.5 ± 0.6	15.1
0.200	8.78 ± 0.20	9.09 ± 0.76	7.90 ± 0.24	8.83
0.300	9.70 ± 0.18	9.09 ± 0.76	5.97 ± 0.20	6.24

^a From the fit of data at each $[H^+]$ individually to eq 2. ^b From the fit of data at all $[H^+]$ simultaneously to eq 2 and 3.

Table II. Values of the Rate Constants k_2 for the Second Step in the Reaction of V(V) with Ti(III) at 25.0° and 0.50 M Ionic Strength

$[H^+], M$	$10^4[Ti(III)], M$	k_2, sec^{-1}	
		Obsd	Calcd ^a
0.05	1.03	2.39	2.37
	2.98	4.81	4.90
	5.03	6.40	6.36
	6.98	7.14	7.23
	9.03	8.00	7.87
0.10	1.03	1.50	1.33
	2.98	3.09	3.07
	5.03	3.36	4.29
	6.98	5.92	5.10
	9.03	6.30	5.75
0.13	10.98	6.54	6.23
	1.03	0.564	0.544
	2.05	0.924	0.994
	2.98	1.43	1.35
	6.98	2.37	2.43
0.20	9.03	2.88	2.82
	1.03	0.171	0.171
	2.98	0.436	0.429
	5.03	0.642	0.635
	6.98	0.734	0.790
0.30	9.03	0.979	0.921
	0.974	0.107	0.111
	1.03	0.115	0.117
	2.02	0.210	0.216
	2.98	0.330	0.302
	5.02	0.495	0.456
	6.98	0.598	0.577
	9.03	0.630	0.683

^a Calculated from eq 4 and the values of the parameters given in Table III.

Table III. Rate Parameters for the Second Step in the Reaction of V(V) with Ti(III) at 25.0° and 0.50 M Ionic Strength

$[H^+], M$	$10^{-3}b, M^{-1} \text{sec}^{-1}$	$b[H^+]^2, M \text{sec}^{-1}$	K, M^{-1}	$K_{\text{calcd}}^a, M^{-1}$
0.050	29.3 ± 0.7	73	2610 ± 121	2570 ± 385
0.100	14.9 ± 3.1	149	1480 ± 68	1660 ± 249
0.130	5.79 ± 0.35	98	946 ± 189	1370 ± 205
0.200	1.81 ± 0.11	72	854 ± 174	972 ± 145
0.300	1.22 ± 0.06	110	676 ± 149	687 ± 102
Av 100 ± 23				

^a $K_{\text{calcd}} = k_2/k_1$ calculated from the fit of data from the first step to eq 2 and 3.

Table IV. Rate Constants for Binuclear Complex Formation between V(V) and Ti(IV) at 25.0° and 0.50 M Ionic Strength

$[H^+], M$	$k_3, M^{-1} \text{sec}^{-1}$		$[H^+], M$	$k_3, M^{-1} \text{sec}^{-1}$	
	Obsd	Calcd ^a		Obsd	Calcd ^a
0.040	483	493	0.200	1470	1500
0.050	545	523	0.300	2630	2700
0.075	665	619	0.350	3510	3460
0.090	687	689	0.400	4430	4330
0.100	731	741			

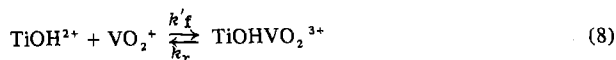
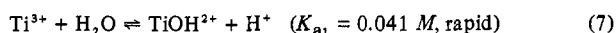
^a Calculated from eq 6 and the values of the parameters given in the text.

yielded values of the parameters: $f = 414 \pm 30 M^{-1} \text{ sec}^{-1}$, $g = 1110 \pm 450 M^{-2} \text{ sec}^{-1}$, and $h = 21,700 \pm 1640 M^{-3} \text{ sec}^{-1}$. The large uncertainty in g in spite of the good agreement between the observed and calculated values of k_3 is not unreasonable since this term never contributes more than *ca.* 15% to the total rate.

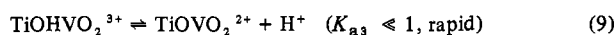
Discussion

A mechanism which will explain all of the observations on the oxidation-reduction reaction with excess Ti(III) is given in eq 7-10.

first step



second step



If the first step is considered to be an approach to equilibrium in a reversible reaction (eq 8) preceded by a rapid acid hydrolysis equilibrium (eq 7), the predicted rate law for the first step is

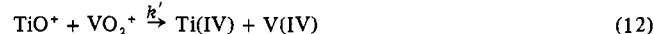
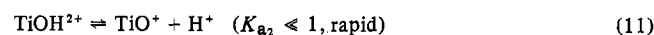
$$k_1 = k_r + k_f'K_{a1}[\text{Ti(III)}](K_{a1} + [\text{H}^+])^{-1}$$

in conformance with the observed rate law for the first step (eq 2 and 3). For the second step, the first step (eq 7, 8) must have reached a state of equilibrium and the acid hydrolysis (eq 9) must be rapid and in a state of equilibrium. Since the first step is at least tenfold more rapid than the second step, these criteria are apparently met. Then the rate law for the second step which is predicted by this mechanism is given by

$$k_2 = kK_{a1}K_{a3}k_f'k_r^{-1}(K_{a1}[\text{H}^+] + [\text{H}^+]^2)^{-1}[\text{Ti(III)}](1 + K[\text{Ti(III)}])^{-1}$$

equivalent to eq 4, with $K = k_f'K_{a1}k_r^{-1}(K_{a1} + [\text{H}^+])^{-1}$, which is of the form required by a rate-determining step preceded by an equilibrium step with equilibrium constant of intermediate size. It was noted earlier that the $[\text{H}^+]$ dependence of the parameter b in eq 4 could not be determined exactly because of experimental scatter but could be either $c[\text{H}^+]^{-2}$ or $d(e[\text{H}^+] + [\text{H}^+]^2)^{-1}$. The latter form, demanded by the above mechanism, has $e = K_{a1} = 0.041 M$ and $d = kK_{a3}K_{a1}k_f'k_r^{-1}$ with $kK_{a3} = b[\text{H}^+]/K$ then having the value $0.58 \pm 0.12 M \text{ sec}^{-1}$. The above mechanism suggests that the species TiOHVO_2^{3+} is an intermediate in the reaction.

An alternate mechanism, which does not require this and which is equally consistent with the rate data, would involve the replacement of eq 9 and 10 by eq 11 and 12, with the



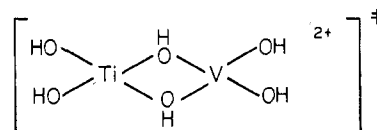
only difference in the rate laws being $d = k'K_{a1}K_{a2}$.

Several aspects of these mechanisms need to be examined carefully. The interpretation of the $[\text{H}^+]$ dependence for the first step requires a value for the Ti^{3+} acid dissociation constant of $0.041 \pm 0.012 M$. An independently measured value¹⁸ of K_{a1} in 0.50 M KBr solution is 0.012 or 0.015 M, depending on the activity coefficients used²⁸ (*i.e.*, for KBr or LiCl solution). Considering the differences which might

arise from the change in ionic medium, especially in the change from K^+ to Li^+ , the value of K_{a1} determined here is probably in reasonably good agreement with that measured independently. The direction of the deviation is consistent with differences in the value of K_{a1} in KI and KBr solutions.¹⁸ A further possible source of deviation is the possibility of slight complexation of Ti^{3+} by Cl^- ,^{14,18,29} although in each check of a possible $[\text{Cl}^-]$ effect on rate made here as well as in the reactions of Ti^{3+} with HCrO_4^- ,⁵ UO_2^{2+} ,¹⁵ and $\text{Co}(\text{NH}_3)_5\text{N}_3^{2+}$,¹³ no effect was observed as long as reaction times were short enough to preclude reduction of ClO_4^- . This is in agreement with the Cl^- complexation constant which is estimated to be quite small at 25°.^{14,29}

A number of other kinetic studies of the oxidation of Ti(III) have established TiOH^{2+} to be a reactive species but have involved simple inverse dependences on $[\text{H}^+]$.^{6,7,9-12} These results are consistent with the present value of K_{a1} since the $[\text{H}^+]$ range in the systems which have been published in detail was not sufficiently low to pick up a major contribution from K_{a1} .

A second point to be considered is the loss of the second proton, as in eq 9 or 11, prior to the rate-determining step (eq 10 or 12). It is not unusual for metal ions to lose H^+ prior to electron transfer; *e.g.*, VOH^{2+} is the reactive species in many V(III) reductions, and TiOH^{2+} is a reactive species in the reduction of I_2 ,^{6,7} Hg^{2+} ,⁹ Pu^{4+} ,¹¹ and PuO_2^{2+} .¹⁰ However, it is difficult to understand the loss of the second proton by Ti(III). It is generally true that if a metal ion is going to lose protons on oxidation it will lose one or more before it is oxidized. In a reaction such as the present however, assuming TiO^{2+} to be the predominant Ti(IV) species, there should presumably be offsetting loss of H^+ by Ti(III) and gain of H^+ by V(V) prior to electron transfer. Unfortunately, there is still considerable uncertainty about the predominant forms of Ti(IV) in acidic aqueous solution. Various studies³⁰ have yielded widely disparate results, with values of protonation constants differing by as much as two orders of magnitude. Evidence has been advanced³⁰ for the species in perchlorate solutions: TiOH^{3+} , $\text{Ti}(\text{OH})_2^{2+}$ (or TiO^{2+}), $\text{Ti}(\text{OH})_3^+$, and $\text{Ti}(\text{OH})_4$ (or TiO_2), any one of which might be the initial product of oxidation of Ti(III). If the initial product were $\text{TiO}_2(\text{aq})$, the observed $[\text{H}^+]$ dependence might be explicable in terms of the attainment of a symmetric transition state $[\text{O-Ti-O-V-O}^{2+}]^\ddagger$, which is frequently a configuration favorable to electron transfer. However, such arguments assume knowledge of the structures of Ti(IV) and V(V) as oxo ions rather than, *e.g.*, tetrahedrally coordinated hydroxy complexes. If the latter situation obtains for both metal ions, an alternate formulation for a symmetric transition state can also be made as



ignoring possible solvent participation. The origin of either sort of transition state formulated in this manner would presumably be related to the transfer of oxy or hydroxy groups during electron transfer to accomplish the necessary configurational changes. The kinetic data unfortunately provide no information regarding the possible role of the binuclear complex TiOHVO_2^{3+} as a reaction intermediate

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and so do not distinguish between inner-sphere and outer-sphere mechanisms. The rate of water exchange on Ti(III) is sufficiently large³¹ that the inner-sphere mechanism cannot be excluded on the basis of arguments related to the rate of substitution. At any rate, such arguments have been shown to be insufficient for V(V) and Cr(VI) oxidations.¹⁻³

With regard to $[H^+]$ dependence, it is of interest to compare the Ti(III)-V(V) reaction to the V(III)-V(V) reaction. The major paths for the latter reaction have orders of -1 and -2 in $[H^+]$,³² in spite of the fact that overall no H^+ is consumed or released. Apparently the configurational changes accompanying electron transfer are not the sole factors determining the $[H^+]$ dependence. In other respects there is apparently little similarity between the two reactions. No evidence was found for binuclear complex formation between V(III) and V(V), although arguments were advanced for an inner-sphere configuration of the transition state.³²

Titanium(IV) appears to have particular tendency to form binuclear complexes. Complexes are known with titanium(III)-³³ and cobalt(III)-ammine complexes¹² in SO_4^{2-} media, Ti(IV) has been reported to polymerize,²⁷ and we have observed complexation with V(V) and Cr(VI).⁵ Considering the uncertainty in the formulation of Ti(IV) in solu-

tion as well as in that of the Ti(IV)-V(V) binuclear complex observed here, it would be presumptive to attempt to identify the reactions corresponding to each of the terms in the complexation rate law (eq 5, 6). These terms may well correspond to reactions with Ti(IV) (and/or V(V)) in different states of protonation, in which case some information could be surmised regarding the existence of such species and the magnitude of the equilibrium constants relating their concentrations. It is interesting that the formation of a complex between Ti(IV) and H_2O_2 ³⁴ follows a rate law of the same form as eq 5 and 6. The similarity extends to the magnitude of the rate constants as well, in particular that of the acid-independent term f , which has a value of $414 M^{-1} sec^{-1}$ for V(V) and of $120 M^{-1} sec^{-1}$ for H_2O_2 in perchlorate solutions of 3.0 M ionic strength.³⁴ Whether these similarities have any mechanistic significance must await further kinetic studies of complexation reactions of Ti(IV).

Registry No. Vanadium, 7440-62-2; titanium, 7440-32-6.

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Complex Fluoro Anions in Solution. I. Homo- and Heteropolyfluoro Anions of Niobium and Tantalum

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The compounds (TBA)MNF₁₁, where TBA is tetra-*n*-butylammonium, M is tantalum or niobium, and N is tantalum, niobium, or antimony, have been prepared in solution and characterized by their fluorine resonance spectra. A comparison is made between these compounds and the corresponding ones where M and N are arsenic and antimony.

Introduction

Fluorine bridging between atoms of a transition metal in its binary fluoride or as a complex fluoro anion has been well documented by X-ray diffraction studies of crystalline compounds.¹ In solution most of the evidence for fluorine bridging is obtained from fluorine magnetic resonance spectroscopy. It has been demonstrated for antimony pentafluoride² and the anions $Sb_nF_{5n+1}^-$,³ $As_2F_{11}^-$,^{4,5} $AsSbF_{11}^-$,⁵ and $B_2F_7^-$ ⁶ that it is possible to obtain information about the structure of the fluorine-bridged entity provided that

fluorine exchange is not too rapid on the nuclear magnetic resonance time scale. Since fluorine bridging has been observed in the solid fluorides of niobium and tantalum, there appeared to be a distinct possibility that complex fluoro anions could be found for these elements as with $As_2F_{11}^-$ and $Sb_2F_{11}^-$. This has been realized, and details of the fluorine magnetic resonance spectra are presented. TBA will be used as an abbreviation for the tetra-*n*-butylammonium ion.

Experimental Section

All sample preparation and handling was done with standard vacuum-line techniques or by using a vacuum drybox. Solvent purification and storage were accomplished as previously described.⁵ At no time was any evidence found for hydrolysis of these sensitive compounds. Fluorine resonance spectra were obtained on a Varian Associates HA 100 spectrometer operating at 94.1 MHz. Some spectra were also obtained at 25.1 MHz to distinguish with certainty between chemical shift or spin-coupling origin for certain line splittings. Chemical shifts are reported as ppm from internal $CFCl_3$. Infrared spectra of the compounds dispersed in potassium

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