Titanium(III) Chemistry: Electron-Transfer Reactions with Ground-State Poly(pyridine)osmium(III) Complexes, Quenching Reactions with Excited-State Poly(pyridine)ruthenium(II) Complexes, and Formal Reduction Potentials
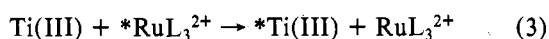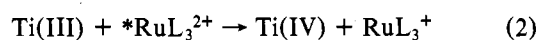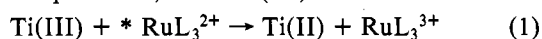
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Potentiometric titrations of aquotitanium(III) with ferric ions have been performed in hydrochloric acid solution. The potentiometric data are described by E (V vs. NHE) = 0.03 − 0.059 log ([Ti(III)]/[Ti(IV)][H$^+$]^2) at 25 °C and 3.0 M ionic strength and are consistent with the interpretation that Ti^{3+}(aq) and TiO^{2+} are the principal titanium(III) and titanium(IV) species, respectively, present at acid concentrations of 0.1–3.0 M. Rate constants for the oxidation of titanium(III) by a series of osmium(III) complexes, OsL$_3^{3+}$, where L is a bipyridine or phenanthroline derivative, have been determined at 25 °C and 3.0 M ionic strength. The rates are interpreted in terms of the reactions of Ti^{3+}(aq) and TiOH^{2+}. The rate constants are correlated with the Marcus theory, and the exchange rate constants for the Ti$^{4+,3+}$(aq) and TiOH$^{3+,2+}$ couples are estimated. The rate constants for the reaction of titanium(III) with the excited states of the ruthenium(II) complexes RuL$_3^{2+}$ are insensitive to the reduction potentials of the ruthenium(II) complexes. Arguments are presented to show that the quenching reactions proceed predominantly by energy-transfer mechanisms. The implications of these results for the production of Ti^{2+}(aq) in quenching reactions are discussed.

Introduction

There is currently considerable interest in developing systems in which metal complexes sensitize the photodecomposition of water.[1–3] One of our strategies[4] has been to use the charge-transfer excited state of tris(2,2′-bipyridine)ruthenium(II), *Ru(bpy)$_3^{2+}$, to generate reduced metal complexes capable of undergoing two-electron oxidations. With this in mind we have studied the quenching of the charge-transfer excited states of substituted poly(pyridine)ruthenium(II) complexes by aquotitanium(III) ions. The hope was that the potent two-electron reductant titanium(II)[5] would be formed in these reactions and that the subsequent reactions of this reductant with water or hydronium ions would yield hydrogen.

By analogy with the reactions of the charge-transfer excited states of the poly(pyridine)ruthenium(II) complexes, *RuL$_3^{2+}$, with various quenchers, titanium(III) reactions 1–3 need to

$$\text{Ti(III)} + {}^*\text{RuL}_3^{2+} \rightarrow \text{Ti(II)} + \text{RuL}_3^{3+} \quad (1)$$

$$\text{Ti(III)} + {}^*\text{RuL}_3^{2+} \rightarrow \text{Ti(IV)} + \text{RuL}_3^{+} \quad (2)$$

$$\text{Ti(III)} + {}^*\text{RuL}_3^{2+} \rightarrow {}^*\text{Ti(III)} + \text{RuL}_3^{2+} \quad (3)$$

be considered.[6–13] The first two reactions both involve electron transfer and should be governed by the same parameters that are important in electron transfer between ground-state species.[14,15] On the other hand, the third reaction is an energy-transfer process, and the efficiency of this process should depend on the spectral overlap of the donor and acceptor complexes.[16] Evidently the reaction yielding titanium(II) has to compete with two other excited-state reactions.

The reactions of titanium(III) with a number of oxidants have been studied recently;[17–23] however, there has been little systematic investigation of the dependence of the rates of these reactions on their driving forces. In order to examine this dependence, the electron-transfer reactions of titanium(III) with poly(pyridine)osmium(III) complexes were studied. These thermal reactions should be good models for the reductive quenching of *RuL$_3^{2+}$ (eq 2). The reduction potentials and self-exchange rates of the osmium(III)/osmium(II) couples are similar to those of the corresponding ruthenium(II)*/ruthenium(I) couples.[24] Further, the sizes of the complexes, their hydrophobic shells, and the symmetry of the transferring electron are the same for the ruthenium and osmium complexes. Consequently the importance of the reductive-quenching pathway in the reactions of *RuL$_3^{2+}$ with titanium(III) can be assessed from a comparison of the observed quenching rate constants with the rate constants for the reactions of OsL$_3^{3+}$ with Ti(III). The energy-transfer

pathway should show only a small dependence on the excited-state potentials.[8] The rate of the oxidative-quenching pathway (eq 1), by contrast, should increase with decreasing reduction potential of the ruthenium(III)/ruthenium(II)* couple.[8] These considerations, in addition to flash-photolysis studies of the quenching products, should enable the relative contributions of the different quenching pathways to be assessed.

Experimental Section

Materials. A stock solution of titanium(III) was prepared by dissolving titanium metal in 3 M HCl and was stored under argon. The titanium concentration was determined both spectrophotometrically (ϵ_{505} 3.97)[17,18] and by X-ray fluorescence. The titanium(IV) present in the stock solution was estimated spectrophotometrically from the absorbance at 340 nm ($\epsilon_{Ti(III)}$ <0.02; $\epsilon_{Ti(IV)}$ ~5 M^{-1} cm^{-1}).[17] The acid concentration was determined by titration with NaOH.[22b] The ruthenium and osmium complexes are those used in previous studies.[8,25]

Potentiometric Titrations. The potentiometric titrations of titanium(III) solutions (0.01 M) with ferric ammonium sulfate solutions (0.01 M) were carried out in an argon atmosphere at 25 °C with a graphite or a hanging mercury drop electrode (HMDE) and an SCE as reference. The potentials were measured on a PAR 173 potentiostat. For measurements with the HMDE a few drops of mercury were expelled from the electrode just prior to each measurement and the potential was read after about 1 min. Readings with the graphite electrode were found to drift over long periods, and after 12 h the potential still drifted slowly (~2 mV/h). The ionic strength in some of the measurements was adjusted to 3.0 M with LiCl.

Kinetic Measurements. All of the solutions for the kinetic runs were prepared by diluting the stock solution with HCl or Li$_2$CO$_3$ to produce the desired concentration and pH. The solutions were handled anaerobically by using platinum needles. The kinetic runs were performed on a modified Durrum (Dionex) stopped-flow apparatus;[26] the reactions were studied with titanium(III) in excess and semilogarithm plots of the absorbance changes were linear for more than 2 half-lives. The disappearance of the poly(pyridine)osmium(III) complexes was followed by monitoring the absorbance changes at 500 nm. The quenching of the poly(pyridine)ruthenium(II) complexes was determined from emission lifetime measurements with a neodymium laser flash photolysis system.[8] The ionic strength was maintained at 3.0 M (LiCl) and the temperature at 25 °C in all the kinetic studies.

Results

The Formal Potential of the Titanium(IV)/Titanium(III) Couple. The potentiometric titrations of titanium(III) with iron(III) gave curves similar to the one shown in Figure 1. When the potentials before the equivalence point were plotted against log ([Ti(III)]/[Ti(IV)]) a straight line with slope 58
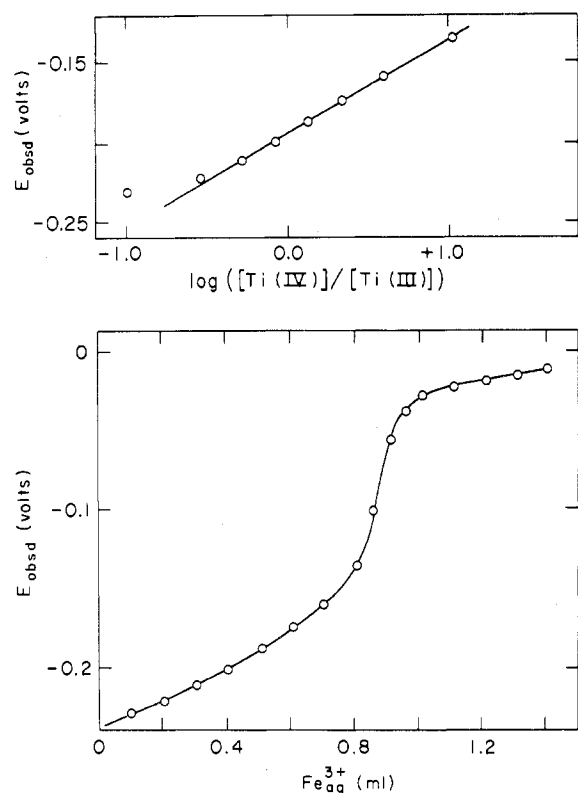
Figure 1. Bottom: plot of E_{obsd} vs. volume of iron(III) added in the potentiometric titration of titanium(III) by iron(III). Top: plot of E_{obsd} vs. log ([Ti(IV)]/[Ti(III)]) ratio.

Table I. Formal Reduction Potentials for the Titanium(IV)/Titanium(III) Couple in Aqueous Solution

[HCl], M	medium ionic strength,[a] M	T, °C	$E_{1/2}$, mV[b]	ref
0.04	0.04	18	−100	c
0.04	0.44 (NaCl)	18	−120	c
0.14	0.14	18	−80	c
0.44	0.44	18	−20	c
0.55	0.5	room ?	−55 ± 10	d
0.1	3.0 (LiCl)	25	−72 ± 10	e
0.5	3.0 (LiCl)	25	−5 ± 10	e
1.0	1.0	25	−16 ± 10	e
1.0	3.0 (LiCl)	25	+33 ± 10	e
1.5	3.0 (LiCl)	25	+50 ± 10	e
2.0	2.0	25	+36 ± 10	e
2.0	3.0 (LiCl)	25	+60 ± 10	e
3.0	3.0	25	+86 ± 10	e
3.0	3.0	room ?	+100	f
4.0	4.0	25	+170	g
4.0	4.0	20	+125	h
6.0	6.0	20	+169	h
6.0	6.0	25	+220	g
8.0	8.0	20	+225	h
10.0	10.0	20	+285	h
2.1	4.5 (TiCl$_3$, TiCl$_4$)	18	+56	i
2.1	2	18	+125	i
2.0	2	20	+92	h
3.0	3	20	+110	h
4.0	4	20	+130	h
4.0	4	25	+237	f

[a] The ionic strength is due to the acid if the medium is not specified. [b] Potential vs. NHE. [c] Reference 28. [d] Tribalat, S.; Delafosse, D. *Anal. Chim. Acta* **1958**, *19*, 74. [e] This work. [f] Verbeek, F.; Eeckhavt, Z. *Bull. Soc. Chem. Belg.* **1959**, *68*, 303. [g] Lingane, J. J.; Kennedy, J. H. *Anal. Chim. Acta* **1956**, *15*, 294. [h] Bock, V. R.; Günter, G., Z. *Anorg. Allg. Chem.* **1958**, *295*, 61. [i] Diethelm, B.; Foerster, F. Z. *Phys. Chem.* (*Leipzig*) **1908**, *62*, 129.

± 5 mV was obtained at all acid concentrations. The formal half-cell potentials for the titanium(IV)/titanium(III) couple were evaluated from the intercepts of these plots and are presented in Table I. The potentials after the equivalence point never reached that for the $Fe^{3+,2+}$ couple in 1 M HCl when the HMDE was used. Rather the potentials reached a final value between −20 and +40 mV vs. SCE with the more positive values obtaining at lower acid concentration. One titration in 1 M HCl was performed with a graphite electrode. The potential after 2 equiv of iron(III) had been added was 680 mV vs. NHE. However, the potentials measured before the equivalence point never stabilized. The potential of a solution of titanium(III) to which half an equivalent amount of iron(III) had been added still drifted toward more negative values after 12 h; at this time the potential measured with the graphite electrode was 00 mV vs. NHE (and −10 mV vs. NHE measured with the HMDE).

The formal potentials of the titanium(IV)/titanium(III) couple determined from the potentiometric titrations depended on both the acid concentration and the ionic strength (Table I). The fact that the potential measured after 2 equiv of iron(III) had been added was relatively low is probably due to the creation of a calomel electrode at the HMDE. This interpretation is supported by the fact that the potential measured in 1 M HCl is 40 mV vs. SCE which is the potential of a 1 M KCl calomel electrode.[27] The titanium(IV)/titanium(III) potentials measured by other workers are also included in Table I. If the potentials determined in HCl are plotted vs. pH, most of the data lie on a smooth curve: the potential is −100 mV at pH 1.5 and increases to over +200 mV in 6 M HCl.

Kolthoff[28] has attempted to fit the potential data for the titanium(IV)/titanium(III) couple from pH 0 to 6. He found that, despite the formation of precipitates, the use of complexing buffers, and a changing ionic strength, the data showed a first-order hydrogen-ion dependence. The present mea-

surements along with the other data presented in Table I show that a plot of $E_{1/2}$ (the potential at which the formal concentration of titanium(IV) equals that of titanium(III)) vs. the negative logarithm of the acid concentration from 1.5 to −1 is not linear. This is probably due to the changing chloride concentration and ionic strength.

We have also measured $E_{1/2}$ for [H$^+$] between 0.1 and 3.0 M at an ionic strength of 3.0 M maintained with LiCl. When these data are plotted vs. log [H$^+$], a straight line with a slope of 0.11 mV is obtained (Figure 2). Thus the potentiometric data are consistent with a quadratic hydrogen-ion dependence (eq 4) and provide good evidence that TiO^{2+} is the principal

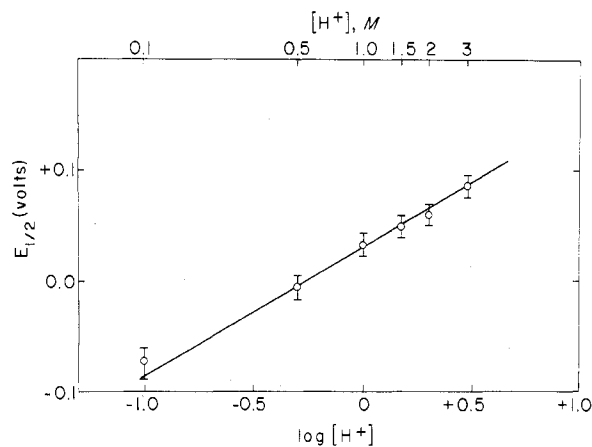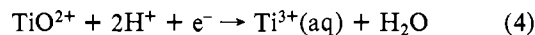**Figure 2.** Plot of $E_{1/2}$ for the titanium(IV)/titanium(III) couple vs. log [H$^+$] at 25 °C in 3.0 M ionic strength (LiCl).

$$TiO^{2+} + 2H^+ + e^- \rightarrow Ti^{3+}(aq) + H_2O \qquad (4)$$

Table II. Excited-State Lifetimes and Rate Constants for the Quenching of Poly(pyridine)ruthenium(II) Complexes $(RuL_3{}^{2+})$ by Titanium(III)[f]

| L	$10^6\tau_0$,[a] s	$10^{-6}k_q$, M^{-1} s^{-1}	$*E°_{3+,2+}$,[c] V	$*E°_{2+,+}$,[d] V
5-Cl(phen)	0.72	6.2	−0.77	1.00
bpy	0.53	6.0	−0.84	0.84
phen	0.72	6.2	−0.87	0.79
4,7-$(CH_3)_2$phen	1.27	3.8	−1.01	0.67
3,4,7,8-$(CH_3)_4$phen	1.0[b]	3.7	−1.11	0.55[e]

[a] Errors estimated to be ±7%. [b] Extrapolated value from the $1/\tau$ vs. [Ti(III)] plot. [c] Reference 8. [d] Reference 9. [e] Estimated from plot of $*E°_{3+,2+}$ vs. $*E°_{2+,+}$ for other poly(pyridine)ruthenium complexes. [f] In 1.5 M HCl at 25 °C and 3.0 M ionic strength (LiCl).

titanium(IV) species present in the solutions under the conditions used.

Reactions of $*RuL_3{}^{2+}$ Complexes with Titanium(III). The quenching of the ruthenium(II) emission by titanium(III) gave linear Stern-Volmer plots. However, in the case of Ru(3,-4,7,8-$(CH_3)_4$phen)$_3{}^{2+}$ the intercept of the Stern–Volmer plot was not 1.0. When the reciprocals of the measured lifetimes were plotted vs. the titanium(III) concentration, all of the points except the one at zero titanium(III) concentration fell on a straight line. The quenching rate constant for this complex was therefore calculated from the slope of this line and the extrapolated intercept was taken as τ_0.

The lifetimes and quenching rate constants determined in this work are summarized in Table II. The lifetimes of $*Ru(bpy)_3{}^{2+}$ showed only a small increase as the pH was raised (~10% increase on going from pH −0.2 to 2.0). The quenching rate constant also changed only slightly upon raising the pH to ~1.5. The quenching of $*Ru(phen)_3{}^{2+}$ gave no products which could be detected spectrophotometrically following excitation with a 20-ns laser pulse (Δabs < 0.003 at 500 and 370 nm, the isosbestic points for Ru(phen)$_3{}^{2+}$ and $*Ru(phen)_3{}^{2+}$, corresponding to a quantum yield for the production of either Ru(III) or Ru(I) of <0.2).
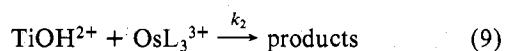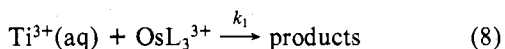
Flash photolysis of a solution containing Ru(bpy)$_3{}^{2+}$, Eu^{2+}(aq) (0.1 M), and titanium(III) (0.1 M) showed the presence of Ru(bpy)$_3{}^+$ generated by reaction 5. The Ru-

$$*Ru(bpy)_3{}^{2+} + Eu^{2+}(aq) \rightarrow Ru(bpy)_3{}^+ + Eu^{3+}(aq) \quad (5)$$
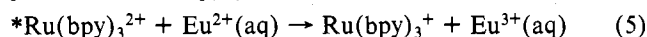
(bpy)$_3{}^+$ back-reacted with Eu^{3+}(aq) ($k \approx 3 \times 10^7$ M^{-1} s^{-1}[9]). No evidence was found for the reaction of Ti^{3+}(aq) with Ru(bpy)$_3{}^+$. Thus we estimate the rate constant for reaction 6 to be $<1 \times 10^6$ M^{-1} s^{-1}.

$$Ru(bpy)_3{}^+ + Ti^{3+}(aq) \rightarrow Ru(bpy)_3{}^{2+} + Ti^{2+}(aq) \quad (6)$$
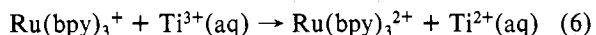
Reactions of $OsL_3{}^{3+}$ Complexes with Titanium(III). The rate of oxidation of titanium(III) by the poly(pyridine)osmium(III) complexes was first order in both the osmium(III) complex and titanium(III) concentrations. The second-order rate constants for the electron-transfer reactions varied with acidity in the pH range −0.2 to +2.5 (Table III). In order to correct for the hydrolysis of titanium(III), the quantity $k_{obsd}(1 + K_h/[H^+])$ was plotted vs. $1/[H^+]$ by using 2.3×10^{-3} M for the hydrolysis constant (K_h) of titanium(III).[20,29,30] The plots were linear with well-defined intercepts (Figure 3). The values of k_1 and k_2 (eq 7–9) calculated from the slope (k_2K_h)

$$Ti^{3+}(aq) + H_2O \underset{}{\overset{K_h}{\rightleftharpoons}} TiOH^{2+}(aq) + H^+ \quad (7)$$

$$Ti^{3+}(aq) + OsL_3{}^{3+} \overset{k_1}{\longrightarrow} products \quad (8)$$

$$TiOH^{2+} + OsL_3{}^{3+} \overset{k_2}{\longrightarrow} products \quad (9)$$

and the intercept (k_1) of these plots are presented in Table III.
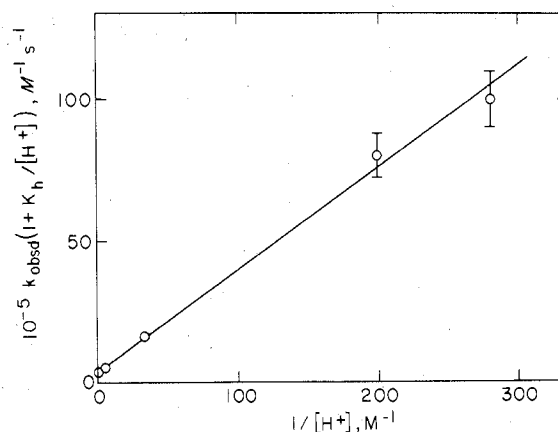
Figure 3. Plot of $k_{obsd}(1 + K_h/[H^+])$ vs. $1/[H^+]$ for the oxidation of titanium(III) by tris(bipyridine)osmium(III) in hydrochloric acid solution at 25 °C and 3.0 M ionic strength (LiCl).

Table III. Rate Constants for the Oxidation of Titanium(III) by Poly(pyridine)osmium(III) Complexes $(OsL_3{}^{3+})$[a]

L	[HCl], M	$10^{-5}k_{obsd}$, M^{-1} s^{-1}
4,4'-$(CH_3)_2$bpy	1.5	0.14
	0.06	0.90
	0.03	1.74
	0.0039	6.8
bpy	1.5	3.7
	0.3	5.1
	0.03	16
	0.005	56
	0.0036	61
5-Cl(phen)	1.5	22

[a] In HCl at 25 °C and 3.0 M ionic strength (LiCl).

The value of $E°_{3+,2+}$ for the Os(4,4-$(CH_3)_2$bpy)$_3{}^{3+,2+}$ couple was found to be 630 mV vs. NHE in 0.5 M H_2SO_4. The cyclic voltammograms were reversible with a peak separation of 70 mV on a graphite electrode.

Discussion

The Hydrolysis Constants of Titanium(III) and -(IV). Sykes et al.[31,32] have presented evidence that TiO^{2+} is the principal titanium(IV) species present in solution at [H$^+$] > 0.1 M. This evidence is based upon the reduction of titanium(IV) by Cr^{2+}(aq)[31] and the ligand substitution reactions of titanium(IV).[32] Our work suggests that the equilibrium constant for reaction 10 is greater than 25 M^2 since no deviation from

$$Ti^{4+}(aq) + H_2O \rightleftharpoons TiO^{2+} + 2H^+ \quad (10)$$

a straight line is seen in the $E_{1/2}$ vs. pH plot up to [H$^+$] = 3 M. The interpretation that TiO^{2+} is the principal titanium(IV) species present under our conditions is consistent with the results of the ion-exchange studies of Nabivanets et al.[33] and of Beukenkamp et al.[34] On the other hand, solvent extraction studies[35,36] suggest that a TiOH^{3+} species predominates in 1 M HClO$_4$.

The values of the first and second hydrolysis constants (K_{h1} and K_{h2}) of titanium(IV) are not known. As stated above, our work gives $K_{h1}K_{h2} > 25$ M^2 with $K_{h1} \leq K_{h2}$ (if $K_{h1} \gg K_{h2}$, then the slope of $E_{1/2}$ vs. log [H$^+$] should be 0.06 V). We estimate that K_{h2} may be greater than K_{h1} since the formation of an oxotitanium(IV) species should stabilize the second hydrolysis product. K_{h2} has been estimated by various workers to be 10^{-2},[35] ~0.5,[36] >2,[34] and 10^3 M.[37]

Because of the smaller size of titanium(IV), its hydrolysis constants should be larger than those of hafnium(IV) and zirconium(IV). Table IV lists the hydrolysis constants of a

Table IV. Hydrolysis Constants for M^{4+} Ions in Aqueous Solution at 25 °C

ion	radius,[a] Å	EC[b]	K_{h_1}, M	K_{h_2}, M	ionic strength, M	ref
Ti^{4+}	0.605	[Ar]	≥5	≥5 (~8)	3.0	c
Zr^{4+}	0.72	[Kr]	6.0	10	1	d,e
			0.6	0.24	2	f
			0.3		4	g
Hf^{4+}	0.71	[Xe]$4f^{14}$	0.1		4	g
Pu^{4+}	0.86	[Rn]$5f^4$	0.02		2	g
Ce^{4+}	0.87	[Xe]	0.2		1.5	g
			8	0.08	2	h
Np^{4+}	0.87	[Rn]$5f^3$	0.005		2	g
U^{4+}	0.89	[Rn]$5f^2$	0.03		1	g
			0.008		3	h
Pa^{4+}	0.90	[Rn]$6d^1$	0.72	0.04	3	g
Th^{4+}	0.94	[Rn]	6×10^{-5}	3×10^{-4}	1	g
			1×10^{-5}	2×10^{-4}	3	h

[a] Shannon, R. D. *Acta Crystallogr., Sect A* 1976, *32*, 751. [b] Electron configuration. [c] This work. [d] Calculated from data in ref *e* by using $pK_w = 13.79$ at $\mu = 1$ M. [e] Solovkin, A. S.; Tsvetkova, Z. N.; Ivantsov, A. I. *Russ. J. Inorg. Chem. (Engl. Transl.)* 1967, *12*, 326. [f] Solovkin, A. S.; Tsvetkova, Z. N. *Ibid.*, 1962, *31*, 655. [g] Smith, R. M.; Martell, A. E. "Critical Stability Constants"; Plenum: New York, 1976; Vol. 4. [h] Baes, C. F.; Mesmer, R. "Hydrolysis of Cations"; Wiley-Interscience: New York, 1976.

number of 4+ ions together with their ionic radii. Our estimate of the hydrolysis constants of titanium(IV) seems to lie in the correct range. Since K_h, the hydrolysis constant of titanium(III), is $\sim 2.3 \times 10^{-3}$ M (see below), the concentration of hydrolyzed titanium(III) species can be neglected under the conditions used.

A detailed study of the effect of chloride on the $E_{1/2}$ values was not made. In general, $E_{1/2}$ increases with increasing chloride ion concentration and ionic strength. If this increase is due to chloride complexing, then chloride is bound less strongly by titanium(IV) than by titanium(III). The equilibrium constant for the reaction of titanium(III) with chloride is 0.07–0.2 M.[38] On this basis we estimate that between 20 and 60% of the titanium(III) has a coordinated chloride under the conditions used. The percentage of titanium(IV) containing a coordinated chloride is presumably lower.

The above discussion serves to illustrate some of the problems involved in knowing exactly what species are present in the titanium solutions. However, if the question of chloride complexing is ignored (i.e., if we assume that the amount of chloride complexing of both titanium species is small), then we can use the data to estimate the formal potentials of the $Ti^{4+,3+}$(aq) and $TiOH^{3+,2+}$ couples. The potential data at ionic strength 3 M are described by eq 11. This implies that the

$$E = +0.03 - 0.059 \log ([Ti(III)]/[Ti(IV)][H^+]^2) \quad (11)$$

potential for the reduction of Ti^{4+}(aq) (eq 12) is greater than

$$Ti^{4+}(aq) + e^- \rightleftharpoons Ti^{3+}(aq) \quad (12)$$
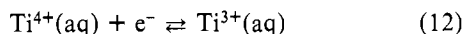
+110 mV vs. NHE ($K_{h1}K_{h2} \approx 25$ M^2) and that the potential for the reduction of $TiOH^{3+}$ (eq 13) is more positive than −80

$$TiOH^{3+} + e^- \rightleftharpoons TiOH^{2+} \quad (13)$$
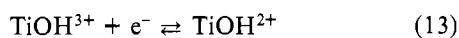
mV vs. NHE ($K_{h2} \approx 8$ M; $K_h \approx 2.3 \times 10^{-3}$ M).

Oxidation of Titanium(III) by Poly(pyridine)osmium(III) Complexes. The oxidation of titanium(III) by the poly(pyridine)osmium(III) complexes can be assigned an outer-sphere mechanism based on the substitution-inert nature of the osmium(III) complexes and the absence of a bridging group in poly(pyridine) ligands. Since the osmium(III) complexes exhibit no pK around pH 2.5, the inverse hydrogen-ion dependence of the rates can be attributed to $TiOH^{2+}$
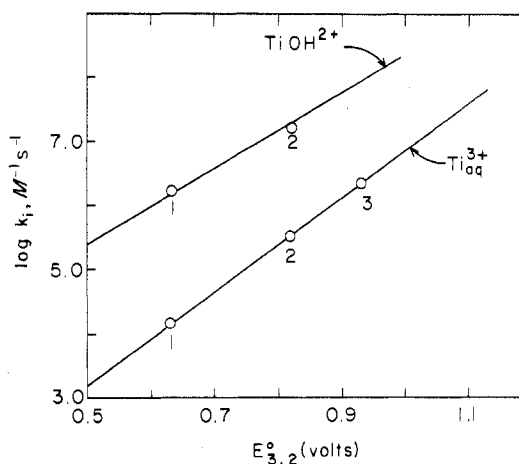
Figure 4. Plot of the logarithms of the rate constants for the oxidation of Ti^{3+}(aq) and $TiOH^{2+}$ by poly(pyridine)osmium(III) complexes (OsL_3^{3+}) vs. the reduction potentials of the osmium(III) complexes: L = (1) 4,4'-$(CH_3)_2$bpy, (2) bpy, (3) 5-Cl(phen).

rather than Ti^{3+}(aq) being the active reductant. The oxidation of titanium(III) by ruthenium(III) and cobalt(III) ammine complexes,[19,22] by poly(pyridine)cobalt(III) complexes[19,23] and by vanadium(III)[17] all feature rates which show an inverse acid dependence. These have all been ascribed to reduction by $TiOH^{2+}$. In only a few studies[17,20] has the acid-independent path been observed (i.e., $k_1 > 0$), and in these cases k_1 is usually 2 orders of magnitude smaller than k_2.

The value of K_h used here (2.3×10^{-3} M) is consistent with the values of 1.6×10^{-3} M measured in 3 M KCl[29] and 2.8×10^{-3} M measured in 3 M KBr[30] and falls within the range of K_h values used to interpret other redox reactions of $TiOH^{2+}$ (i.e., $K_h = (1.5–5) \times 10^{-3}$ M[17-23]). The value is somewhat lower than that measured by Pecsok and Fletcher (5×10^{-3} M in 0.75 M KI).[39] The effect of chloride ion on the reaction rate was not studied since chloride has only a small effect on other titanium(III) reactions.[17]

We next consider the correlation of the rate constants with the driving forces for the reactions. In Figure 4, log k_1 and log k_2 are plotted vs. $E°_{3+,2+}$ of the poly(pyridine)osmium(III) complexes. It will be seen that both log k_1 and log k_2 are linearly dependent on the driving force with slopes of 6.2 and 7.4, respectively. The Marcus cross-reaction relation[40] predicts this type of linear behavior (eq 14) where k_{12} is the cross-

$$k_{12} = (k_{11}k_{22}K_{12}f_{12})^{1/2} \quad (14)$$

$$\log f_{12} = (\log K_{12})^2/4 \log (k_{11}k_{22}/Z^2)$$

reaction rate constant, k_{11} and k_{22} are the self-exchange rate constants of the couples, and K_{12} is the equilibrium constant. Equation 14 predicts a slope of 8.4 for the plot of log k_{12} vs. $\Delta E°$. The agreement of the results of the present study with Marcus theory is satisfactory considering the large driving force for the reactions.[15] A plot of log k_1 vs. $E_{1/2}$ that includes all of the outer-sphere oxidation reactions of $TiOH^{2+}$ that have been studied can be constructed if corrections are made for the self-exchange rates. Unfortunately only a few of the relevant exchange rates are known. These data are plotted in Figure 5 as log k_{12} vs. log ($K_{12}k_{11}f_{12}$) and give a line of slope 0.40.[41] Thus over a wide potential range $TiOH^{2+}$ acts in a manner reasonably consistent with the Marcus theory.

The self-exchange rates of the $Ti^{4+,3+}$(aq) and $TiOH^{3+,2+}$ couples can be estimated from the data in Table V by using the potentials of the two couples estimated above. The calculated exchange rate constants are $\geq 10^{-8}$ and 3×10^{-7} M^{-1} s^{-1}, respectively.[42] Recent work on cross-reactions between metals in which one partner is an aquo ion and the other a
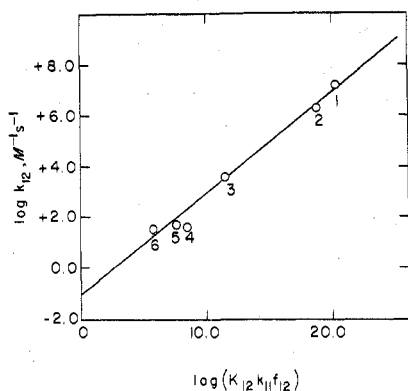
Figure 5. Plot of the logarithms of the observed rate constants for the oxidation of TiOH^{2+} by various oxidizing agents vs. log $(K_{12}k_{11}f_{12})$, where k_{11} is the self-exchange rate of the oxidizing agent: 1, Os-(bpy)$_3$$^{3+}$; 2, Os(4,4'-(CH$_3$)$_2$bpy)$_3$$^{3+}$; 3, Ru(NH$_3$)$_5$py^{3+}; 4, Co(phen)$_3$$^{3+}$; 5, Co(tpy)$_2$$^{3+}$; 6, Ru(NH$_3$)$_6$$^{3+}$.

Table V. Rate Constants for the Oxidation of Ti^{3+}(aq) and TiOH^{2+} by Poly(pyridine)osmium(III) Complexes (OsL$_3$$^{3+}$)^c

L	$10^{-5}k_1$, M^{-1} s^{-1}	$10^{-6}k_2$,^{a} M^{-1} s^{-1}	*E$^\circ_{3+,2+}$, V
4,4'-(CH$_3$)$_2$bpy	0.14	2.0	+0.63
bpy	3.4	17	+0.82^b
5-Cl(phen)	22		+0.93^b

^{a} Calculated by assuming $K_h = 2.3 \times 10^{-3}$ M. ^{b} Hoselton, M. A.; Lin, C.-T.; Schwarz, H. A.; Sutin, N. *J. Am. Chem. Soc.* **1978**, *100*, 2383. ^{c} At 25 °C and 3.0 M ionic strength.

ruthenium or osmium poly(pyridine) complex suggests that the exchange rate estimated in this manner may be as much as 10^6 too slow.[43,44] The TiOH$^{3+,2+}$ exchange rate can also be obtained from the intercept of the plot in Figure 5. This plot gives an exchange rate constant of $\geq 10^{-2}$ M^{-1} s^{-1}. Evidently the rate constant calculated from the OsL$_3$$^{3+}$ reactions is 3 × 10^4 times lower than the value calculated from Figure 5 which includes cross-reactions with relatively small driving forces. In general, reactions of the latter type do not show large deviations from eq 14.[44] Thus the present data suggest a rate constant of $\geq 10^{-2}$ M^{-1} s^{-1} for the TiOH$^{3+,2+}$ exchange and $>3 \times 10^{-4}$ M^{-1} s^{-1} for the Ti$^{4+,3+}$(aq) exchange.

Reactions of Titanium(III) with the Excited States of the Poly(pyridine)ruthenium(II) Complexes. As discussed in the Introduction, the reactions of OsL$_3$$^{3+}$ provide a good model for the reductive quenching reactions of *RuL$_3$$^{2+}$. The reduction potential of the *Ru(phen)$_3$$^{2+,1+}$ couple is +0.79 V (Table II) which is close to the potentials of the osmium complexes used. On this basis a rate constant of ~1.6 × 10^5 M^{-1} s^{-1} is expected for the oxidation of Ti^{3+}(aq) by *Ru-(phen)$_3$$^{2+}$ and ~1 × 10^7 M^{-1} s^{-1} for the oxidation of TiOH^{2+}. The measured quenching constant in 1.5 M HCl is 6 × 10^6 M^{-1} s^{-1} which is 40 times faster than the rate expected for reductive quenching. This suggests that a reaction that involves the reduction of the excited ruthenium(II) complex by titanium(III) does not constitute the predominant quenching mode. This conclusion is supported by the results of the flash-photolysis experiments: since no electron-transfer products were detected following flash photolysis of the titanium(III)–RuL$_3$$^{2+}$ solutions,[46] it follows that oxidative quenching and/or energy transfer provide the principal quenching pathways.

Additional information concerning the quenching mechanism is provided by the dependence of the quenching rate constant on the driving force. Figure 6 shows a plot of log k_q vs. *E$^\circ_{3+,2+}$ and *E$^\circ_{2+,+}$. Although there is a weak dependence of log k_q on *E$^\circ_{3+,2+}$, the rate constants *decrease* with increasing driving force. While an inverse relationship
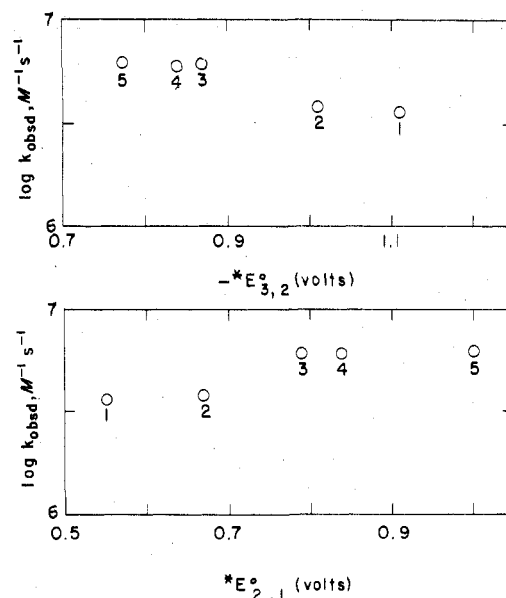
Figure 6. Plot of the logarithms of the rate constants for the quenching of the poly(pyridine)ruthenium(II) (RuL$_3$$^{2+}$) emission by titanium(III) in 1.5 M HCl at 25 °C and 3.0 M ionic strength (LiCl) vs. the excited state potentials of the ruthenium(II) complexes: L = (1) 3,4,7,8-(CH$_3$)$_4$phen, (2) 4,7-(CH$_3$)$_2$phen, (3) phen, (4) bpy, (5) 5-Cl(phen).

of this type is predicted for very exothermic electron-transfer reactions,[47] it is not expected in this case (since, as discussed below, the driving force for oxidative quenching is relatively small).

The above implies that the rate of the oxidative-quenching pathway (eq 1) is also considerably slower than the observed quenching rate. This is probably due to Ti^{3+}(aq) being a very poor oxidant. While the Ti$^{3+,2+}$(aq) potential has been reported to be −0.37 V by Forbes and Hall,[5] more recent work has yielded a value of −1.3 V vs. SCE in acetonitrile and an estimate of ~−2 V vs. NHE in water.[48] George and McClure[49] have also argued that the potential for the Ti$^{3+,2+}$(aq) couple is much more negative than that measured by Forbes and Hall. The rate constant of $\leq 10^6$ M^{-1} s^{-1} determined in this work for the reaction of Ru(bpy)$_3$$^+$ with titanium(III) allows an estimate of the Ti$^{3+,2+}$(aq) potential to be made by using eq 14. Assuming that the rate constant for the Ti$^{3+,2+}$(aq) exchange is ~10^{-2} M^{-1} s^{-1} (similar to that for the V$^{3+,2+}$(aq)^{50} exchange) and using −1.28 V and $\geq 10^8$ M^{-1} s^{-1} for the reduction potential and exchange rate of the Ru(bpy)$_3$$^{2+,+}$ couple, respectively,[24] we calculate the reduction potential of the Ti$^{3+,2+}$(aq) couple to be <−0.7 V.[51] In view of this very negative potential, and, more significantly, the relatively slow rate of the reaction of titanium(III) with Ru(bpy)$_3$$^+$, it is not surprising that we find no evidence for the oxidative-quenching pathway (eq 1). The only quenching mechanism left, therefore, is energy transfer. This mechanism is consistent with the relatively small variation of the quenching rates with the nature of the excited ruthenium(II) complex.[8,43] For example, the rates of the quenching of the excited ruthenium(II) complexes by Cr^{3+}(aq) (which is believed to proceed by energy transfer) vary by only 40% for the series of ruthenium(II) complexes used in this work.[8] In the quenching of the same series of ruthenium(II) complexes by chromium(III) ammine complexes, the rates vary by a factor of 3 and correlate with the average frequency maximum of the ruthenium emission.[11]

In further support of the energy-transfer interpretation, it should be noted that there is considerable overlap between the ruthenium(II) emission and the Ti^{3+}(aq) absorption spectra. In Ru(phen)$_3$$^{2+}$ the emission band (half-width) is from 570 to 660 nm while the Ti^{3+} absorption band (maximum 500 nm)

has a shoulder at ~575 nm. Energy-transfer rate constants of ~10^9 M^{-1} s^{-1} have been measured for ions with this amount of spectral overlap.[11]

In conclusion, the present study shows the utility of using thermal electron-transfer reactions to help elucidate the quenching reactions of excited-state molecules. We have shown that reactions involving the oxidation of $Ti^{3+}(aq)$ and $TiOH^{2+}$ are normal in a Marcus sense and that their reactions with the ruthenium(II) excited state leading to production of $Ti^{2+}(aq)$ are slow. In order to drive the $Ti^{3+,2+}(aq)$ reaction, a couple with a considerably lower reduction potential is needed.

Registry No. TiO^{2+}, 12192-25-5; $Ti^{3+}(aq)$, 17524-20-8; $TiOH^{3+}$, 23335-62-8; $TiOH^{2+}$, 21029-47-0; $Ru(5-Cl(phen))_3^{2+}$, 47860-47-9; $Ru(bpy)_3^{2+}$, 15158-62-0; $Ru(phen)_3^{2+}$, 22873-66-1; $Ru(4,7-(CH_3)_2phen)_3^{2+}$, 24414-00-4; $Ru(3,4,7,8-(CH_3)_4phen)_3^{2+}$, 64894-64-0; $Os(4,4'-(CH_3)_2bpy)_3^{3+}$, 47838-06-2; $Os(bpy)_3^{3+}$, 23648-06-8; $Os-(5-Cl(phen))_3^{3+}$, 70101-70-1.

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(41) Figure 5 was constructed by using the following data: $Ru(NH_3)_5py^{3+,2+}$, $k_{11} = 4.3 \times 10^5$ M^{-1} s^{-1}, $E^{\circ}_{3+,2+} = 305$ mV;[44] $Ru(NH_3)_6^{3+,2+}$, $k_{11} = 4.3 \times 10^3$ M^{-1} s^{-1}, $E^{\circ}_{3+,2+} = 51$ mV;[44] $Co(phen)_3^{3+,2+}$, $k_{11} = 40$ M^{-1} s^{-1}, $E^{\circ}_{3+,2+} = 370$ mV;[44] $Co(tpy)_2^{3+,2+}$, $k_{11} = 40$ M^{-1} s^{-1}, $E^{\circ}_{3+,2+} = 310$ mV.[45]
(42) The rate constants are the average of the logarithms of the exchange rate constants calculated for each OsL_3^{3+} reaction by using the potentials for the $OsL_3^{3+,2+}$ couples listed in Table V and a rate constant of 2×10^9 M^{-1} s^{-1}[24] for the $OsL_3^{3+,2+}$ exchange reaction.
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(51) Calculated with an effective exchange rate of 3×10^{-7} M^{-1} s^{-1} for the $Ti^{3+,2+}(aq)$ couple.

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Multistep Redox Series of the Tris(*o*-semiquinone)chromium(III) Complexes

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Neutral complexes of chromium(III) with tetrachloro-1,2-benzoquinone, 9,10-phenanthrenequinone, and 3,5-di-*tert*-butyl-1,2-benzoquinone chelated as semiquinone ligands have been examined by using cyclic voltammetry. All three complexes show reversible or quasi-reversible redox series corresponding to complexes of form $Cr(quinone)_3{}^n$, where n ranges from 3+ to 3−. EPR spectra on the 1+ and 1− members of the series show quite similar $\langle g \rangle$ and ^{53}Cr hyperfine values indicating substantial metal character in the ground states of both types of complexes. These results are compared with $V(O_2C_6Cl_4)_3$ where the ground state is principally ligand and explained in terms of VB and MO views of bonding.

Introduction

There is considerable interest in the modification of electrode surfaces with electroactive complexes to serve as electron-transfer agents.[1] Various problems centered about the rapid, reversible reduction of small molecules (i.e., O_2, N_2) require electrocatalysts which are capable of providing the large numbers of electrons involved. Two approaches may be taken in the design of electroactive complexes which are capable of

supporting reversible multielectron redox series. The approach used in the development of systems which serve as analogues for various biological electron-transfer agents has been to incorporate two or more electroactive metal centers within a molecular complex unit so they may act in concert.[2] A second approach involves the complexation of electroactive ligands to a single metal center. In systems of this type a multielectron redox series can be supported which involves the oxidation or