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General Mechanism for Ruthenium(III)-Titanium(III) Electron-Transfer Reactions: Reductions Involving Sulfato Ligands

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Ru(III)-Ti(III) redox reactions exhibit several patterns of kinetic behavior and involve various mechanisms. These differences can be interpreted in terms of a single, unified conceptual scheme. The major source of multiplicity of kinetic patterns is variation, among possible bridging ligands, of the tendency to facilitate cross-bridge electronic interaction. Reactions between Ti(III) and $(NH_3)_5RuX^{(3-n)+}$ ($X = SO_4^{2-}$, $S_2O_3^{2-}$, $NH_2SO_3^-$) were studied in 1.0 M LiCl at 25 °C. $(NH_3)_5RuSO_4^+$ is reduced with the following rate law: $k_{obsd} = k_a[Ti(III)]/[H^+]$, where $k_a = 0.25\ s^{-1}$. Comparison with previously investigated systems indicates that the mechanism of reaction is outer-sphere reduction by $TiOH^{2+}$. The rate law for the reduction of $(NH_3)_5RuNH_2SO_3^{2+}$ by Ti(III) follows: $k_{obsd} = (k_c + k_d[H^+]^{-1})[Ti(III)]$, where $k_c = 86\ M^{-1}\ s^{-1}$ and $k_d = 6.0\ s^{-1}$. Both Ti^{3+} and $TiOH^{2+}$ reduce $(NH_3)_5RuNH_2SO_3^{2+}$ via outer-sphere mechanisms. Reduction of $(NH_3)_5RuS_2O_3^+$ by Ti(III) proceeds in two stages. The rate law for the faster process is $k_{obsd} = k_e[Ti(III)]/(K + [H^+])$, where $k_e = 2.4 \times 10^3\ M^{-1}\ s^{-1}$ and $K = 0.03$ M. The slower stage is dependent on [Ti(III)] and relatively independent of $[H^+]$. The faster step involves formation of an unstable binuclear intermediate, followed by fast intramolecular electron transfer within the conjugate base of that intermediate. The slower stage is decomposition of the successor complex thus produced. Although SO_3 is an efficient electron-mediating group in redox reactions that involve e_g redox orbitals, all three systems of present interest consistently indicate that SO_3 is inefficient as an electron mediator for Ru(III)-Ti(III) electron transfer, which involves t_{2g} orbitals as both electron-donor and electron-acceptor orbitals.

Introduction

Two types of outer-sphere Ru(III)-Ti(III) redox processes occur. If an electron-delocalizing ligand is present on the oxidant, then both Ti^{3+} and $TiOH^{2+}$ function as reductants. Otherwise, the aquo ion is ineffective[1] as a reductant. Inner-sphere Ru(III)-Ti(III) redox reactions display a variety of types of dependence on $[H^+]$ and on [Ti(III)]. When the ruthenium(III) oxidant is $RuX^{(3-n)+}$ (where $X^{n-} = CH_3COO^-$, NCS^-, salycilate, and $C_2O_4^{2-}$) the rate constants for the reductions are linearly dependent on [Ti(III)] and acid-independent.[2,3] In these cases, measured redox rates correspond to rates of substitution on Ti(III), and redox rates vary with charge-type of the reactants as expected for that relatively simple reaction. When the ruthenium(III) oxidant is $(pd)_2Ru(fpd)$ (where pd designates the pentane-2,4-dionate ion and fpd is the 3-formylpentane-2-4-dionate ion), reaction with Ti(III) occurs in two stages.[4] The rate of the faster step (taken to include electron transfer) is linear in both $[Ti^{3+}]$ and in $[H^+]^{-1}$. The reaction of $Ru_2(CH_3COO)_2(C_2O_4)_2^+$ with Ti^{3+} also occurs[5] in two stages, but the faster steps shows mass law retardation both with respect to $[H^+]^{-1}$ and also with respect to [Ti(III)]. In an effort to rationalize these reactivity patterns, we studied Ru(III)-Ti(III) redox reactions involving sulfato ligands as candidate bridging groups.

Sulfate ion is an effective bridging ligand in Co(III)-Cr(II)[6] and Co(III)-Ti(III)[7] redox reactions. Reaction[8] between $Co(NH_3)_5SSO_3^+$ and Cr^{2+} involves attack by Cr^{2+} on oxygen remote from the site of coordination and subsequent electron transfer. In contrast, $NH_2SO_4^-$ does not function as a bridge for inner-sphere Co(III)-Cr(II) electron transfer.[9] Chloride ion is an effective bridging ligand for inner-sphere electron transfer in Co(III)-Cr(II) reactions, but it is quite ineffective as a bridging ligand in Ru(III)-Ti(III) redox reactions;[10] NCS^-, on the other hand, though similar to Cl^- as a bridge for inner-sphere electron transfer in the Co(III)-Cr(II) cases, is much more effective than chloride for inner-sphere electron transfer in Ru(III)-Ti(III) cases. Thiocyanate ion is so effective for these t_{2g}-t_{2g} reactions, in fact, that the rate-limiting step in the redox reaction is formation of the binuclear complex.[2a] We set out to determine whether related differences in reactivity patterns occurred for sulfato ligands as candidate bridges in Ru(III)-Ti(III) redox reactions.

Experimental Section

In the following, coordinated waters are generally omitted and **Ru** represents $Ru(NH_3)_5$. Reagents and procedures were as previously described.[1-5] Kinetic data are shown in Table I.

$[\mathbf{RuOSO_3}]Cl$ was prepared by the procedure of Isied and Taube.[11] Elemental analyses and spectra are consistent with those reported. Alternatively, $\mathbf{RuOSO_3}^+$ was prepared in situ by reacting either $\mathbf{RuCl}^{2+}$ or freshly prepared $\mathbf{RuOH_2}^{3+}$ with H_2SO_4 solution (pH 2.0). The reaction mixture was heated at 70 °C, with stirring, for 5 h. The resulting yellow solution was cooled to room temperature (its pH adjusted to 1.0), transferred to an ion-exchange resin (BioRad 50W-X2, Li^+ form), and eluted with 0.25 M Li_2SO_4 (pH adjusted to 1.0). The equilibrium constant for

$$\mathbf{RuOSO_3H}^{2+} \rightleftharpoons \mathbf{RuOSO_3}^+ + H^+ \tag{1}$$

was determined spectrophotometrically to be 0.06 (±0.01) M. The UV spectra of acidified $\mathbf{RuOSO_3}^+$ solutions change slowly (over several hours).

$[\mathbf{RuNHSO_3}]Cl$ was prepared according to the method of Armor and Taube.[12] Elemental analyses and spectra are consistent with those reported. The equilibrium constant for

$$\mathbf{RuNH_2SO_3}^{2+} \rightleftharpoons \mathbf{RuNHSO_3}^+ + H^+ \tag{2}$$

was determined spectrophotometrically to be 2.0 (±0.5) × 10^{-3} M. Protonation of $\mathbf{RuNHSO_3}^+$ was complete within 4 ms ($k_2 > 7 \times 10^2\ s^{-1}$). Approximately 5% change is observed in the UV spectrum of a $\mathbf{RuNH_2SO_3}^{2+}$ solution within 15 min, but less than 1% change is observed for $\mathbf{RuNHSO_3}^+$ over 24 h.

$[\mathbf{RuS_2O_3}]Cl$ was prepared by the method of Armor and Taube.[12] Elemental analyses and spectra agreed with prior reports. There was no spectral evidence for an acid-base equilibrium.

Cyclical voltammograms of the three complexes were measured in a variety of media with use of a glassy-carbon electrode. Reductions were quasi-reversible. Reduction potentials (millivolts vs NHE, averages of anodic and cathodic peak potentials at 25 °C): $\mathbf{RuOSO_3}^+$ (in 0.1 M HCl/0.9 M LiCl), +64; $\mathbf{RuNH_2SO_3}^{2+}$ (pH 1.0, I = 1.0 M (Na_2SO_4/H_2SO_4)), +230; $\mathbf{RuS_2O_3}^+$ (1 < pH < 4, 1 M LiCl), -145. The potential (as above) measured for $Ru(NH_3)_6^{3+}$ (0.10 M LiCl, pH 2.0) was -6 mV vs NHE at 25 °C.

Kinetic measurements were made at 25.0 °C, generally in 1 M LiCl. Ti(III) was in at least 10-fold excess in kinetic runs. Pseudo-first-order rate constants, k_{obsd}, were reproducible to within 5%. All reductions were

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Table I. Kinetic Data for Reduction of Ru(III) Complexes by Ti(III) in 1 M LiCl at 25.0 °C

A. **Ru**OSO$_3^{+}$[a]

[Ti(III)], mM	[H$^+$], mM	$10^2\ k_{obsd}$, s^{-1}	[Ti(III)], mM	[H$^+$], mM	$10^2\ k_{obsd}$, s^{-1}	[Ti(III)], mM	[H$^+$], mM	$10^2\ k_{obsd}$, s^{-1}
2.2	19.6	2.86	4.6	39.5[c]	5.67	5.3	50.2[b]	4.8
9.3	25.0	9.36	5.3	39.5[b]	5.68	5.3	71.5[b]	3.1
4.6	27.0	4.40	4.6	39.5[d]	6.19	5.3	85.0[b]	3.7
16.5	30.0	14.0	4.6	48.0	2.44	6.0	85.0[b]	3.9
20.0	33.0	14.5	4.6	48.0	2.43	10.3	85.0[b]	6.7
5.3	39.2[b]	6.8	5.5	48.0	2.82	10.3	85.0[b]	6.7
4.6	39.5	3.13	9.5	48.0	4.91	12.2	85.0[b]	7.4
4.6	39.5	2.93	12.8	48.0	6.85	14.2	85.0[b]	9.1
4.6	39.5	5.03	13.6	48.0	7.21			

B. **Ru**NH$_2$SO$_3^{+}$[e]

[Ti(III)], mM	[H$^+$], mM	k_{obsd}, s^{-1}	k_2, M^{-1} s^{-1}	[Ti(III)], mM	[H$^+$], mM	k_{obsd}, s^{-1}	k_2, M^{-1} s^{-1}
3.5	10.0	2.28	651	13.6	53.0	2.66	196[g]
3.5	11.5	2.32	663	6.25	57.2	1.09	174
3.5	12.5	2.04	583	6.25	57.2	1.13	181
3.0	15.0	1.42	473	2.5	69.0	0.41	166
13.6	16.0	6.65	489	2.5	69.0	0.43	171[f]
3.0	17.7	1.27	423	8.5	69.0	1.43	168
3.5	21.7	1.35	385	8.5	69.0	1.49	184
3.5	25.8	1.12	320	12.0	69.0	2.21	184
3.5	25.8	1.14	326	19.0	69.0	3.48	183
3.5	25.8	1.16	331	19.0	69.0	3.53	186[g]
3.5	30.0	0.93	266	26.0	69.0	4.65	179[f]
3.5	30.0	1.01	288[f]	26.0	69.0	4.98	191
13.6	37.0	4.00	294	13.6	69.7	1.94	143
13.6	37.0	4.19	308	13.6	69.7	2.04	150
27.5	40.0	7.87	286	4.8	83.4	0.61	127[g]
16.0	45.0	4.34	271	13.6	112.0	1.29	95
13.6	53.0	2.81	207				

C. **Ru**S$_2$O$_3^{+}$[h]

[Ti(III)], mM	[H$^+$], mM	k_f, s^{-1}	k_s, s^{-1}	[Ti(III)], mM	[H$^+$], mM	k_f, s^{-1}	k_s, s^{-1}
4.8	5.6	9.8	0.56	10.0	23.1	16.1	3.53
6.0	8.6	12.9	4.73	12.1	23.1	17.8	3.83
8.0	11.5	14.9	4.44	18.1	25	22.4	4.26
8.0	13	14.5	3.69	18.1	28.7	21.9	5.49[i]
9.0	14.3	14.2	2.78	10.0	35	13.4	5.84
9.0	14.3	14.5	3.1[i]	5.3	46	5.6	1.94
7.8	14.5	12.3	3.07	5.3	46	5.9	2.44
5.3	21	8.6	1.94	5.3	66	4.35	1.53
4.2	23	5.5	1.61	5.3	110	2.88	0.51
8.0	23	12.0	2.75				

[a] [**Ru**OSO$_3^+$] = 0.20 ± 0.08 mM. [b] Added [SO$_4^{2-}$] = 20 mM. [c] Added [SO$_4^{2-}$] = 18 mM. [d] Added [SO$_4^{2-}$] = 29 mM. [e] [**Ru**NH$_2$SO$_3$] = 0.35 ± 0.15 mM. [f] In situ preparation. [g] LiCF$_3$SO$_3$ medium. [h] [**Ru**S$_2$O$_3^+$] = 0.25 ± 0.07 mM. [i] Ion-exchange eluent used as oxidant rather than solution prepared from solid.

found to have first-order specific rate constants that were linearly dependent on [Ti(III)].

Colorless **Ru**OSO$_3^+$ solutions turn yellow on addition of Ti(III). Polarography on the dme showed that 1.00 ± 0.02 mol of Ru(III)/mol of Ti(III) added is reduced. Rate was monitored by decrease in absorbance at 310 nm, the wavelength of maximum absorbance of **Ru**OSO$_3^+$. Pseudo-first-order plots were linear for at least 3 half-lives. For replicate runs, rate constants obtained with **Ru**OSO$_3^+$ and **Ru**OSO$_3^+$ (in situ preparation) solutions that were used within 30 min of preparation agreed within 5%. Smaller rates were measured by using solutions that had aged for longer periods. Second-order rate constants, k_b, increase with decreasing hydrogen ion concentration according to $k_b = k_a[\mathrm{H}^+]^{-1}$, where $k_a = 0.25\ \mathrm{s}^{-1}$. The value of k_{obsd}, at [H$^+$] = 39.5 mM and [Ti(III)] = 5.3 mM, increased with increasing added [SO$_4^{2-}$] according to

$$k_{obsd} = \frac{a + b[\mathrm{SO_4}^{2-}]}{1 + c[\mathrm{SO_4}^{2-}]} \tag{3}$$

where a, b, and c are 0.030 ± 0.001 s^{-1}, 7.6 ± 0.1 M^{-1} s^{-1}, and 105 ± 2 M^{-1}.

RuNH$_2$SO$_3^{2+}$ solutions turn yellow on addition of Ti(III). Polarography (dme) led to the conclusion that 1.0 mol of Ru(III)/mol of Ti(III) added is consumed. The rate of reaction was monitored by measuring the decrease in absorbance at 290 nm, a wavelength close to the absorbance maximum for **Ru**NH$_2$SO$_3^{2+}$, and also at 398 nm, the wavelength of maximum absorbance for **Ru**NHSO$_3^+$. To avoid complications due to aquation, reactions were generally initiated by acidifying solutions of **Ru**NHSO$_3^+$ (pH 6.5). Pseudo-first-order plots were linear for at least 3 half-lives. Rate constants obtained in 1.0 M LiCl and in 1.0 M LiCF$_3$SO$_3$ media agree within 5%. Second-order rate constants, k_b, increase with decreasing hydrogen ion concentration. The data follow

$$k_b = k_c + k_d[\mathrm{H}^+]^{-1} \tag{4}$$

where $k_d = 6.0 \pm 0.2\ \mathrm{s}^{-1}$ and $k_c = 86 \pm 7\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$.

Orange-red **Ru**S$_2$O$_3^+$ solutions fade on addition of Ti(III). The resulting solution has the odor of sulfur dioxide. Isosbestic points occur at 428 and 555 nm. Absorbance changes are consistent with a one-to-one stoichiometry. When lead acetate solution is added to the product solution within 10 s of mixing, a black precipitate forms, indicating that sulfide ions are among the final products. Kinetics were monitored by decrease in absorbance at 488 nm, the wavelength of maximum absorbance of **Ru**S$_2$O$_3^+$. The reactions were adequately described by a double exponential absorbance decrease, yielding two rate constants, k_f (for the faster relaxation, which accounted for the larger absorbance change) and k_s (for the slower relaxation, which accounted for the smaller absorbance change). Linear-least-squares programs were used to obtain initial estimates of parameters. Calculated absorbance vs time curves were compared to experimental data by using a CRT. Parameters were adjusted until differences between calculated and experimental curves were within experimental uncertainty. Reproducibility of rate constants thus obtained is ±8%.

Results

The IR spectrum of [**Ru**OSO$_3$]Cl indicates that sulfate is monodentate. Our results are consistent with Armor and Taube's[12]

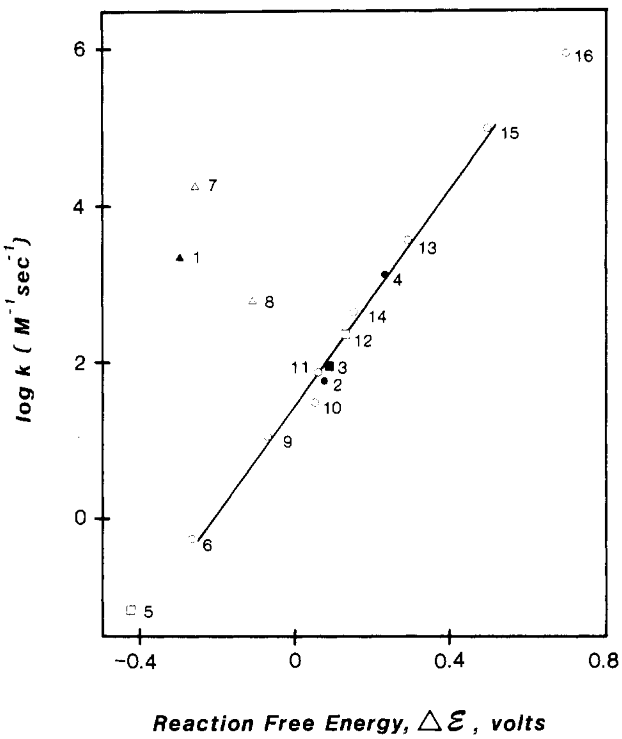

Figure 1. Second-order rate constant for Ti(III) reduction of Ru(III) complexes as a function of reaction free energy. Squares denote reactions of Ti^{3+}, circles indicate reactions of $TiOH^{2+}$, and triangles represent reactions of Ti^{3+} that are interpreted as inner-sphere reactions. The line has a slope of 0.5. Filled symbols correspond to reactions reported in this paper. Oxidants are as follows (**Ru** denotes $Ru(NH_3)_{5(or 4)}$): (1) $\mathbf{Ru}SSO_3^+$; (2) $\mathbf{Ru}SO_4^+$; (3, 4) $\mathbf{Ru}NH_2SO_3^{2+}$; (5, 6) $Ru(pd)_3$; (7) $\mathbf{Ru}C_2O_4^+$; (8) $\mathbf{Ru}OOCCH_3^{2+}$; (9) $\mathbf{Ru}Cl^{2+}$; (10) $\mathbf{Ru}NH_3^{3+}$; (11) $\mathbf{Ru}H_2O^{2+}$; (12, 13) $Ru_2(OOCCH_3)_4^+$; (14) **Ru**(pyridine)$^{3+}$; (15) **Ru**(pyrazine)$^{3+}$; (16) **Ru**(isonicotinamide)$_2^+$.

conclusion that $[\mathbf{Ru}NH_2SO_3]Cl_2$ involves coordination to ruthenium(III) through NH_2. Spectra also indicate coordination via sulfur for $\mathbf{Ru}SSO_3^+$.

Second-order rate constants for the reduction of $\mathbf{Ru}OSO_3^+$ by Ti(III) are inversely proportional to $[H^+]$. This behavior is observed for Ti(III) reduction of a number of Ru(III) complexes that lack bridging ligands[10] but is contrary to the behavior of complexes that carry adequate bridging ligands. This suggests that $TiOH^{2+}$ reduces $\mathbf{Ru}OSO_3^+$ in an outer-sphere mechanism. For $K_a = 4 \times 10^{-3}$ M, the rate constant for reduction of $\mathbf{Ru}OSO_3^+$ by $TiOH^{2+}$ is $k_b = 64\ M^{-1}\ s^{-1}$. This fits on the linear free energy relationship between log (rate constant) and reaction driving force (hereafter, LFER) for outer-sphere reduction (by $TiOH^{2+}$) of a series of Ru(III) complexes (Figure 1). This supports the interpretation that $TiOH^{2+}$ is the reductant in an outer-sphere reduction of the $\mathbf{Ru}OSO_3^+$ complex by Ti(III) and that Ti^{3+} is ineffective as a reductant.[13]

The kinetic results for reduction of $\mathbf{Ru}NH_2SO_3^{2+}$ by Ti(III) indicate[14] that both Ti^{3+} and $TiOH^{2+}$ are effective reductants. The rate constant corresponding to the reduction of $\mathbf{Ru}NH_2SO_3^{2+}$ by $TiOH^{2+}$, $1.5 \times 10^3\ M^{-1}\ s^{-1}$, lies on the LFER (Figure 1). The rate constant, corresponding to the Ti^{3+} reduction of $\mathbf{Ru}NH_2SO_3^{2+}$, 86 $M^{-1}\ s^{-1}$, also fits the LFER. This reactivity pattern was observed[1] for the Ti^{3+} reduction of $Ru(pd)_3$ and $Ru_2(OAc)_4^+$. The kinetic results on the reduction of $\mathbf{Ru}NH_2SO_3^{2+}$ are best interpreted as indicating outer-sphere mechanisms for which the ligand on the oxidant functions as an electron-withdrawing group.

In contrast to the linear dependence on inverse acid concentration found for the two reactions just discussed, the second-order rate constant, k_b^f, for the faster relaxation in the reduction of $\mathbf{Ru}S_2O_3^+$ by Ti(III) showed mass law retardation by $[H^+]$

$$k_b^f = \frac{kK}{[H^+] + K} \tag{5}$$

with $K = 0.03$ M and $k = 2.4 \times 10^3\ M^{-1}\ s^{-1}$. (In 2.0 M LiCl, k and K were 46 s^{-1} and 0.030 M.) As with the other two oxidants, the rate constant for this reaction is linearly dependent on [Ti(III)].

Ru(III)–Ti(III) reactions for which both inverse-[acid] and [reductant] dependences are nonlinear have previously been observed,[5] as have cases for which both are linear, but this is the first with a linear dependence on [reductant] and a nonlinear inverse-[acid] dependence. The limiting second-order rate constant for the reduction of $\mathbf{Ru}S_2O_3^+$ by Ti(III), $2.4 \times 10^3\ M^{-1}\ s^{-1}$ in 1.0 M LiCl ($1.3 \times 10^3\ M^{-1}\ s^{-1}$ in 2.0 M LiCl), lies above the LFER; that is, the observed value is considerably greater than the rate constant predicted for outer-sphere reduction by $TiOH^{2+}$. This requires that reduction of $\mathbf{Ru}S_2O_3^+$ by Ti(III) involve an inner-sphere mechanism.

Second-order rate constants for the Ti^{3+} reduction of $\mathbf{Ru}X^{(3-n)+}$ ($X^{n-} = CH_3COO^-, NCS^-$, salycilate, $C_2O_4^{2-}$) also lie above the LFER.[2,3] In these cases, variation of rate constant with charge type of the oxidant is consistent with variation of Ti(III) substitution rate with charge type of the entering ligand, as determined in independent studies. The rate constant for the thiosulfato oxidant is about 1 order of magnitude less than the corresponding rate constants for two corresponding oxalato oxidants, indicating that factors in addition to those regulating rate of formation of the binuclear complex are involved in reaction of $\mathbf{Ru}S_2O_3^+$ with Ti^{3+}.

A mechanism that is consistent with our results for reduction of $\mathbf{Ru}S_2O_3^+$ by Ti(III) is

$$\mathbf{Ru}S_2O_3^+ + Ti^{3+} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathbf{Ru}S_2O_3Ti^{4+} \tag{6}$$

$$\mathbf{Ru}S_2O_3Ti^{4+} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \mathbf{Ru}S_2O_3TiOH^{3+} + H^+ \tag{7}$$

$$\mathbf{Ru}^{III}S_2O_3Ti^{III}OH^{3+} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} \mathbf{Ru}^{II}S_2O_3Ti^{IV}OH^{3+} \tag{8}$$

$$\mathbf{Ru}^{II}S_2O_3Ti^{IV}OH^{3+} \xrightarrow{k_4} \text{products} \tag{9}$$

The rate law derived on the basis of this mechanism and assumptions that k_3 is rate-determining and that the two prior reactions are relatively rapid equilibria requires that all conditions that yield less than first-order dependence on $[H^+]^{-1}$ also yield less than first-order dependence on [Ti(III)]. The same rate law and the same conclusion follow from the use of Castellan's method,[15] which assumes that all significant reactions are near equilibrium. An alternative assumption, that electron transfer has a rate constant comparable to those of reactions preceding electron transfer, suggests applying the steady-state approximation to concentrations of both intermediates, $\mathbf{Ru}S_2O_3Ti^{4+}$ and $\mathbf{Ru}S_2O_3TiOH^{3+}$. This leads to the rate law

$$k_f = k_1k_2k_3[Ti^{3+}]/\{k_3(k_{-1} + k_2) + (k_2 + k_3)k_1[Ti^{3+}] + (k_{-1} + k_1[Ti^{3+}])k_{-2}[H^+]\} \tag{10}$$

When k_{-1} becomes large ($k_{-1} > k_2$, $k_1[Ti]^{3+}$), that is, if an unstable intermediate is formed between $\mathbf{Ru}S_2O_3^+$ and Ti^{3+}, eq 10 reduces to

$$k_f = \frac{K_1k_2k_3[Ti^{3+}]}{k_3 + k_{-2}[H^+]} \tag{11}$$

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[13] On the basis of the assumption that formation constants of the sulfato complexes of Ti(III) are the same as those of the corresponding oxalato complexes,[16] second-order rate constants for reductions by $Ti(H_2O)_5SO_4^+$ and $Ti(H_2O)_5SO_4H^{2+}$ of 0.2 and 14 $M^{-1}\ s^{-1}$ respectively, are inferred from the effect of added sulfate on the rate of reaction. These should be regarded as upper limits, since it is likely that the sulfate complexes are less stable than the corresponding oxalato complexes.

[14] Alternative interpretations involving deprotonation of the oxidant and/or an inner-sphere mechanism were considered, but none of our results requires such complications.

[15] Castellan, G. W. *Ber Bunsen-Ges. Phys. Chem.* **1963**, *67*, 898.

This requires linear dependence on $[\mathrm{Ti}^{3+}]$ and nonlinear dependence on $[\mathrm{H}^+]^{-1}$, the behavior observed in the reduction of $\mathbf{Ru}\mathrm{S_2O_3}^+$ by Ti(III).

From the slope of a plot of $[\mathrm{Ti(III)}][\mathrm{H}^+]^{-1}/k_f$ vs $[\mathrm{H}^+]^{-1}$, the product K_1k_2 is 2.4×10^3 M^{-1} s^{-1}. Using this result and the intercept of the same plot, we find $k_{-2} = 29k_3$. On the reasonable assumption that protonation of the conjugate base of the intermediate is diffusion-controlled, we take $k_{-2} = 10^{10}$ M^{-1} s^{-1} and compute k_3, the rate of intramolecular electron transfer, as 10^8 s^{-1}. Using the acidity constant for Ti^{3+}, 4×10^{-3} M, for the acid dissociation constant, K_2, of the binuclear complex, we obtain the value of k_2, the rate constant for deprotonation of the binuclear complex, as 4×10^7 s^{-1} and the formation constant of the intermediate as $K_1 = 6 \times 10^{-5}$ M^{-1}. The intermediate is unstable to dissociation. (The effect of changing the medium from 1 M LiCl to 2 M LiCl can be fitted by the single change of a decrease in K_1 to 3×10^{-5} M^{-1}.) Using an estimated rate constant for the substitution reaction between Ti^{3+} and a cation of unit charge[16] (3×10^4 M^{-1} s^{-1}) for k_1, we calculate the value of k_{-u}, the rate of breakup of the binuclear complex between $\mathbf{Ru}\mathrm{S_2O_3}^+$ and Ti^{3+}, to be 5×10^8 s^{-1}.

The second-order rate constant for the slower process, k_b^s, is 290 ± 10 M^{-1} s^{-1} in the range 0.014 M < [H$^+$] < 0.050 M. The slower relaxation is assigned to the breakup of the successor compllex $\mathbf{Ru}^{\mathrm{II}}\mathrm{S_2O_3Ti^{IV}OH^{3+}}$ (eq 9). Applying the steady-state approximation to the concentrations of the three intermediates, we obtain the rate law for the slower process:

$$k_s = \frac{k_1k_2k_3k_4[\mathrm{Ti}^{3+}]}{k_{-1}k_{-2}[\mathrm{H}^+](k_{-3} + k_4) + k_3k_4(k_{-1} + k_2) + k_1[\mathrm{Ti}^{3+}]A} \qquad (12)$$

where $A = (k_{-2}[\mathrm{H}^+] + k_2)(k_{-3} + k_4) + k_3(k_4 + k_2)$.

When $k_{-1} \rightarrow \infty$, eq 12 reduces to

$$k_s = \frac{k_1k_2k_3k_4[\mathrm{Ti}^{3+}]}{k_{-2}[\mathrm{H}^+](k_{-3} + k_4) + k_3k_4} \qquad (13)$$

A plot of k_s (at constant hydrogen ion concentration) vs $[\mathrm{Ti}^{3+}]$ should be linear. At [H$^+$] = 23 mM the data show the expected trend and are consistent with a k_4/k_{-3} ratio of 0.1. The slow process accounts for less than 10% of the total absorbance change. The precision of the data do not warrant discussion of the acid dependence of the slower process.

Discussion

TiOH^{2+} reduces $\mathbf{Ru}\mathrm{OSO_3}^+$, but we detect no evidence that Ti^{3+} acts as a reducing agent toward that ion. In contrast, both Ti^{3+} and TiOH^{2+} reduce $\mathbf{Ru}\mathrm{NH_2SO_3}^{2+}$. Rate constants for these three processes fit well on the LFER, supporting the conclusion that all three reactions involve outer-sphere mechanisms. Conversely, the kinetics indicate that reduction of $\mathbf{Ru}\mathrm{S_2O_3}^+$ by Ti^{3+} involves an inner-sphere mechanism with formation of an unusually *un*stable binuclear intermediate and fast intramolecular electron transfer within the conjugate base of that intermediate.

The kinetic difference between the sulfato and amido sulfato complexes is similar to differences between $\mathrm{Ru(NH_3)_6}^{3+}$ and $\mathrm{Ru_2(CH_3COO)_4}^+$. This indicates that the electron-acceptor orbital is more accessible in the $\mathrm{NH_2SO_3}$ case. This requires that the outer-sphere reactions of $\mathbf{Ru}\mathrm{NH_2SO_3}^{2+}$ involve close approach of the reductant to the coordinated amido group.

Sulfate ion is an effective bridging ligand in Co(III)–Ti(III)[7] and Co(III)–Cr(II) redox reactions. The rate of formation and formation constant for the binuclear intermediate for inner-sphere reduction of $\mathrm{M(NH_3)_5SO_4}^+$ by Ti^{3+} ought to be similar for both Co(III) and Ru(III) oxidants. Absence of an inner-sphere path for the reaction of present interest indicates a substantial barrier to intramolecular electron transfer in the Ru(III)–Ti(III) case.

Both chloride ion and sulfate ion are effective bridging ligands in Co(III)–Cr(II) but not in Ru(III)–Ti(III)[10] redox reactions. Even though driving force is greater for Co(III)–Cr(II) reactions than for Ru(III)–Ti(III) reactions, the latter are much faster. Since activation barriers are high for Co(III)–Cr(II) reactions, the reaction rate is quite sensitive to specific electronic effects. The difference between the two couples (with respect to effectiveness of Cl$^-$ and SO$_4$ as bridges) seems best interpreted as indicating that although sulfate and chloride are effective in mediating σ–σ (e_g–e_g) electron transfer, they are ineffective in mediating π-electron (t_{2g}–t_{2g}) transfer. This difference, in turn, seems best ascribed to lack (on these ligands) of vacant electronic orbitals of appropriate symmetry and energy for facilitating interaction of electron-donor and electron-acceptor metal-centered orbitals of π symmetry. Unoccupied π orbitals have high energies for both Cl$^-$ and SO$_3$.

In contrast to the three reactions discussed above, the reduction of $\mathbf{Ru}\mathrm{S_2O_3}^+$ by Ti^{3+} involves an inner-sphere electron-transfer mechanism. Both coordinated sulfur and remote oxygen are potential sites for attack by Ti^{3+} on $\mathbf{Ru}\mathrm{S_2O_3}^+$. Lability of Ti(IV) prevents direct determination of the bonding mode of Ti(IV) by product analysis. Ti(III), a "hard acid", would be expected to form weaker complexes with sulfur donors than with oxygen donors and weaker complexes with chlorine donors than with fluorine donors. This expectation is borne out in reactions[17] of titanium(III) halides with organo ethers and organo thioethers and also by the observation that titanium(III) reacts with $\mathbf{Co}\mathrm{F}^{2+}$ by an inner-sphere mechanism but with $\mathbf{Co}\mathrm{Cl}^{2+}$ by an outer-sphere mechanism.[7,18] On this basis, thermodynamic stability of the intermediate favors attack of Ti(III) on remote oxygen rather attack on adjacent sulfur. The unusual acid dependence of the rate constants for this reaction requires an *unstable* intermediate; this suggests that the less stable rather than the more stable binuclear complex is involved. Our results support the interpretation that, in the reduction of $\mathbf{Ru}\mathrm{S_2O_3}^+$ by Ti(III), the Ti^{3+} interaction that is involved in the electron-transfer reaction includes attack at sulfur rather than at oxygen. This is consistent with the low tendency of SO$_3$ to act as a bridging ligand for Ru(III)–Ti(III) electron transfer that is demonstrated by the three reactions first discussed above. The complex in which Ti(III) is coordinated to (remote) oxygen may be more stable than its isomer in which Ti(III) is bound to (adjacent to Ru(III)) sulfur, but the former has a higher barrier to intramolecular electron transfer than has the latter; hence, the oxygen-bound complex is a "dead-end", not on the redox reaction coordinate.

The difference between the Co(III)–Cr(II) and Ru(III)–Ti(III) systems in the case of thiosulfate is parallel to the difference in the case of thiocyanate and chloride ions. The SO$_3$ group, like the chloride ion, is adequate as a bridge for σ–σ electron transfer, but it is not efficient for π–π electron transfer; coordinated sulfur, however, *is* an efficient π-bridging ligand.

A Unified Treatment for Ru(III)–Ti(III) Redox Reactions

Equation 10 can be used to account for the behavior of all inner-sphere Ru(III)–Ti(III) redox reactions studied thus far. When k_{-1}, the rate of breakup of the binuclear intermediate, is large, eq 10 reduces to eq 11. This behavior is observed for $\mathbf{Ru}\mathrm{S_2O_3}^+$ and[19] $\mathrm{Ru(C_2O_4)_3}^{3-}$. When k_2, the rate of deprotonation of the binuclear complex, and k_3, the rate of intramolecular electron transfer, are large, eq 10 reduces to

$$\lim_{k_2,k_3\to\infty} k_f = k_1[\mathrm{Ti}^{3+}] \qquad (14)$$

Linear dependence of redox rate on $[\mathrm{Ti}^{3+}]$ and absence of acid dependence are observed for the Ti(III) reductions of $\mathbf{Ru}\mathrm{X}^{(3-n)+}$, where $\mathrm{X}^{n-} = \mathrm{C_2O_4}^{2-}$, $\mathrm{CH_3COO^-}$, $\mathrm{NCS^-}$, and salicylate ion. When k_1, the rate of substitution onto Ti^{3+}, and also k_3, the rate of

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intramolecular electron transfer, are small, eq 10 reduces to

$$\lim_{k_1,k_3\to 0} k_f = K_1K_2k_3[\mathrm{Ti}^{3+}]/[\mathrm{H}^+] \qquad (15)$$

Linear dependence of redox rate on $[\mathrm{Ti}^{3+}]$ and inverse hydrogen ion dependence have been observed[4] for reduction of $(pd)_2Ru(fpd)$ by Ti(III). When k_3, the rate of intramolecular electron transfer, is small, eq 10 reduces to

$$\lim_{k_3\to 0} k_f = \frac{k_3K_1K_2[\mathrm{Ti}^{3+}]}{[\mathrm{H}^+] + K_1[\mathrm{Ti}^{3+}][\mathrm{H}^+] + K_1K_2[\mathrm{Ti}^{3+}]} \qquad (16)$$

which has the same form as the rate law determined for the Ti^{3+} reduction[5] of $Ru_2(OAc)_2(C_2O_4)_2^+$. Equation 16 is a special case of eq 10 that applies when the system is at or near[11] equilibrium.

Present understanding of Ru(III)–Ti(III) reactions can be summarized as follows. In reductions of $Ru^{III}X$ complexes by Ti(III), outer-sphere electron transfer prevails when X is NH_3, H_2O, Cl^-, pyridine, ethylenediamine, pentane-2,4-dionate, or sulfate. Some of these ligands have no open coordination position, but others, such as Cl^- and SO_4^{2-}, have residual coordinating ability. Lack of bridging effectiveness in these cases must have a different explanation. Insufficiency of interaction between electron-donor and electron-acceptor orbitals within the assembled binuclear intermediate must be invoked. This, in turn, seems due to inappropriate energy of ligand orbitals that have correct symmetry for mixing the electron-donor and electron-acceptor orbitals on the redox partners.

All known outer-sphere Ru(III)–Ti(III) redox reactions display $TiOH^{2+}$ paths, but reaction of Ti^{3+} with ruthenium(III) oxidants that lack electron-delocalizing ligands is not observed (such Ti^{3+} reactions are anomalously slow; this has been ascribed[1] to nonadiabaticity arising from lack of effective overlap between electron-donor and electron-acceptor orbitals). On the other hand, when X is a ligand such as oxalate, acetate, thiocyanate, or salicylate that has a coordination position to bind the reductant and also has a delocalized π-orbital system, inner-sphere electron transfer predominates and substitution on Ti^{3+} is rate-limiting. An extraordinarily unstable binuclear intermediate (as in the case of the thiosulfato complex reported here) can reduce observed rate constants even if electron transfer is rapid. When an oxidant-linked ligand has a vacant coordination site but there is a barrier to electron transfer, more complex rate behavior is observed, as required by eq 10. This occurs in the Ti^{3+} reductions of $(pd)_2Ru(fpd)$[4] and of $Ru_2(OAc)_2(C_2O_4)_2^+$.[5] The kinetics indicate that the formation constant of the binuclear complex between $(pd)_2Ru(fpd)$ and Ti^{3+} is small ($K_f \geq 1\ M^{-1}$), whereas a relatively stable trinuclear complex (K_f = ca. $5 \times 10^2\ M^{-1}$) is involved in reduction of $Ru_2(OAc)_2(C_2O_4)_2^+$. The differences in kinetic behavior observed can be understood on this basis.

The Ru(III)–Ti(III) couple exhibits a wide variety of kinetic patterns, but these differences in kinetic behavior follow understandable patterns.

Registry No. Ti^{3+}, 22541-75-9; $Ru(NH_3)_5SO_4^+$, 113322-96-6; $Ru(NH_3)_5S_2O_3^+$, 76790-96-0; $Ru(NH_3)_5NH_2SO_3^{2+}$, 51259-40-6.

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Volume Profiles as Mechanistic Information for the Trans ⇌ Cis Isomerizations of $Co(en)_2(H_2O)X^{n+}$ ($X = H_2O, OH^-, NCS^-, NH_3, NO_2^-, Br^-, N_3^-$) and $Co(en)_2(OH)Y^{n+}$ ($Y = OH^-, NH_3$)

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Activation volumes (ΔV^*) and reaction volumes (ΔV) have been obtained for the title reactions. The magnitudes of ΔV are close to zero (−6 to +2 $cm^3\ mol^{-1}$), and correlation exists between the ΔV for $Co(en)_2(H_2O)X^{n+}$ and the order of X in the spectrophotochemical series. Values of ΔV^* are in the range 5–8 $cm^3\ mol^{-1}$ for isomerizations of $Co(en)_2(H_2O)X^{n+}$ ($X = H_2O, OH^-, NCS^-, NH_3, N_3^-$). These include three reactions ($X = H_2O, OH^-, NCS^-$) that are known to proceed with exchange of coordinated water with the solvent. By contrast, ΔV^* is conspicuously large (18 $cm^3\ mol^{-1}$) for the isomerization of $Co(en)_2(OH)NH_3^{2+}$, which is known to proceed without exchanging OH^- or NH_3. We interpret the relatively small ΔV^* (2.1 $cm^3\ mol^{-1}$) for the isomerization of $Co(en)_2(H_2O)Br^{2+}$ in light of the relative lability of the Br^- ligand. On this basis, we consider that isomerizations of $Co(en)_2(H_2O)X^{n+}$ ($X = H_2O, OH^-, NCS^-, NH_3, Br^-, N_3^-, SeO_3H^-, SeO_3^{2-}, CH_3COO^-, Cl^-$) proceed through the $Co–OH_2$ bond dissociation by an interchange mechanism.

Introduction

Recently, activation volumes (ΔV^*) have been considered as useful mechanistic information for inorganic reactions.[2] Concerning the isomerization of a Co^{III} complex, Stranks and Vanderhoek followed the isomerization of *trans*-$Co(en)_2(H_2O)_2^{3+}$

$$trans\text{-}Co(en)_2(H_2O)_2^{3+} \rightleftharpoons cis\text{-}Co(en)_2(H_2O)_2^{3+}$$

in acidic solution at high pressure up to 138 MPa and obtained ΔV^*.[3] They compared this magnitude of ΔV^* with that for the water-exchange reaction[4]

$$trans\text{-}Co(en)_2(H_2O)(H_2{}^{18}O)^{3+} + H_2O \rightarrow trans\text{-}Co(en)_2(H_2O)_2^{3+} + H_2{}^{18}O$$

They explained that the $\Delta V^* = 12.6–14.3\ cm^3\ mol^{-1}$ of the isomerization corresponded to a dissociative water release in the transition state yielding a trigonal-bipyramidal configuration and that in contrast the $\Delta V^* = 5.9 \pm 0.2\ cm^3\ mol^{-1}$ of the water exchange corresponded to a water release in the transition state by an interchange mechanism yielding a tetragonal-pyramidal configuration.[3,4] They emphasized that the mechanistic difference between the isomerization and the water exchange, as originally pointed out by Kruse and Taube, was revealed by these magnitudes of ΔV^*.[5] Subsequently, ΔV^* has been obtained for the following isomerizations:[6,7]

$$trans\text{-}Co(en)_2(H_2O)X^{n+} \rightleftharpoons cis\text{-}Co(en)_2(H_2O)X^{n+}$$

$$X = SeO_3H^-, SeO_3^{2-}, CH_3COO^-, Cl^-$$

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