on the basis of experimental evidence. Studies of the rate of dissociation of CH_3CN from this complex, path B (there is no evidence for the formation of a dicarbonyl product which would result from path A), indicate this process to have a first-order rate constant of ca. 1.8×10^{-2} s^{-1} at 15.5 °C. Moreover, while the expected dicarbonyl products, *cis*,*trans*,*cis*-(phen)(L)$_2$(CO)$_2$Mo, are well-known,[7] they are produced only under reaction conditions far more rigorous (>100 °C) than those employed here. The dissociation of CO in competition with that of CH_3CN in *fac*-(CH_3CN)(phen)Mo(CO)$_3$ also is not expected on the basis of both ground-state[8] and transition-state[9] bonding arguments.

There is evidence, on the other hand, which implicates the competitive pathways (C) and (D) (Scheme I) in these systems.

(a) The stereoselectivity of the introduction of the ^{13}CO label is quite temperature dependent, the labeling being highly stereoselective (>95% axial) at 0 °C, but much less so (ca. 75% axial) at 25 °C. This observation would indicate significant differences in the temperature sensitivity, i.e., in ΔH^*, for the processes leading to each geometrical isomer. For competing associative and dissociative paths such as (C) and (D), the dissociative path, which leads to formation of the species containing the equatorial label, will exhibit greater temperature sensitivity, as is observed.[10]

(b) Enrichment studies using various mixtures of ^{13}CO/N$_2$ indicate that the fraction of ^{13}CO label incorporation decreases with decreasing ^{13}CO pressure. This observation is consistent with the decreasing accessibility of the associative path (C) relative to a dissociative path such as (D) as the concentration of ^{13}CO decreases.

(c) Evidence for the presence of *two* labels in some labeled molecules, consistent with the accessibility of path D as that which leads to the equatorial enrichment, comes from the observation of a weak band in the carbonyl stretching spectrum of (phen)Mo(CO)$_4$ prepared from *fac*-(CH_3CN)(phen)Mo(CO)$_3$ (25 °C), at 1788 cm^{-1}. This band is attributable to the antisymmetric stretch of the two equatorial ^{13}CO's (B_2 mode in the C_{2v} local symmetry of the complex).[11] No splitting attributable to ^{13}C–^{13}C coupling was observed in the ^{13}C FT NMR spectrum of the complex. Such splitting would be indicative of the presence of two labels in the same molecule, rather than two species each containing an axial or equatorial label. However, such splitting also was not observed for (phen)Mo(CO)$_4$ prepared from Mo(CO)$_6$ containing ca. 30 mol % ^{13}CO, statistically distributed,[12] although this complex is more highly enriched than is that prepared from *fac*-(CH_3CN)(phen)Mo(CO)$_3$.

It would appear probable that the dissociation of the second carbonyl is from the apical position of the five-coordinate, square-pyramidal intermediate on the basis both of "cis labilization" arguments[13] and strong π-bonding in the equatorial plane, which should inhibit carbonyl dissociation from such a position.

The proposed mechanism is of interest in its relationship to decomposition of substituted metal carbonyls. For example, it has been suggested that (amine)M(CO)$_5$ complexes decompose via initial amine dissociation, followed by a bimolecular interaction of [M(CO)$_5$] and (amine)M(CO)$_5$.[14] A successive dissociation mechanism such as is indicated here would also seem reasonable.

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Registry No. *fac*-(CH_3CN)(phen)Mo(CO)$_3$, 15492-80-5; [(phen)Mo(CO)$_2$], 85735-65-5; CH_3CN, 75-05-8; CO, 630-08-0.

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Articles

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Nonadiabaticity in Ruthenium(III)–Titanium(III) Outer-Sphere Electron-Transfer Reactions

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$Ru_2(OAc)_4^+$ is reduced by Ti(III) (at 25 °C, in 1 M $LiCF_3SO_3$–HCF_3SO_3) by a two-term rate law, indicating that both Ti^{3+} and $TiOH^{2+}$ are effective reductants for this oxidant. Rate constants are 2.3×10^2 and 3.4×10^3 M^{-1} s^{-1}, respectively. Tris(pentane-2,4-dionato)ruthenium(III) is reduced by Ti(III), in 1 M LiCl–HCl at 25 °C, by the same general rate law with rate constants of 0.08 M^{-1} s^{-1} for Ti^{3+} and 0.7 M^{-1} s^{-1} for $TiOH^{2+}$. Ti^{3+} is *not* an effective reductant for Ru(III) oxidants that lack delocalized π electrons: we take this as indicating that such reactions would be nonadiabatic.

Previous papers from this laboratory have demonstrated that Ru(III)–Ti(III) redox reactions proceed by both outer-sphere[1] and inner-sphere (bridged)[2] electron-transfer (ET) mechanisms, depending on the ligand coordinated to Ru(III). In the

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previously studied outer-sphere reactions, $Ti(H_2O)_5OH^{2+}$ (hereafter $TiOH^{2+}$) was the reductant and the rates of reaction followed a linear free energy relationship. In contrast, $Ti(H_2O)_6^{3+}$ (hereafter Ti^{3+}) was ineffective as a reductant for these oxidants. We now report two reactions in which both Ti^{3+} and its conjugate base are effective reductants. We attribute the gross difference in reactivity pattern between the oxidants of present interest and those studied earlier to differences in adiabaticity of the ET reactions of Ti^{3+} with the two sets of oxidants. We conclude that adiabaticity of Ru(III)–Ti(III) ET requires at least one ligand capable of electron delocalization on one of the metal ions. This requirement is taken to arise from necessity for effective overlap of electron-donor and electron-acceptor orbitals prior to the ET step.

Experimental Section

Trifluoromethanesulfonic acid (3M Co.), hereafter HTFMS, was distilled twice under vacuum before use. LiTFMS was prepared by neutralization of lithium carbonate with HTFMS. Titanium(III)–TFMS solution was made by dissolving 5 g of titanium hydride in 2 M HTFMS (150 mL) maintained, under nitrogen, at 40–50 °C for 1 day. Cyclic voltammograms were recorded at 25 °C with use of a glassy-carbon working electrode and a Ag/AgCl or calomel reference electrode. Other techniques were as described elsewhere.[1,2]

Tetrakis(μ-acetato)diruthenium(II,III) chloride (hereafter $Ru_2(OAc)_4Cl$) was synthesized according to the literature method.[3] Ruthenium analysis and the extinction coefficient at 425 nm in D_2O (ϵ = 695 M^{-1} cm^{-1}) agree with literature values. This salt was converted to the TFMS salt with use of a Dowex 50W-X2 column (which had been prepared in 0.01 M HTFMS) and was eluted with 0.5 M NaTFMS in 0.01 M HTFMS. Slow evaporation of the eluate gave reddish brown microcrystals. Anal.[4] Calcd for $Ru_2(OAc)_4CF_3SO_3{\cdot}2H_2O$: Ru, 32.42; C, 17.34; H, 2.57. Found: Ru, 32.2; C, 17.21; H, 2.48. Tetrakis(μ-acetato)diaquodiruthenium(II,III) tetrafluoroborate was prepared by an analogous procedure.[5a]

The UV–vis–near-IR spectra of $Ru_2(OAc)_4Cl$, $Ru_2(OAc)_4CF_3SO_3{\cdot}2H_2O$, and $[Ru_2(OAc)_4(H_2O)_2]BF_4$ in 0.9 M $LiCF_3SO_3$–0.1 M CF_3SO_3H all exhibit bands at 310 (sh), 425, and 1000 nm, and the extinction coefficients for all these complexes are quite similar to each other. The spectrum of $Ru_2(OAc)_4Cl$ in solution is markedly different from its solid-state spectrum. It has been suggested that, in aqueous solutions, two axial positions are aquated.[5b] The similarity of the solution-phase spectra of the three substances mentioned above supports this view. The common cation present in all these solutions will be designated $Ru_2(OAc)_4^+$. Cyclic voltammograms showed a peak separation of 75 mV between reduction and oxidation waves of $Ru_2(OAc_4)^+$ in 0.9 M $LiCF_3SO_3$–0.1 M CF_3S_3H and gave a formal reduction potential of 0.29 V vs. NHE. The voltammogram is unchanged by changing the medium to 0.5 M $LiCF_3SO_3$–0.5 M CF_3SO_3H.

Tris(pentane-2,4-dionato)ruthenium(III) (hereafter $Ru(pd)_3$) was prepared in 66% yield by using a modification of Barbieri's method.[6] Ruthenium trichloride trihydrate (Matthey, Bishop, Inc.) (10 g) was dissolved in freshly distilled 2,4-pentanedione; 12.2 g of $KHCO_3$ was added and the mixture refluxed, with stirring, for 5 h. After 1 h the color of the reaction mixture had changed from green to magenta. The product was extracted with hot trichloromethane. On cooling, deep red, rhombic crystals formed. These were dried and recrystallized from benzene–hexane (50/50 vol/vol). Anal.[4] Calcd for $Ru(pd)_3$: Ru, 25.38; C, 45.20; H, 5.27. Found: Ru, 24.85; C, 45.50; H, 5.27.

Table I. Kinetic Data for Reduction of Ruthenium Complexes by Ti(III) (25.0 °C, Ionic Strength = 1.0 M)

$[H^+]$, mM	$[Ti^{3+}]$, mM	10^2k_{obsd}, s^{-1}	$[H^+]$, mM	$[Ti^{3+}]$, mM	10^2k_{obsd}, s^{-1}
A. $Ru_2(OAc)_4^+$, 0.5–1.2 mM in LiTFMS-HTFMS					
100	12.2	42.7	25	3.8	25.0
101	16.3	57.1	25	5.8	40.0
85	16.3	62.8	25	7.7	52.4
63	16.3	66.0	25	11.9	78.0
45	16.3	77.4	24	16.3	110.0
44	12.2	58.6	14	16.3	153
25	2.4	16.5			
B. $Ru(pd)_3$, 0.2 mM in LiCl-HCl					
4	10	0.054	41	10	0.015
8	10	0.024	78	10	0.013
8	10	0.021	83	10	0.011
15	10	0.021	83	10	0.010
21	10	0.017	80	10	0.0096
40	10	0.015			

Polarography in 0.1 M HCl–0.9 M LiCl gave a half-wave potential of −0.278 V vs. NHE for $Ru(pd)_3$. This is in agreement with prior reports.[7] The electronic spectra also agreed with reported values.[8,9]

Color changes rapidly ensue when Ti(III) solutions are added to acidified solutions of either $Ru_2(OAc)_4^+$ or $Ru(pd)_3$. Following the initial change in the case of $Ru_2(OAc)_4^+$, subsequent changes occur on a much longer time scale. Formation of insoluble products complicated absorbance–time traces for this slow reaction.

For both oxidants, titrations indicated that the stoichiometry of the initial reaction is 1:1, within 5%. Rate measurements were made under pseudo-first-order conditions, with Ti(III) in at least 10-fold excess. Pseudo-first-order rate plots for the initial reaction were linear, generally for at least 3 half-times. In a few experiments at low [Ti(III)], the rate constant was computed from the data taken during the first half-time. Repeated determinations using the same solutions yielded rate constants agreeing within 3%. With different solutions, reproducibility of better than 5% was obtained.

Results

The spectrum of $Ru_2(OAc)_4^+$ in TFMS media changes with change in pH of the medium. At pH values less than 4.0, isosbestic points at 415 and 450 nm are maintained as pH changes. A plot of absorbance vs. pH shows a point of inflection at about pH 3. At pH values near 10, a further gross change in spectrum occurs, and the previously yellow solution turns green. The initial rates of the slow reactions that lead to the ultimate reaction products for $Ru_2(OAc)_4^+$ are insensitive to changes in $[H^+]$ or in $[Ti^{3+}]$.

Table I contains values of observed pseudo-first-order rate constants, k_0, for the initial rapid change in spectrum. The rate constant for reduction of the dimeric oxidant increases linearly with [Ti(III)]. Second-order rate constants are computed as $k_2 = k_{obsd}/[Ti(III)]$. Values of k_2 decrease with increasing acidity but do not approach zero at the highest acid concentrations. Although the dimeric oxidant has an acidity constant that is close to that of Ti^{3+}, it seems highly probable that base catalysis in both these cases is due to $Ti(OH)^{2+}$ functioning as a reductant, as is usual in Ti(III) reductions. The data were fitted to the rate law

$$k_2 = (k[H^+] + k'K)/([H^+] + K)$$

where k and k' are second-order rate constants for the reactions of Ti^{3+} and $TiOH^{2+}$ with the oxidants, and K is the acidity constant of Ti^{3+}, previously measured[10] under our conditions

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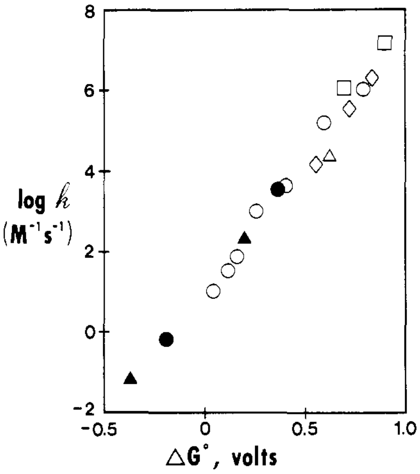

Figure 1. Variation of rate constant with free energy of reaction for reduction of some Ru(III) and Os(III) oxidants by Ti(III) species. Filled symbols indicate rate constants reported in this work; open symbols refer to previous work (ref 1 for Ru(III), ref 12 for Os(III). Triangles refer to reaction of Ti^{3+} with Ru(III) oxidants, and lozenges refer to reactions of Ti^{3+} with Os(III) oxidants. Circles and squares refer to reactions of $TiOH^{2+}$ with Ru(III) and Os(III) oxidants, respectively. For $TiOH^{2+}$, oxidants are entered in order of increasing rate: $Ru(pd)_3^{3+}$, $Ru(NH_3)_6^{3+}$, $Ru(NH_3)_5Cl^{2+}$, $Ru(NH_3)_5(H_2O)^{2+}$, $Ru(en)_3^{3+}$, $Ru(NH_3)_5(py)^{3+}$, $Ru_2(OAc)_4^+$, $Ru(NH_3)_5(py)^{3+}$, $Ru(NH_3)_4(i\text{-nic})_2^{3+}$, $Os(4,4'\text{-}(CH_3)_2bpy)_3^{3+}$, $Os(bpy)_3^{3+}$. For the Ti^{3+} reactions, points are in the following order: $Ru(pd)_3^{3+}$, $Ru_2(OAc)_4^+$, $Ru(NH_3)_4(i\text{-nic})_2^{3+}$, $Os(4,4'\text{-}(CH_3)_2bpy)_3^{3+}$, $Os(bpy)_3^{3+}$, $Os(5\text{-}Cl\text{-}phen)_3^{3+}$. *For the other oxidants, the reaction with* Ti^{3+} *is too slow to be detected* (*see text*).

as 4×10^{-3} M. Plots of $k_2(K + [H^+])$ vs. $[H^+]$ were linear and yielded the values $k = 2.3 \times 10^2$ M^{-1} s^{-1} and $k' = 3.4 \times 10^3$ M^{-1} s^{-1} for $Ru_2(OAc)_4^+$ and $k = 0.08$ M^{-1} s^{-1} and $k' = 0.7$ M^{-1} s^{-1} for $Ru(pd)_3$.

Discussion

The slow changes that lead to the ultimate products of the $Ru_2(OAc)_4^+$ reaction occur at rates that are consistent with assignment of this reaction as decomposition of a Ru(II) dimer.[11] The corresponding reaction of $Ru(pd)_3^-$ has been reported to be slow.[5b] The initial changes correspond to Ru(III)–Ti(III) redox reactions.

By analogy with previously studied systems, the acid-independent terms in the two rate laws are taken as resulting from a reaction channel that involves reaction of Ti^{3+} and each of the two oxidants. Titration data indicate that there is a deprotonation of $Ru_2(OAc)_4^+$ that occurs near pH 3, but we favor the interpretation that base catalysis of the reactions of both oxidants results from the reaction of $TiOH^{2+}$. Figure 1 shows a linear free energy relationship between the logarithm of the second-order rate constant for reactions of $TiOH^{2+}$ with various Ru(III) oxidants and the overall reaction free energy, computed from cyclic voltammetric data. Also included in the figure are data for various osmium(III) oxidants[12] reacting with both $TiOH^{2+}$ and Ti^{3+}. The presently reported rate constants for reduction by $TiOH^{2+}$ correlate well with the corresponding rate constants for the other Ru(III) oxidants, and also with those for the Os(III) oxidants, and the present rate constants for reaction of Ti^{3+} correlate well with the corresponding rates for Os(III) reactions. This agreement supports our interpretation that base catalysis of the reduction of the dimer results from deprotonation of the reductant rather than of the oxidant. In contrast to the systems of present interest, all but one of the previously studied outer-sphere Ru(III) oxidants reacted with Ti(III) in strictly base-catalyzed reactions, without an acid-independent term in the rate law. It is clear that both Ti^{3+} and $TiOH^{2+}$ are effective reductants for the present two oxidants but that only $TiOH^{2+}$, and *not* Ti^{3+}, is effective for those previously studied. The source of the anomaly must be sought in reactions of the Ti^{3+} with $Ru(NH_3)_6^{3+}$ and similar oxidants.

Our data lead us to conclude that the reaction between $Ti(H_2O)_6^{3+}$ and $Ru(NH_3)_6^{3+}$ is slower than would be expected on the basis of the correlation shown in Figure 1. Anomalous behavior of hexaaquo cations in redox reactions has been noticed previously.[13] Two main classes of explanation have been offered for such behavior. Entropy effects connected with solvent reorganization should be more significant for aquo ion reactions than for others, and some have suggested that this is the main contributing factor to unusually slow electron-transfer reactions of aquo ions.[13,14] On the other hand, Taube[15] and others[16] have suggested that some such anomalies involve lack of adiabaticity in the outer-sphere electron-transfer step.

Our data are not consistent with an interpretation based on solvent structuring alone, since the effect we note is *not* correlated with the charge type of the reaction partners. On the other hand, our results are fully consistent with explaining the unusually slow reactions of Ti^{3+} with some (but not all) Ru(III) oxidants as being due to nonadiabaticity arising from lack of effective overlap between electron-donor and electron-acceptor orbitals prior to the transition state of electron transfer. This interpretation, and only this interpretation, rationalizes *which* reactions show nonzero intercepts of plots of rate constant vs. inverse acid concentration and which reactions do not display such intercepts. Effective interaction between electron-donor and electron-acceptor orbitals appears to require at least one ligand that can delocalize electronic orbitals away from the metal centers.[17] Hydroxide is sufficiently effective to satisfy this requirement. If hydroxide is not present, some other ligand may supply this function.

Linck and Sullivan[18] reported that the rate of reduction of $Co(pd)_3$ was more sensitive to the nature of the reductant than was the rate of reduction of $Co(NH_3)_5Cl^{2+}$ or $Co(en)_3^{3+}$. This they ascribe to orbital interaction between the oxidant and reductant centers, through the π-electron system of the pd ring. The two oxidants of present interest, and all the Os(III) complexes shown in Figure 1, contain ligands with delocalized electrons, capable of bringing about interaction between donor orbitals and acceptor orbitals. The Ru(III) complexes studied previously (and also shown in Figure 1) that did not contain such ligands did not react with Ti^{3+} at rates detectable by our experiments. The one oxidant that does display a high-acid intercept contains two isonicotinamide ligands, which could serve the required purpose. All of the complexes that lack acid-independent terms in their rate laws also lack suitable electron-delocalizing ligands. Reactions of the hexaaquotitanium(III) cation with these oxidants are slow in our view because of deficient orbital overlap. We predict that these reactions would be greatly accelerated by increased pressure.[19]

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Our conclusion suggests that hydroxide ion plays a crucial role in outer-sphere redox reactions of conjugate-base forms of aquo ions. At least in these Ti(III)–Ru(III) cases, hydroxide ion functions as an outer-sphere electron mediator, a kind of "bridging ligand". Since electronic reorganizations are rapid with respect to vibration times, such an interaction is quite possible even in a short-lived "encounter complex".[20] The requirement of hydroxide mediation of electrons does imply that the hydroxo ligand is physically located near the line joining the centers of the Ru and Ti atoms. This geometric requirement indicates that electron transfer could occur in only a small fraction (e.g., 0.1%) of collisions between reacting cations. The reactions of present interest are sufficiently slow as to be consistent with a factor of that magnitude.

Registry No. Ru, 7440-18-8; $Ru(acac)_3$, 14284-93-6; $Ru_2(OAc)_4$, 30553-94-7; Ti, 7440-32-6.

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Effect of the Nature of Other Ligands on the Rate of Nitrito-to-Nitro Linkage Isomerization of Octahedral Cobalt(III)–Amine Complexes in Aqueous Solution

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The spontaneous nitrito-to-nitro linkage isomerziation was followed spectrophotometrically for a variety of octahedral (nitrito)(amine)cobalt(III) complexes in aqueous solution to examine the effect of ligands other than the reacting nitrito group on the isomerization rate. The following characteristics were found: (i) The isomerization is retarded relative to that of $[Co(NH_3)_5(ONO)]^{2+}$ for the complexes with chelate rings trans to each other, but it is accelerated for those with chelate rings in other forms. (ii) An increase in the chelate ring size has little effect on the rate constant. (iii) The isomerization rate of *cis*-$[Co(en)_2(X)(ONO)]^{n+}$ is relatively insensitive to the nature of X ligands, while that of *trans*-$[Co(en)_2(X)(ONO)]^{n+}$ differs greatly for different X ligands trans to the ONO group. (iv) A change in net charge on the complex has no appreciable effect on the rate constant. These findings were discussed in the light of the reaction mechanisms proposed so far.

Introduction

It is well-known[1] that the nitrite ion NO_2^- is coordinated through either its O or N atom in Co(III) complexes and that the O-bound nitrito complexes isomerize spontaneously and stereoretentively[2] to the more stable N-bound nitro complexes both in the solid state and in solution. Furthermore, this reaction (called a nitrito-to-nitro linkage isomerization[3]) is confirmed to be an intramolecular process[4,5] for which a seven-coordinated[1,5-7] or six-coordinate π-bonded species[8] has been proposed as a reaction intermediate. However, little attention has been paid to the kinetic aspects of this reaction in solution. In fact, only a limited number of nitrito Co(III) complexes have been subjected to kinetic measurements: $[Co(NH_3)_5(ONO)]^{2+}$,[7-10] *trans*-$[Co(NH_3)_2(py)_2(ONO)_2]^+$,[11] *cis*- and *trans*-$[Co(en)_2(ONO)_2]^+$,[12-14] *cis*-$[Co(en)_2(NO_2)(ONO)]^+$,[10] *cis*-$[Co(NH_3)_4(ONO)_2]^+$,[15] and *cis*-$[Co(NH_3)_4(OH_2)(ONO)]^{2+}$ [15] in aqueous solution.

By contrast, acid hydrolysis reactions, for example, have been extensively studied for a huge number of chloro(amine)cobalt(III) complexes to elucidate the factors determining the rate of chloride ion release, the factors examined so far being net charge of the complex, the number, size, and conformation of chelate ligands including various types of macrocyclic amines (and imines), and the electronic nature of the ligands cis and trans to the leaving Cl^- ion.[16-26] Furthermore, optically active complexes have been successfully utilized to obtain the information on the steric course of the reaction.[27,28] These elaborate studies have made signifciant

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