HPLC chromatogram has thus been assigned to $RSSO_3H$.

On the basis of eq 2-5, the calculated yields of RSO_3H, $RSSO_3H$, and unhydrolyzed $(H_2O)_5Cr(SO_2)R^{2+}$ are 40%, 40%, and 20%, respectively. The satisfactory agreement between the observed (25-45%) and calculated (~40%) yields of both RSO_3H and $RSSO_3H$ and, in particular, the formation of comparable amounts of the two products strongly support the proposed mechanism.

We assign the formula $(H_2O)_5Cr(SO_2)R^{2+}$ to the green species produced in 20 ± 10% yield in the reaction of $(H_2O)_5CrR^{2+}$ with SO_2. The visible spectra of these complexes show only low-intensity bands typical of inorganic complexes of chromium(III). The UV region indicates the presence of bound SO_2 (the band at 260 nm) and the alkyl group (strong absorption for R = benzyl). Base hydrolysis at pH 10 of the ion-exchanged complex formed in the reaction of SO_2 with the 2-propylchromium yields 2-propanesulfonic acid, probably by the sequence of reactions 6, 3,

$$(H_2O)_5Cr(SO_2)CH(CH_3)_2^{2+} \xrightarrow{H_2O} (H_2O)_6Cr^{3+} + (CH_3)_2CHSO_2^- \quad (6)$$

and 4. As expected, the decomposition of 2-propanesulfinic acid in the absence of SO_2/HSO_3^- yielded no $(CH_3)_2CHSSO_3H$. The concentrations were too low, however, to attempt the identification of $(CH_3)_2CHSSO_2CH(CH_3)_2$ by NMR.

Reaction according to eq 2 gives rise to two distinctly different chromium(III) products, $Cr(H_2O)_6^{3+}$ and the insertion product, $(H_2O)_5Cr(SO_2)R^{2+}$. The relative amounts of the two are apparently determined by the competition between a molecule of solvent and the nucleophilic site on the leaving ligand for the coordination site on the metal center. A similar situation occurs in the reactions of several functionalized alkylchromium complexes with Hg^{2+}.[21] In the alternative scheme[1] the transition state collapses to the contact ion pair $\{(H_2O)_5Cr^{3+}, RSO_2^-\}$. The recombination of the fragments within the ion pair to yield the Cr-O or Cr-S product and their escape into the solvent are then responsible for the formation of the two products.

The insertion of SO_2 into the metal-carbon bonds by electrophilic substitution often yields the O-bonded product, which subsequently isomerizes. The data available in the present case are insufficient to distinguish between the O- and S-bonded species. If the initial product is indeed O-bonded, the isomerization might not take place, given the hard/soft properties of the pentaaquochromium(III) entity, sulfur, and oxygen. On the other hand, the isomerization to the S-bonded isomers has been observed for a number of related cobalt(III) and chromium(III) complexes of the type $L_5MOSO_2^+$.[22-24]

Acknowledgment. This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Chemical Sciences Division, under Contract W-7405-Eng-82.

Registry No. $(H_2O)_5CrCH_3^{2+}$, 32108-96-6; $(H_2O)_5CrC_2H_5^{2+}$, 52653-39-1; $(H_2O)_5Cr$-*n*-$C_3H_7^{2+}$, 52653-40-4; $(H_2O)_5Cr$-*i*-$C_3H_7^{2+}$, 60764-48-9; $(H_2O)_5Cr$-c-$C_5H_9^{2+}$, 84559-49-9; $(H_2O)_5CrCH_2OH^{2+}$, 32108-95-5; $(H_2O)_5CrCH_2OCH_3^{2+}$, 78402-17-2; $(H_2O)_5CrCH_2CH_2CN^{2+}$, 76068-69-4; $(H_2O)_5CrCH_2Cl^{2+}$, 17477-09-7; $(H_2O)_5CrCH_2C_6H_4$-*p*-OCH_3, 71605-13-5; $(H_2O)_5CrCH_2C_6H_4$-*p*-CH_3, 53150-36-0; $(H_2O)_5CrCH_2Ph^{2+}$, 34788-74-4; $(H_2O)_5CrCH_2C_6H_4$-*p*-Br, 53150-37-1; $(H_2O)_5CrCH_2C_6H_4$-*p*-CF_3^{2+}, 53150-38-2; $(H_2O)_5CrCH_2C_6(CH_3)_5^{2+}$, 110903-70-3; $(H_2O)_5CrCH_2C_6H_2$-2,4,6-$(CH_3)_3^{2+}$, 110903-71-4; $(H_2O)_5Cr(SO_2)C_2H_5^{2+}$, 110934-38-8; $(H_2O)_5Cr(SO_2)$-*i*-$C_3H_7^{2+}$, 110934-39-9; $(H_2O)_5Cr(SO_2)CH_2OCH_3^{2+}$, 110934-40-2; $(H_2O)_5Cr(SO_2)CH_2Ph^{2+}$, 110934-41-3; CH_3SO_3H, 75-75-2; $C_2H_5SO_3H$, 594-45-6; *n*-$C_3H_7SO_3H$, 5284-66-2; *i*-$C_3H_7SO_3H$, 14159-48-9; c-$C_5H_9SO_3H$, 19247-73-5; $HOCH_2SO_3H$, 75-92-3; $CH_3OCH_2SO_3H$, 110874-69-6; $NCCH_2CH_2SO_3H$, 107-67-5; $ClCH_2SO_3H$, 40104-07-2; CH_3O-*p*-$C_6H_4CH_2SO_3H$, 110874-70-9; CH_3-*p*-$C_6H_4CH_2SO_3H$, 110874-71-0; $C_6H_5CH_2SO_3H$, 100-87-8; Br-*p*-$C_6H_4CH_2SO_3H$, 110874-72-1; CF_3-*p*-$C_6H_4CH_2SO_3H$, 110874-73-2; $(CH_3)_5C_6CH_2SO_3H$, 110874-74-3; 2,4,6-$(CH_3)_3C_6H_2CH_2SO_3H$, 4496-98-4; $Cr(H_2O)_6^{3+}$, 14873-01-9; SO_2, 7446-09-5.

---

(21) Kita, P.; Jordan, R. B. *Inorg. Chem.* **1986**, *25*, 4791.

(22) Van Eldik, R. *Inorg. Chim. Acta* **1980**, *42*, 49.

(23) Moritzen, P. A.; El-Awady, A. A.; Harris, G. M. *Inorg. Chem.* **1985**, *24*, 313.

(24) Dash, A. C.; El-Awady, A. A.; Harris, G. M. *Inorg. Chem.* **1981**, *20*, 3160.

Contribution from the Rudjer Bosković Institute, 41000 Zagreb, Croatia, Yugoslavia,
and Ames Laboratory and Department of Chemistry, Iowa State University, Ames, Iowa 50011

Reduction of Titanium(IV) and Oxidation of Titanium(III) by 1-Hydroxy-1-methylethyl Radicals

Andreja Bakac,*[1a] James H. Espenson,*[1a] Jasna Lovrič,[1b] and Matko Orhanovič*[1b]

Received June 10, 1987

Kinetic competition between TiO^{2+} and $Co(NH_3)_6^{3+}$ was used to study the reduction of titanium(IV) by the indicated aliphatic radical. The second-order rate constant is $(1.1 \pm 0.1) \times 10^6$ M^{-1} s^{-1} at 25 °C and 1.0 M ionic strength in aqueous 1 M 2-propanol. The rate constant is independent of $[H^+]$ over the range 0.03-0.08 M. The method of "stored free radicals", based on the homolysis of $CrC(CH_3)_2OH^{2+}$, was used to study the oxidation of titanium(III) by the same radical. The apparent second-order rate constant increases markedly with decreasing $[H^+]$. The inverse $[H^+]$ dependence, unprecedented for oxidations by this radical, suggests that a transient intermediate is stabilized by the incipient formation of titanium(IV) already partly deprotonated, thus assisting in the formation of the species TiO^{2+}. Schemes by which this can be accomplished are suggested.

Introduction

Reactions in which aliphatic radicals reduce and oxidize transition-metal aquo cations proceed by a diversity of mechanisms. Reduction reactions appear to occur by "simple" electron transfer, with metal-carbon bond formation known but rare.[2] The mechanisms for oxidation include, for example, metal-carbon bond formation (eq 1) and hydrogen atom abstraction from a coordinated water molecule (eq 2). The intervention of an organometallic intermediate has been verified for Cr^{2+} [3-5] and Cu^+,[6,7]

$$M(H_2O)_n^{x+} + {}^\bullet R \rightarrow \{(H_2O)_m M\text{-}R^{x+}\} \xrightarrow{H_3O^+} M(H_2O)_n^{x+1} + RH \quad (1)$$

$$M(H_2O)_n^{x+} + {}^\bullet R \rightarrow (H_2O)_m M\text{-}OH^{x+} + RH \quad (2)$$

---

[1] (a) Iowa State University. (b) Rudjer Bosković Institute.

[2] (a) Elroi, H.; Meyerstein, D. *J. Am. Chem. Soc.* **1978**, *100*, 5540. (b) Mulac, W. A.; Meyerstein, D. *J. Am. Chem. Soc.* **1982**, *100*, 4124.

whereas strong circumstantial evidence points to hydrogen atom abstraction for $V(H_2O)_6^{2+}$[8] and Eu_{aq}^{2+}.[9] Kinetic data for these and other ions have recently been summarized.[10,11]

The situation for titanium(III) is ambiguous at present, in part because data are so scarce.[12–14] The mechanism for titanium(III) oxidation should be of additional interest, because (unlike the case for other metal ions studied) one-electron oxidation yields the oxo cation TiO^{2+}, not a simple hydrated ion.[15,16] Thus protons may play an unusual role in the activated complex. The earlier investigations[12–14] of reactions between Ti(III) and aliphatic radicals were conducted at high and constant [H^+], providing no data on this point.

Oxidation of $Ti(H_2O)_6^{3+}$ by the radicals investigated occurs so slowly that methods based on the production of a "burst" of radicals are, at best, marginal. To circumvent these limitations, we adopted the "stored free radical" method,[8–9,17–19] based on the production of the free radical by homolysis of an organochromium(2+) cation. The oxidation of $Ti(H_2O)_6^{3+}$ by $^{\bullet}C(CH_3)_2OH$, eq 3, was investigated with particular emphasis on the kinetic dependences on [Ti(III)] and [H^+].

$$Ti(H_2O)_6^{3+} + {}^{\bullet}C(CH_3)_2OH = (H_2O)_5TiO^{2+} + (CH_3)_2CHOH + H^+ \quad (3)$$

Closely related to this chemistry is the reduction of titanium(IV) by the same radical, eq 4. The source of the radical is again

$$TiO_{aq}^{2+} + {}^{\bullet}C(CH_3)_2OH + H^+ = Ti(H_2O)_6^{3+} + (CH_3)_2CO \quad (4)$$

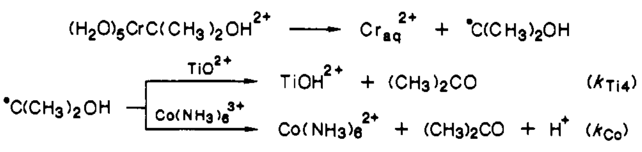
$CrC(CH_3)_2OH^{2+}$, but now the other reactions require that the rate constants be evaluated by kinetic competition methods.

Experimental Section

Materials. A stock solution of titanium(IV) was prepared by dissolving $TiOSO_4$ (Merck analytical grade) in 0.5 M HCl and standardized spectrophotometrically at 410 nm by using the H_2O_2 method.[20]

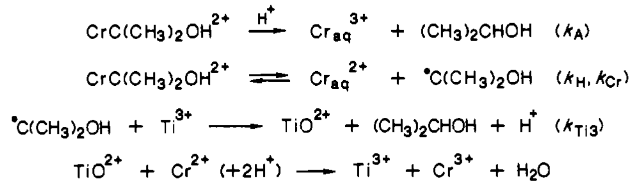
A stock solution of titanium(III) in chloride medium was prepared by dissolving titanium metal (Alfa Inorganic m3N+ Sponge) in ~3.3 M HCl at 30–40 °C under anaerobic conditions.[21] It was filtered, divided into portions, and stored in a freezer. Several preparation attempts were made to obtain a solution containing a negligible amount of titanium(IV) (~0.07%) and a favorable ratio of titanium(III) and H^+ concentrations (0.97 and 0.37 M, respectively). A given Ti(III) stock solution was discarded when its Ti(IV) content exceeded 0.1% as assessed spectrophotometrically. The titanium(III) concentration was determined spectrophotometrically in 1 M HCl at 502 nm (ϵ = 3.9 M^{-1} cm^{-1}), and the amount of Ti(IV) checked at 310 nm ($\epsilon_{Ti(III)}$ = 0.3 M^{-1} cm^{-1}, $\epsilon_{Ti(IV)}$ = 15.2 M^{-1} cm^{-1}).[22]

Scheme I



$$(H_2O)_5CrC(CH_3)_2OH^{2+} \longrightarrow Cr_{aq}^{2+} + {}^{\bullet}C(CH_3)_2OH$$
$${}^{\bullet}C(CH_3)_2OH \xrightarrow{TiO^{2+}} TiOH^{2+} + (CH_3)_2CO \quad (k_{Ti4})$$
$${}^{\bullet}C(CH_3)_2OH \xrightarrow{Co(NH_3)_6^{3+}} Co(NH_3)_6^{2+} + (CH_3)_2CO + H^+ \quad (k_{Co})$$

Scheme II



$$CrC(CH_3)_2OH^{2+} \xrightarrow{H^+} Cr_{aq}^{3+} + (CH_3)_2CHOH \quad (k_A)$$
$$CrC(CH_3)_2OH^{2+} \rightleftharpoons Cr_{aq}^{2+} + {}^{\bullet}C(CH_3)_2OH \quad (k_H, k_{Cr})$$
$${}^{\bullet}C(CH_3)_2OH + Ti^{3+} \longrightarrow TiO^{2+} + (CH_3)_2CHOH + H^+ \quad (k_{Ti3})$$
$$TiO^{2+} + Cr^{2+} (+2H^+) \longrightarrow Ti^{3+} + Cr^{3+} + H_2O$$

Lithium chloride (Merck analytical grade) was recrystallized two times from water. The same stock solution of lithium perchlorate as in a previous study was used.[23] All other chemicals used were of analytical grade. Redistilled water was used throughout. Oxygen-sensitive materials were handled under an oxygen-free argon atmosphere by syringe–septa methods.

The organochromium complex $(H_2O)_5CrC(CH_3)_2OH^{2+}$, which is the source of the radical, was prepared as described earlier[24] by the reaction between $Cr(H_2O)_6^{2+}$ and H_2O_2 in acidic solution containing 1 M 2-propanol. The alcohol was distilled as needed, at least weekly. Solutions of Cr^{2+} were prepared by zinc amalgam reduction of $Cr(H_2O)_6^{3+}$ under argon.

Techniques. The kinetics of the oxidation of titanium(III) by $^{\bullet}C(CH_3)_2OH$ were followed spectrophotometrically with a Cary 219 instrument at an absorption maximum for $CrC(CH_3)_2OH^{2+}$, λ = 311 nm (ϵ = 2500 M^{-1} cm^{-1}), as described previously.[23] The reaction followed pseudo-first-order kinetics, since both reactants competing for the radicals, Cr^{2+} and Ti(III), were present in substantially higher concentrations over that of the organochromium cation.

The rate constant for the reduction of titanium(IV) by $^{\bullet}C(CH_3)_2OH$ was determined by analysis of the cobalt(II) produced after allowing a mixture of $Co(NH_3)_6^{3+}$ and Ti(IV) to compete for the radicals. The Co^{2+} was determined by the thiocyanate method,[25] both for competing runs and blanks. The latter involved reaction with $Co(NH_3)_6^{3+}$ only.

Results

Reduction of Ti(IV). The fast reaction between TiO^{2+} and Cr^{2+} required the use of a method based on the analysis of the amounts of products formed in competitive reactions. The reaction between $Co(NH_3)_6^{3+}$ and $^{\bullet}C(CH_3)_2OH$, known from earlier work,[26] proved to be a useful calibration reaction, since it is otherwise uninvolved chemically. The reactions proceed as shown in Scheme I. After each experiment, a quantitative analysis was performed for $Co(H_2O)_6^{2+}$; note that Cr^{2+} and $Co(NH_3)_6^{3+}$ react so slowly that this reaction need not be included in the data analysis. This concentration, $[Co(II)]_r$, is less than that in a corresponding blank experiment with titanium(IV) absent, $[Co(II)]_b$.

The expression in eq 5 allows the calculation of k_{Ti4} in each experiment, since other values are known. (At 1.0 M ionic

$$\frac{k_{Ti4}[TiO^{2+}]}{k_{Co}[Co(NH_3)_6^{3+}]} = \frac{[Co(II)]_b - [Co(II)]_r}{[Co(II)]_r} \quad (5)$$

strength $k_{Co} = 4.1 \times 10^5$ M^{-1} s^{-1} at 25.0 °C.)[26] The data obtained are presented in Table I. The average value of k_{Ti4} is $(1.1 \pm 0.1) \times 10^6$ M^{-1} s^{-1} at 25.0 °C and 1.0 M ionic strength. This rate constant is independent of [H^+] over the concentration range 0.030–0.80 M.

Oxidation of Ti^{3+}. The reaction rate was determined by measuring the effect of Ti^{3+} on the decomposition of $CrC(CH_3)_2OH^{2+}$. The chemical reactions involved are presented in Scheme II, in which any [H^+] dependences are for the moment ignored. The reaction between Ti(IV) and Cr(II) occurs rapidly

---

(3) Cohen, H.; Meyerstein, D. *Inorg. Chem.* **1974**, *13*, 2434.

(4) Espenson, J. H. *Adv. Inorg. Bioinorg. React. Mech.* **1983**, *1*, 1–69.

(5) Blau, R. J.; Espenson, J. H.; Bakac, A. *Inorg. Chem.* **1984**, *23*, 3526.

(6) Buxton, G. V.; Green, J. C. *J. Chem. Soc., Faraday Trans. 1* **1978**, *74*, 697.

(7) Freiberg, M.; Mulac, W. A.; Schmidt, K. H.; Meyerstein, D. *J. Chem. Soc., Faraday Trans. 1* **1980**, *76*, 1838.

(8) Chen, J.-T.; Espenson, J. H. *Inorg. Chem.* **1983**, *22*, 1651.

(9) Muralidharan, S.; Espenson, J. H. *Inorg. Chem.* **1984**, *23*, 636.

(10) Ross, A. B.; Neta, P. *Natl. Stand. Ref. Data Ser.* (*U.S. Natl. Bur. Stand.*) **1982**, *NSRDS-NBS70*.

(11) Landolt-Börnstein. *Physical and Chemical Tables*; Springer-Verlag: West Berlin, 1984; New Series II, Vol. 13B.

(12) Behar, D.; Samuni, A.; Fessenden, R. W. *J. Phys. Chem.* **1973**, *77*, 2055.

(13) Micic, O. I.; Menadovic, M. T. *J. Chem. Soc., Dalton Trans.* **1979**, 2011.

(14) Ellis, J. D.; Green, M.; Sykes, A. G.; Buxton, G. V.; Sellers, R. M. *J. Chem. Soc., Dalton Trans.* **1973**, 1724.

(15) Orhanović, M.; Earley, J. E. *Inorg. Chem.* **1975**, *14*, 1478.

(16) (a) Ellis, J. D.; Thomson, G. A. K.; Sykes, A. G. *Inorg. Chem.* **1976**, *15*, 3172. (b) Grätzel, M.; Rotzinger, F. P. *Inorg. Chem.* **1985**, *24*, 2320. (c) Comba, P.; Merbach, A. *Inorg. Chem.* **1987**, *26*, 1315.

(17) Shimura, M.; Espenson, J. H. *Inorg. Chem.* **1983**, *22*, 334.

(18) Bakac, A.; Butković, V.; Espenson, J. H.; Marcec, R.; Orhanović, M. *Inorg. Chem.* **1986**, *25*, 341.

(19) Espenson, J. H.; Bruhn, S. L.; Bakac, A. *Inorg. Chem.* **1984**, *23*, 3668.

(20) Snell, F. D.; Snell, C. T. *Colorimetric Methods of Analysis*; Van Nostrand: New York, 1953.

(21) Bakac, A.; Orhanović, M. *Inorg. Chim. Acta* 1977, *21*, 173.

(22) Ellis, J. P.; Sykes, A. G. *J. Chem. Soc. Dalton Trans.* 1973, 2553.

(23) Bakac, A.; Butković, V.; Espenson, J. H.; Marcec, R.; Orhanović, M. *Inorg. Chem.* **1986**, *25*, 2562.

(24) Kirker, G. W.; Bakac, A.; Espenson, J. H. *J. Am. Chem. Soc.* **1982**, *104*, 1249.

(25) Kitson, R. F. *Anal. Chem.* **1950**, *22*, 664.

(26) Espenson, J. H.; Shimura, M.; Bakac, A. *Inorg. Chem.* **1982**, *21*, 2537.

Table I. Concentrations and Rate Constants Obtained for the Reductions of TiO^{2+} by 1-Hydroxy-1-methylethyl Radicals at 25 °C and μ = 1.0 M in 1 M 2-Propanol[a]

$10^3Ti(IV)]_0/M$[b]	$10^3[Ti(IV)]_\infty/M$[c]	$10^3[Co(NH_3)_6^{3+}]/M$	$([Co(II)]_b - [Co(II)]_r)/[Co(II)]_r$	$10^{-6}k_{Ti4}/M^{-1}\ s^{-1}$[d]
		$[H^+]$ = 0.80 M		
0.86	0.71	5.19	0.50	1.3
2.50	2.35	10.0	0.79	1.3
1.56	1.40	5.19	0.805	1.2
2.06	1.90	5.19	1.0	1.1
5.47	5.31	10.0	1.5	1.1
		$[H^+]$ = 0.50 M		
1.56	1.50	5.19	0.76	1.1
4.07	3.90	10.0	1.1	1.1
2.88	2.73	54.19	1.3	1.0
3.14	2.98	5.19	1.7	1.2
		$[H^+]$ = 0.10 M		
3.0	2.84	10.0	0.915	1.3
1.95	1.79	5.19	1.05	1.2
4.37	4.22	10.0	1.3	1.2
		$[H^+]$ = 0.060 M		
2.38	2.22	10.0	0.67	1.2
3.6	3.44	10.0	0.83	1.0
1.99	1.83	5.27	0.97	1.1
		$[H^+]$ = 0.030 M		
1.1	0.94	5.27	0.61	1.3
1.62	1.46	5.27	0.79	1.1
1.79	1.63	5.27	1.0	1.3

[a] $[(H_2O)_5CrC(CH_3)_2OH^{2+}]$ = 1.6 × 10^{-4} M. [b] [Ti(IV)] at zero reaction time. [c] [Ti(IV)] at the end of the reaction. [d] Calculated by use of average [Ti(IV)] in each run.

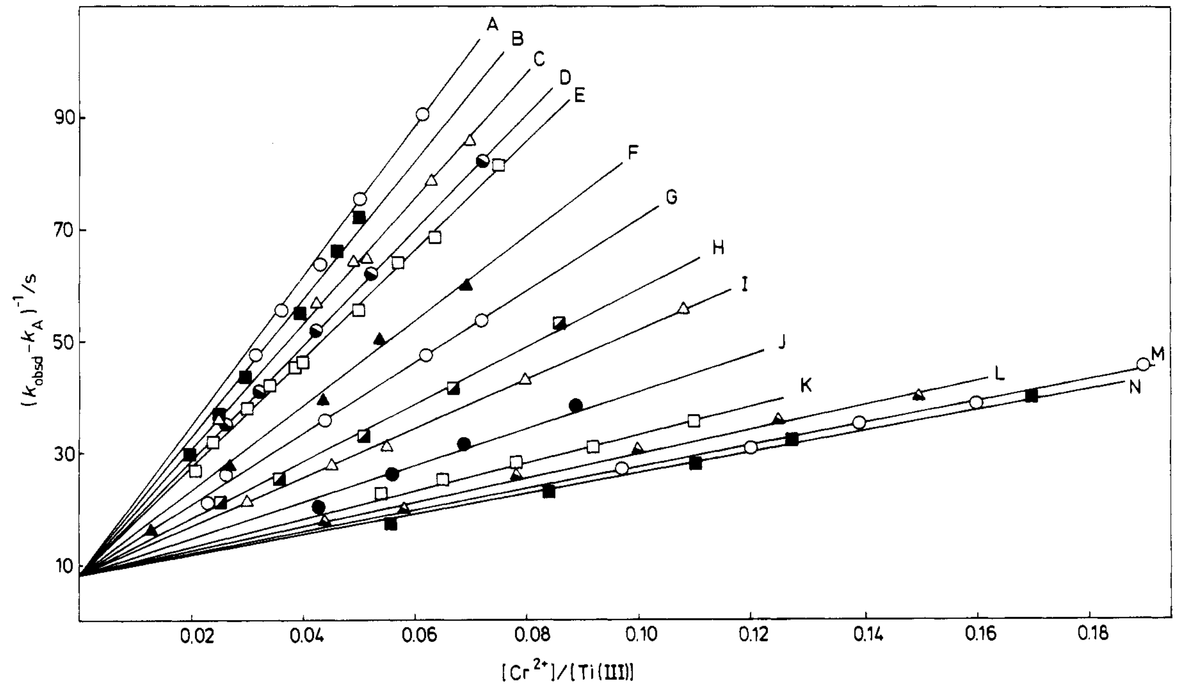


Figure 1. Plot of the kinetic data for the oxidation of Ti^{3+} by $\cdot C(CH_3)_2OH$ according to eq 9. Data are shown in lines A–N for $[H^+]$ = 85, 70, 60, 40, 10, 5.0, 3.2, 1.9, 1.2, 1.0, 0.90, 0.83, 0.72, and 0.60 mM in 0.10 M Cl^- (lines A, C, D, K, and M) and 0.10 M ClO_4^- (lines B, E–J, L, and N).

under these conditions (k = 7.5 × $10^3\ M^{-1}\ s^{-1}$),[16] but it influences only the overall stoichiometry and not the rate.

With the steady-state approximation for the concentration of the free radical, the reaction rate can be expressed as in eq 6.

$$\frac{-d\ln[CrC(CH_3)_2OH^{2+}]}{dt} = k_{obsd} = k_A + \frac{k_H k_{Ti3}[Ti(III)]}{k_{Cr}[Cr^{2+}] + k_{Ti3}[Ti(III)]} \quad (6)$$

Since Ti^{3+} and Cr^{2+} were used at concentrations high compared to that of the organochromium cation, the disappearance of $CrC(CH_3)_2OH^{2+}$ is expected to follow pseudo-first-order kinetics. The value of k_{obsd} is thus a composite quantity, which can be rearranged to eq 7.

$$\frac{1}{k_{obsd} - k_A} = \frac{1}{k_H} + \frac{k_{Cr}}{k_H k_{Ti3}} \frac{[Cr^{2+}]}{[Ti(III)]} \quad (7)$$

The values of the known rate constants are k_A/s^{-1} = 3.31 × 10^{-3} + 4.91 × $10^{-3}[H^+]$,[24] k_H = 0.127 s^{-1},[24] and k_{Cr} = 5.1 × $10^7\ M^{-1}\ s^{-1}$.[2] The data for the oxidation of titanium(III) were analyzed at each acidity according to eq 6 and 7. Figure 1 presents a plot of $(k_{obsd} - k_A)^{-1}$ versus $[Cr^{2+}]/[Ti(III)]$ at each $[H^+]$. The least-squares slopes of the straight lines obtained are summarized

Table II. Kinetic Data for the Oxidation of Titanium(III) Aquo Ions by 1-Hydroxy-1-methylethyl Radicals at 25 °C and $\mu = 0.1$ M ($HClO_4 + LiClO_4$ or $HCl + LiCl$) in 1 M Aqueous 2-Propanol

$10^3[H^+]$/M (added)	$10^3[H^+]_{eq}$/M (calcd[a])	10^{-2} × slope/$s^{b,c}$	$10^{-5}k_{Ti3}$/ $M^{-1}\ s^{-1}$
85[d]	85.3	13.2 ± 0.3	3.05
70[d]	70.2–70.4	11.9 ± 0.4	3.35
60[d]	60.5	11.2 ± 0.1	3.6
40[d]	40.5	10.5 ± 0.2	3.8
10.01	11.0–12.0	9.6 ± 0.1	4.2
5.0	8.85	7.4 ± 0.3	5.4
3.24	5.65	6.3 ± 0.2	6.35
1.93	4.53	4.9 ± 0.2	8.2
1.25	3.08	4.34 ± 0.07	9.3
1.00	2.59	3.28 ± 0.17	12.2
0.90[d]	1.90	2.59 ± 0.06	15.5
0.83	1.86	2.21 ± 0.05	18.2
0.72[d]	1.61	1.93 ± 0.03	20.8
0.60	1.50	1.90 ± 0.09	21.1

[a] Calculated by using $K_a = 7.3 \times 10^{-3}$ M for $Ti(H_2O)_6^{3+}$ at 25 °C and $\mu = 0.1$ M. [b] Uncertainties quoted are standard deviations. [c] The slope of plots of $(k_{obsd} - k_A)^{-1}$ vs $[Cr^{2+}]/[Ti(III)]$. [d] Chloride medium.

in Table II, along with the values of k_{Ti3} calculated from each set of runs at different $[H^+]$.

The effect of using perchlorate versus chloride is negligible, as shown by the data, which include a considerable number of experiments in each medium.

Effects of $[H^+]$. Although the reduction of titanium(IV) was independent of $[H^+]$, the rate of oxidation of titanium(III) increases markedly with decreasing $[H^+]$. To account for this phenomenon, it is first necessary to allow for the increase in $[H^+]$ from its nominal value (i.e., that added as perchloric acid) to the equilibrium value in a given solution. This requires allowance for the acid ionization of $Ti(H_2O)_6^{3+}$, an acid of appreciable strength (eq 8; $K_a = 7.3 \times 10^{-3}$ M at 0.1 M ionic strength), which

$$Ti(H_2O)_6^{3+} = (H_2O)_5TiOH^{2+} + H^+ \quad (K_a) \qquad (8)$$

is present at significant concentration in the reaction solutions. This effect can be quite substantial, especially at low acidity and high Ti(III) concentration. The concentrations so calculated are the values labeled $[H^+]_{eq}$ in Table II.

Interpretation and Discussion

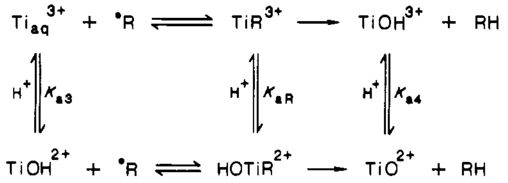
The reduction of titanium(IV) converts TiO^{2+} to Ti^{3+}. This may be accomplished within a single transition state, assisted by proton transfer from the radical accompanying electron transfer, since net proton release accompanies the conversion of $^{\bullet}C(CH_3)_2OH$ to $(CH_3)_2CO$. That point aside, a relatively simple electron-transfer process accounts for the data, and the lack of an appreciable kinetic effect of varying $[H^+]$ is quite consistent with this picture.

On the other hand, the complex effect of $[H^+]$ variation on the rate of Ti^{3+} oxidation signals a much more intricate process. *To our knowledge, this is the only base-catalyzed reduction of this aliphatic radical.* It should be noted, however, that base-catalyzed hydrolyses are known; for example, the heterolytic solvolysis of $[(H_2O)_5CrC(CH_3)_2OH]^{2+}$ has been reported.[27]

Whatever the details, the qualitative interpretation seems clear: the intermediate(s) is (are) stabilized by incipient formation of hydrolyzed products. This is certainly consistent with TiO^{2+} being the predominant titanium(IV) species.[15,16]

Even then, there are two sources for the kinetic effect of $[H^+]$ variation, and they tend to be intermingled (and perhaps confused) in the analysis of the results obtained. One source is the change in rate caused by the shift in the proportions of the species Ti_{aq}^{3+} and $TiOH^{2+}$ by virtue of equilibrium in eq 8; the other, the effect (if any) of varying $[H^+]$ on the kinetic parameters of the mechanism by which the reaction proceeds.

Scheme III



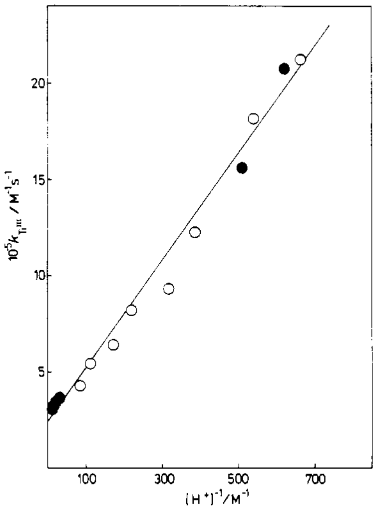


Figure 2. Plot of the second-order rate constant for the oxidation of Ti^{3+} by $^{\bullet}C(CH_3)_2OH$ versus $[H^+]^{-1}$ in 0.1 M ClO_4^- (○) and 0.10 M Cl^- (●).

Two possibilities, both of which represent the results satisfactorily, will be considered. In one, three parallel reactions are considered, those being the bimolecular reactions[28] between the aliphatic radical and Ti_{aq}^{3+}, $TiOH^{2+}$, and $Ti(OH)_2^+$ (or TiO^+). The equation applicable to that model is given in eq 9; a nonlinear

$$k_{Ti3}(1 + K_a/[H^+]) = k_1 + k_2/[H^+] + k_3/[H^+]^2 \qquad (9)$$

least-squares fit represents the data adequately, and gives the following parameters (M, s units): k_1 3.6×10^5, $k_2 = 1.8 \times 10^3$, and $k_3 = 25$ at 0.1 M ionic strength and 25 °C when K_a is taken as 7.3×10^{-3} M.

An alternative consists of the chemical equations shown in Scheme III, in which parallel hydrolytic pathways of an organotitanium(IV) intermediate are invoked to arrive at a dependence on $[H^+]$ that is consistent with the experimental formulation. The numerical assignments are less clear, although on the basis of literature data it is likely that the rate constants for radical binding to Ti^{3+} and $TiOH^{2+}$ are nearly the same. That is, an element of substitution control is inferred from the model given. Note that a plot of the *uncorrected* value of k_{Ti3} (i.e., the apparent second-order rate constant without allowance for the changing distribution of Ti(III) between $Ti(H_2O)_6^{3+}$ and $(H_2O)_5TiOH^{2+}$ over the range of $[H^+]$) is a linear function of $1/[H^+]$ (Figure 2). Once again, the rate is accelerated at low $[H^+]$ since the transition states are stabilized by incipient TiO^{2+} formation.

Acknowledgment. This work was supported in part by the U.S. Department of Energy through the Joint U.S.-Yugoslav Board for Scientific Cooperation, by the Research Council (SIZ) of S.R. Croatia, and by the U.S. Department of Energy, Office of Basic Energy Sciences, Chemical Sciences Division, under Contract W-7405-Eng-82.

Registry No. Ti^{3+}, 22541-75-9; Ti^{4+}, 16043-45-1; TiO^{2+}, 12192-25-5; $Co(NH_3)_6^{3+}$, 14695-95-5; $(H_2O)_5CrC(CH_3)_2OH^{2+}$, 74065-16-0; 1-hydroxy-1-methylethyl radical, 5131-95-3.

---

(27) Cohen, H.; Meyerstein, D. *Inorg. Chem.* **1984**, *23*, 84.

(28) The data will not fit to a simpler model in which only the two species Ti^{3+} and $TiOH^{2+}$ react in parallel with $^{\bullet}C(CH_3)_2OH$.