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Kinetics of Outer-Sphere Electron Transfer in Some Ru(II)–Ru(III) Reactions

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The rates of reduction of *cis*-(oxalato)tetraammineruthenium(III) and (oxalato)- and (acetato)pentaammineruthenium(III) by hexaammine- and aquapentaammineruthenium(II) have been measured at 25 °C and $I = 0.10$ mol dm^{-3} (LiOTs). The rates of reduction of these complexes increase with increasing acid concentration. This and the sensitivity of their absorption spectra to acid concentration suggest substantial protonation of these complexes in solution. LFE log–log plots are linear for these reactions and are used to suggest outer-sphere mechanisms for them.

Introduction

Studies of the reduction of ruthenium(III) ammine complexes by Cr(II),[1-3] U(III),[4] Eu(II)[1], V(II),[1] and Ti(III)[5,6] have been reported. Apart from the reduction of hexaammineruthenium(III)[7] and the halopentaammineruthenium(III)[8] complexes by ruthenium(II) previously reported, little thought has been given to reduction of ruthenium(III) by ruthenium(II). More reports on ruthenium(II)–ruthenium(III) reactions are desirable, since in the reduction of (carboxylato)ruthenium(III) complexes by metal ion reductants[1,6] for instance, reoxidation of the aquated (carboxylato)ruthenium(II) products, by (carboxylato)ruthenium(III) could be an important competing reaction. Moreover, the (carboxylato)pentaammineruthenium(III) complexes are now synthesized by the ruthenium(II)-catalyzed[1,6] substitution of the carboxylato ligand on inert chloropentaammineruthenium(III). The free carboxylato ligand is complexed first to the ruthenium(II) catalyst, and then electron transfer occurs between the two oxidation states of the metal. In a situation in which a (carboxylato)pentaammineruthenium(III) complex is being reduced by ruthenium(II), it is not clear if the carboxylato ligand is substituted into the coordination sphere of the ruthenium(II) prior to electron transfer. We have studied the reduction of the oxalato and acetato complexes of ruthenium(III) by hexaammine- and aquapentaammineruthenium(II) in an attempt to clarify the points of mechanistic interest outlined above.

Oxalate and acetate are good bridging ligands in many electron-transfer reactions involving cobalt(III)[9,10] and ruthenium(III),[1,6] and aquapentaammineruthenium(II) is more labile than the inert and outer-sphere hexaammineruthenium(II) reductant.[11,12]

Table I. Stoichiometry of the Reaction between (Acetato)pentaammineruthenium(III) and the Ruthenium(II) Species[a, b]

$10^4 \times$ [oxidn]$_0$	$10^4 \times$ [redn]$_0$	$10^4 \times$ [oxidn]$_\infty$	$10^4\Delta$-[oxidn]	Δ[oxidn]/Δ[redn]
		(A) $Ru(NH_3)_6^{2+}$ | $Ru(NH_3)_5OAc^{2+}$		
0.63	0.30	0.34	0.29	0.97
1.25	0.62	0.60	0.65	1.08
2.50	1.26	1.27	1.23	0.98
3.75	1.26	2.54	1.21	0.96
				av 1.00 ± 0.03
		(B) $Ru(NH_3)_5H_2O^{2+}$ | $Ru(NH_3)_5OAc^{2+}$		
1.10	0.56	0.53	0.57	1.02
1.70	0.56	1.16	0.54	0.96
2.20	0.56	1.62	0.58	1.04
2.20	1.12	1.14	1.06	0.95
3.25	1.12	2.14	1.11	0.99
				av 0.99 ± 0.02

[a] $t = 25.0 \pm 0.1$ °C, $I = [H^+] = 0.10$ mol dm^{-3} (HOTs), $\lambda = 295$ nm, concentration in mol dm^{-3}. [b] Oxidant concentrations were calculated from their absorbances at 295 nm, where the reductants, their oxidized products, and $Ru(NH_3)_5H_2O^{2+}$, the aquated product of the oxidant, have negligible absorbance compared to the parent ruthenium(III) oxidant.

Experimental Section

Materials. $[Ru(NH_3)_6]Cl_3$ (Johnson Matthey Chem. Ltd.) was purified as described[4] previously. $[Ru(NH_3)_5Cl]Cl_2$ was prepared from the purified hexaammineruthenium(III) as described in the literature.[4] Aquapentaammineruthenium(II) was prepared by the reduction of acidic solution of the chloropentaammineruthenium(III) with the use of Zn amalgam in an atmosphere of pure argon gas.[12] The acetato and oxalato complexes were prepared as described previously.[1,6] They were certified pure by their characteristic UV absorption spectra and elemental analysis.[6]

p-Toluenesulfonic acid (BDH) was recrystallized several times. LiOTs was prepared by the neutralization of a saturated solution of purified *p*-toluenesulfonic acid with AnalaR grade lithium carbonate and recrystallized several times. The water used to make all solutions was triply distilled.

Kinetics. All kinetic measurements were performed on a Pye Unicam SP 500 spectrophotometer by monitoring decreasing absorbances at the UV absorbance peak of the following oxidants.[6] $Ru(NH_3)_5OAc^{2+}$: $\lambda = 295$ nm, $\epsilon = 1.61 \times 10^3$ dm^3 mol^{-1} cm^{-1}. $Ru(NH_3)_5C_2O_4^{+}$: $\lambda = 288$ nm, $\epsilon = 2.60 \times 10^3$ dm^3 mol^{-1} cm^{-1}. *cis*-$Ru(NH_3)_4C_2O_4^{+}$: $\lambda = 287$ nm, $\epsilon = 3.01 \times 10^3$ dm^3 mol^{-1} cm^{-1}. The reductant concentration was always in sufficient excess over the oxidant concentration to ensure pseudo-first-order condition, and due to air sensitivity of the reductants, an argon atmosphere was used throughout. The temperature was maintained at 25.0 ± 0.1 °C by circulating water from a regulated water bath around the cell compartments. The ionic strength was maintained at 0.1 mol dm^{-3} with LiOTs and not $LiClO_4$ because perchlorate slowly oxidizes ruthenium(II),[2,12] and chloride medium was not used, to avoid complications arising from ruthenium(II)-catalyzed substitution of Cl^- onto ruthenium(III).[6] Low ionic strength was used as a result of the limited solubility of ruthenium(II) species.[8,12-14] All reactions were followed to at least 8 half-lives, and logarithmic plots of the oxidant absorbances against time (under pseudo-first-order condition) were linear throughout. That the reactions were clean to completion as judged

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Table II. Acid Dependence of the Observed Second-Order Rate Constants for the Reduction of the Oxalato and Acetato Complexes of Ruthenium(III) by Hexaammine- and Aquapentaammineruthenium(II)[a]

$[H^+]$, mol dm^{-3}	k_{obsd}, dm^3 mol^{-1} s^{-1}	$[H^+]$, mol dm^{-1}	k_{obsd}, dm^3 mol^{-1} s^{-1}
A(i). $Ru(NH_3)_6^{2+} + Ru(NH_3)_5C_2O_4^+ \mid Ru(NH_3)_5C_2O_4H^{2+}$ $[Ru(NH_3)_6^{2+}] = (2.0–3.0) \times 10^{-4}$ mol dm^{-3} $[Ru(III)] = 2 \times 10^{-5}$ mol dm^{-3}			
0.008	2.3	0.015	3.4
0.010	2.5	0.020	4.1
0.013	3.0		
A(ii). $Ru(NH_3)_5H_2O^{2+} + Ru(NH_3)_5C_2O_4^+ \mid Ru(NH_3)_5C_2O_4H^{2+}$ $[Ru(NH_3)_5H_2O^{2+}] = (2.4–7.5) \times 10^{-4}$ mol dm^{-3} $[Ru(III)] = 2.0 \times 10^{-5}$ mol dm^{-3}			
0.008	1.3	0.015	2.3
0.010	1.8	0.020	2.6
0.013	2.0		
B(i). $Ru(NH_3)_6^{2+}$ + *cis*-$Ru(NH_3)_4C_2O_4^+ \mid$ *cis*-$Ru(NH_3)_4C_2O_4H^{2+}$ $[Ru(NH_3)_6^{2+}] = (2.0–3.0) \times 10^{-4}$ mol dm^{-3} $[Ru(III)] = (1.5–2.0) \times 10^{-5}$ mol dm^{-3}			
0.008	2.1	0.013	3.4
0.010	2.8	0.020	4.8
B(ii). $Ru(NH_3)_5H_2O^{2+}$ + *cis*-$Ru(NH_3)_4C_2O_4^+ \mid$ *cis*-$Ru(NH_3)_4C_2O_4H^{2+}$ $[Ru(NH_3)_5H_2O^{2+}] = (2.1–4.5) \times 10^{-4}$ mol dm^{-3} $[Ru(III)] = 2.0 \times 10^{-5}$ mol dm^{-3}			
0.008	1.4	0.015	2.6
0.010	1.7	0.020	3.2
0.013	2.2		
C(i). $Ru(NH_3)_6^{2+} + Ru(NH_3)_5OAc^{2+} \mid Ru(NH_3)_5OAcH^{3+}$ $[Ru(NH_3)_6^{2+}] = (1.8–3.1) \times 10^{-4}$ mol dm^{-3} $[Ru(III)] = (3.0–6.0) \times 10^{-5}$ mol dm^{-3}			
0.008	11.2	0.015	18.6
0.010	13.5	0.020	22.9
0.013	16.4		
C(ii). $Ru(NH_3)_5H_2O^{2+} + Ru(NH_3)_5OAc^{2+} \mid Ru(NH_3)_5OAcH^{3+}$ $[Ru(NH_3)_5H_2O^{2+}] = (1.8–3.1) \times 10^{-4}$ mol dm^{-3} $[Ru(III)] = (3.0–6.0) \times 10^{-5}$ mol dm^{-3}			
0.008	6.4	0.015	10.6
0.010	7.8	0.020	13.2
0.013	9.4		

[a] $t = 25.0 \pm 0.1$ °C, $I = 0.10$ mol dm^{-3} (LiOTs).

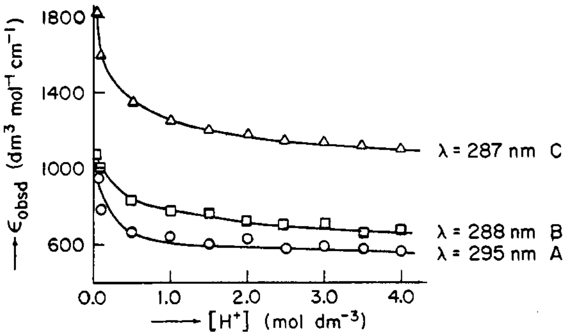

Figure 1. Variation of the molar absorbances of oxalato and acetato complexes of ruthenium(III) with acid concentration in 4.0 mol dm^{-3} LiOTs/HOTs mixture: A = $Ru(NH_3)_5OAc^{2+} \mid Ru(NH_3)_5OAcH^{3+}$; B = $Ru(NH_3)_5C_2O_4^+ \mid Ru(NH_3)_5C_2O_4H^{2+}$; C = *cis*-$Ru(NH_3)_4C_2O_4^+ \mid$ *cis*-$Ru(NH_3)_4C_2O_4H^{2+}$.

Table III. Spectrophotometric Protonation Constants K_s for the Ruthenium(III) Species[a]

Ru(III) species	wavelength, nm	K_s, dm^3 mol^{-1}
$Ru(NH_3)_5OAc^{2+} \mid Ru(NH_3)_5OAcH^{3+}$	295	17.8
$Ru(NH_3)_5OAc^{2+} \mid Ru(NH_3)_5OAcH^{3+}$	302	18.5
$Ru(NH_3)_5C_2O_4^+ \mid Ru(NH_3)_5C_2O_4H^{2+}$	288	24.2
$Ru(NH_3)_5C_2O_4^+ \mid Ru(NH_3)_5C_2O_4H^{2+}$	293	25.8
cis-$Ru(NH_3)_4C_2O_4^+ \mid$ *cis*-$Ru(NH_3)_4C_2O_4H^{2+}$	287	12.8
cis-$Ru(NH_3)_4C_2O_4^+ \mid$ *cis*-$Ru(NH_3)_4C_2O_4H^{2+}$	281	12.1

[a] $I = 0.1$ mol dm^{-3} (LiOTs), $t = 25$ °C.

from the absorbance changes of the oxidant species being consumed is supported by the stoichiometric data (see below; Table I).

Results

Stoichiometry was ascertained for each reaction from the amount of Ru(III) oxidant consumed at its UV absorbance peak under conditions of (2–3)-fold excess Ru(III) over Ru(II). In each case, there was no deviation from 1:1 stoichiometry. Table I shows typical data for the reduction of $Ru(NH_3)_5OAc^{2+}$ by $Ru(NH_3)_6^{2+}$ and $Ru(NH_3)_5H_2O^{2+}$. The kinetic data conform to rate law 1 with no systematic trend

$$-d[Ru(III)]/dt = k_{obsd}[Ru(III)][Ru(II)] \tag{1}$$

in the second-order rate constant k_{obsd} for various concentrations of the oxidant and reductant at constant acid concentration and temperature. The linearity of the pseudo-first-order rate plots and the complete consumption of ruthenium(II) by excess ruthenium(III) as observed from absorbance changes, thus giving 1:1 stoichiometry, show that the reactions are free of complications.

The observed second-order rate constants k_{obsd} for the reduction of *cis*-(oxalato)tetraamine-, (oxalato)pentaammine-, and (acetato)pentaammineruthenium(III) increase with increasing acid concentration in the range 0.008–0.020 mol dm^{-3}, an effect not previously reported for reactions of this class of ruthenium(III) complexes (Table II). Spectral evidence was sought for the protonation of the ruthenium(III) complexes by measuring their peak UV absorbance at various acid concentrations in the range 0.01–4.00 mol dm^{-3} at constant ionic strength (4.00 mol dm^{-3} HOTs/LiOTs). The observed molar extinction coefficients at various acid concentrations are plotted in Figure 1. If the protonation equilibrium is represented by eq 2 (where M = $Ru^{III}(NH_3)_5$ or $Ru^{III}(NH_3)_4$, n = 1 or 2,

$$ML^{n+} + H^+ \overset{K_s}{\rightleftharpoons} MLH^{(n+1)+} \tag{2}$$

and L = OAc^- or $C_2O_4^{2-}$), it can be shown that eq 3 applies

$$a = (a_0 + a_1K_s[H^+])/(1 + K_s[H^+]) \tag{3}$$

(where a_0, a_1, and a are the molar extinction coefficients of the unprotonated, the protonated, and the equilibrium mixture of the protonated and the unprotonated ruthenium(III) species, respectively). Equation 3 can be rearranged to the form (4).

$$(a - a_0)/[H^+] = -aK_s + a_1K_s \tag{4}$$

A plot of $(a - a_0)/[H^+]$ against $-a$ should be linear with slope K_s. Spectrophotometric measurements of K_s were therefore made at two different wavelengths (the absorption peak and one other close wavelength for each ruthenium(III) oxidant), by measuring absorbances at varying acid concentrations, under the same conditions used in the kinetics measurements. The results at the two wavelengths agree within 5%. The mean values of the K_s obtained spectrophotometrically are listed in column 2 of Table III.

If reactions 5 and 6 are assumed to be the rate-determining

$$ML^{n+} + Ru(II) \xrightarrow{k_1} \text{products} \tag{5}$$

$$MLH^{(n+1)+} + Ru(II) \xrightarrow{k_2} \text{products} \tag{6}$$

steps, the rate law becomes

$$\frac{-d[Ru(III)]}{dt} = \frac{k_1 + k_2K_s[H^+]}{1 + K_s[H^+]}[Ru(III)][Ru(II)] \tag{7}$$

with

$$k_{obsd} = (k_1 + k_2K_s[H^+])/(1 + K_s[H^+]) \qquad (8)$$

If $k_1 \ll k_2K_s[H^+]$, eq 8 reduces to eq 9.

$$k_{obsd} = k_2K_s[H^+]/(1 + K_s[H^+]) \qquad (9)$$

If this equation is valid, a plot of the reciprocal of k_{obsd} against the reciprocal of $[H^+]$ will yield a straight line of slope $1/k_2K_s$ and intercept $1/k_2$. Such plots of the data in Table II yield straight lines, and those for the reactions of hexaammine- and aquapentaammineruthenium(II) with (acetato)pentaammineruthenium(III) are shown in Figure 2. K_s and k_2 computed from the data are listed in Table IV. Agreement between spectrophotometric K_s (Table III) and the kinetic K_s (Table IV) is very satisfactory. k_1 (Table IV) was obtained from the data (using computed values of k_2 and K_s) for k_{obsd} $(1 + K_s[H^+])$ against $[H^+]$, with use of eq 8. The temperature variation of k_{obsd} was not investigated due to its complex form which does not permit sufficiently accurate estimates of k_1. k_1 is much smaller than k_2 (Table IV).

Discussion

The data obtained for the reduction of the oxalato and acetato complexes of ruthenium(III) by ruthenium(II) suggest that the active oxidants are a mixture of the protonated and unprotonated ruthenium(III) species in each case (Tables II and IV), with the protonated species reacting faster. Spectral data presented in Figure 1 support the protonation of these oxalato and acetato complexes in acid solution. The kinetic evidence in favor of the protonation of these carboxylato complexes of ruthenium(III) comes from the fact that the protonation constants K_s obtained (Table IV) for the reduction of a common oxidant by the two different reductants $Ru(NH_3)_6^{2+}$ and $Ru(NH_3)_5H_2O^{2+}$ are approximately the same but are different for two different oxidants with a common reductant. The satisfactory agreement between the spectrophotometric K_s and the kinetic K_s makes us believe that the data obtained in this study and the consequent interpretation of the protonation effects are reliable. The acid effects observed in the reduction of some (carboxylato)pentaamminecobalt(III) complexes[10,15,16] by Cr^{2+} and Eu^{2+}, *cis*- and *trans*-bis(acetato)tetraamminecobalt(III)[17] by V^{2+} and $Ru(NH_3)_6^{2+}$, and of (oxalato)pentaamminecobalt(III)[15] by $Ru(NH_3)_6^{2+}$ have been interpreted in terms of protonation of the carboxylato ligand of the oxidants. Vleck[18] has provided evidence that the reduction of the bis(acetato) complex of cobalt(III) at the dropping-mercury electrode involves the pick-up of protons, and Taube et al.[10a] had provided spectral evidence for the protonation of (acetato)pentaamminecobalt(III) in its reduction by Cr^{2+}. It is interesting that kinetic and spectral data presented here suggest the protonation of analogous (carboxylato)ruthenium(III) complexes in acid solution too.

In the reduction of (oxalato)pentaaminecobalt(III) by $Ru(NH_3)_6^{2+}$, the protonated oxalato complex reacts faster than the unprotonated species.[14] This is not surprising since bridging is not involved and $Ru(NH_3)_6^{2+}$ is a typical outer-sphere reductant.[12,13,17] $Co(NH_3)_5OAcH^{3+}$ reacts slower than $Co(NH_3)_5OAc^{2+}$ in the inner-sphere Cr^{2+} reduction of (acetato)pentaamminecobalt(III)[10a] since bridging is involved. An exception to the two consistent observations above is the inner-sphere Cr^{2+} reduction of the (fumarato)pentaamminecobalt(III), in which the protonated form reacts faster than the unprotonated form.[16] Taube et al.[16] had explained this in terms of a remote attack by Cr^{2+} of the protonated ligand through conjugation in the fumarate. In a recent study,[6] the monopositive oxalato complexes of ruthenium(III)—cis $Ru(NH_3)_4C_2O_4^+$ and $Ru(NH_3)_5C_2O_4^+$—were found to be more reactive toward Ti(III) than the dipositive $Ru(NH_3)_5OAc^{2+}$ cation. This is consistent with the "bridging" mechanism proposed[6] since the stabilities of the precursor complexes in the transition state are affected by the coulombic interactions of the charges on the reacting partners. In the reduction of these complexes by hexaammine- and aquapentaammineruthenium(II), the reverse is found (Tables II and IV). This and the greater reactivity of the protonated than the unprotonated species (Table IV) therefore suggest that bridging is not involved in the Ru(II)–Ru(III) systems studied here.

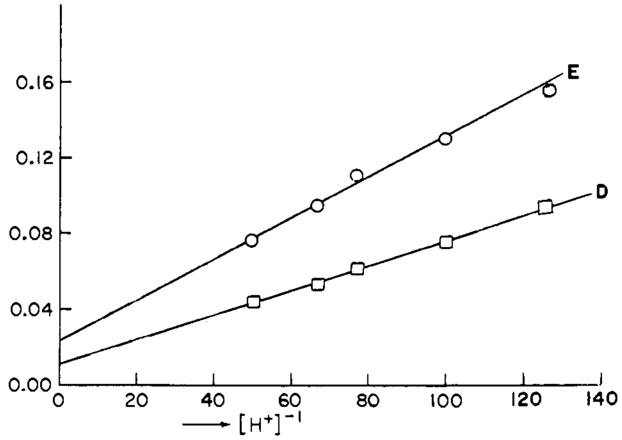

Figure 2. Reciprocal of the observed second-order rate constant for the reduction of (acetato)pentaammineruthenium(III) by hexaammine- and aquapentaammineruthenium(II) as a function of the reciprocal of the hydrogen ion concentration: D = $Ru(NH_3)_5H_2O^{2+}$; E = $Ru(NH_3)_6^{2+}$ (a = ionic strength = 0.10 mol dm^{-3} (LiOTs), t = 25 °C).

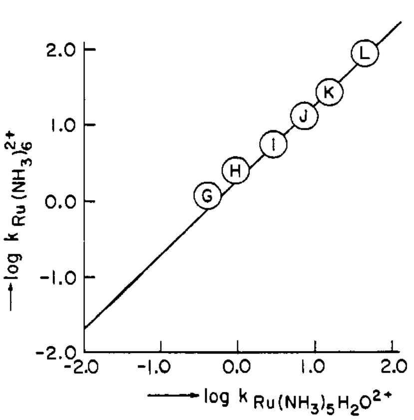

Figure 3. log–log plots for the reduction of the oxalato and acetato complexes of ruthenium(III) by hexaammine- and aquapentaammineruthenium(II): G = $Ru(NH_3)_5C_2O_4^+$; H = *cis*-$Ru(NH_3)_4C_2O_4^+$; I = $Ru(NH_3)_5OAc^{2+}$; J = $Ru(NH_3)_5C_2O_4H^{2+}$; K = *cis*-$Ru(NH_3)_4C_2O_4H^{2+}$; L = $Ru(NH_3)_5OAcH^{3+}$.

log–log plots, based on linear free energy correlations, have now been used extensively to distinguish between mechanisms[12,13,19–25] for any given pair of reductants reacting with

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Table IV. Second-Order Rate Constants and Protonation Constants for the Reduction of Acetato and Oxalato Complexes of Ruthenium(III) by Hexaamine- and Aquapentaammineruthenium(II)

reaction	K_S, dm^3 mol^{-1}	k_1, dm^3 mol^{-1} s^{-1}	k_2, dm^3 mol^{-1} s^{-1}
$\mathrm{Ru(NH_3)_6^{2+} + Ru(NH_3)_5OAc^{2+} \vert Ru(NH_3)_5OAcH^{3+}}$	18.9 ± 2.3	4.8 ± 1.4	82.5 ± 7.6
$\mathrm{Ru(NH_3)_5H_2O^{2+} + Ru(NH_3)_5OAc^{2+} \vert Ru(NH_3)_5OAcH^{3+}}$	20.1 ± 1.9	2.6 ± 0.8	42.8 ± 4.0
$\mathrm{Ru(NH_3)_6^{2+} + Ru(NH_3)_5C_2O_4^{+} \vert Ru(NH_3)_5C_2O_4H^{2+}}$	27.4 ± 3.1	1.3 ± 0.3	13.6 ± 1.2
$\mathrm{Ru(NH_3)_5H_2O^{2+} + Ru(NH_3)_5C_2O_4^{+} \vert Ru(NH_3)_5C_2O_4H^{2+}}$	28.0 ± 3.2	0.5 ± 0.2	7.5 ± 0.7
$\mathrm{Ru(NH_3)_6^{2+}} + cis\text{-}\mathrm{Ru(NH_3)_4C_2O_4^{+} \vert} cis\text{-}\mathrm{Ru(NH_3)_4C_2O_4H^{2+}}$	11.8 ± 1.4	3.6 ± 0.5	26.4 ± 2.4
$\mathrm{Ru(NH_3)_5H_2O^{2+}} + cis\text{-}\mathrm{Ru(NH_3)_4C_2O_4^{+} \vert} cis\text{-}\mathrm{Ru(NH_3)_4C_2O_4H^{2+}}$	13.3 ± 1.2	0.8 ± 0.2	12.8 ± 1.3

a common series of closely related cobalt(III) complexes or any pair of oxidants reacting with a common series of reductants. In each case, when a pair of reductants reduces a common series of oxidants by the same mechanism, a linear relationship of the form

$$\log k_a = x \log k_b \pm c \qquad (10)$$

is obtained (where k_a and k_b are the rate constants for the reduction of the common oxidants by reductants a and b and x and c are constants with $x \approx 1$). The data in Table IV have been plotted in this manner (Figure 3), and a relationship of the form

$$\log k_{\mathrm{Ru(NH_3)_6^{2+}}} = 0.97 \log k_{\mathrm{Ru(NH_3)_5H_2O^{2+}}} + 0.20 \qquad (11)$$

is obtained. $\mathrm{Ru(NH_3)_6^{2+}}$ is substitution-inert and must therefore react with the ruthenium(III) species by outer-sphere mechanism.[12,13,17] The good linear log–log correlation obtained here suggests that $\mathrm{Ru(NH_3)_5H_2O^{2+}}$, which is more substitution labile[11,12] than $\mathrm{Ru(NH_3)_6^{2+}}$, reacts with these ruthenium(III) complexes by an outer-sphere mechanism too. Hexaammineruthenium(II) is more reactive toward the oxalato and acetate complexes of ruthenium(III) than the aquapentaammineruthenium(II) (Table II and IV). This is understandable since the redox potentials of these reductants[11,12] ($\mathrm{Ru(NH_3)_6^{2+}}$, −0.10 V; $\mathrm{Ru(NH_3)_5H_2O^{2+}}$, −0.16 V) suggest that hexaammineruthenium(II) should be a faster outer-sphere reductant than aquapentaammineruthenium(II).

Aquation of the primary (carboxylato)pentaammineruthenium(II) products of the reactions may be represented by eq 12. Reaction 12 and the reoxidation of Ru(NH$_3$)$_5$H$_2$O^{2+} by $\mathrm{Ru(NH_3)_5X^{2+}}$ ($\mathrm{X = OAc^-, C_2O_4^{2-}}$) do not affect the reactions studied here since pseudo-first-order rate plots are linear to completion in all cases, otherwise autocatalysis would have been observed in the rate plots. Electron-transfer rate constants (dm^3 mol^{-1} s^{-1}) for the reduction of the (acetato)pentaammineruthenium(III) by Cr(II),[1] V(II),[1] Eu(II),[1] and Ti(III)[6] are 2.6×10^4 (10 °C, $I = 0.10$ mol dm^{-3} (LiClO$_4$)), 5.6×10^2 (25 °C, $I = 0.10$ mol dm^{-3} (LiClO$_4$)), 1.7×10^5 (25 °C, $I = 0.10$ mol dm^{-3} (LiClO$_4$)), and 7.0×10^2 (25 °C, $I = 1.0$ mol dm^{-3} (LiCF$_3$SO$_3$)), respectively, and that for the reduction of (oxalato)pentaammineruthenium(III) by Ti(III)[6] is 2.5×10^4 dm^3 mol^{-1} s^{-1} (25 °C, $I = 0.10$ mol dm^{-3} (LiCl)). When all rate constants are extrapolated to 25 °C and $I = 0.10$ mol dm^{-3} (our experimental conditions for the Ru(II)/Ru(III) systems), they are much higher than the electron-transfer rate constants k_1 and k_2 for the Ru(II)/Ru(III) reactions (Table IV). Competition from the Ru(II)/Ru(III) cross reactions in the Cr(II), V(II), Eu(II), and Ti(III) reductions[1,6] are probably insignificant and therefore not observed. Reductions using less reactive reductants than those cited above could further access the importance of the Ru(II)/Ru(III) reactions reported here.

$$\mathrm{Ru(NH_3)_5X^+ + H_2O \rightarrow Ru(NH_3)_5H_2O^{2+} + X^-} \qquad (12)$$
$$(\mathrm{X = OAc^-, C_2O_4^{2-}})$$

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Registry No. $\mathrm{Ru(NH_3)_6^{2+}}$, 19052-44-9; $\mathrm{Ru(NH_3)_5H_2O^{2+}}$, 21393-88-4; $\mathrm{Ru(NH_3)_5OAc^{2+}}$, 38744-91-1; $\mathrm{Ru(NH_3)_5C_2O_4^{+}}$, 69765-81-7; *cis*-$\mathrm{Ru(NH_3)_4C_2O_4^{+}}$, 45976-96-3; $\mathrm{Ru(NH_3)_5OAcH^{3+}}$, 76479-94-2; $\mathrm{Ru(NH_3)_5C_2O_4H^{2+}}$, 76479-95-3; *cis*-$\mathrm{Ru(NH_3)_4C_2O_4H^{2+}}$, 76479-96-4.

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Charge-Transfer Excited States as Molecular Photodiodes

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The results of experiments are described in which a series of sequential electron-transfer reactions are induced by oxidative or reductive quenching of the emitting charge transfer (CT) excited state of $\mathrm{Ru(bpy)_3^{2+}}$ (bpy is 2,2′ = bipyridine). The excited state is shown to have the innate properties of electronic charge separation and ability to undergo facile electron and electron-hole loss which allow it to mimic the behavior expected of a photodiode at the molecular level. By adding a chemically linked electron acceptor to the basic chromophore, as in the complex $\mathrm{[(bpy)_2Ru(NC_5H_4C_5H_4NCH_3)_2]^{4+}}$, it is possible to introduce a directed charge-transfer character to the excited state.

Introduction

The absorption of light at the molecular level leads to an electronic redistribution and the formation of an excited state. By the nature of the transition, an electron is excited to a higher level where the binding energy is decreased, and a hole is created in a lower level. As a consequence, when compared to the ground state, an excited state has enhanced properties both as oxidant and reductant. For a charge-transfer (CT) excited state, the absorption of light leads to a transient redox asymmetry where separated oxidizing and reducing sites exist simultaneously within the same molecule. The redox asymmetry inherent in charge-transfer excited states may be of importance in the charge separation step or steps in photosynthesis, in the design of solar energy conversion systems based on molecular excited states, and possibly in the design of molecular level devices. Aviram and Ratner have discussed

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