the doubly reduced 2− cluster could have most interesting magnetic and low-energy electronic absorption spectral properties.

Changes in the terminal ligands on the periphery of the cluster such as exchanging pyridines for methanol or going from symmetrical, $[Ru_3O(OAc)_6(py)_3]^{n+}$, to unsymmetrical, $[Ru_3O(OAc)_6(py)_2pyr]^{n+}$, clusters lead to relatively slight but understandable changes in cluster properties. However, in the neutral carbonyl cluster $[Ru_3O(OAc)_6(py)_2CO]$, the single CO group creates a large electronic asymmetry and the properties of the CO cluster are significantly modified. The importance of Ru → CO back-bonding is seen in the lability of the CO group following oxidation to the 1+ cluster, a reaction which can be exploited synthetically to give unsymmetrically substituted clusters and, ultimately, dimers and higher oligomers. Because of the effect of the CO group, the electronic structure and chemical properties of this cluster may be understandable in terms of interacting but reasonably localized Ru–CO and Ru–O–Ru dimeric sites.

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Linear Free Energy Relationship for Outer-Sphere Reduction of Ruthenium(III) Amine Complexes by Titanium(III)

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Second-order rate constants k have been measured for reactions by which various Ru(III) complexes are reduced to corresponding Ru(II) complexes by $TiOH^{2+}$. At 25 °C, in media of 1 M ionic strength, values of k ($M^{-1}\ s^{-1}$) are as follows: $Ru(NH_3)_5H_2O^{3+}$, 66; $Ru(NH_3)_5py^{3+}$, 4.2×10^3; $Ru(NH_3)_5pyr^{3+}$ (pyr = pyrazine), 1.5×10^5; *cis*-$Ru(NH_3)_4(isn)_2{}^{3+}$ (isn = isonicotinamide), 1×10^6. For the last-named complex, a path involving reduction by Ti^{3+} ($k^\circ = 2 \times 10^4\ M^{-1}\ s^{-1}$) was also observed. The values of k are found to follow a linear free energy relationship with slope near $^1/_2$, when plotted against the reduction potentials of the Ru(III) complexes. The variation in rate constant with $\mathcal{E}^\circ$ is mainly due to a variation in enthalpy of activation.

Introduction

Rates of redox reactions of inorganic ions are often sensitive to variation in thermodynamic driving force. Even before mechanistic and theoretical understanding was well developed, it had been shown that certain redox systems followed linear free energy relationships (LGR); that is, straight lines were obtained when log k was plotted against ΔG°.[1] Sutin,[2] and later other workers, demonstrated that a number of sets of reactions involving the outer-sphere electron-transfer mechanism follow LGR. We have also shown[3] that Cr(II)–Cr(III) electron-transfer reactions (which involve the inner-sphere mechanism) follow a LGR with a slope near $^1/_2$. When free-energy data are not available, "indirect" LGR (involving either or both mechanisms) can sometimes be obtained by comparing rates of reduction of various reductants with a series of common oxidants.[4]

Chow, Creutz, and Sutin[5] have called attention to a number of factors which could complicate interpretation of rates of electron-transfer reactions in terms of theory. One such factor is variation in the extent of electron-donor orbital, electron-acceptor orbital interaction in the transition state. Since both of these orbitals have t_{2g} symmetry for Ru(III)–Ti(III) reactions, such overlap is favored. This effect has previously[6a] been invoked to explain one of the chemical peculiarities which is common to Ru(II) and Ti(III), that is, facile reduction of ClO_4^- ion. The present paper deals with simple outer-sphere

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processes; subsequent publications will deal with inner-sphere processes for reduction of Ru(III) complexes by Ti(III).[6b]

Experimental Section

Titanium(III) Solutions. Stock solutions of Ti(III) in chloride and trifluoromethanesulfonate media were prepared as previously described. They were standardized by oxidation to Ti(IV) with Cr(VI), excess Cr(VI) being determined iodometrically. Hydrogen ion concentrations of titanium(III) stock solutions were determined by two independent methods. In one method, aliquot portions were passed down an oxygen-free cation exchange column [Amberlite IR 120 (H)] and the total acid content of the eluent solution was determined by titration with standard base. Another method was direct NaOH titration (carried out slowly with constant stirring) of diluted Ti(III) stock solution. A white deposit of $TiO_2(s)$ was observed. The $[H^+]$ present in the Ti(III) stock solution was obtained from the relation $[OH^-] = [H^+] + 3[Ti(III)]$, assuming quantitative conversion to $TiO_2(s)$ by $4Ti^{3+} + O_2 + 12OH^- \rightarrow 4\ TiO_2(s) + 6H_2O$. More rapid addition of base to Ti(III) solutions gave a blue, presumably polymeric, titanium-containing material and nonreproducible titration results. The acidity of the Ti(III) stock as determined by the two methods was found to be in good agreement (±1%).

Preparation of Ruthenium Complexes. The complexes $[Ru(NH_3)_5Cl]Cl_2$,[7] $[Ru(NH_3)_5py](ClO_4)_3$,[8] *cis*-$[Ru(NH_3)_4(isn)_2](ClO_4)_2$,[8] and $[Ru(NH_3)_5pyr](ClO_4)_2$ were prepared by published procedures. $[Ru(NH_3)_5H_2O](ClO_4)_3$ was obtained by dissolving $[Ru(NH_3)_5Cl]Cl_2$ (0.1 g) in concentrated NH_3 (~2 mL) with warming to 40 °C. The resulting pink solution was filtered, cooled in ice, and carefully acidified by dropwise addition of 60% $HClO_4$. The resulting white solid was twice recrystallized from 0.1 M $HClO_4$ and washed with methanol. Fresh samples of the solid were prepared daily. The spectrum of the complex, λ 269 (ϵ 768), λ 325 (ϵ 91), was in good agreement with published data. The pyrazine and bis(isonicotinamide)ruthenium(III) complexes were prepared in solution by oxidation of the corresponding Ru(II) complexes using a suspension of PbO_2. A solution of Ru(II) (10^{-4}–10^{-5} M) in 1.0 M $LiClO_4$ was treated with $PbO_2(s)$ and filtered. The resulting Ru(III) solution, after deoxygenation, was used directly in the kinetic experiments. Addition of Ti(III) to such solutions resulted in quantitative regeneration of Ru(II), indicating no apparent interference from dissolved PbO_2, the concentration of which was very low. Spectra of the ruthenium complexes were in good agreement with literature values:[8,9] $Ru(NH_3)_5py^{3+}$, λ 262 (ϵ 4.55×10^3), λ 253 (ϵ 4.50×10^3); $Ru(NH_3)_5pyr^{2+}$, λ 473 (ϵ 1.2×10^4), λ 258 (ϵ 0.64×10^4); *cis*-$Ru(NH_3)_4(isn)_2^{2+}$, λ 480 (ϵ 1.45×10^4), λ 415 (ϵ 1.11×10^4), λ 260 (ϵ 8.7×10^3).

Other Materials. CF_3SO_3H, from the 3M Co., was twice distilled under reduced pressure from an all-glass, grease-free apparatus, prior to use. $LiClO_4$, LiCl, and $LiCF_3SO_3$ were prepared by neutralization of Li_2CO_3 with the appropriate acid. Stock solutions were analyzed by passage of aliquot portions through a cation exchange column [Amberlite IR 120 (H)], the eluent being determined with standard base. Argon, for exclusion of oxygen, was passed through Cr(II) scrubbers. For some of the more rapid reactions, N_2 was used.

Kinetic Measurements. Rate measurements on the complex $Ru(NH_3)_5OH_2^{3+}$ were made by following changes in absorbance at 310 nm using a Gilford 240 spectrophotometer equipped with a thermostable 10-cm cell compartment and a fast-scanning recorder. The reaction was studied at 1.0 M ionic strength in $LiCF_3SO_3/CF_3SO_3H$ media. A Durrum stopped-flow spectrophotometer coupled to a Biomation transient recorder and a Hewlett-Packard X-Y recorder with a time base was used to measure the faster reaction rates of the other complexes. Absorbance increases accompanying the reduction of $Ru(NH_3)_5py^{3+}$, $Ru(NH_3)_5pyr^{3+}$, and *cis*-$Ru(NH_3)_4(isn)_2^{3+}$ were followed at 408, 540, and 480 nm, respectively. These reactions were also studied at 1.0 M ionic strength but in mixed $LiClO_4$/LiCl media. The Ru(III) complexes at 1.0 M ionic strength ($LiClO_4/HClO_4$) were mixed in the stopped-flow instrument with Ti(III) solutions which had also been adjusted previously to an ionic strength of 1.0 M, but with LiCl.

Stoichiometry was checked for each reaction by carrying out one or more experiments with initial [Ti(III)] comparable to that of Ru(III). In all cases checked, the stoichiometry Ru(III) + Ti(III) → Ru(II) + Ti(IV) was followed.

All reactions for which rate constants are reported were carried out under pseudo-first-order conditions with Ti(III) present in at least a 10-fold excess. Specific rates (k_0) were calculated from the slopes of standard plots which were linear to at least 3 half-lives. The temperature during reaction was maintained in all cases to ±0.2 °C. Replicate runs agreed within 5%.

Table I. Rate Constants for the Reduction of $Ru(NH_3)_5OH_2{}^{3+}$ by Ti(III) at 25 °C and 1.0 M Ionic Strength ($LiCF_3SO_3$)

$[H^+]$, mM	[Ti(III)], mM	10^4[Ru(III)], M	10^3k_0,[a] s^{-1}	k_2,[b] M^{-1} s^{-1}	k',[c] s^{-1}
20.0	2.53	2.3	55.9	22.1	0.44
20.5	2.05	2.0	34.5	16.8	0.35
29.8	2.57	2.1	27.5	10.7	0.32
42.2	5.06	4.1	43.0	8.50	0.36
60.0	4.88	4.4	26.7	5.46	0.33
79.2	4.88	4.3	22.0	4.51	0.36
102	5.06	4.1	16.8	3.32	0.34
121	6.11	3.9	15.2	2.49	0.30
204	4.88	4.1	7.1	1.45	0.30

[a] k_0 is the observed pseudo-first-order rate constant. [b] $k_2 = k_0/[Ti(III)]$. [c] $k' = k_2[H^+]$.

Most of the reactions were studied in media in which Cl^- was the dominant anion but which also contained amounts of ClO_4^-. Previous work[10,11] has shown that chloride is an innocent medium anion for Ti(III) oxidations. The rates of the reactions studied here were generally much faster than the rate of reduction of ClO_4^- by Ti(III) so that no complication from the reaction was expected, and none was observed. In the case of $Ru(NH_3)_5H_2O^{3+}$, however, reduction was rather slow so that presence of ClO_4^- was avoided as a precaution. Also, in Cl^- media, reduction of $Ru(NH_3)_5H_2O^{3+}$ by Ti^{3+} yields an autocatalytic reaction, presumably due to formation of $Ru(NH_3)_5Cl^{2+}$ by Cl^- anation of the initial Ru(II) product, followed by rapid Ru(II)–Ru(III) electron exchange.[5] For this reason, the reduction of this oxidant was studied in poorly complexing $CF_3SO_3^-$ media. Estimates of k based on initial values in Cl^- media were consistent with more precisely measured values for reactions in $CF_3SO_3^-$ solutions. The autocatalytic path was not observed in Cl^- media in cases for which rates of Ru(III) reduction were faster than anation rates of the initial Ru(II) product. Reductions of $Ru(NH_3)_5H_2O^{3+}$ in solutions containing CF_3SO_3H which had not been redistilled gave poorly reproducible kinetic data and early deviations from pseudo-first-order kinetics. Strong absorption in the region 390–440 nm characterized the products of such experiments.

Results

Tables I, II, and III show the variation of observed pseudo-first-order rate constant with [Ti(III)] and $[H^+]$. All reactions follow the rate law rate = k_2[Ru(III)][Ti(III)], where the second-order rate constant decreases with increasing $[H^+]$. With one exception, all of the reactions have rates which are satisfactorily regarded as being inversely proportional to $[H^+]$; that is, $k'(=k_2[H^+])$ is constant, within experimental error. For the $Ru(NH_3)_4(isn)_2^{3+}$ complex, however, k' increases with increasing $[H^+]$. It seems most reasonable to ascribe this to a small contribution from an acid-independent path. Similar contributions have been reported in other reactions of Ti^{3+}.[10,12] The precision of our data is not sufficient to unambiguously rule out other interpretations. For this oxidant only, the rate law which best fits our data is $k_2 = k^\circ + k''/[H^+]$. Except at the highest acidities, the second term predominates.

For most of the reactions, the acid-inverse path is clearly best interpreted[13] as corresponding to a reduction by $Ti(OH)^{2+}$, but in the case of the reduction of $Ru(NH_3)_5H_2O^{3+}$ there is some ambiguity. The proton lost during the activation process for reduction of the aquo ion might come from either the oxidant or the reductant. Using 4.0 as the pK_a of $Ru(NH_3)_5H_2O^{3+}$, the data of Table I yield a value of 4×10^3 M^{-1} s^{-1} for the rate of reduction of $Ru(NH_3)_5OH^{2+}$ by Ti^{3+}. In the event that this mechanism were operative, a term inverse second order in $[H^+]$ might be expected.[15] We have observed[16] such a term in the Ti^{3+} reduction of *cis*-$Co(en)_2(H_2O)_2^{3+}$. There is no evidence of such a term in this case; therefore we

Table II. Rate Constants for the Ti(III) Reduction of Ruthenium(III) Oxidants at 1.0 M Ionic Strength[a]

$[H^+]$, mM	$[Ti(III)]$, mM	$10^5[Ru(III)]$, M	T, °C	$10^{-3}k_2$,[b] $M^{-1}\ s^{-1}$	$10^{-2}k'$,[c] s^{-1}
		$Ru(NH_3)_5py^{3+}$			
24.1	3.45	3.9	25.0	0.862	0.21
51.4	2.76	7.0	25.0	0.386	0.20
76.4	3.45	3.9	25.0	0.284	0.22
108	2.76	7.0	25.0	0.198	0.21
151	3.45	3.9	25.0	0.142	0.21
205	2.76	7.0	25.0	0.101	0.21
24.1	3.45	3.9	12.2	0.285	0.069
76.4	3.45	3.9	12.2	0.102	0.078
151	3.45	3.9	12.2	0.0485	0.073
24.1	3.45	3.9	39.7	2.22	0.54
76.4	3.45	3.9	39.7	0.881	0.67
151	3.45	3.9	39.7	0.395	0.60
		$Ru(NH_3)_5pyr^{3+}$			
24.1	3.45	0.83	25.0	23.9	5.8
51.4	2.76	1.5	25.0	14.7	7.5
76.4	3.45	0.83	25.0	9.34	7.1
108	2.76	1.5	25.0	6.63	7.2
151	3.45	0.83	25.0	4.86	7.3
205	2.76	1.5	25.0	3.49	7.2
24.1	3.45	0.83	14.9	12.0	2.9
76.4	3.45	0.83	14.9	4.24	3.2
151	3.45	0.83	14.9	2.23	3.4
24.1	3.45	0.83	35.0	47.5	11.4
76.4	3.45	0.83	35.0	18.6	14.2
151	3.45	0.83	35.0	9.9	14.9
24.1	3.45	0.83	43.9	77.3	18.6
76.4	3.45	0.83	43.9	34.6	26.4
151	3.45	0.83	43.9	18.6	28.1

[a] $LiCl/LiClO_4$ medium, 25.0 °C. [b] $k_2 = k_0/[Ti(III)]$, where k_0 is the observed pseudo-first-order rate constant. [c] $k' = k_2[H^+]$.

Table III. Rate Constants for the Ti(III) Reduction of $Ru(NH_3)_4(isn)_2{}^{3+}$ at 1.0 M Ionic Strength[a]

$[H^+]$, mM	$[Ti(III)]$, mM	$10^5[Ru(III)]$, M	10^3k_2,[b] $M^{-1}\ s^{-1}$	$10^{-2}k'$,[c] s^{-1}	$10^{-2}k''$,[d] s^{-1}
24.2	0.965	4.8	227	55	50
58.0	0.965	6.0	110	63	52
70.9	1.17	3.0	84	60	45
70.9	5.52	3.0	90	64	49
70.4	3.45	3.0	78	55	41
81.4	0.965	4.8	91	74	57
119	0.965	6.0	65	77	53
160	0.965	4.8	52	83	51
198	0.965	6.0	41	82	41

[a] $LiCl/LiClO_4$ medium, 25.0 °C. [b] $k_2 = k_0/[Ti(III)]$, where k_0 is the observed pseudo-first-order rate constant. [c] $k' = k_2[H^+]$. [d] $k'' = (k_2 - k^\circ)/[H^+]$ where k°, an acid-independent rate constant, is $2 \times 10^4\ M^{-1}\ s^{-1}$.

Table IV. Summary of Data on $TiOH^{2+}$ Reduction of Ru(III) Amine Oxidants at 25.0 °C

oxidant	k,[a] $M^{-1}\ s^{-1}$	$\mathcal{E}^\circ$,[b] mV vs. NHE
cis-$Ru(NH_3)_4(isn)_2{}^{3+}$	1×10^6 [c]	700
$Ru(NH_3)_5pyr^{3+}$	1.5×10^5	490
$Ru(NH_3)_5py^{3+}$	4.2×10^3	305
$Ru(NH_3)_5H_2O^{3+}$	66	66
$Ru(NH_3)_6{}^{3+}$ [d]	35	51
$Ru(NH_3)_5Cl^{2+}$ [d]	12	−42

[a] For reduction by $TiOH^{2+}$ on the assumption that K_a for acid dissociation of Ti^{3+} (at 25 °C) is 5×10^{-3} M, $k = k'/K_a$. [b] Data from ref 12, 25 °C; see original for media. Ru(III)/Ru(II). [c] Calculated from k'', an inverse acid rate constant obtained from $k_2 = k^\circ + k''/[H^+]$, where k° is $2 \times 10^4\ M^{-1}\ s^{-1}$. That is, $k = k''/K_a$. [d] Data from ref 11.

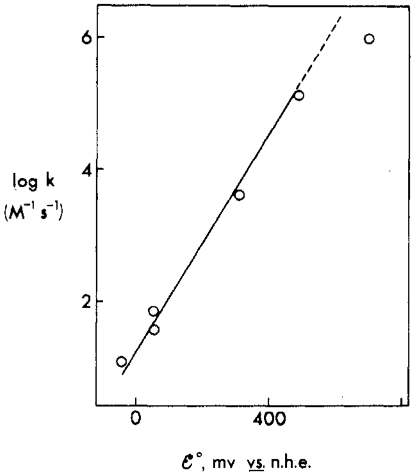

Figure 1. Variation of second-order rate constant for reduction of certain Ru(III) complexes by $TiOH^{2+}$, with reduction potential for the Ru(III) complexes, in saline (1 M) aqueous media at 25 °C. See Table IV for further details.

prefer to interpret the reduction of the aquo ion, as with the other reactions, as a reduction of Ru(III) by $Ti(OH)^{2+}$.

Table IV shows values of k, the rate constant for reduction by $TiOH^{2+}$ obtained from k' (or k'') using 5×10^{-3} M as the value of K_a for Ti^{3+} appropriate[11] to our conditions. Also shown in the table are reduction potentials for the Ru(III) oxidants. Data pertaining to temperature dependencies are shown in Table V. Pecsok and Fletcher[13b] studied the effect of temperature on the K_a of Ti^{3+} by potentiometric titration, but they stated that their results were not precise enough to determine ΔH° and ΔS° for the acid dissociation. The value of ΔH° for the acid dissociation of V^{3+} is about 42 kJ mol^{-1}, and other M^{3+} ions are similar in this respect. If we assume that this value applies to Ti^{3+} as well, then the activation parameters $\Delta H^\ddagger$ and $\Delta S^\ddagger$ which pertain to reduction by $TiOH^{2+}$, would be those shown in the last two columns of Table V. Corresponding data for $Ru(NH_3)_6{}^{3+}$ and $Ru(NH_3)_5Cl^{2+}$ are included in Tables IV and V.

Figure 1 shows that the five points corresponding to lower values of Ru(III) reduction potential follow the relationship of eq 1 ($2.30\,RT/\mathcal{F}$ is 59 mV at 25 °C). Since the point for

$$\log k = 1.30 + 0.48\mathcal{E}/59 \qquad (1)$$

$Ru(NH_3)_4(isn)_2{}^{3+}$ falls significantly below that line, there is a suggestion that

$$\log k - \log {}^0k = \alpha(\mathcal{E}/59) + \beta(\mathcal{E}/59)^2 \qquad (2)$$

where ${}^0k$ is the rate constant at the zero of potential, might be a more appropriate form. Since the data are well fitted by a straight line, the value of β in eq 2 would be small. It seems that 0.01 is a reasonable estimate of the upper limit of the magnitude of β which would be consistent with the data. The precision of our data, especially that of the deviant point, does not seem great enough to warrant more extensive treatment.

Discussion

Lack of ligands which can function as electron-transfer bridging groups restricts $Ru(NH_3)_6{}^{3+}$, $Ru(NH_3)_5py^{3+}$, and probably $Ru(NH_3)_5H_2O^{3+}$, to the outer-sphere mechanism. The existence of a linear free energy relationship involving these complexes and some others suggests that the others also follow the same mechanism. It might be expected that $Ru(NH_3)_5pyr^{3+}$ would function as an inner-sphere oxidant, since $Ru(NH_3)_5pyr^{2+}$ functions as a good ligand to Ru-

Table V. Kinetic Parameters for Reaction of Ru(III) Oxidants with Ti(III)

oxidant	k', s^{-1} (25 °C)	$\Delta H^{\ddagger\prime}$, kJ/mol	$\Delta S^{\ddagger\prime}$, J/(deg mol)	k,[a] $M^{-1}\ s^{-1}$	$\Delta H^{\ddagger}$,[b] kJ/mol	$-\Delta S^{\ddagger}$,[b] J/(deg mol)
$Ru(NH_3)_5pyr^{3+}$	7.3×10^2	54 ± 2	−10 ± 8	1.5×10^5	12 ± 6	~95
$Ru(NH_3)_5py^{3+}$	21.0	56 ± 2	−33 ± 13	4.2×10^3	14 ± 6	~120
$Ru(NH_3)_6^{3+}$ [c]	0.175	82 ± 4	17 ± 12	35	41 ± 10	~70
$Ru(NH_3)_5Cl^{2+}$ [c]	0.061	75 ± 4	−17 ± 12	12	33 ± 10	~100

[a] For reduction by $TiOH^{2+}$ on the assumption that K_a for Ti^{3+} is 0.005 M. [b] For reduction by $TiOH^{2+}$ on the assumption that K_a for Ti^{3+} is 0.005 M and the corresponding ΔH° is 42 kJ mol^{-1}. [c] Data from ref 11.

$(NH_3)_5H_2O^{2+}$ and other divalent metals (Cu^{2+}, Zn^{2+}, Ni^{2+}) and since photoinduced electron transfer across pyrazine bridges in such binuclear complexes is known.[17] On the other hand, the inner-sphere mechanism necessarily involves substitution in the first coordination sphere of Ti(III), and Diebler[18] reported the second-order rate constants for the substitution of NCS^- on Ti^{3+} to be 8×10^3 $M^{-1}\ s^{-1}$ and for HC_2O_4 to be 4×10^5 $M^{-1}\ s^{-1}$, at 10 °C. Rates of substitution on $TiOH^{2+}$ seem to be little faster (less than a factor of 5) than those on Ti^{3+}. $Ru(NH_3)_5pyr^{3+}$ is at least 1.5 orders of magnitude less basic than free pyrazine, although $Ru(NH_3)_5pyr^{2+}$ is 2 orders of magnitude more basic than the free ligand.[19] The low basicity of the Ru(III) species may be taken to indicate low nucleophilicity. Diebler has concluded that Ti(III) substitutions are associative, with rate dependent on entering-group nucleophilicity. The rate of substitution of $Ru(NH_3)_5pyr^{3+}$ onto $TiOH^{2+}$ should thus be $<10^4$ $M^{-1}\ s^{-1}$. Since the rate constant for the redox reaction is larger, we consider an inner-sphere mechanism unlikely. Similar arguments could be made for the bis(isonicotinamide) complex, which is reduced even more rapidly.

Extrapolation of our k vs. $\mathcal{E}^\circ$ plot to −42 mV, the $Ru(NH_3)_5OH^{2+/1+}$ potential, yields a predicted second-order rate constant of 2×10^{-3} $M^{-1}\ s^{-1}$ for the $Ti(OH)^{2+}$ outer-sphere reduction of $Ru(NH_3)_5OH^{2+}$. Such a pathway would account for less than 0.1% of the reduction of $Ru(NH_3)_5H_2O^{3+}$ at the lowest acidity we used. In contrast, in the Cr(II) reduction of $Ru(NH_3)_5H_2O^{3+}$, the reduction of the conjugate base, through[17b] a bridge mechanism, competes effectively with the outer-sphere reduction of the aquo ion. Hydroxide is not as efficient a bridging ligand in the Ti(III)–Ru(III) system as it is in the Cr(II)–Ru(III) system.

Indirect linear free energy relationships, for both outer-sphere and inner-sphere reactions, have been obtained by comparing the rates of reduction of a series of Co(III) oxidants by one reductant to the rates of reduction of the same series of oxidants by a second reductant. For outer-sphere reductions, slopes of such log k_M vs. log k_N plots (M and N being different reductants) are usually near unity. That is, selectivity (with respect to oxidant $\mathcal{E}^\circ$) is generally the same for various reductants. With respect to Co(III) oxidants, however, $TiOH^{2+}$ functioning as an outer-sphere reductant is only half as selective as other reductants.[20] No such effect is observed in the Ru(III)–Ti(III) systems reported here, so that the lower selectivity is not simply a property of Ti(III) but is a joint property of titanium and cobalt. The slope of near $^1/_2$ which we observed is the same as that which is usually observed in outer-sphere LGR and as the slope we have observed for Cr(II)–Cr(III) inner-sphere reactions.

Equilibrium potentials of electrodes are only slowly attained for Ti(III)–Ti(IV) mixtures in Cl^- media.[21] At the dropping mercury electrode, Ti(III) in Cl^- media is oxidized in a wave which has a reversible shape, but Ti(IV) is reduced in a drawn-out wave at more cathodic potentials.[22] Added ligands such as SCN^- engender reversible waves.[23] The lack of reversibility of the couple seems best understood as being due to polymerization of the Ti(IV) species which is the initial product of the electrode reaction. It has been found[24] that the half-wave potential for oxidation of Ti(III) in our media follows the relationship (V vs. NHE)

$$\mathcal{E}_{1/2} = (0.06 \pm 0.01) - 0.08\text{pH} \tag{3}$$

Using 0.005 M for K_a of Ti^{3+}, one obtains

$$TiOH^{2+} \Leftrightarrow TiOH^{3+} + e^- \qquad \mathcal{E}^\circ_H = -0.08\ V \tag{4}$$

The most widely applied result of the Marcus theory is the "cross relation"

$$k_{MN} = (k_{MM}k_{NN}K_{MN}f_{MN})^{1/2} \tag{5}$$

in which

$$\log f_{MN} = (\log K_{MN})^2/4 \log (k_{MM}k_{NN}/Z^2)$$

where $Z = 10^{11}$ s^{-1} and K_{MN} and k_{MN} refer to an electron-transfer reaction such as

$$M^+ + N \rightarrow M + N^+ \tag{6}$$

and k_{MM} refers to an electron-interchange reaction such as

$$M^+ + M \rightarrow M + M^+ \tag{7}$$

Equation 5 assumes that work terms are negligible. An equivalent form of eq 5 is[25]

$$\Delta G^*_{MN} = \lambda_{MN}/4 + \tfrac{1}{2}\Delta G^\circ_{MN} + \Delta G^\circ{}_{MN}{}^2/(4\lambda_{MN}) \tag{8}$$

in which

$$\lambda_{MN} = (\lambda_{MM} + \lambda_{NN})/2 = 2\Delta G^*_{MM} + 2\Delta G^*_{NN} \tag{9}$$

where ΔG^*_{MM} is the activation energy associated with k_{MM}. The parameter λ measures the stiffness of the system to the vibration which transforms the "precursor" complex into the activated complex. The free energy of the overall redox reaction can be computed from the potentials of the two couples involved. The cross relation (eq 5) involves the assumption that the λ for a redox reaction is the average of the values of λ for the related electron-exchange reactions (eq 9).

In our case, the oxidation potential for $TiOH^{2+}$ is close to zero, so that the overall free energy of the reaction is nearly proportional to the reduction potential of the Ru(III) oxidants. Equation 5 can be rewritten in terms of potentials (mV) as eq 10. At the zero of potential, the value of λ (denoted λ^0)

$$\ln k = -\lambda/(4RT) + \mathcal{F}\mathcal{E}/(2RT) - \mathcal{F}^2\mathcal{E}^2/(4\lambda RT) \tag{10}$$

can be computed from the rate constant (denoted ^0k) (eq 11).

$$\lambda^0 = -4RT \ln {}^0k \tag{11}$$

Inserting (11) into (10) ($RT/\mathcal{F}$ = 59 mV at 25 °C), we obtain eq 12. The use of λ^0 for λ in eq 10 amounts to the assumption

$$\log k = \log {}^0k + \frac{\mathcal{E}}{118} - \frac{1}{16 \log {}^0k}\left(\frac{\mathcal{E}}{59}\right)^2 \tag{12}$$

that both λ_{NN} and λ_{MM} are constants. Although λ_{NN} is a constant for our reactions, it has been reported[5,26] that the rate of Ru(III)–Ru(II) electron exchange increases (and hence λ_{MM} decreases) as $\mathcal{E}$ for Ru(III) reduction increases. The value of λ thus decreases below λ^0 and the magnitude of the coefficient of the $\mathcal{E}^2$ term would be expected to increase above[29] 0.04, the value predicted by (12). Equation 12 is of the same form as eq 2, but the predicted value of the coefficient of the

$\mathcal{E}^2$ term is much larger than the observed upper limit of β. Our results indicate that eq 5 and 8 overestimate the importance of the $\Delta G^{\circ 2}$ term in calculations of ΔG^* for these Ru(III)–Ti(III) outer-sphere reactions.

Anson[27] has observed that the variation of ΔG^* with ΔG° for reduction of Cr(III) at electrodes is also more linear than theory would predict, and he suggests that anharmonicity in metal–ligand vibrations may account for this. Eigen[28] has explained a related phenomenon in proton-transfer reactions by invoking cooperative effects. The large variation of $\mathcal{E}$ with the nature of the ligands indicates that there is strong interaction of metal and ligand orbitals in one or both oxidation states of ruthenium. The derivation of eq 5 and 8 assumes that the interaction (H_{RP}) between electron-donor and electron-acceptor orbitals in the transition state is real but small. If the variations which cause an increase in $\mathcal{E}$ also cause a significant increase in H_{RP}, deviation from eq 9 would be expected. Chow, Creutz, and Sutin[5] have provided a number of other examples of such effects. Why the variation of log k with $\mathcal{E}$ should be linear (with slope $^1/_2$) over such a large range is not clear. Systematic variations in the transition-state distance between metal centers may occur along with increase in H_{RP}.

As previously noted,[11] calculation of k_{NN} from the cross relation and K_{MM}, k_{MN}, and k_{MM} for the hexaammine complex gives a reasonable result. The same calculation in the case of $Ru(NH_3)_5py^{3+/2+}$, however, gives values of k_{NN} that are several orders of magnitude higher. It has often been observed that high negative values of ΔG° give rise to deviation[2] from the theory; in the present case similar effects occur even for low values of ΔG°. This may be due to the low value of λ associated with electron interchange between Ru(II) and Ru(III).

In the case of inner-sphere Cr(II)–Cr(III) electron transfers,[4] both enthalpy and entropy variations occur along the linear free energy relationship. In the $TiOH^{2+}$–Ru(III) case, as Table IV shows, the variation in k arises mainly from an enthalpy variation. In the Cr(II)–Cr(III) case, both oxidant and reductant undergo large geometric changes which involve solvent and solvent structure. In the present case, the titanium atom undergoes solvent-connected geometric change but the ruthenium atom does not. Although much of the magnitude of the activation barrier arises from the titanium (and hence would involve an entropic contribution), the variation in the barrier among the reactions studied is principally connected with metal–ligand electronic effects on ruthenium and hence is an enthalpy effect.

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Registry No. *cis*-$Ru(NH_3)_4(isn)_2^{3+}$, 50573-22-3; $Ru(NH_3)_5pyr^{3+}$, 38139-16-1; $Ru(NH_3)_5py^{3+}$, 33291-25-7; $Ru(NH_3)_5H_2O^{3+}$, 25590-52-7; $TiOH^{2+}$, 21029-47-0.

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