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Inner-Sphere Electron Transfer in Some Ruthenium(III)–Titanium(III) Reactions

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The kinetics of oxidation of Ti^{3+} by $Ru(NH_3)_5OOCCH_3^{2+}$, $Ru(NH_3)_5C_2O_4^{+}$, and $Ru(NH_3)_4C_2O_4^{+}$ have been measured in aqueous media (μ = 1 M, 25 °C). For the first-named cation, $LiCF_3SO_3$–HCF_3SO_3 media were used; for the others, LiCl–HCl media. All reactions follow second-order kinetics with rate constant dependent on acidity according to the rate law $k_b = k\kappa/(\kappa + [H^+])$. Values of k ($M^{-1}\ s^{-1}$) are 7×10^2, $2._5 \times 10^4$, and $3._6 \times 10^4$. Values of κ (M) are 0.2_1, 0.2_3, and 0.1_3. The reduction potentials (mV vs. NHE) of the complexes are +44, –109, and –88. The values of k are too large to be consistent with an outer-sphere mechanism and indicate that the redox reaction proceeds via electron transfer in a deprotonated binuclear intermediate. The rate-limiting process is substitution on Ti(III), and k may be identified as the rate constant for that process. Comparison of the values of k for these oxidants with corresponding values for Co(III) oxidants indicates a significant degree of cross-bridge electronic interaction prior to the transition state for the Ru(III)–Ti(III) reactions.

Introduction

Reduction of low-spin d^5 Ru(III) complexes by d^1 Ti(III) complexes involves t_{2g} metal orbital as both the electron-donor and electron-acceptor orbitals. In previous papers,[1] we have shown that many Ru(III)–Ti(III) reactions proceed via outer-sphere reductions by $Ti(OH)^{2+}$ (rather than Ti^{3+}) and that a series of such reactions follow a linear free energy relationship. Another earlier paper[2] showed that oxalate ion functions as an electron-transfer bridging ligand for Co(III)–Ti(III) redox reactions. We have previously suggested that some of the remarkable properties of Ti(III) and Ru(II) (such as the ability to reduce perchlorate ion)[3] can be understood as involving unusually extensive overlap between t_{2g} electron-donor and -acceptor orbitals. This effect should be more prominent in inner-sphere than in outer-sphere reactions. We previously showed[4] that inner-sphere Cr(II)–Cr(III) reactions also follow linear free energy relationships. It is of interest to examine the effect of t_{2g} orbital overlap on inner-sphere Ru(III)–Ti(III) electron-transfer processes. It is anticipated that such effects will be useful in developing understanding of the details of the electron-transfer process. The magnitude of interaction between electron-donor and electron-acceptor orbitals, in or prior to the transition state, should be important in deciding whether or not Marcus' theory[5] is applicable and clearly would be important in the consideration of such reactions on a molecular orbital basis.[6]

Experimental Section

Methods used were generally similar to those reported earlier.[1,2] Ti(III) stock solutions were prepared by dissolving Ti metal in HCl or HCF_3SO_3, as appropriate. Perchlorate salts of (acetato)- and (oxalato)pentaammineruthenium(III) cations were prepared from $[Ru(NH_3)_5Cl]Cl_2$ by using the method of Stritar and Taube.[7] The oxalato cation does not appear to have been prepared previously. The dithionate salt of *cis*-(oxalato)tetraammineruthenium(III) cation was prepared by the method of Pell and Armor.[8] Wavelengths (in nm) of maximum absorption (and of log extinction coefficients) for the three cations are 295 (3.20), 288 (3.49), and 287 (3.67). Anal.[9] Calcd for $[Ru(NH_3)_5OOCCH_3](ClO_4)_2$: Ru, 22.8; C, 5.4; N, 15.8. Found: Ru, 22.6; C, 5.4; N, 15.7. $[Ru(NH_3)_5C_2O_4]ClO_4$: Ru, 27.1; C, 6.4; N, 18.7. Found: Ru, 27.0; C, 6.7; N, 18.8. *cis*-$[Ru(NH_3)_4C_2O_4]_2S_2O_6$: Ru, 30.0; C, 7.1; N, 16.6. Found: Ru, 30.3; C, 7.0; N, 16.5. Reduction potentials for each cation were measured, with apparatus previously described,[3] in trifluoroacetate buffers. The depolarizers of interest in this paper yielded voltammograms corresponding to reversible (or quasi-reversible) reductions. For comparison purposes $Ru(NH_3)_6^{3+}$ and $Ru(NH_3)_5Cl^{2+}$ were also studied. As previously reported,[10] the former yields a reversible wave but the voltammogram of the latter ion is more complicated.

Rates of reaction were measured by monitoring decrease in absorbance at the UV absorbance peak of the oxidants. Preliminary experiments indicated 1/1 stoichiometry for each reaction. Subsequent experiments were carried out with Ti(III) at least tenfold in excess. $LiCF_3SO_3$ media were used for the acetato complex in order to avoid complications due to side reactions subsequent to the electron-transfer step. The reductions of the oxalato complexes were rapid with respect to Ru(II) substitution[11] so that Cl^- media could be used without complication. Pseudo-first-order rate plots were linear for over 85% of reaction. Replicate experiments agreed within 5%. The measured pseudo-first-order rate constant will be denoted k_0.

Results

On the basis of changes in absorption in the UV region which occur along with (and after) the decrease in UV absorption attributable to reduction of Ru(III), we conclude that the Ti(IV) species which is the initial product of the redox process undergoes subsequent reaction with the consequent formation of Ti(IV) species with a higher degree of polymerization. As in the case of olated Cr(III) species,[12] the larger polymers are more opaque in the UV region than are the lower molecular weight forms. This process is more rapid in $CF_3SO_3^-$ media than in Cl^- media and is more rapid in less acidic media than in more acidic media. This phenomenon imposes a lower limit on the acidities which can be used in these studies.

For runs at the same acid concentration, rate increased as [Ti(III)] increased. Table I lists values of the second-order rate constant k_b obtained by dividing the measured pseudo-first-order rate constant by [Ti(III)]. As the data shown in the table indicate, there is no large or systematic variation in the second-order rate constants thus obtained, if $[H^+]$ is held constant. The value of the second-order rate constant increases with decreasing acid concentration. As Figure 1 indicates, the plots of the reciprocal of k_b vs. $[H^+]$ are linear, consistent with a rate law of the form

$$k_b = k\kappa/([H^+] + \kappa) \qquad (1)$$

Values of k and κ for each of the oxidants are shown in Table II, along with measured values of $\mathscr{E}^\circ$. For comparison, the corresponding values for Ti(III) reduction of $Ru(NH_3)_6^{3+}$ and $Ru(NH_3)_5Cl^{2+}$ are also included.

In addition to the results reported in the table, we carried out preliminary experiments on two additional systems. For the purpose of discussion, a summary of the results of these preliminary experiments is included here. The anion $Ru(C_2O_4)_3^{-3}$ is reduced by Ti(III) with a second-order rate constant more than an order of magnitude larger than that for $Ru(NH_3)_4C_2O_4^+$. When $Ru(NH_3)_5OOCCH_3^{2+}$ is reduced[13] by $TiEDTA^-$, the rate is independent of $[H^+]$ and close to the limiting (low acid) rate of reduction of $Ru(NH_3)_4C_2O_4^+$.

Discussion

Rate laws of the form observed for these reactions (eq 1) are quite common for redox reactions of Ti(III). Frequently

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Table I. Rate Constants for Reduction of Ru(III) Cations by Ti(III) at 25.0 °C in Aqueous Media ($\mu = 1.0$)

$[H^+]$, mM	[Ti(III)], mM	$10^{-4}k_b$,[f] $M^{-1}\ s^{-1}$	$[H^+]$, mM	[Ti(III)], mM	$10^{-4}k_b$,[f] $M^{-1}\ s^{-1}$
(A) *cis*-$Ru(NH_3)_4C_2O_4^+$ [a,b]					
26.9	2.7	2.8	96.8	2.8	1.9
41.0	2.7	2.5	125	2.7	1.6_5
67.3	2.8	2.2	153	2.8	1.4
83.1	2.7	2.1	181	2.7	1.3
83.1	5.3	2.1_5	200	2.8	1.2_5
83.1	7.9	2.0	223	2.8	1.1
83.1	10.6	2.1			
(B) $Ru(NH_3)_5C_2O_4^+$ [a,c]					
18.5	3.8	2.3_5	154	3.8	1.5
27.0	3.8	2.2	215	3.8	1.3_5
35.9	3.8	2.1_5	215	9.5	1.27
52.3	3.8	2.0	215	19.0	1.32
86.0	3.8	1.9	215	28.5	1.43
120	3.8	1.6	221	3.8	1.3_5
(C) $Ru(NH_3)_5OOCCH_3^{2+}$ [d,e]					
44.5	3.2	0.059	164	4.8	0.040
55.4	3.2	0.056	192	4.8	0.038
76.0	3.2	0.052	249	5.6	0.033
103	3.2	0.046	306	5.6	0.028
131	3.2	0.043	354	6.4	0.026

[a] LiCl media. [b] (5–9) × 10^{-5} M. [c] (3–4) × 10^{-5} M. [d] $LiCF_3SO_3$ media. [e] (6–9) × 10^{-5} M. [f] Observed first-order rate constant divided by [Ti(III)], $k_b = k_0/[\mathrm{Ti(III)}]$.

Table II. Kinetic and Electrochemical Parameters for Reduction of Some Ru(III) Cations at 25.0 °C in Aqueous Media

oxidant	$\mathcal{E}°$,[a] mV vs. NHE	$10^{-3}k$, $M^{-1}\ s^{-1}$	κ, M
cis-$Ru(NH_3)_4C_2O_4^+$	−88	36[b]	0.1_3[b]
$Ru(NH_3)_5C_2O_4^+$	−110	25[b]	0.2_3[b]
$Ru(NH_3)_5OOCCH_3^{2+}$	+44	0.7[b]	0.2_1[b]
$Ru(NH_3)_5Cl^{2+}$	−59 (−42)[c]	0.035[c]	0.005[d]
$Ru(NH_3)_6^{3+}$	+54 (+51)[c]	0.012[c]	0.005[d]

[a] Average of cathodic and anodic peak potentials in ~1 M $CF_3COOH-LiCF_3COO$ solutions, pH 2–3, sweep rate ~20 V/s. [b] This work. [c] Reference 10, see original for conditions and media. [d] Reference 1b.

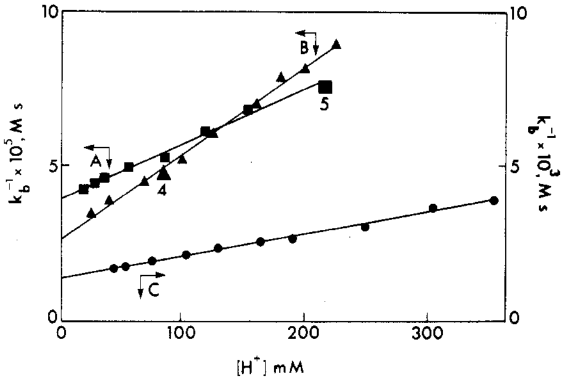

Figure 1. Variation of k_b^{-1} with $[H^+]$: (A) ■, $Ru(NH_3)_5C_2O_4^+$; (B) ▲, $Ru(NH_3)_4C_2O_4^+$; (C) ●, $Ru(NH_3)_5OOCCH_3^{2+}$ (right scale). The large triangle labeled 4 covers four points and the square labeled 5, five. Conditions are as described in Table I.

the constant κ turns out to have a value that can be identified as the acid-dissociation constant of Ti^{3+}. When this is the case, the best interpretation is often that the reaction consists of outer-sphere (direct) electron transfer from $TiOH^{2+}$ as reductant.[1] In the case of reduction of $Co(NH_3)_5F^{2+}$ and some other Co(III) oxidants containing good electron-transfer bridging groups,[14] the value of κ is far too large to correspond to K_a of Ti^{3+} and this is taken as good evidence that there is an inner-sphere (bridged) electron-transfer mechanism operative. However, in the cases of Ti(III) reduction of $Co(NH_3)_4C_2O_4^+$ [15] and $Co(NH_3)_5OOCCH_3^{2+}$,[16] the rate is inversely proportional to $[H^+]$, indicating a value of κ near 0.005 M, but the magnitude of k indicates that an inner-sphere mechanism operates.

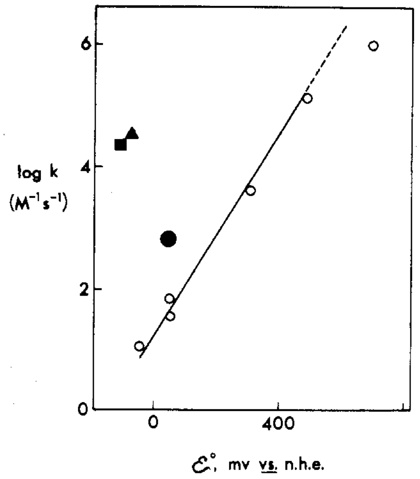

Figure 2. Variation of rate constant with redox potential of the oxidant for Ti(III) reductions of Ru(III) complexes. Filled points denote inner-sphere electron-transfer constants (low-acid limits): ■, $Ru(NH_3)_5C_2O_4^+$; ▲, $Ru(NH_3)_4C_2O_4^+$; ●, $Ru(NH_3)_5OOCCH_3^{2+}$. Open points denote rate constants for reductions by $TiOH^{2+}$(l) (left to right): $Ru(NH_3)_5Cl^{2+}$, $Ru(NH_3)_6^{3+}$, $Ru(NH_3)_5H_2O^{3+}$, $Ru(NH_3)py^{3+}$ (py = pyridine), $Ru(NH_3)_5pyr^{3+}$ (pyr = pyrazine), *cis*-$Ru(NH_3)_4(isn)_2^{3+}$ (isn = isonicotinamide). Conditions are as described in Table I.

Figure 2 shows the values of k for the three reactions studied here and electron-transfer rate constants for a number of $Ru^{III}-Ti(OH)^{2+}$ reactions, plotted against $\mathcal{E}°$ for the reduction of the oxidants. The outer-sphere reactions correlate well with each other, but the three reactions of interest here are clearly faster than would be predicted from the reduction potential of the oxidants, by using the correlation between rate constant and $\mathcal{E}°$ determined from the previously studied outer-sphere processes. A further difference between the systems of present interest and the outer-sphere reactions is that the value of κ is much larger in the present system than the acid-dissociation constant of Ti^{3+}. It is apparent that a mechanism other than simple outer-sphere electron transfer from $TiOH^{2+}$ is involved in the reactions of interest here.

Recent evidence[17] indicates that the three cationic oxidants of interest here are protonated in highly acidic solutions.[18] A mechanism which is sufficient to fit our data is

$$\mathrm{RuXH}^{(n+1)+} \overset{K}{\rightleftharpoons} \mathrm{RuX}^{n+} + \mathrm{H}^+ \qquad (2)$$

$$\mathrm{RuX}^{n+} + \mathrm{Ti}^{3+} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \mathrm{RuXTi}^{(3+n)+} \qquad (3)$$

$$\mathrm{RuXTi}^{(3+n)+} \xrightarrow{k_{\mathrm{et}}} \text{products} \qquad (4)$$

Applying the steady-state assumption to the concentration of the binuclear intermediate, one obtains the observed rate law with $\kappa = K$ and $k = k_1k_{\mathrm{et}}/(k_2 + k_{\mathrm{et}})$.

Substitution reactions like eq 3 usually involve outer-sphere complexes as precursors, so that one may write $k_1 = K_0k_x$, where K_0 is the formation constant for an outer-sphere complex involving the oxidant and reductant, and k_x is the rate constant for water exchange between the coordination sphere of the reductant and the solvent. Diebler has studied a number of substitution reactions of Ti^{3+}, including the formation of oxalato complexes.[19] The activation energy associated with k_x for Ti^{3+} has been reported to be unusually low.[20] This suggests an associative substitution mechanism so that k_x may also depend on the nature of the entering group. The EDTA complexes of Cr(III)[21] and Ru(III)[22] are more labile toward substitution than are $Cr(H_2O)_6^{3+}$ and $Ru(H_2O)_6^{3+}$. The increased rate (relative to Ti^{3+}) of oxidation of $Ti(EDTA)^-$ by $Ru(NH_3)_5OOCCH_3^{2+}$ may be caused by increased lability of the reductant (in an inner-sphere reaction) or increased prior association of the oxidant and reductant (either inner- or outer-sphere mechanisms[23]).

Reduction of oxalato complexes by Cr^{2+} often involves the radical–ion mechanism,[24] and this mechanism operates when Ti(III) reduces Co(III) complexes with ligands which are easy to reduce.[25] The reducing power of Ti(III)[1a] does not seem sufficient for this mechanism to be operative in the reactions of present interest. Although the reduction potential of $Ru(C_2O_4)_3^{3-}$ is quite negative ($\mathcal{E}°_{SCE} = -0.8$ V[26]), the reduction of that ion by Ti^{3+} goes to completion and does so rapidly.[27] Among factors which could contribute to this result are high stability of titanium–oxalate interactions in either or both reductant or product states and interference with the reverse reaction by rapid polymerization of the initial Ti(IV) product.

Among the Ti(III) redox reactions for which inner-sphere mechanisms have been demonstrated, those involving oxidants of less positive charge are more rapid than those involving oxidants of more positive charge. However, there are substantial variations in rate among oxidants of the same charge type.[14] The rate constant we observe in the case of $Ru(NH_3)_5OOCCH_3^{2+}$ is higher than that observed for any Ti(III) reduction of a dipositive Co(III) oxidant. The rate constants we observe for the monopositive oxalato complexes are more than an order of magnitude larger than that observed for Ti(III) reduction of $Co(C_2O_4)_3^{3-}$.[2] The variation (among themselves) of the rate constants for inner-sphere Ti(III) reductions of Co(III) complexes and, separately, the variation (among themselves) of the rate constants for Ti(III) reductions of Ru(III) complexes are each understandable on the basis of differences in equilibrium constants for prior association (K_0) or of Coulombic influences on rates of substitution k_x. But there is a systematic difference between observed rates for Ru(III) complexes as compared with corresponding Co(III) complexes which *cannot* be explained on such grounds. The Ru(III) rate constants are consistently larger than the rate constants for the corresponding Co(III) oxidants.

The most satisfactory interpretation of the observation that acid-independent rate constants for inner-sphere reactions of Ti^{3+} are consistently larger for Ru(III) oxidants than for the corresponding Co(III) oxidants is that cross-bridge electronic interaction is greater in the case of Ru(III) than in the case of Co(III) oxidants. In the case of Ru(III), efficient superexchange interaction (through the π-electron system of the bridge) between electron-donor and electron-acceptor orbitals causes the rate of electron transfer to be large with respect to the rate of breakup of the complex ($k_{et} > k_2$) so that $k \approx k_1$. In the case of Co(III), less efficient interaction occurs and $k_3/(k_2 + k_3) < 1$ so that $k < k_1$.[28]

The (substitution-limited) acid-independent rate constants for Ti(III) reduction of the oxalate–ammine complexes are 4 orders of magnitude larger than the rate constants for $TiOH^{2+}$ reduction of outer-sphere oxidants of comparable $\mathcal{E}°_H$. The rate constant for intracomplex electron transfer must be larger still. Cross-bridge electronic interaction reduces the activation barrier for electron transfer by at least 20 kJ/mol. The reduction of the barrier in the case of Ti^{3+} reduction of $Ru(C_2O_4)_3^{3-}$ may be even larger.[27]

Some of our observations seem pertinent to the mechanism of the technologically important phenomenon of stress corrosion cracking of titanium metal and its alloys.[29] Corrosion of titanium involves formation of Ti(III) from the metal and is retarded by formation of titanium(IV) oxide on the metal surface. When Ti is in contact with water, the tendency for stress corrosion cracking is increased by the presence of chloride ion. These facts have usually been interpreted by mechanisms involving chloro complexes of Ti(III). Our experience has been that Ti^{3+} has a low affinity for Cl^- but that Cl^- has a strong effect on the rate of polymerization (and eventual precipitation) of Ti(IV). It seems likely that the dramatic influence of halide ions (in sea water, for instance) on the stress corrosion cracking of titanium is more due to their effect on Ti(IV) aggregation than on any complex formation involving Ti(III).

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Registry No. Ti^{3+}, 22541-75-9; $Ru(NH_3)_5OOCCH_3^{2+}$, 38744-91-1; $Ru(NH_3)_5C_2O_4^+$, 69765-81-7; $Ru(NH_3)_4C_2O_4^+$, 45976-96-3.

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