Ion Association and Electron Transfer in Reactions between Copper and Pentaamminepyridineruthenium Complexes

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Abstract: Cuprous ion reduction of several $(NH_3)_5Ru^{III}L^{3+}$ complex ions, where L is pyridine or 4-substituted pyridines, is described. With 4-vinylpyridine as ligand it is possible to measure separately preequilibrium binuclear ion formation and electron transfer. Ion association is attributed to Cu(I) π complexation of the olefin substituent on the organic ligand from comparison of binding parameters with values for other similar olefin-bound Cu(I) ions. Electron transfer is identified as intramolecular, i.e., taking place through the bridging ligand in the binuclear ion, from comparison with rate behavior exhibited by the $(NH_3)_5Ru^{III}$-4-ethylpyridine, Cu(I) and $(NH_3)_5Ru^{III}$-pyridine, Cu(I)-allyl alcohol redox pairs. Rate parameters for the reverse reaction were determined from kinetic studies of Cu(II)-catalyzed autoxidation of the $(NH_3)_5Ru^{II}$-4-vinylpyridine ion. The redox equilibrium constant determined from the kinetic data agrees well with that calculated from reduction potentials of the reactants. Contributions to enthalpies and entropies for binuclear ion formation arising from the electrostatic work required for ion association were estimated assuming a simple Coulomb interaction potential. Comparison of thermodynamic parameters "corrected" for the work terms with available data for other binuclear ions suggest that entropy losses from conversion of translational and rotational degrees of freedom to internal motions in ion association are $\Delta S \simeq -(4-8)$ eu and, for the ions considered, effects arising from solvent restructuring in the ion hydration lattice are small. It follows from the model that $\Delta S^{\ddagger}$ for electron transfer gives a measure of the probability for electron transfer in the activated complex, values near zero indicating that transfer is adiabatic, or nearly so.

Introduction

Electron transfer between metal ions is complex, generally involving a series of discrete reaction steps.[1-3] Characterization of these elementary reactions offers a potentially fruitful means for detailed examination of the molecular forces controlling reactivity. Several experimentally tractable redox systems in which separation of reaction steps is possible have been described;[4-12] a noteworthy feature of some of them[6,7,10-12] is that the structure of reactant binuclear ions, hence, electron transfer pathways, can be unambiguously assigned.

In the present report, we describe the reaction between Cu(I) and $(NH_3)_5Ru^{III}$-4-vinylpyridine ions, for which intramolecular electron transfer is preceded by Cu(I) π complexation to the pendant olefin group of the organic ligand.[13] Thermodynamic parameters for the reaction steps are discussed in relation to information available from other studies. A method based upon simple electrostatic considerations is developed which provides a self-consistent assessment of charge effects in several diverse binuclear ion-association and complexation reactions.

Experimental Section

Materials. Reagent grade chemicals were used throughout. Pyridine compounds used as ligands were distilled under reduced pressure immediately before use. Aqueous solutions were prepared with reverse-osmosis deionized water. Stock solutions of cupric ion in trifluoroacetic acid (TFA) were obtained by dissolving $Cu(ClO_4)_2$ in aqueous TFA, then precipitating perchlorate by addition of KOH; Cu(II) concentrations were determined by the method of Kitson.[14] Chromic trifluoroacetate reagent solutions were prepared by reducing potassium dichromate in TFA with hydrogen peroxide after adding the molar equivalence of perchloric acid to precipitate potassium ions; Cr(III) concentrations were determined by oxidation to CrO_4^{2-} with alkaline peroxide.[15] Chromous ion solutions were obtained by anaerobic (Ar) reduction with zinc analgam; Cu(I) by reaction of Cr(II) with Cu(II).[16]

Ruthenium coordination complexes containing pyridine ligands were prepared from $(NH_3)_5RuCl_3$ by methods similar to that of Gaunder and Taube.[17] However, explicit application of their procedures to synthesis of the ion containing 4-vinylpyridine led to extensive decomposition/polymerization of the ligand and isolation of a complex product mixture, as witnessed by formation of copious quantities of insoluble material in initial isolation steps and anomalous spectroscopic properties, reduced shelf life, and erratic kinetic behavior of the final product. These problems could be largely avoided if the A_5Ru^{III}-chloro[18] ion were reduced in the absence of 4-vinylpyridine, then transferred anaerobically to a solution containing the ligand. The following protocol was found to give consistently reproducible syntheses: ca. 200 mg of A_5RuCl_3 in 15 mL of dilute TFA (pH 4-5) was reduced in an argon atmosphere over zinc amalgam. Reduction required 20-30 min to reach completion. The Ru(II)-containing solution was then transferred to an argon-flushed solution (ca. 10 mL) containing the ligand in ethanol (1:3 v/v), which was then cooled in an ice bath and extracted twice with diethyl ether, and the complex was precipitated by adding solid NH_4PF_6. The salt was twice recrystallized from warm (40-45 °C) water and washed with ethanol and ether. The complex was oxidized to the corresponding Ru(III) ion by addition of a stoichiometrically equivalent amount of Ag(I) ion, the latter prepared by dissolving Ag_2O in ca. 0.5 mL of TFA, then diluting tenfold with H_2O. The mixture was cooled and filtered through Celite to remove Ag(0), solid $NaClO_4$ was added to the filtrate, and the volume was reduced under vacuum at ca. 40 °C on a rotary evaporator until complex precipitation occurred. The product, $((NH_3)_5Ru^{III}$-4-vinylpyridine$)(ClO_4)_3$, was recrystallized from warm water and washed with ethanol and ether. Prepared in this way, the compound was stable for several days when stored at 0 °C as judged by the criterion of reactivity with Cu(I). Slight decomposition, imperceptible by other criteria, gave markedly catalyzed rates. The Ru(II) complex, as the PF_6^- salt, showed appreciably greater stability at room temperature. Critical features of the synthesis are (1) separation of 4-vinylpyridine from Zn(Hg) during the initial reduction step, (2) maintenance of relatively high pH during reduction, and (3) use of scrupulously cleaned glassware. Treatment of A_5RuCl_3 with 2 equiv of Ag(I) to solubilize the salt prior to Zn(Hg) reduction[17] gave less consistent results, suggesting interference from small amounts of Ag(I) in the coordination step. Ruthenium complexes containing 4-ethylpyridine and pyridine ligands were treated identically, except that it was not necessary to add ethanol to pyridine to maintain solution homogeneity. Infrared absorption spectra (KBr) of the 4-vinylpyridine complex salts gave bands characteristic of A_5Ru^{II} and A_5Ru^{III} ions;[19] in particular, for Ru(III), $\delta(NH_3)$(sym) was found at 1340 cm^{-1}, $\rho(NH_3)$ at 790 cm^{-1}; for Ru(II), $\delta(NH_3)$ (sym) was at 1280 cm^{-1}, $\rho(NH_3)$ at 740 cm^{-1}. All major bands attributable to NH_3 and counterion vibrations were present, with weaker bands ascribable to the coordinated ligand evident at 1500-1510, 1430-1440, 1415-1420, 1025-1035, 990, and ca. 930 cm^{-1}. The ^1H NMR spectrum of the Ru(II) salt in Me_2SO-d_6 was nearly identical with that for uncomplexed 4-vinylpyridine, the bands being broadened slightly and shifted downfield by coordination. Additional broad bands arising from *trans*- and *cis*-NH_3 protons appeared at δ 2.95 and 2.30, respectively, relative to Me_4Si, but no extraneous peaks were detected.

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Electronic absorption spectra for the A_5RuL complexes (λ_{max} (log ϵ_λ)) in 0.1 M TFA, 24 °C, are as follows: L = 4-vinylpyridine, Ru(III), 420 (2.67), 317 (3.63), 251 (4.08); Ru(II), 453 (3.99_6), 255 (3.97), 241 (4.09); L = 4-ethylpyridine, Ru(III), 251 (3.78); Ru(II), 394 (3.70), 245 (3.81); L = pyridine, Ru(III), 261 (3.67), 255 (3.67), 248 (3.67); Ru(II), 407 (3.89), 245 (3.66). Spectra of the pyridine-containing complexes are identical with previously reported values;[17] energies of the visible charge-transfer bands of the Ru(II)-substituted pyridine ions are consistent with behavior exhibited by Ru(II) complexes of other pyridine derivatives.[20] Elemental analysis for $((NH_3)_5Ru^{II}$–4-vinylpyridine$)(PF_6)_2$ follows. Anal. Calcd: C, 14.46; H, 3.81; N, 14.46. Found: C, 14.40; H, 4.00; N, 14.49. The ruthenium(III) perchlorate salt was too explosive to obtain analysis.

The pentaamminecobalt(III) (Ro) complex ion of 4-vinylpyridine was prepared by heating Ro-DMF$(ClO_4)_3$ in 1:1 4-vinylpyridine–dry DMF for 2 h at 55 °C; the reaction was carried out over molecular sieve in a nitrogen atmosphere. The resulting gelatinous mass was extracted sequentially with H_2O and acetone to give yellow solutions which, upon condensation, acidification, and addition of NaI, gave yellow solids with identical visible spectra. The combined solids were recrystallized several times, then converted to the perchlorate salt by addition of $AgClO_4$ and $HClO_4$. The product was recrystallized from dilute $HClO_4$. ^1H NMR spectra in D_2O gave spectral patterns diagnostic of coordinated 4-vinylpyridine and amine groups; apart from signals due to trace quantities (<5%) of Ro-DMF ion, no impurity peaks were seen. Visible absorption spectra at 477 nm (ϵ 68.2) and 344 (77.0) are nearly identical with values found for Ro complexes of other substituted pyridines.[21]

Apparatus. Rapid kinetic measurements were made on a stopped-flow instrument of conventional design,[22] except that the Lucite block housing the observation tube was channeled to permit circulation of thermostating water; with this arrangement temperatures far from ambient could be controlled to ±0.1 °C. Reagents were prepared in anaerobic (Ar) reservoirs and loaded directly into the drive syringes without exposure to air. Kinetic studies for runs with half-times greater than ca. 15 s and equilibrium binding studies were made on a recorder-interfaced Cary 16 spectrophotometer. Reactions were initiated by syringe transfer of the limiting reagent into serum-stoppered optical cells containing anaerobic solutions of the excess reagent. Sufficient time was given to ensure thermal equilibration of the reactant solutions in the cell compartment before mixing. Rates were determined by following changes in light intensities at the visible absorption maxima for the $A_5Ru^{II}L$ ions. Reagent concentrations were adjusted to maintain first-order conditions.

^1H NMR and absorption infrared spectra were taken on Varian HA-100 and Perkin-Elmer 621 instruments, respectively. Instrumentation used for measuring cyclic voltammograms has been described;[23] platinum wire, platinum foil, and silver wire in 0.01 M $AgNO_3$ were used as working, counter, and reference electrodes, respectively.

Calculations. Copper(I)-olefin binding constants were determined from the measured intensities of Cu(I) → olefin(π^*) near-UV bands, which are diagnostic of π complexation;[23] anaerobic reactant solutions were mixed directly in optical cells using syringe-transfer methods. Temperatures of the thermally equilibrated cells were established with copper–constantan thermocouple junctions taped to the cuvette walls.

Contributions of electrostatic forces to overall equilibrium binding energies were estimated assuming a simple Coulomb potential expression:[24]

$$\Delta G_{elec} = N^\circ z_A z_B e_0^2/\epsilon a + RT\sum \nu_i \ln \gamma_i \qquad (1)$$

where N° = Avogadro's number, z_i are the electrical charges of the various ionic species, e_0 is the electronic charge, ϵ is the solvent dielectric constant, a is the distance of closest approach of the charge centers, ν_i are the stoichiometric coefficients of the components taking part in the reaction, and γ_i are their activity coefficients. Electrostatic contributions to the other thermodynamic parameters were estimated from

$$\begin{aligned}\Delta S_{elec} &= -(\partial \Delta G_{elec}/\partial T)\\ &= (N^\circ z_A z_B e_0^2/\epsilon a)\partial(\ln \epsilon)/\partial T\\ &\quad - R\sum \nu_i \ln \gamma_i - RT\sum \nu_i \partial(\ln \gamma_i)/\partial T \qquad (2)\end{aligned}$$

$$\Delta H_{elec} = \Delta G_{elec} + T\Delta S_{elec} \qquad (3)$$

For the binuclear ions discussed, internuclear distances were estimated from crystallographic structures of similar mononuclear complexes or, with the $[(Ro\text{-}py)Fe(CN)_6]^-$ ion, calculated from the measured ion-association constant.[25] The solvent was treated as a continuum, with ϵ corrected for the ionic medium according to $\epsilon = \epsilon_w + 2\bar{\delta}c$, where ϵ_w is the dielectric constant of water and c is the electrolyte concentration.[26] For TFA and $HClO_4$, $\bar{\delta}$ was estimated to be −12; for $NaClO_4$, $\bar{\delta} \simeq -7.5$. Activity coefficients were estimated from the Davies equation,[27] assuming that individual ionic coefficients could be equated to $\gamma_\pm$, i.e.

$$\log \gamma_i = -Az_i^2[\mu^{1/2}/(1 + \mu^{1/2}) - 0.30\mu]$$

Since TFA is essentially completely dissociated in 0.1 M solutions,[28] this value was also taken for the ionic strength (μ). The parameter, $\partial(\ln \gamma_i)/\partial T$, was estimated in two ways: (1) from the temperature dependence[29] of the Debye–Hückel coefficient (A) in the Davies equation, $\partial(\ln \gamma_i)/\partial T = -4.3 \times 10^{-4}$ deg^{-1} at 23 °C, (2) from $\partial(\ln \gamma_\pm)/\partial T = -\bar{L}_2/2RT^2 \leqslant -5.5 \times 10^{-4}$ deg^{-1}, valid for uni-univalent electrolytes, where partial molar heat contents of several common salts are $\bar{L}_2 \leqslant 190$ cal/mol at $\mu = 0.1$ M;[30] for the calculations we took $\partial(\ln \gamma_i)/\partial T \simeq -5 \times 10^{-4} z_i^2$ deg^{-1}. Also, $\partial(\ln \epsilon)/\partial T = -4.54 \times 10^{-3}$ deg^{-1} at 23 °C.[31]

Scheme I

$$\begin{tikzcd}
Cu(I) + Ru(III) \arrow[rr, shift left, "K_a"] \arrow[dr, "k_b"'] & & Cu(I)\cdot Ru(III) \arrow[ll, shift left] \arrow[dl, "k_a"] \\
& Cu(II) + Ru(II) &
\end{tikzcd}$$

Results

Kinetic Studies. Cuprous ion reduction of A_5Ru^{III}–4-vinylpyridine ion exhibits "saturation" kinetics, changing from second to first order with increasing concentrations of reactants. Rate data are reproduced in Figure 1. This behavior is attributable to association of the reactant ions and can be fitted to Scheme I.

The measured rate constant (k_0) is given by $k_0 = k'/(1 + 1/K_a[Ru(III)])$, $k' = k_a + k_b/K_a$, when $[Ru(III)]_0 \gg [Cu(I)]_0$ and a symmetrically equivalent relationship holds when $[Cu(I)]_0 \gg [Ru(III)]_0$. The kinetic parameters k' and K_a were evaluated from plots of k_0^{-1} vs. $[Ru(III)]^{-1}$, which were found to be linear. Data are recorded in Table I. Reduction of the other A_5Ru^{III}py ions by Cu(I) and the Cu(I)-allyl alcohol π-complex ion exhibited strictly second-order kinetics over the experimentally accessible concentration ranges, i.e., $d[Ru(II)]/dt = k[Cu(I)][Ru(III)]$. Representative data, obtained for the reaction of A_5Ru^{III}–4-ethylpyridine with Cu(I), are given in Figure 2; kinetic results are summarized in Table I.

Reduction of the A_5Ru^{III}-py complexes was well behaved. For each of the redox systems investigated, reactant concentrations were varied over (10–400)-fold ranges; rate constants were independent of the identity of reactant held in excess (Ru(III)/Cu(I) ≃ 0.1–10) and no systematic deviation from the rate laws was apparent. Kinetic plots were linear to better than 3 half-lives. For runs with Ru(III) in excess, Ru(II) product concentrations calculated from total absorbancy changes were 90–100% the stoichiometric equivalence of added Cu(I), indicating the overall reactions to be

$$Cu(I) + Ru(III) \rightarrow Cu(II) + Ru(II)$$

Oxidation of A_5Ru^{II}–4-vinylpyridine ion by Cu(II) was studied in the presence of excess O_2, which served to oxidize Cu(I) formed and thereby drive the reaction to completion, viz., the sequence

$$Ru(II) + Cu(II) \underset{k_2}{\overset{k_1}{\rightleftharpoons}} Ru(III) + Cu(I)$$

$$Cu(I) + {}^1\!/_4 O_2 \xrightarrow[k_3]{} Cu(II) + {}^1\!/_2 H_2O$$

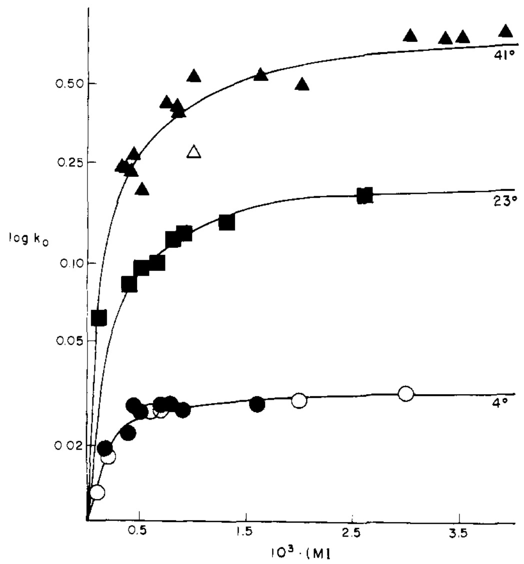

Figure 1. Cu(I) reduction of $(NH_3)_5Ru^{III}$-4-vinylpyridine ion in 0.1 M TFA. Solid symbols, data points representing averages of three to six individual runs with Ru(III) in excess; open symbols, with Cu(I) in excess. The solid lines give theoretical k_0 value calculated for the mechanism given in Scheme I using the best fit values of K_a and k' (Table I).

Table I. Kinetic Parameters for Copper-Ruthenium Redox Reactions[a]

reactants[b]	t, °C	k[c]	
Ru^{III}vpy, Cu^{I}[d]	4	$10^{-3}K_a = 6.2 \pm 0.5$	$k' = 0.032 \pm 0.006$
	23	1.3 ± 0.3	$0.24 \pm 0.01_5$
	41	0.77 ± 0.11	0.94 ± 0.04
Ru^{III}etpy, Cu^{I}[d]	4	2.6 ± 0.1	
	23	5.4 ± 0.3	
	41	11.2 ± 0.9	
Ru^{III}py, Cu^{I}-π[d,e]	4	0.10 ± 0.01	
	24	0.40 ± 0.04	
	47	3.7 ± 0.1	
Cu^{II}, Ru^{II}vpy	4	0.57 ± 0.06	
	24	2.3 ± 0.3	
	47	7.7 ± 0.3	

[a] In 0.1 M TFA. [b] Abbreviations: Ru = $(NH_3)_5Ru$, vpy = 4-vinylpyridine, etpy = 4-ethylpyridine, py = pyridine, π = allyl alcohol. [c] Units: k ($M^{-1}s^{-1}$), K_a (M^{-1}), k' (s^{-1}). [d] Solutions contained additionally Cu(II) = 0.1 mM. [e] Solutions contained additionally ($CH_2{=}CHCH_2OH$) = 5 mM.

Because the latter step is extremely rapid,[32] i.e., $k_3 \gg k_2$, Ru(II)-Cu(II) electron transfer is rate limiting. The reaction was studied over the concentration ranges [Cu(II)] = 1.0-50 mM, [Ru(II)] = 0.05-0.10 mM and found to adhere to the rate law $-d[Ru(II)]/dt = k[Ru(II)][Cu(II)]$. Slow, direct oxidation of Ru(II) by O_2 also occurs in the absence of Cu(II).[33] This reaction was briefly studied to provide correction for its contribution to the measured overall rate. In the presence of excess oxygen, the reaction follows first-order kinetics with $k_{O_2} = 0.64$, 3.2, and 14×10^{-4} s^{-1} at 3, 23, and 43 °C, respectively. Only under extreme conditions of high temperature and low Cu(II) concentrations was it necessary to apply the correction, which was at most 15% of the overall rate. Corrected rate data for the Ru(II)-Cu(II) reaction are summarized in Table I.

Thermodynamic and activation parameters for the reactions evaluated from their temperature dependencies are given in Table II; the plots (ln K vs. T^{-1}, ln k/T vs. T^{-1}) were linear.

Equilibrium Studies. A. Cu(I)-Olefin Binding. Molar extinction coefficients for the Cu(I) → olefin (π^*) absorption bands were determined by adding Cu(I) to solutions containing sufficient ligand (~10^{-2} M) to completely coordinate the metal ion. Values obtained, for 4-vinylpyridine, λ_{max} (log ϵ_λ) 352 nm (3.57_5), for Ro-4-vinylpyridine, 340 (3.67), were independent of temperature (3-43 °C), acidity (pH 1-2), and time for periods up to several hours. As with previous systems studied,[23] thermal electron transfer from Cu(I) to RoL is exceedingly slow. Equilibrium constants were evaluated from absorption intensities for solutions of reagents whose concentrations ranged from 0.05 to 2.0 mM, with Cu(I)/(L) = 0.1-10. The data were adequately fitted assuming 1:1 binding stoichiometry and are summarized in van't Hoff plots given in Figure 3; for Cu(I)-4-vinylpyridine association, $\Delta H = -12 \pm 1.7$ kcal/mol, $\Delta S = -23 \pm 6$ eu; for Cu(I)-RoL binuclear ion formation, $\Delta H = -9.6 \pm 3.0$ kcal/mol, $\Delta S = -16 \pm 10$ eu. The relatively large errors cited for the thermodynamic constants reflect scatter in individual data points which is a consequence of strong bonding; hence the necessity for working at low reagent concentrations where exclusion of adventitious oxygen is difficult. The values obtained are quite similar in magnitude to those determined from kinetic analysis of the Cu^{I}-$A_5Ru^{III}L$ redox reaction, i.e., $\Delta H_{K_a} = -9.7 \pm 1.7$ kcal/mol, $\Delta S_{K_a} = -18 \pm 6$ eu (Table II).

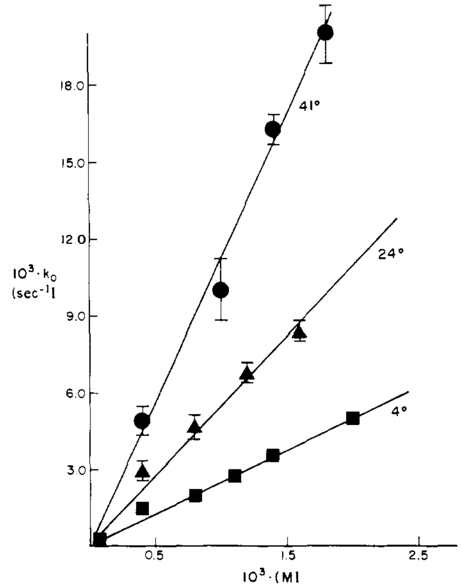

Figure 2. Cu(I) reduction of $(NH_3)_5Ru^{III}$-4-ethylpyridine ion in 0.1 M TFA. Data points are averages of three to six individual runs with either Cu(I) or Ru(III) held in excess. Error limits shown are average deviations from the mean values. The solid lines were drawn using simple linear regression analysis of the data points and were constrained to go through the graph origin.

Table II. Activation Parameters for the Redox Reactions[a]

reactants[b]	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$,[c] eu
Ru^{III}vp, Cu^{I}	$(-9.7 \pm 1.7, 15.1 \pm 0.2)$[d]	$(-18 \pm 6, -10 \pm 4)$[e]
Ru^{III}etpy, Cu^{I}	5.5 ± 0.5	-36 ± 3
Ru^{III}py, Cu^{I}-π	14.6 ± 1.4	-11 ± 5
Cu^{II}, Ru^{II}vp	10.2 ± 0.1	-22 ± 1

[a] In 0.1 M TFA. [b] Abbreviations as in Table I. [c] At 23 °C. [d] $(\Delta H_{K_a}, \Delta H_{k'}{}^{\ddagger})$. [e] $(\Delta S_{K_a}, \Delta S_{k'}{}^{\ddagger})$.

B. Redox Equilibrium for the A_5Ru^{III}-4-Vinylpyridine-Cu(I) Reaction. The half-wave reduction potential ($E_{1/2}$) for the Ru(III) ion in 0.1 M TFA was calculated from cyclic voltammographic curves to be $(E_{p,a} - E_{p,c})/2 = 302$ mV vs. NHE at 23 °C; a nearly identical value has been reported for the A_5Ru-pyridine$^{3+/2+}$ couple.[34] Peak separations were

Table III. Thermodynamic Parameters for Binuclear Ion Formation

ion[a]	a, Å	enthalpies, kcal/mol[b]			entropies, eu[c]			conditions	
		ΔH	ΔH_{elec}	ΔH_{bond}	ΔS	ΔS_{elec}	ΔS_{bond}	(μ, t)	ref[d]
H-4-vp-Cu^I	6.2_5	−12.0	−0.06	−11.9	−23	−1.6	−21	0.1 M TFA, 23 °C	*e*
A_5Ru^{III}-4-vp-Cu^I	7.2	−9.7	−0.1	−9.6	−18	−2.5	−14.5	0.1 M TFA, 23 °C	*e*
Ro-4-vp-Cu^I	7.0_5	−9.6	−0.03	−9.6	−16	−2.6	−14	0.1 M TFA, 23 °C	*e*
Ro-fum-Cu^I	5.4	−11.5	−0.4	−11.1	−22	−7.1	−14	1.0 M $HClO_4$, 23 °C	*f*
$[A_5Ru^{II}]_2N_2$	4.98	−11.2	−0.5	−10.7	−20	−9.5	−10.5	0.1 M Na/HCl, 25 °C	*g*
$A_5Ru^{II}N_2$		−10.1	0	−10.1	−13	0	−13	0.1 M Na/HCl, 25 °C	*g*
Ro-py·$Fe^{II}(CN)_6$	6.3	~0	0.8	−0.8	15	19	−4	0.1 M Na/$HClO_4$, 25 °C	*h*
HgSCN	3.8	−11.9	0.6	−12.5	1.7	9.4	−7.7	1.0 M Na/$HClO_4$, 25 °C	*i*
CrNCSHg	7.1_3	−8.0	−0.3	−7.7	−7.3	−7.1	−0.2	1.0 M Na/$HClO_4$, 25 °C	*j*
Ro(SCN)Hg	4.6	−5.2	−0.9	−4.3	−17	−14.5	−2.5	1.0 M Na/$HClO_4$, 25 °C	*k*

[a] Abbreviations: vp = vinylpyridine, fum = fumarate, py = pyridine. [b] $\Delta H = \Delta H_{\text{elec}} + \Delta H_{\text{bond}}$. [c] $\Delta S = \Delta S_{\text{elec}} + \Delta S_{\text{bond}}$. [d] For values of ΔH, ΔS. [e] This work. [f] Reference 23. [g] Reference 49. [h] Reference 5. [i] Ahrland, S.; Kullberg, L. *Acta Chem. Scand.* **1971,** *25,* 3692–3704. [j] Armor, J. N.; Haim, A. *J. Am. Chem. Soc.* **1971,** *93,* 867–873. [k] Reference 53.

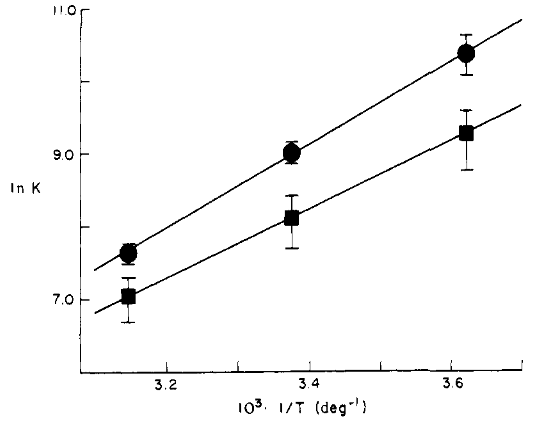

Figure 3. Temperature dependence of Cu(I)-olefin association constants in 0.1 M TFA. Circles, L = 4-vinylpyridine; squares, L = Ro-4-vinylpyridine ion.

slightly larger ($\Delta E_p \simeq 80$ mV) than expected for a reversible process ($\Delta E_p = 58$ mV),[35] but were independent of scan rates from 10 to 200 mV/s. Similar electrochemical behavior has been reported for other pyridine-containing ruthenium complexes and some possible reasons for the anomalous peak separations have been suggested.[36] Anodic to cathodic peak current ratios ($i_{p,a}/i_{p,c}$) were approximately unity.

Taking $E_{1/2} \simeq E_r^0$ for the A_5Ru-4-vinylpyridine$^{3+/2+}$ couple with $E_r^0 = 153$ mV for $Cu^{2+/+}$,[37] we calculate K = [Ru(II)][Cu(II)]/[Ru(III)][Cu(I)] = 344; from rate data (Table I) we calculate K = 186, in reasonable agreement with the thermodynamic results.

Discussion

Electron Transfer Pathways. For Cu(I) reduction of A_5Ru^{III}-4-vinylpyridine ion, the ion-association step (K_a, Scheme I) is clearly attributable to Cu(I) π complexation of the olefin substituent group in 4-vinylpyridine. This claim is substantiated on the following grounds: (1) thermodynamic parameters for ion association are nearly identical with those for other complex ions which form olefin π-bonded binuclear ions (Table III); (2) no evidence of ion association was found in the kinetic behavior of the corresponding reactions of Cu(I) or Cu(I)-olefin complexes with Ru(III) ions incapable of π bonding the reductant.

Since Cu(I)-olefin ligand association rates are rapid, approaching diffusion-controlled limits,[38] binuclear ion formation can be treated as a preequilibrium step to rate-limiting electron transfer. Electron transfer can in principle occur both by intramolecular pathways (k_a) in the binuclear ion and by other, intermolecular (k_b) pathways (Scheme I). In the present case, electron transfer must be almost completely intramolecular, as is evident from the following argument. Reduction of A_5Ru^{III}-4-ethylpyridine ion by Cu(I) provides an estimate of reaction by k_b pathways; this reaction has now been studied for a wide variety of 4-alkyl substituents and found to give essentially invariant rate constants,[39] so the ethyl group does not present unusual steric constraints to electron transfer. Furthermore, olefin coordination per se does not confer enhanced reactivity upon Cu(I), as is apparent from the reduced rate of electron transfer between Cu(I)-π-allyl alcohol and A_5Ru^{III}py ions (Table I). Taking $k_b \simeq 5.4$ M^{-1} s^{-1} at 23 °C, one calculates from $10^2 k_b/K_a k'$ less than 2% reaction by pathway b and, therefore, $k' \simeq k_a$.

Given that the reaction proceeds by a pathway involving the intermediacy of the π-complexed binuclear ion, the possibility exists that this coordination geometry is not maintained in the activated complex for electron transfer. Lifetimes of Cu(I)-olefin complexes are sufficiently short ($\tau \simeq$ microseconds)[38] that dissociation or substitution for the olefin bond could occur in approaching the transition state, i.e., as in

$$\mathrm{Ru^{III}L + Cu^{I}} \overset{K_a}{\rightleftarrows} \mathrm{Ru^{III}L(\pi)Cu^{I}}$$
$$\overset{\text{fast}}{\rightleftarrows} \mathrm{Ru^{III}L \cdot Cu^{I}} \overset{\text{slow}}{\rightleftarrows} \mathrm{Ru^{II}L + Cu^{II}}$$

However, it is difficult to imagine in this system the circumstance whereby prior olefin binding and subsequent release of Cu(I) leads to formation of associated ions ($Ru^{III}L{\cdot}Cu^I$) with geometries unattainable by direct pairing. Without the prospect of special stabilization of a reactant pair and/or reduction of the activation barrier for electron transfer for a complex formed in this way, the system gains no energetic advantage by obligatory binding and release of Cu(I) from the π complex prior to electron transfer. The overall rate constant remains k_b, which has been shown to be too small to account for the measured reaction rate. It is almost certain, then, that the Cu(I)-olefin π bond remains intact in the activated complex.

In 5×10^{-3} M allyl alcohol, Cu(I) is essentially completely coordinated to the π complex ($K = 5 \times 10^4$ M^{-1} at 23 °C, μ = 0.1 M).[40] The activation free energy for Cu(I)-allyl alcohol ion reduction of A_5Ru^{III}-py is greater than that for Cu(I) reduction of A_5Ru^{III}-4-ethylpyridine by 1.4 kcal/mol at 23 °C; the slower rate for the π-complexed reductant is readily ascribable to the reduced driving force for this reaction, since olefin binding stabilizes the Cu(I) oxidation state by 6.4 kcal/mol.

Ion Association Thermodynamics. Enthalpies and entropies for Cu(I)-olefin binuclear ion formation are given in Table III along with reported values for other equilibria. Electrostatic contributions arising from the work required to bring the ions

Table IV. Activation Parameters for Intramolecular Electron Transfer

ion	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$,[c] eu	ref
A_5Ru^{III}-4-vinylpyridine·Cu^{I}	$15.1 \pm 0.2_5$	-10 ± 4[d]	this work
Ro-4,4′-bipyridine-$A_4Ru^{II}OH_2$, etc.[a]	20	+3 to −1	10
Ro-NTA-Fe^{II} [b]	18.7 ± 1.3	0 ± 4	4
$(en)_2Co^{III}(SCH_2CO_2)Cu^{I}$ (S-bridged)	21.4 ± 0.4	1.0 ± 2.5	11
Ro-py·$Fe^{II}(CN)_6$	21.7 ± 2.2	5.8 ± 7	5

[a] For π-conjugated bridging ligands. [b] NTA = nitrilotriacetate. [c] At 25 °C, except where noted. [d] 23 °C.

together (ΔH_{elec}, ΔS_{elec}) were estimated from eq 1–3, assuming the metal–metal internuclear distances listed. Crystallographic distances for the diruthenium dinitrogen dimer are known.[41] For the Cu(I)-vinylpyridine complexes, distances were calculated assuming Cu(I)-olefin,[42] Ru(III)-nitrogen,[43] and Co(III)-nitrogen[43] distances of 1.97, 2.09, and 1.94 Å, respectively, and a coordination geometry comprising the Cu(I) π bond directed perpendicularly to the linear Ru(III)-vinylpyridine chain. For the Ro-fumarate ion, cobalt carboxylate geometry was assumed to be identical with that for Ro-acetato complexes.[44] In each instance, interatomic distances for the bridging ligand were taken to be equal to tabulated representative bond distances for similar organic compounds.[45] Calculations for the mercuric ion containing systems were made assuming Hg-S bonding in all instances, with Hg-S,[46] Co(III)-S,[47] and Cr(III)-S[48] distances of 2.38, 2.27, and 2.37 Å, and SCN distances and bonding angles given by the X-ray structures.[46,47] Our calculation of the metal-metal distance in the Ro-py·$Fe(CN)_6^-$ ion pair from the Fuoss equation[25] differs somewhat from the previously reported value because we made explicit correction for the activities of each charged species.

The calculations are subject to the usual reservations associated with assumptions implicit in classical models, i.e., dielectric continuum, use of mean ionic activities, and, in some instances, their unwarranted extrapolation to high ionic strengths. In the present case, there is reason to believe that errors arising from these sources will be relatively small. Charge separation distances in the binuclear ions are large so that dielectric saturation effects should be minimal and the calculations make use of activity coefficient ratios so that errors in values for the individual ions tend to cancel. However, a major uncertainty in the calculations for the ions forming covalent bonds arises from the use of an ion-pairing model which takes no account of the redistribution of electronic charge accompanying bond formation. Such electronic rearrangement can be expected to have ameliorating effects on the electrostatic forces and, thereby, reduce the magnitudes of their contributions to the binding parameters. Nonetheless, because what follows from the calculations presents an interesting molecular view of the binding process, we retain them as "first-order" approximations of the electrostatic contributions.

The most prominent feature of the electrostatic enthalpy terms (ΔH_{elec}, Table III) is their small magnitude; electrostatic effects appear principally in the entropies of association (ΔS_{elec}, Table III). Entropies for Cu(I)-olefin binuclear ion formation (ΔS_{bond}, Table III) appear remarkably constant; the diruthenium dinitrogen dimer also gives a binding entropy similar to that for simple N_2 coordination when corrected for electrostatic effects. For dinitrogen coordination, the equilibrium reaction is

$$A_5RuN_2^{2+} + A_5RuOH_2^{2+} \rightleftarrows (A_5Ru)_2N_2^{4+} + H_2O$$

As has been pointed out,[49] a major portion of the measured association entropy arises from assigning the standard state for H_2O as the pure liquid, rather than 1 M. Correcting for this factor ($\Delta S = R \ln 55.5 = 8.0$ eu) leaves $\Delta S \simeq -(2\text{–}3)$ eu for the changes in motional entropies in binuclear ion formation. According to at least one model,[50] differences in librational entropy between a water molecule coordinated to an ion and hydrogen bonded to solvent are small, so that the summation of remaining entropy changes for binuclear ion formation, including loss of translational and rotational degrees of freedom, changes in internal bonding, and solvent reorganization, comprises less than $\Delta S \simeq -5$ eu. Assuming that Cu(I)-olefin binding is accompanied by release of coordinated water, as seems likely, an entirely analogous analysis for these binuclear ions suggests $\Delta S \simeq -8$ eu from these contributions. Finally, the value for Ro-py^{3+}, $Fe(CN)_6^{4-}$ ion pairing, unencumbered by questions of consideration of H_2O in the primary coordination spheres of reactant ions, is also comparable ($\Delta S \simeq -4$ eu).

Changes in vibrational entropies likely contribute negligibly to the sums. Since loss of translational and rotational motion accompanying ion association undoubtedly gives rise to negative entropies of at least this magnitude, we might tentatively conclude that the net change in entropy due to specific solvent-structuring changes is also small. Corrected enthalpies of association should then be principally measures of intrinsic bond strengths in the associated ions. This interpretation appears quite plausible from the data. Values of ΔH_{bond} for Cu(I)-olefin bonding appear constant for the various ligands, and are nearly identical with values measured for simple Cu(I)-olefin ligation in nonaqueous solutions,[51] Ru(II) binding to N_2 is comparable in the two dinitrogen complexes, and the net binding enthalpy for the Ro-py^{3+}, $Fe(CN)_6^{4-}$ ion pair is $\Delta H \simeq 0$, as expected for electrostatic association.[52]

The data for Hg(II) binding are less reliable on several counts. Binding geometries for the $Ro(SCN)Hg^{4+}$ ion are unknown,[53] medium effects ($\mu = 1.0$ M) are not easily accounted for, and explicit consideration of changes in solvent coordination is difficult. The data are consistent with the qualitative picture presented, however, if variations in ΔH_{bond} are attributable to decrease in the Hg-S bond strength through the series, SCN^-, CrNCS (end-on), Ro-SCN (S-bridged).[53]

Translational-rotational entropy losses ($\Delta S \simeq -(4\text{–}8)$ eu) estimated for binuclear ion formation in the present analysis are somewhat smaller than values generally assumed for association of coordination complexes,[54] and appear to be markedly less than for association of neutral molecules in nonpolar solvents.[55] The absence of thermodynamic effects attributable to changes in solvent structuring is perhaps not surprising for these equilibria since they comprise mostly cases for which inner-sphere complex formation occurs between soft donors and acceptors; the one instance of complex formation between hard ions is outer sphere. In the former case, reactant ions are expected to be weakly hydrated and, in the latter, charge redistribution is relatively small, requiring minimal changes in the hydration lattice.[52]

Electron Transfer Dynamics. Activation parameters for intramolecular electron transfer in several binuclear ions are listed in Table IV. Excepting the Cu(I)-Ru(*III*) ions, $\Delta S^{\ddagger}$ values are all near zero. Since the activation process likely requires simultaneous compression of reductant and stretching of oxidant metal-ligand bonds, entropy changes associated with these vibrational motions will tend to compensate; in any event, they will be small. In view of the apparent lack of specific solvation effects in binuclear ion formation (above), one would anticipate only a small contribution to $\Delta S^{\ddagger}$ from solvent restructuring attending the relatively minor charge redistribution in approaching the electron transfer transition state. These qualitative arguments receive some basis of support from recent theoretical calculations on the ferrous-ferric ion exchange reaction, for which solvent and ion atmosphere reorganization in the activation process contribute approximately 0.5 eu to $\Delta S^{\ddagger}$.[54] Electronic effects associated with low probabilities of electron transfer within the lifetime of the activated complex (nonadiabaticity) can potentially give rise to negative $\Delta S^{\ddagger}$ terms.[56] For the reactions with $\Delta S^{\ddagger} \simeq 0$, since contributions from inner- and outer-sphere reorganization are probably negligible, it would appear that electron transfer is adiabatic.

The redox activation entropy for the A_5Ru^{III}-4-vinylpyridine-Cu(I) ion is significantly less than zero, suggesting nonadiabatic electron transfer. However, since the coordination geometry of Cu(I) changes upon oxidation, it is possible that $\Delta S^{\ddagger}$ reflects these geometrical constraints, i.e., ordering of solvent in the transition state. Use of solvent perturbation methods may provide the means for distinguishing between these effects. If solvent reorganization contributes significantly to $\Delta S^{\ddagger}$, then this term should be sensitive to changes in structure of the bulk solvent; moreover, enthalpy-entropy compensation should be reflected in $\Delta H^{\ddagger}$.[57] If the negative $\Delta S^{\ddagger}$ arises from nonadiabatic electron transfer, any changes in $\Delta S^{\ddagger}$ with solvent structure should be largely uncompensated in $\Delta H^{\ddagger}$.

Overall activation parameters for electron transfer, i.e., for the reaction

$$A_5Ru^{III}\text{-4-vinylpyridine} + Cu^{I} \rightleftarrows A_5Ru^{II}\text{-4-vinylpyridine} + Cu^{II}$$

are $\Delta H^{\ddagger} = \Delta H_{K_a} + \Delta H_{k'}{}^{\ddagger} = 5.4 \pm 1.9$ kcal/mol, $\Delta S^{\ddagger} = \Delta S_{K_a} + \Delta S_{k'}{}^{\ddagger} = -28 \pm 10$ eu (Table II). Values of this magnitude are commonly found for oxidation-reduction reactions between like-charged ions.[58]

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(18) Abbreviations used: A = ammine, Ro = pentaamminecobalt(III) moiety, TFA = trifluoroacetic acid, DMF = *N,N*-dimethylformamide, Me_4Si = tetramethylsilane, py = pyridine, Me_2SO = dimethyl sulfoxide.
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