Electron-Transfer Reactions of Copper(I) and (2,9-Dimethyl-1,10-phenanthroline)copper(II) with Some Ammine Complexes of Ruthenium(III) and -(II)

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Second-order rate constants have been determined for the oxidation of $Cu(aq)^+$ by various Ru(III) complexes in perchlorate solutions at 25 °C and 1.0 M ionic strength. Values of the rate constants (M^{-1} s^{-1}): $Ru(NH_3)_5py^{3+}$, 46.6; $Ru(NH_3)_5isn^{3+}$, 540; $Ru(NH_3)_4bpy^{3+}$, 3.8×10^3; $Ru(NH_3)_4(isn)_2^{3+}$, 4.4×10^4. These data and previously measured values of $Cu(aq)^+$–Ru(III) reactions follow a linear free energy relationship between log k_2 and $E°$, the reduction potential of the Ru(III) complexes. Rate constants for the one-electron oxidations of $Ru(NH_3)_5py^{2+}$, $Ru(NH_3)_5isn^{2+}$, and $Ru(NH_3)_4bpy^{2+}$ by the (2,9-dimethyl-1,10-phenanthroline)copper(II) ion, $Cu(dmp)_2^{2+}$, were found to be 5.50×10^5, 4.55×10^5, and 3.86×10^5 M^{-1} s^{-1}, respectively, in an MES-buffered 0.10 M $LiCF_3CO_2$ medium between pH 5.1 and 7.0. Activation enthalpies, ΔH^* = 21.6, 22.6, and 23.7 kJ mol^{-1}, and activation entropies, $\Delta S^* = -64, -59$, and -58 J mol^{-1} K^{-1}, were measured for the same reactions. Application of the Marcus relations leads to estimated exchange rate constants of 2×10^{-4} and 4×10^4 M^{-1} s^{-1} for the $Cu(aq)^+/Cu(aq)^{2+}$ and $Cu(dmp)_2^+/Cu(dmp)_2^{2+}$ couples. The exchange rates are discussed in terms of the inner-shell reorganizations at the copper centers.

Introduction

The relationship between the rate and thermodynamic driving force of redox reactions of inorganic ions has been systematically explored for a number of reaction series, and the dependence found has in most instances been successfully correlated with theoretical treatments of electron-transfer rates.[1–5] Ruthenium ammine and bipyridine complexes have found particular application in such studies since both the II and III oxidation states are inert to substitution and the wide range of complexes amenable to study has provided considerable flexibility in the choice of reactants and in the desired variation in $\Delta G°$. The availability of many Ru(II)/Ru(III) self-exchange rate constants has also enabled self-exchange rates of other participating couples to be estimated through the Marcus cross-reaction relations[5,6] and has allowed observed rate constants to be compared with theory.[7–9]

The wide variation that is found in the values of electron-exchange rate constants of transition-metal redox couples is generally interpreted in terms of the reorganization of the inner-coordination shells of the reactants (including polarization of the surrounding solvent), which is necessary in attaining the nuclear configuration of the activated complex.[10,11] This structural barrier to electron transfer usually manifests itself through changes in metal–ligand bond lengths, though spin-state changes and solvent-related entropic effects appear as contributing factors in some reactions also. Less commonly encountered are redox reactions in which a change in coordination geometry at one of the metal centers necessitates major inner-shell reorganizations. Copper(I) and copper(II) redox reactions are unusual in that significant differences exist in both the coordination number and stereochemistry of the two oxidation states. With the aim of providing a better

understanding of such redox systems, we have studied the kinetics of oxidation of aqueous Cu(I) by Ru(III) complexes and the oxidations of Ru(II) complexes by (2,9-dimethyl-1,10-phenanthroline)copper(II), where structural change at the copper center is restricted by the geometric requirements of the ligand.[12]

Experimental Section

Materials. Stock solutions of copper(II) were prepared from $Cu(ClO_4)_2 \cdot 6H_2O$ and were standardized iodometrically with sodium thiosulfate. Chromium(II) solutions were obtained by dissolving chromium metal (99.999%) in excess perchloric acid. The solutions were standardized by oxidation with potassium dichromate, the excess chromium(VI) being determined iodometrically. CF_3SO_3H, from the 3M Co., was purified by reduced-pressure distillation. Dilute aqueous solutions of CF_3SO_3H, CF_3CO_2H, and $HClO_4$ were standardized by titration with base. $LiClO_4$, $LiCF_3SO_3$, and $LiCF_3CO_2$ 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 (Dowex 50W-X8(H)), the eluent being determined with standard base. Solutions of 2,9-dimethyl-1,10-phenanthroline (dmp), from the G. F. Smith Co., were made from the solid hemihydrate, which had been recrystallized from warm aqueous methanol. Stock solutions were stored in the dark. The ligands 2,2′-bipyridine, 1,10-phenanthroline, and isonicotinamide were recrystallized from hot water and stock solutions prepared by weight. MES (2-morpholinoethanesulfonic acid) buffer was obtained from the Sigma Chemical Co. All solutions were prepared by using a double redistillate of water than had been deionized and distilled from alkaline permanganate.

Ruthenium Complexes. The complexes $[Ru(NH_3)_5py](ClO_4)_2$, $[Ru(NH_3)_5isn](ClO_4)_2$ (isn = isonicotinamide), $[Ru(NH_3)_5bpy](ClO_4)_2$ (bpy = 2,2′-bipyridine), $[Ru(NH_3)_5py](ClO_4)_3$, $[Ru(NH_3)_5isn]-(ClO_4)_3$, $[Ru(NH_3)_4bpy](ClO_4)_3$, and cis-$[Ru(NH_3)_4(isn)_2](ClO_4)_3$ were prepared by published procedures.[13,14] Spectra of the ruthenium complexes were in good agreement with literature values[9,13] [λ, nm (ε)]: $Ru(NH_3)_5py^{2+}$, 407 (7.80×10^3), 244 (4.6×10^3); $Ru(NH_3)_5py^{3+}$, 261 (4.57×10^3), 254 (4.50×10^3); $Ru(NH_3)_5isn^{2+}$, 478 (1.08×10^4), 258 (3.86×10^3); $Ru(NH_3)_5isn^{3+}$, 278 (6.1×10^3); $Ru(NH_3)_4bpy^{2+}$, 522 (3.48×10^3), 367 (5.7×10^3), 336 (2.72×10^3); $Ru(NH_3)_4bpy^{3+}$, 313 (1.3×10^4), 302 (1.04×10^4); $Ru(NH_3)_4(isn)_2^{2+}$, 478 (1.37×10^4), 412 (1.1×10^4).

Reaction Solutions. Solutions of Cu^+ were prepared in the concentration range 1×10^{-3}–1×10^{-4} M by the procedure of Espenson and Parker[15] in which the reaction of Cr^{2+} and Cu^{2+} is allowed to

(1) For example see: (a) Ford-Smith, M. H.; Sutin, N. *J. Am. Chem. Soc.* **1961**, *83*, 1830. (b) Dulz, G.; Sutin, N. *Inorg. Chem.* **1963**, *2*, 917. (c) Diebler, H.; Sutin, N. *J. Phys. Chem.* **1964**, *68*, 174.
(2) Davies, K. M.; Earley, J. E. *Inorg. Chem.* **1976**, *15*, 1074.
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(4) Lin, C.-T.; Bottcher, W.; Chou, M.; Creutz, C.; Sutin, N. *J. Am. Chem. Soc.* **1976**, *98*, 6536.
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(6) Bottcher, W.; Brown, G. M.; Sutin, N. *Inorg. Chem.* **1979**, *18*, 1447.
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(8) Chou, M.; Creutz, C.; Sutin, N. *J. Am. Chem. Soc.* **1977**, *99*, 5615.
(9) Brown, G. M.; Sutin, N. *J. Am. Chem. Soc.* **1979**, *101*, 883.
(10) Marcus, R. *Annu. Rev. Phys. Chem.* **1966**, *15*, 155.
(11) (a) Sutin, N. *Annu. Rev. Nucl. Sci.* **1962**, *12*, 285. (b) Sutin, N. *Acc. Chem. Res.* **1968**, *1*, 225.

(12) James, B. R.; Williams, R. J. P. *J. Chem. Soc.* **1961**, 2007.
(13) Gaunder, R. G.; Taube, H. *Inorg. Chem.* **1970**, *9*, 2627.
(14) Ford, P. C.; Rudd, De F. P.; Gaunder, R.; Taube, H. *J. Am. Chem. Soc.* **1968**, *90*, 1187.

proceed to >99% completion, as calculated from the known rate constants. The Cu(I) solution was generated immediately before use either directly in the reaction cell or in one of the volumetric flasks used as a solution reservoir in the stopped-flow experiments. Provided metal surfaces were avoided and Cu^{2+} was maintained in greater than a 3-fold excess over Cu^+, solutions of Cu^+ could be kept for up to 1 h without disproportionation. With repeated use of the same cell or flask, premature precipitation of copper metal tended to occur.[16] Thorough cleaning with nitric acid usually eliminated this problem. Oxygen was rigorously excluded from all reaction solutions containing Cu(I) by passage of Cr^{2+}-scrubbed N_2 or Ar. The copper(II) oxidant, $Cu(dmp)_2^{2+}$, was generated in solution by mixing Cu^{2+}, ligand, and buffer at the required pH. The concentration of the complex was computed from the published equilibrium data[17] on Cu(II)–dmp complexes.

Kinetic Measurements. Rate measurements on the very fast reactions were made with a thermostated Aminco-Morrow stopped-flow spectrophotometer coupled to a Gould-Biomation transient recorder and an X-Y recorder with time base. A Beckman Acta C-III recording spectrophotometer was used for monitoring the slower reactions. The reaction solutions, in cylindrical quartz cells, were thermostated to ±0.05 °C with a water-jacketed cylindrical cell holder. Rate studies with Cu^+ were made by monitoring absorbance increases at 408, 478, and 522 nm accompanying the reduction of $Ru(NH_3)_5py^{3+}$, $Ru(NH_3)_5isn^{3+}$, $Ru(NH_3)_4(isn)_2^{3+}$, and $Ru(NH_3)_4bpy^{3+}$, respectively. These reactions were studied at 1.0 M ionic strength in $LiClO_4$–$HClO_4$ media with the temperature maintained at 25.0 ± 0.05 °C. Pseudo-first-order conditions were employed with Cu(I) present in at least a 10-fold excess. Rates were followed at acidities in the range 0.10–0.40 M. Three separate runs were usually performed for each pair of solutions in the stopped-flow apparatus. Rate constants generally agree to within 5%. When copper metal was not deposited, rate constants obtained from duplicate determinations agreed to within 10%. Rates of the $Cu(dmp)_2^{2+}$ oxidations of $Ru(NH_3)_5py^{2+}$, $Ru(NH_3)_5isn^{2+}$, and $Ru(NH_3)_4bpy^{2+}$ were monitored spectrophotometrically at one or more appropriate wavelengths where $Cu(dmp)_2^+$ (λ_{max} 454 nm, ϵ 6.2 × 10^3 M^{-1} cm^{-1}) or the Ru(II) reductant absorbed strongly. The reactions were carried out under pseudo-first-order conditions with a greater than 10-fold excess of copper complex over the Ru(II) reductant. In some experiments the Ru(II) complex was present in excess. Pseudo-first-order plots were linear to at least 3 half-lives in all cases. The second-order rate constants determined with either Ru(II) or Cu(II) in excess were found to be in good agreement. In all cases, reaction solutions were adjusted to the required pH with 0.01 M MES buffer and were maintained at an ionic strength of 0.10 M with $LiCF_3CO_2$. In initial experiments employing $LiCF_3SO_3$ or $LiClO_4$ to maintain the ionic strength, appreciable turbidity was noted in the reaction solution due to precipitation of the Cu(I) product. A Corning 125 pH meter and Cambridge 5-700 combination electrode were used for pH measurements. The pH of the reaction solutions employed in the kinetic experiments was determined in duplicate experiments. Analyses for Cu^+ were made through the reaction of Cu^+ with $Co(NH_3)_5Br^{2+}$. The Co^{2+} produced was determined spectrophotometrically as the thiocyanate complex in 50 vol % acetone (ϵ 1842 M^{-1} cm^{-1} at 623 nm), with corrections being made for Ru(II) absorbance where appropriate.

Results

Reaction of Ru(III) Complexes. Stoichiometric measurements were carried out with both Ru(III) and Cu(I) in excess. The excess Ru(III) was determined spectrophotometrically, while Cu^+ in excess was analyzed by its reaction with $Co(NH_3)_5Br^{2+}$. In all cases checked, the stoichiometry was consistent with Ru(III) + Cu(I) → Ru(II) + Cu(II).

Table I shows representative kinetic data for reactions of the Ru(III) complexes $Ru(NH_3)_5py^{3+}$, $Ru(NH_3)_5isn^{3+}$, $Ru(NH_3)_4bpy^{3+}$, and $Ru(NH_3)_4(isn)_2^{3+}$ with Cu^+. All reactions follow the rate law rate = $k_2[Ru(III)][Cu(I)]$, with the second-order rate constant, k_2, independent of [H$^+$], for [HClO$_4$] between 0.10 and 0.40 M. The rate also showed no dependence on the excess Cu^{2+} concentration when present in the

(15) Parker, O. J.; Espenson, J. H. *J. Am. Chem. Soc.* **1969**, *91*, 1968.
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Table I. Rate Constants for the Cu(I) Reduction of Ruthenium(III) Ammine Oxidants at 25.0 °C and 1.0 M Ionic Strength[a]

[H$^+$], M	initial concn × 10^5, M			k_2,[b] M^{-1} s^{-1}
	[Cu$^+$]	[Ru(III)]	[Cu^{2+}]	
	$Ru(NH_3)_5py^{3+}$			
0.205	11.2	1.04	140	48.7
0.205	18.6	1.04	140	48.7
0.205	34.6	1.50	140	40.1
0.205	63.4	1.50	137	48.8
0.211	19.8	0.86	137	51.9
0.410	19.2	1.30	140	50.1
0.101	34.3	1.60	268	45.9
	$Ru(NH_3)_5isn^{3+}$			
0.201	48.5	2.00	510	571
0.201	110	4.00	920	532
0.410	48.5	2.00	490	538
0.201	10.5	0.502	85.0	519
	$Ru(NH_3)_4bpy^{3+}$			
0.201	97	2.00	410	3.4 × 10^3
0.502	49	2.00	460	4.1 × 10^3
0.201	25	2.00	280	3.7 × 10^3
0.102	49	2.00	460	4.0 × 10^3
	$Ru(NH_3)_4(isn)_2^{3+}$			
0.201	88	2.00	410	4.2 × 10^4
0.201	49	2.00	462	4.6 × 10^4
0.201	35	2.00	265	4.5 × 10^4

[a] $LiClO_4$–$HClO_4$ medium. [b] $k_2 = k_1/[Cu^+]$, where k_1 is the pseudo-first-order rate constant.
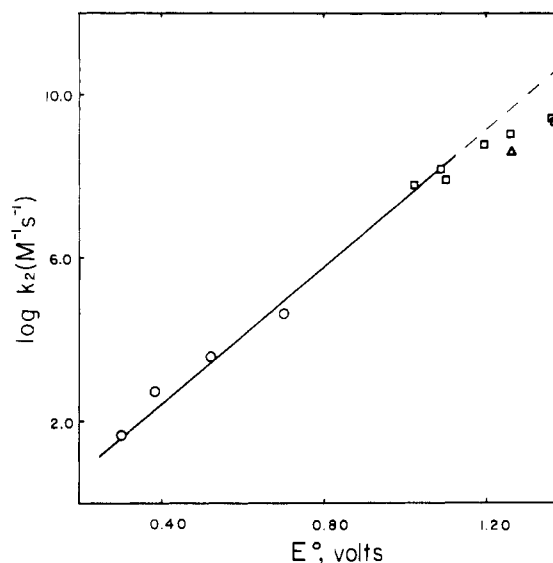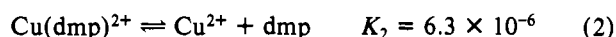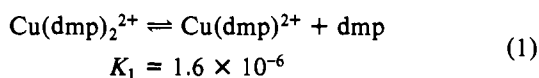

Figure 1. Plot of the logarithms of the observed rate constant for oxidation of Cu^+ by ruthenium(III) oxidants vs. the formal reduction potentials of the ruthenium(III) complexes (all data at 25.0 °C): (O) rate data at 1.0 M ionic strength ($LiClO_4$/$HClO_4$) from Table IV, standard potentials from ref 13 and 23; (□) 0.5 M $HClO_4$; (△) 0.5 M H_2SO_4, data from ref 23.

range (1.40–2.68) × 10^{-3} M. A summary of the second-order rate constants for the Cu^+ reduction of ruthenium(III) complexes is shown in Table IV, and the correlation of the rate constants with the thermodynamic driving force for the reactions is illustrated in Figure 1, where log k_2 is plotted against $E°$, the standard reduction potential of the Ru(III) oxidants.

$Cu(dmp)_2^{2+}$–Ru(II) Reactions. On the basis of the reported stability constants,[17] $Cu(dmp)_2^{2+}$ is the predominant Cu(II) species present under the experimental conditions. The involvement of $Cu(dmp)^{2+}$ or $Cu(dmp)_3^{2+}$ in the reactions is

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Table II. Rate Constants for the Oxidation of Ruthenium(II) Ammine Complexes by $Cu(dmp)_2^{2+}$ at 0.10 M Ionic Strength $(LiCF_3CO_2)^a$
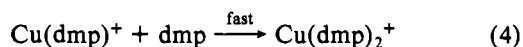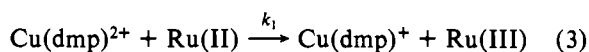
	initial concn × 10^5, M				
[Ru(II)]	[Cu-(dmp)$_2$$^{2+}$]	[dmp]$_T$	pH	temp, °C	$10^{-5}k_2$, M^{-1} s^{-1}
Ru(NH$_3$)$_5$isn^{2+}					
51.0	2.04	7.5	6.1	25.0	4.29
22.7	2.04	15.0	6.1	25.0	4.59
22.7	2.04	7.5	6.1	25.0	4.23
22.7	1.02	7.5	6.1	25.0	4.63
1.03	12.3	28.3	6.1	25.0	4.56
1.07	10.8	62.9	6.1	25.0	5.16
1.02	10.2	55.6	7.0	25.0	4.69
1.03	12.3	59.4	5.5	25.0	4.53
1.05	12.3	60.4	5.1	25.0	4.35
1.07	10.8	62.9	6.1	14.9	3.66
1.07	10.8	62.9	6.1	4.4	2.68
1.07	10.8	62.0	6.1	35.5	8.06
22.2	2.45	20.0	6.0	25.0	5.47^b
1.03	12.3	61.0	6.1	25.0	1.17^b
Ru(NH$_3$)$_5$py^{2+}					
32.8	1.5	15.0	6.1	25.0	5.80
16.4	1.5	15.0	6.1	25.0	5.20
16.4	1.5	15.0	6.1	14.5	3.52
16.4	1.5	15.0	6.1	4.2	2.13
16.4	1.5	15.0	6.1	35.2	6.01
26.3	2.45	20.0	6.1	25.0	11.7^b
103	4.0	20.0	6.1	25.0	0.93^c
44.5	2.5	25.0	6.1	25.0	1.07^c
23.2	2.0	10.0	6.1	25.0	0.97^c
Ru(NH$_3$)$_4$bpy^{2+}					
1.10	20.4	111	6.1	25.0	4.08
1.10	20.4	111	6.1	15.0	2.65
1.10	20.4	111	6.1	4.2	2.04
1.10	20.4	111	6.1	34.5	5.52
1.05	16.9	89.6	6.1	25.0	3.97
1.06	12.3	41.8	6.1	25.0	3.90
1.42	14.3	84.6	7.0	25.0	3.62
1.42	14.3	84.6	5.1	25.0	3.72

^{a} All data at 0.10 M ionic strength $(LiCF_3CO_2)$ in an MES buffer, unless otherwise indicated. ^{b} $LiCF_3SO_3$ media. ^{c} Ionic strength maintained with a 0.10 M acetate buffer.

Table III. Activation Parameters for the Oxidation of Ru(II) Complexes by $Cu(dmp)_2^{2+}$ at 0.10 M Ionic Strength $(LiCF_3CO_2)$

reductant	$\Delta H^{\ddagger}$, kJ mol^{-1}	$\Delta S^{\ddagger}$, J mol^{-1} K^{-1}
Ru(NH$_3$)$_5$py^{2+}	21.6 ± 4.4	−64 ± 15
Ru(NH$_3$)$_5$isn^{2+}	22.6 ± 4.2	−59 ± 16
Ru(NH$_3$)$_4$bpy^{2+}	23.7 ± 3.8	−58 ± 13

Since the reaction product, characterized by an absorption maximum at 454 nm (ϵ 6.1 × 10^3 M^{-1} cm^{-1}), is identified as $Cu(dmp)_2^+$, the bis Cu(II) complex, $Cu(dmp)_2^{2+}$, is taken to be the Cu(II) oxidant in the reactions. Davies and Loose[18,19] have previously concluded that the most rapid reactions of Cu(II)–dmp species are those that result in the direct formation of the thermodynamically stable $Cu(dmp)_2^+$ complex as primary product.

Table II shows second-order rate constants determined for the oxidation of Ru(NH$_3$)$_5$py^{2+}, Ru(NH$_3$)$_5$isn^{2+}, and Ru-(NH$_3$)$_4$bpy^{2+} by $Cu(dmp)_2^{2+}$ in a 0.10 M $LiCF_3CO_2$ medium. All reactions follow the second-order rate law, rate = k_2[Ru(II)][Cu(II)], with the specific rate constant independent of acidity between pH 5.1 and 7.0. The reaction rates were not affected by variations of the monitoring wavelength, buffer concentrations, or the presence of oxygen. For reactions buffered in a sodium acetate–acetic acid medium at μ = 0.10 M, a 5-fold reduction in rate was noted with both Ru-(NH$_3$)$_5$py^{2+} and Ru(NH$_3$)$_5$isn^{2+}. Data pertaining to temperature dependencies are shown in Table III. The values of ΔH^* and ΔS^* reported were calculated from a linear least-squares fit of the data ot the Eyring absolute rate equation.

The stoichiometry of the $Cu(dmp)_2^{2+}$–Ru(II) reactions, which was determined spectrophotometrically, was consistent with the reaction $Cu(dmp)_2^{2+}$ + Ru(II) → $Cu(dmp)_2^+$ + Ru(III) in all cases checked.

Discussion

The substitution-inert nature of the Ru(III) complexes and the absence of suitable bridging ligands require an outer-sphere mechanism in the Cu$^+$ reduction of Ru(NH$_3$)$_5$py^{3+} and Ru-(NH$_3$)$_4$bpy^{3+}. Though inner-sphere transfer is possible for the isonicotinamide complexes and inner-sphere mechanisms appear to operate in several previously studied Cu$^+$ reactions,[15,20] the existence of a linear free energy dependence involving all four Ru(III) oxidants points strongly to the same mechanism being followed in all reactions. In the Cu$^+$ reduction of (4-vinylpyridine)pentaammineruthenium(III),[21] Hurst observed extensive ion association between Cu$^+$ and the Ru(III) oxidant preceding electron transfer. This is attributed to the high binding affinity of Cu(I) for olefin bonds. A similar effect was not observed with the corresponding 4-ethylpyridine complex, Ru(NH$_3$)$_5$py-4-C$_2$H$_5$$^{3+}$, where Cu(I) π-bonding interactions are precluded and no evidence for such interactions was found in the present study. Though the formal reduction potential of the 4-ethylpyridine complex has not been reported, it is expected to be somewhat less positive than the value of 0.30 V reported for Ru(NH$_3$)$_5$py^{3+}.[22] The rate constant for the Ru(NH$_3$)$_5$py-4-C$_2$H$_5$$^{3+}$ reaction (k_2 = 9.7 M^{-1} s^{-1} in 0.1 M CF$_3$CO$_2$H at 23 °C) should, therefore, fit close to the solid line drawn in Figure 1 and lends further support to the linear dependence of log k_2 on $E°$, the reduction potential of the Ru(III) oxidant, for outer-sphere Cu(I)–Ru(III) reactions.

Included in Figure 1 are rate constants, reported by Hoselton, Lin, Schwarz, and Sutin[23] for reactions of poly(pyri-

unexpected in view of the low concentrations of these species. Calculations using the equilibrium data in eq 1 and 2 indicate

$$Cu(dmp)_2^{2+} \rightleftharpoons Cu(dmp)^{2+} + dmp$$
$$K_1 = 1.6 \times 10^{-6} \quad (1)$$

$$Cu(dmp)^{2+} \rightleftharpoons Cu^{2+} + dmp \quad K_2 = 6.3 \times 10^{-6} \quad (2)$$

that $Cu(dmp)^{2+}$ accounts for <1.6% of the analytical Cu(II) concentration in the reactions. Oxidation by $Cu(dmp)^{2+}$ via eq 3 and 4 follows the rate law given in eq 5, which reduces

$$Cu(dmp)^{2+} + Ru(II) \xrightarrow{k_1} Cu(dmp)^+ + Ru(III) \quad (3)$$

$$Cu(dmp)^+ + dmp \xrightarrow{fast} Cu(dmp)_2^+ \quad (4)$$

$$rate = \frac{k_1 K_2 [dmp][Cu^{2+}]_T [Ru(II)]}{[dmp]^2 + K_2[dmp] + K_1 K_2} \quad (5)$$

to rate = $k_1 K_2 [Cu^{2+}]_T[Ru(II)]/[dmp]$ for the experimental conditions employed, where [dmp] ≥ 10^{-4} M. The observation that the reaction rate did not change with variation in the excess ligand concentration ([dmp]$_T$/[Cu^{2+}] = 20.0–6.2) is therefore inconsistent with a significant proportion of the reaction occurring through $Cu(dmp)^+$ as oxidant. The involvement of the tris complex is very unlikely since no experimental evidence exists to indicate that $Cu(dmp)_3^{2+}$ is ever present at significant concentrations in aqueous solutions.

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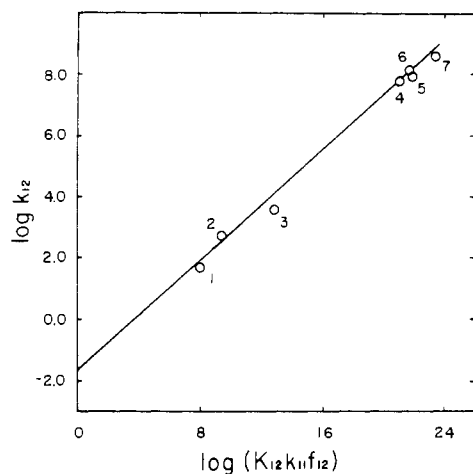
Figure 2. Plot of the logarithms of the second-order rate constants for the reduction of ruthenium(III) complexes by Cu^+ vs. log $(K_{12}k_{11}f_{12})$, where k_{11} is the self-exchange rate constant of the oxidant: 1, $Ru(NH_3)_5py^{3+}$; 2, $Ru(NH_3)_5isn^{3+}$; 3, $Ru(NH_3)_4bpy^{3+}$; 4, Ru-$(3,4,7,8-(CH_3)_4phen)_3^{3+}$; 5, $Ru(4,4'-(CH_3)_2bpy)_3^{3+}$; 6, $Ru(4,7-(CH_3)_2phen)_3^{3+}$; 7, $Ru(bpy)_3^{3+}$.

dine)ruthenium(III) complexes, RuL_3^{3+} with Cu^+, where L is a bipyridine or phenanthroline (phen) derivative. The reactions were monitored during flash-photolysis experiments on RuL_3^{2+} solutions containing Cu^{2+} ions, where Cu^+ and RuL_3^{3+} were generated through the electron-transfer quenching of the luminescent excited state of RuL_3^{2+}. The rate constants reported for the Cu^+ reductions of RuL_3^{3+} complexes, where L = $3,4,7,8-(CH_3)_4phen$, $4,4'-(CH_3)_2bpy$, and $4,7-(CH_3)_2phen$, together with the rate constants measured in the present study clearly establish a linear free energy relationship for outer-sphere $Cu^+-Ru(III)$ reactions over a wide potential range. For the strongly exothermic reactions shown in Figure 1, a leveling off in rate is noted as the diffusion-controlled limit is approached at high driving force. The Marcus cross relation (eq 6), where k_{12} is the cross-reaction

$$k_{12} = (k_{11}k_{22}K_{12}f_{12})^{1/2} \qquad (6)$$

$$\log f_{12} = (\log K_{12})^2/[4 \log (k_{11}k_{22}/Z^2)]$$

rate constant, k_{11} and k_{22} are the self-exchange rate constants of the $Ru(III)/Ru(II)$ and $Cu(II)/Cu(I)$ couples, K_{12} is the equilibrium constant, and Z is a collision number (taken to be 10^{11} M^{-1} s^{-1}), predicts a linear dependence of log k_{12} on $\Delta E°$ with a slope of 8.4. The slope obtained from the plot shown in Figure 1 has a value of 7.9, in good agreement with the theoretically predicted value. Electron-transfer reactions between Cu^+ and $Ru(III)$ ions thus appear to conform to the predictions of the Marcus theory over a wide range of driving force for the reactions.

Since the self-exchange rate constants are known for most of the ruthenium complexes employed in the present study, eq 3 allows for estimation of the self-exchange rate of the Cu^+/Cu^{2+} couple. The plot of log k_{12} vs. log $(K_{12}k_{11}f_{12})$ shown in Figure 2, where k_{11} is the self-exchange rate constant for $Ru(II)/Ru(III)$,[24] has a slope of 0.45, in reasonable agreement with the value of 0.50 predicted by eq 3. Obtained from the intercept of the plot is a Cu^+/Cu^{2+} exchange rate constant of 1.9×10^{-4} M^{-1} s^{-1}. The slowness of the Cu^+/Cu^{2+} exchange reflects the severity of the internal energy barrier to electron exchange arising from the considerable structural differences

Table IV. Summary of Rate Data for $Cu^+-Ru(III)^a$ and $Cu(dmp)_2^{2+}-Ru(II)^b$ Electron-Transfer Reactions at 25.0 °C

reacn	k_2, M^{-1} s^{-1}
$Cu^+-Ru(NH_3)_5py^{3+}$	46.6
$Cu^+-Ru(NH_3)_5isn^{3+}$	540
$Cu^+-Ru(NH_3)_4bpy^{3+}$	3.8×10^3
$Cu^+-Ru(NH_3)_4(isn)_2^{3+}$	4.4×10^4
$Cu(dmp)_2^{2+}-Ru(NH_3)_5py^{2+}$	5.50×10^5
$Cu(dmp)_2^{2+}-Ru(NH_3)_5isn^{2+}$	4.55×10^5
$Cu(dmp)_2^{2+}-Ru(NH_3)_4bpy^{2+}$	3.86×10^5

^{a} $LiClO_4-HClO_4$ medium at 1.0 M ionic strength. ^{b} $LiCF_3CO_2$ medium at 0.10 M ionic strength in an MES buffer at pH 6.1.

that exist between the two oxidation states. The Cu^+ is believed to have a four-coordinate tetrahedral geometry, whereas Cu^{2+} is six-coordinate and tetragonal.

In contrast to the $Cu^+-Ru(III)$ reactions, the rate constants for the oxidation of ruthenium(II) complexes by $Cu(dmp)_2^{2+}$, shown in Table II, are much less sensitive to changes in the thermodynamic driving force. A less than 2-fold increase in rate is observed for reactions varying by 0.22 V in potential. The similarity in rate constants extends also to the activation parameters shown in Table III. The reactions do not appear to exhibit a normal free energy dependence in the Marcus sense, and exchange rates estimated from the $Cu(dmp)_2^+/Cu(dmp)_2^{2+}$ couple by using eq 6 vary by a factor of ca. 10^2. Values of 54, 6.7×10^2, and 8.3×10^3 M^{-1} s^{-1} for the exchange rate of $Cu(dmp)_2^+$ and $Cu(dmp)_2^{2+}$ have been calculated from the data.[25]

In other instances where self-exchange rate constants calculated by using eq 6 were not constant, values estimated from the more exothermic cross reactions are generally lower than those obtained from reactions with smaller driving forces.[5-8] Since the calculated exchange rate constants are rarely too high, extrapolation of the logarithm of the calculated exchange rate constant to $\Delta E° = 0$ has been used previously as a means of estimating the true rate constant. A value of 4×10^4 M^{-1} s^{-1} is obtained for the $Cu(dmp)_2^+/Cu(dmp)_2^{2+}$ exchange in 0.1 M $LiCF_3CO_2$ at 25.0 °C with this approach. This value is in good agreement with values of 1.9×10^4 and 4.9×10^4 M^{-1} s^{-1} at 25 °C in 0.1 M $NaNO_3$ estimated by Augustin and Yandell[26] from data on reactions of $Cu(dmp)_2^{2+}$ with ferricytochrome $c(II)$ and $Co(phen)_3^{2+}$, respectively.

The exact origin of the weak driving-force dependence for reactions of $Cu(II)-dmp$ complexes is however unclear. Steric interaction between the methyl groups of the dmp complex and the $Ru(II)$ reductant could be affecting the electron-transfer rate by restricting the approach of the $Ru(II)$ complex to the $Cu(II)$ center. Nonbonded interactions between the side chain of the oxidant and the reducing agent have been implicated previously in reactions where adherence to the Marcus model was not found.[27] It appears less likely, however, that the methyl groups would seriously limit the accessibility of the acceptor orbitals in the $Cu(dmp)_2^{2+}$ complex, particularly to $Ru(II)$ reductants where the radial extension of the d orbitals is known to be pronounced.[28]

In the $Cu(dmp)_2^{2+}$ complex, mixing of metal d orbitals with the π^* orbitals of the phenanthroline ligand is expected to result in significant d-electron density residing on the dmp ligands. Mediation of the $Ru(II)-Cu(dmp)_2^{2+}$ electron transfer through overlap of the $Ru(II)$ t_{2g} and $Cu(dmp)_2^{2+}$ π^*

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(24) Electron-exchange rate constants (M^{-1} s^{-1}) used were 4.7×10^5 for $Ru(NH_3)_5py^{3+/2+}$ and $Ru(NH_3)_5isn^{3+/2+}$, 1.2×10^7 for $Ru(NH_3)_4bpy^{3+/2+}$,[9] and 2×10^9 for $RuL_3^{3+/2+}$ complexes.[8]

(25) The following $Ru(III)/Ru(II)$ exchange rate constants at 0.10 M ionic strength (M^{-1} s^{-1}, 25 °C) and formal potentials (V) were used in estimating the $Cu(dmp)_2^{+/2+}$ exchange rate: $Ru(NH_3)_4bpy^{3+/2+}$, 7.72×10^5, 0.52;[7] $Ru(NH_3)_5isn^{3+/2+}$, 1.1×10^5, 0.384; $Ru(NH_3)_5py^{3+/2+}$, 1.1×10^5, 0.30.[7,9]

(26) Augustin, M. A.; Yandell, J. R. *Inorg. Chem.* **1979**, *18*, 577.

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orbitals is therefore likely, particularly if direct access to the copper t_{2g} orbitals is hindered. Although a similar mechanism may operate in the $Cu(dmp)_2{}^+$–$Cu(dmp)_2{}^{2+}$ self-exchange process, electron exchange for the Ru(II) complexes involved in this study almost certainly occurs through direct d–d overlap. Since the Marcus theory is expected to be less effective in treating cross reactions that do not proceed via a pathway which is common to the exchange process of both reactants,[8] some variation in the $Cu(dmp)_2{}^+$–$Cu(dmp)_2{}^{2+}$ exchange rate constants calculated with eq 6 is perhaps to be expected.

The lack of sensitivity to changes in thermodynamic driving force could also be tied to rate control by a nonredox process such as a rearrangement of Ru(II) or Cu(II) prior to the electron-transfer step. A partially rate-determining loss of water from the predominant Cu(II) species in solution, $[Cu(dmp)_2H_2O]^{2+}$, prior to reduction of $Cu(dmp)_2{}^{2+}$ by Ru(II) is such a possibility. Both a five-coordinate complex, $[Cu(dmp)_2H_2O]^{2+}$, and a four-coordinate structure, $Cu(dmp)_2{}^{2+}$, in which the chelating nitrogens assume a flattened tetrahedral geometry have been proposed previously for the Cu(II)–dmp complex.[12,29] Sundararajan and Wehry[30] have earlier invoked the existence of the five-coordinate $Cu(dmp)_2H_2O^{2+}$ cation to explain the photoredox behavior of Cu(II)–dmp solutions.

$$[Cu(dmp)_2H_2O]^{2+} \rightarrow [Cu(dmp)_2]^+ + OH + H^+$$
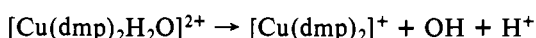
Leupin, Al-Shatti, and Sykes[31,32]3 have proposed that both four- and five-coordinate forms of a related dmp derivative, $Cu(dpmp)_2{}^{2-}$ and $[Cu(dpmp)_2H_2O]^{2-}$ (where dpmp = 2,9-dimethyl-4,7-bis((sulfonyloxy)phenyl)-1,10-phenanthroline) are involved in the oxidation of Ru(II) and Fe(II) complexes. The limiting kinetics that is observed for their reactions is consistent, with both forms being active in the redox change. The recently reported crystal structure of bis(4,4′,6,6′-tetramethyl-2,2′-bipyridine)copper(II) perchlorate dihydrate, $[Cu(tmbp)_2](ClO_4)_2·2H_2O$, which shows a coordinated water molecule in the $[Cu(tmbp)_2H_2O]^{2+}$ cation, would appear to lend support to these conclusions. In the crystal, the $[Cu(tmbp)_2H_2O]^{2+}$ cation has a distorted-trigonal-bipyramidal structure whereas the corresponding Cu(I) ion, $[Cu(tmbp)_2]^+$, is four-coordinate and distorted tetrahedral.[33] In the Cu(II)–dmp oxidations of Ru(II) complexes, a transition from the five-coordinate $[Cu(dmp)_2H_2O]^{2+}$ structure of the dominant solution species to the distorted-tetrahedral $[Cu(dmp)_2]^{2+}$ ion, so as to achieve closer matching to the tetrahedral structure favored by the Cu(I) product, would not appear unreasonable. The relatively small reorganization energy expected for such a change should facilitate a rapid self-exchange rate. The self-exchange rate constant $k_{ex} = 2 \times 10^4$ M^{-1} s^{-1} which is calculated for $Cu(dmp)_2{}^+$/$Cu(dmp)_2{}^{2+}$ is in accord with this expectation.

It is of interest to compare the exchange rates of $Cu(aq)^+$/$Cu(aq)^{2+}$ and $Cu(dmp)_2{}^+$/$Cu(dmp)_2{}^{2+}$ with the ex-

change rate constants of 50 and 250 M^{-1} s^{-1} calculated by Augustin and Yandell[26] for copper phenanthroline and bipyridine complexes. The $Cu(phen)_2{}^{2+}$ and $Cu(bpy)_2{}^{2+}$ complexes are four-coordinate and planar, while the Cu(I) complexes are believed tetrahedral. The structural change required in achieving the nuclear configuration of the activated complex is, therefore, expected to be somewhat intermediate between that required for the $Cu(aq)^{2+}$ ion and the $Cu(dmp)_2{}^{2+}$ complex. The self-exchange rate constants estimated by Augustin and Yandell for $Cu(phen)_2{}^{+/2+}$ and $Cu(bpy)_2{}^{+/2+}$ appear consistent with this rationalization. Values for the $Cu(phen)_2{}^{+/2+}$ and $Cu(bpy)_2{}^{+/2+}$ exchange rates considerably greater than those reported above have been reported by Yoneda, Blackmer, and Holwerda.[34] Data from the oxidation of $Cu(phen)_2{}^+$ and $Cu(bpy)_2{}^+$ by $Co(EDTA)^-$ has yielded self-exchange rate constants of 5×10^7 and 4×10^6 M^{-1} s^{-1} for the $Co(phen)_2{}^{+/2+}$ and $Co(bpy)_2{}^{+/2+}$ couples, respectively. Even with allowance for the effects of opposite charges, these values are still many orders of magnitude greater than those of Augustin and Yandell. A preliminary study of the reaction of $Ru(NH_3)_5py^{3+}$ with $Cu(bpy)_2{}^+$ in this laboratory ($k_2 = 1 \times 10^5$ M^{-1} s^{-1} at 25 °C) has yielded a value for the $Cu(bpy)_2{}^+$/$Cu(bpy)_2{}^{2+}$ exchange rate constant for 28 M^{-1} s^{-1}, in closer accord with the lower value calculated previously.

At least two other instances of rapid Cu(I)/Cu(II) exchange rates have been reported. A rate constant of 5×10^7 M^{-1} s^{-1} has been measured by McConnell and Weaver[35] for electron exchange between copper complexes present in 12 M HCl. The chlorocopper(I) ion $CuCl_4{}^{3-}$ is generally believed to be tetrahedral.[36] Though chlorocopper(II) ions have been shown to assume various geometries in the solid state, a flattened tetrahedral $CuCl_4{}^{2-}$ ion of approximately D_{2d} symmetry is most commonly encountered.[37] The same species has been detected spectroscopically in aqueous solution, though the extent of formation of unhydrated $CuCl_4{}^{2-}$ ions is uncertain even in solutions containing 12 M chloride ion. Though anion effects are likely to be involved, the rapid-exchange rate constant that is found would suggest that a Cu(II) complex, not greatly different in structure from the tetrahedral Cu(I) complex, is the kinetically significant species in the reaction. A similar flattened tetrahedral geometry has been found for the coordination environment of the Cu center in certain blue copper proteins where rapid electron-exchange rates have been noted.[38]

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