presented for B_{12s} reductions of nitrate[3g] and substituted hydroxylamines[10] in acid solution, and an analogous route has been proposed for reduction of N_2O at higher pH.[25] At the same time, however, Bakac and co-workers[14e] have demonstrated that reductions of BrO_3^- and IO_3^- by V^{2+} (which, like B_{12s}, can undergo either 1e or 2e changes) proceed by single-electron transfers, and experimentss of Gordon and Tewari[26] point to the same conclusion for the V^{2+}–ClO_3^- reaction. Reservation of judgment on this point appears to be advisable.

Registry No. B_{12s}, 18534-66-2; B_{12r}, 14463-33-3; ClO_3^-, 14866-68-3; BrO_3^-, 15541-45-4; IO_3^-, 15454-31-6; ClO_2^-, 14998-27-7; *o*-iodosobenzoic acid, 304-91-6.

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Contribution from the Department of Chemistry,
Wayne State University, Detroit, Michigan 48202

Oxidation–Reduction Reactions of Complexes with Macrocyclic Ligands. Role of Kinetic Factors in Distinguishing Mechanistic Pathways in Reactions of Copper(I) Complexes with Coordinated Dioxygen[1]

MEGUMU MUNAKATA and JOHN F. ENDICOTT*

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The rates of reaction between several simple copper(I) complexes and the coordinated dioxygen moiety of $Co([14]aneN_4)(OH_2)O_2^{2+}$ ($[14]aneN_4$ = 1,4,8,11-tetraazacyclotetradecane) have been examined. The very rapid reactions are inferred to span a mechanistic range from simple electron transfer for simple Cu^I(polypyridyl) complexes to transient μ-peroxo (Co–O–O–Cu) adduct formation for $CuCl_3^{2-}$ and $Cu(C_2H_4)^+$. The discrimination between mechanistic pathways is attributed to intrinsic kinetic factors rather than to the thermodynamics of Cu^{II}–(O_2^{2-}) bond formation.

Introduction

Copper-containing enzymes mediate the reduction of dioxygen in several biological systems. The role of the copper is variously ascribed to O_2 binding or to electron transport to the reaction center.[2] Despite the interest in these enzymatic systems, and despite the commonly recognized catalytic role of copper compounds in redox processes, there are many perplexing features of the oxidation–reduction chemistry of copper complexes. For example, the large differences in copper(I) and copper(II) stereochemistry ought to lead to very large reorganizational barriers to oxidation–reduction processes involving complexes in these oxidation states. Thus, electron-transfer reactions of the aquocopper(II)–aquocopper(I) couple are quite sluggish,[3] in apparent contradiction to the often observed catalytic role of copper couples.

Owing to the obvious problems of detecting very small amounts of short-lived, reactive intermediates, there have been few direct studies of the reactions of 1:1 dioxygen adducts of transition-metal complexes. However, we have recently found that the 1:1 adduct of O_2 and $Co([14]aneN_4)(OH_2)_2^{2+}$[4] is relatively strongly absorbing and that $Co([14]aneN_4)(OH_2)O_2^{2+}$ persists long enough in dilute aqueous solution that many of its simple reactions may be investigated.[5] Our work with the $Co([14]aneN_4)(OH_2)O_2^{2+}$ intermediate has shown that the coordinated dioxygen moiety has a relatively small intrinsic barrier to electron transfer, that it is only a mild reducing agent ($E^f \approx 0.3$ V vs. NHE), and that any selectivity of simple inner-sphere over outer-sphere electron-transfer processes has appeared to originate in the very large stability of the M–O bonds of the μ-peroxo products.[5c,d]

We have undertaken the present study to determine whether the reactivity patterns in copper–oxygen systems are dictated largely by product stabilities, as seems the case for many reactions of coordinated superoxide, or whether the differences in copper(I) and copper(II) stereochemisties are important in dictating the reaction pathway.

Experimental Section

Materials. Copper(I) chloride (99.999%) and Cu_2O (99.95%) were obtained from Alfa Chemicals. Tetrakis(acetonitrile)copper(I) perchlorate was synthesized from Cu_2O by the method of Hemmerich and Sigwart.[6]

The macrocyclic ligands $[14]aneN_4$[7] and $Me_6[14]$-4,11-dieneN_4[4,8] and the complexes $[Co(Me_6[14]\text{-}4,11\text{-}dieneN_4)(OH_2)_2](ClO_4)_3$,[9] $[Co(Me_4[14]tetraeneN_4)(OH_2)](ClO_4)_3$,[10] and Co($Me_4$[14]tetrae-

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[1] Partial support of this research by the National Institutes of Health (Grant AM14341) is gratefully acknowledged.

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[4] Ligand abbreviations: $[14]aneN_4$ (cyclam) = 1,4,8,11-tetraazacyclotetradecane; $Me_6[14]$-4,11-dieneN_4 = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene; tpy = 2,2′,2″-terpyridine; 4,4′-Me_2bpy = 4,4′-dimethyl-2,2′-bipyridine; bpy = 2,2′-bipyridine; im = imidazole.

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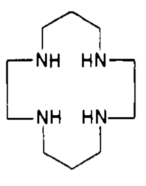
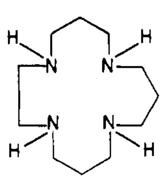
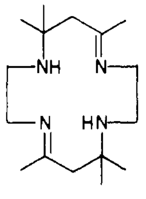
$neN_4)Cl_2]Cl$[11] were prepared by literature methods.



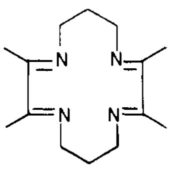
[14]aneN$_4$



[15]aneN$_4$



Me$_6$[14]-4,11-dieneN$_4$



Me$_4$[14]tetraeneN$_4$

Stock solutions containing Co^{II}([14]aneN$_4$) were prepared by mixing $Co(ClO_4)_2 \cdot xH_2O$ with [14]aneN$_4$ anaerobically immediately before each series of kinetic runs. These solutions were continuously purged with Cr^{2+}-scrubbed N_2.

Warning! The perchlorate salts used in this study are dangerous and potentially explosive.

Solid $[Ru(NH_3)_4phen](CF_3SO_3)_2 \cdot H_2O$ was prepared as reported in the literature.[12] Solutions of $Ru(NH_3)_4phen^{3+}$ were generated by PbO_2 oxidations of the ruthenium(II) complex in 0.1 M $HClO_4$.

Solutions containing the copper(I) ethylene complex were prepared in perchloric acid solutions by reduction of aqueous copper(II) with a 10% excess of Cr^{2+} under an ethylene atmosphere.

Solutions (10^{-4} M in $HClO_4$) of the Cu(I) complexes with tpy,[4] Me$_2$bpy,[4] and bpy[4] were prepared by mixing $Cu(CH_3CN)_4ClO_4$ with the ligands anaerobically in an acetone–water mixture (0.5:9.5 v/v). Solutions of copper(I) chloride complexes were prepared by dissolving CuCl anaerobically in 0.1–5 M NaCl solutions containing 0.05 M $HClO_4$.

All solutions were prepared with deionized and distilled water. Acid concentrations were determined by titration. Chromium(II) solutions were prepared by zinc amalgam reduction of $Cr(ClO_4)_3 \cdot xH_2O$ under a nitrogen atmosphere. Deaeration was accomplished by means of a Cr^{2+}-scrubbed nitrogen stream.

Electrical Measurements. Differential pulsed polarography was performed with a Princeton Applied Research Model 174A polarographic analyzer. The electrode system consisted of a saturated calomel reference electrode and either a hanging-mercury-drop or a carbon-paste working electrode. Measurements were made at room temperature, in a closed vessel under an atmosphere of nitrogen, except for study of the Cu^{II,I}-ethylene couple, for which we used ethylene as the purge gas. Values of E^f were obtained from $E^f = (E_r + E_o)/2$. The peak potentials, E_r and E_o, are the potentials of the diffusion current maxima for the reduction and oxidation processes respectively.

Kinetic Methods. The exponential decays of the Co([14]aneN$_4$)$(OH_2)O_2^{2+}$ absorbance at 360 nm were monitored in an Aminco stopped-flow apparatus. The reaction chamber was thermostated, and reactions were run under pseudo-first-order conditions. The values of the experimental rate constants are the means of four separate runs; in general, the rates were reproducible to within 10%.

The $Ru(NH_3)_4phen^{3+}$ oxidations of $CuCl_3^{2-}$ and $Cu(C_2H_4)^+$ were run under pseudo-first-order conditions with [Cu(I)] > [Ru(III)] and monitored by following the appearance of the $Ru(NH_3)_4phen^{2+}$ absorbance, 471 nm, on the stopped-flow apparatus. The Co(Me$_6$-[14]-4,11-dieneN$_4$)$(OH_2)_2^{3+}$–Cu(tpy)$^+$ reaction was monitored at the 430-nm absorbance of Cu(tpy)$^+$.

Apparent second-order rate constants were obtained from the concentration dependencies of the observed first-order time constants. The time constants (τ_{obsd}) for Co([14]aneN$_4$)$(OH_2)O_2^{2+}$ were generally approximate sigmoidal functions of counterreductant concentrations; second-order rate constants have been obtained in the region for which τ_{obsd}^{-1} was proportional to reductant concentration. In some of the very fast reactions it was not possible to achieve this conditions.

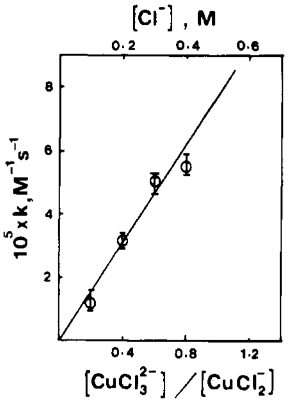


Figure 1. Chloride dependence of the apparent second-order rate constant for the Co([14]aneN$_4$)$(OH_2)O_2^{2+}$–$CuCl_n^{1-n}$ (n = 1, 2) system at 25 °C. Initial concentrations: $[co([14]aneN_4)(OH_2)O_2^{2+}]_i = 6 \times 10^{-4}$ M; $[O_2]_i = 6.3 \times 10^{-4}$ M. (ionic strength 0.4 M (NaCl + $NaClO_4$). The $[CuCl_3^{2-}]$:$[CuCl_2^-]$ ratio is based on association constants from ref 22 and 23. A least-squares fit gives a slope of $(1.1 \pm 0.3) \times 10^6$ M^{-1} s^{-1} and intercept of 0.0 ± 0.4 M^{-1} s^{-1}.

Results

Although copper(I) is substitutionally labile and prone to disproportionate, moderately stable copper(I) complexes can be formed with a wide range of ligands. We have been able to use several such complexes in reductions of Co([14]aneN$_4$)$(OH_2)O_2^{2+}$.

The Copper(I)–Ethylene Complex. Several olefinic complexes of Cu(I) have been reasonably well characterized.[13] The formation constant for the Cu(I)–ethylene complex is 2.2×10^5 M^{-1},[13] and the complex has been isolated as $Cu(C_2H_4)(OH_2)_2ClO_4$.[14] Our reactions were performed with $[C_2H_4(aq)] = 1.1 \times 10^{-3}$ M, so that more than 99% of the total [Cu(I)] was in the form of the ethylenic complex. The $Cu(C_2H_4)^+$ complex was oxidized at $E^f = 0.31 \pm 0.02$ V vs. NHE on a carbon-paste electrode. The differential pulsed polarograms were not very well behaved ($E_{pa} - E_{pc} \simeq 20$ mV) with the cathodic wave having a somewhat larger amplitude than the anodic wave; both waves were broad (full width at half-height, fwhh, for E_a was 131 mV). The shift of the potential implies a formation constant of $\sim 10^3$ M^{-1} for $Cu(C_2H_4)^{2+}$, and many of the features of the polarographic waves must be a consequence of the rapid substitutional equilibration among copper(II) species. Kinetic data for the reactions of $Cu(C_2H_4)^+$ with $Ru(NH_3)_4phen^{3+}$ and Co([14]aneN$_4$)$(OH_2)O_2^{2+}$ are summarized in Tables I and II, respectively. Additionally details may be found in Tables S-I and S-II.[15] The absorption spectrum of the reaction solutions was determined within a few minutes of mixing and had a shoulder at 616 nm and a maximum at 522 nm in accord with the reports[16] for Co([14]aneN$_4$)$(OH_2)O_2H^{2+}$. Since the hydroperoxide was formed in competition with the formation of $[Co([14]aneN_4)(OH_2)]_2O_2^{4+}$, which absorbs relatively strongly in the UV region, a quantitative determination of reaction stoichiometry was not possible. On the basis of the kinetic data in Table S-II and the Geiger and Anson spectroscopic data, at least 60% of the product of the Co([14]aneN$_4$)$(OH_2)O_2^{2+}$–$Cu(C_2H_4)^+$ reaction was Co([14]aneN$_4$)$(OH_2)O_2^{2+}$. A point by point determination of the product spectrum generated after the Co([14]aneN$_4$)$(OH_2)O_2^{2+}$ absorbance decay in stopped-flow studies of the $Cu(C_2H_4)^+$ reactions gave similar results. The reactions were independent of acid in the range 0.1 M ≤ $[H^+]$ ≤ 10^{-4} M.

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Table I. Kinetic Parameters for Simple Electron-Transfer Reactions of Some Copper Complexes (25 °C)

reductant	oxidant	ionic strength,[a] M	$10^{-3}k_{ab}$, $M^{-1}\ s^{-1}$	E^f, V (NHE) oxidant	E^f, V (NHE) Cu(I)	k_{bb},[b] $M^{-1}\ s^{-1}$
$Cu(C_2H_4)^+$	$Ru(NH_3)_4phen^{3+}$	0.10	3.8 ± 0.3	0.533[c]	0.31 ± 0.03	1.3×10^{-3}
$CuCl_3^{2-}$	$Ru(NH_3)_4phen^{3+}$	0.10	11 ± 1	0.533[c]	0.41 ± 0.03	3×10^{-5}
	$Co(Me_4[14]tetraeneN_4)Cl_2^+$	0.20[d]	770 ± 60			
$Cu(tpy)^+$	$Co(Me_6[14]\text{-}4,11\text{-}dieneN_4)(OH_2)_2^{3+}$	0.01[e]	0.53 ± 0.05	0.564[e]	−0.023 ± 0.02	8
$Cu(bpy)_2^+$	$Co(bpy)_3^{3+}$	0.10[f]	2.9 ± 0.2	0.36[e]	0.12 ± 0.02	38
		0.10[g]	4.3 ± 0.3			
		0.01[h,f]	1.8 ± 0.1			
$Cu(phen)_2^+$	$Co(bpy)_3^{3+}$	0.10[f]	2.4 ± 0.1	0.36[e]	0.17 ± 0.02	1.7×10^2
		0.01[h,f]	1.2 ± 0.1			
$Cu(4,4'\text{-}Me_2bpy)_2^+$	$Co(bpy)_3^{3+}$	0.10[f]	49 ± 4	0.36[e]	0.09 ± 0.02	4×10^3
		0.01[h,f]	14 ± 1			
$Cu(4,7\text{-}Me_2phen)_2^+$	$Co(bpy)_3^{3+}$	0.10[f]	18 ± 2	0.36[e]	0.097 ± 0.02	1×10^3
		0.01[h,f]	3.9 ± 0.4			
$Ru(NH_3)_4phen^{2+}$	$Cu(2,9\text{-}Me_2phen)_2^{2+}$	0.01[h,f]	290 ± 20	0.533[c]	0.62 ± 0.02	1.4×10^4

[a] $NaCF_3SO_3$ media except as indicated. [b] Calculated from k_{ab} and literature parameters by using eq 1. [c] Reference 12. [d] HCl and $NaClO_4$ in a 1:1 ratio. [e] Yee, E. L.; Cave, R. J.; Guyer, K. L.; Tyma, P. D.; Weaver, M. J. *J. Am. Chem. Soc.* **1979,** *101,* 1131. [f] Reaction solution contained 10% (v/v) acetone to solubilize the Cu(I) complex. [g] Reaction solution contained 2% (v/v) acetone to solubilize the Cu(I) complex. [h] $NaClO_4$.

Table II. Pseudo-First-Order Rate Constants for the Reaction of $Co([14]aneN_4)(H_2O)O_2^{2+}$-$Cu(C_2H_4)^+$ [a]

$10^4 \times [Co^{II}(N_4)]$,[b] M	$10^4 \times [O_2]$,[b] M	$[H^+]$, M	$10^4 \times [Co^{III}(N_4)O_2^{2+}]$,[b] M	$10^4 \times [Cu^I(C_2H_4)]$,[c] M	k_{obsd}, s^{-1}
3.0	1.3	10^{-4}	0.83	0	33
3.0	1.3	10^{-4}	0.83	3.0	112
3.0	1.3	10^{-4}	0.83	4.0	133
3.0	1.3	10^{-4}	0.83	5.0	156
3.0	1.3	10^{-4}	0.83	6.0	181
3.0	1.3	10^{-3}	0.83	0	39
3.0	1.3	10^{-3}	0.83	3.0	105
3.0	1.3	10^{-3}	0.83	4.0	122
3.0	1.3	10^{-3}	0.83	5.0	161
3.0	1.3	10^{-3}	0.83	6.0	178
3.0	1.3	10^{-2}	0.83	0	41
3.0	1.3	10^{-2}	0.83	3.0	102
3.0	1.3	10^{-2}	0.83	4.0	136
3.0	1.3	10^{-2}	0.83	5.0	151
3.0	1.3	10^{-2}	0.83	6.0	178
3.0	1.3	10^{-1}	0.83	0	56
3.0	1.3	10^{-1}	0.83	3.0	124
3.0	1.3	10^{-1}	0.83	4.0	147
3.0	1.3	10^{-1}	0.83	5.0	170
6.0	6.3	10^{-4}	0.39	0	18
6.0	6.3	10^{-4}	0.39	0.5	28
6.0	6.3	10^{-4}	0.39	1.0	32
6.0	6.3	10^{-4}	0.39	1.5	55

[a] 25 °C and $\mu = 0.1$ ($LiClO_4$). [b] Initial concentration. [c] $[C_2H_4] = 1.1 \times 10^{-3}$ M.

Copper(I) Chloro Complexes. Copper(I) halides and pseudohalides are solubilized by relatively large concentrations of the counter anions:

$$CuX(s) + nX^- \rightleftarrows CuX_{n+1}^{n-} \qquad n = 2\text{–}4$$

Over most practical concentration ranges only the di- and trihalo complexes are formed.[17-21] Association constants of $K_1K_2 = (1.00 \pm 0.05) \times 10^6\ M^{-2}$[22] and $K_3 = 1.95\ M^{-1}$[23] have been reported for

$$K_1K_2 = [CuCl_2^-]/[Cu^+][Cl^-]^2$$

$$K_3 = [CuCl_3^{2-}]/[CuCl_2^-][Cl^-]$$

Kinetic data for the reactions of $CuCl_{n+1}^{n-}$ with several simple electron-transfer agents are summarized in Table I, and additional detail is presented in Table S-III.[15] Pulsed polarographic oxidations of copper(I) in 5 M Cl^- ($[H^+]$ = 1 M) resulted in unsymmetrical waves, broadened at potentials more negative than the peak potentials, and consistent with the presence of several species in equilibrium (fwhh of the anodic peak was 275 mV). The reactions of $Co([14]aneN_4)(OH_2)O_2^{2+}$ with copper(I) in chloride media increased markedly with $[Cl^-]$ (Figure 1); this implies that $CuCl_3^{2-}$ is significantly more reactive than $CuCl_2^-$. Copper(II) had no significant effect on the decay rate of $Co([14]aneN_4)(OH_2)O_2^{2+}$ in chloride media.

Other Copper(I) Reductants. Polypyridyls are well-known to associate strongly with both copper(II) and copper(I), and polypyridyl complexes are relatively well behaved electrochemically.[24] For example, pulsed polarography of $Cu(tpy)^{2+}$ exhibits quasi-reversible behavior ($E_{pa} - E_{pc}$ = 80 mV) and E^f = −0.023 ± 0.006 V (vs. NHE; hanging-mercury-drop electrode; 0.1 M $NaClO_4$). However, the waves are excep-

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Table III. Comparison of the Rate Constants of Oxidation of Copper(I) Complexes by $Co([14]aneN_4)(H_2O)O_2^{2+}$ and O_2 [a]

	k, $M^{-1}\ s^{-1}$			
	by $Co(N_4)(OH_2)O_2^{2+}$)	by O_2	E^f, V [b]	μ [c]
$CuCl_2^-$	$<10^4$	...	~0.28 [d]	0.4
$Cu(CH_3CN)_2^+$	$<10^4$	6.9×10^7 [e-g]	0.31	0.1
$Cu(im)_2^+$	$<10^4$	5.5×10^3 [e,h]	0.35	0.01
$CuCl_3^{2-}$	1.1×10^6	10^3 [i]	0.41	0.4
$Cu(C_2H_4)(H_2O)_2^+$	2.4×10^5	...	0.31	0.1
$Cu(tpy)(H_2O)$	$(\sim 5 \pm 4) \times 10^5$	1.6×10^4 [j]	−0.023	0.01
$Cu(bpy)_2^+$	$<10^4$	6.5×10^3 [k]	0.12	0.01
$Cu(4,4'\text{-}Me_2bpy)_2^+$	$<10^4$		0.09	0.01
$Cu(phen)_2^+$	...	$7 \times 10^{l,m}$	0.17	
hemocyanin	...	1.5×10^7 [n]	...	

[a] 25 °C. [b] Vs. NHE. [c] Ionic strength for reaction $Co([14]aneN_4)(H_2O)O_2^{2+}$ with Cu(I). [d] Kolthoff, I. M., Lingane, J. J., Eds. "Polarography"; Interscience: New York, 1952; Vol. 2, p 494. [e] 30 °C. [f] In $M^{-2}\ s^{-1}$. [g] Gray, R. D. *J. Am. Chem. Soc.* **1969,** *91,* 56. [h] Zuberbühler, A. *Helv. Chim. Acta* **1967,** *50,* 466. [i] Nord, H. *Acta Chem. Scand.* **1955,** *9,* 430. [j] For $Cu(tpy)_2^+$ (Crumbliss, A. L.; Poulos, A. I. *Inorg. Chem.* **1975,** *14,* 1529). [k] Reference 25. [l] Arce, J. A.; Spodine, E.; Zamudio, W. J. *J. Inorg. Nucl. Chem.* **1975,** *37,* 1304. [m] In nitromethane solution. [n] Brunoi, M. *J. Mol. Biol.* **1969,** *46,* 213.

tionally broad (fwhh of the anodic peak was 258 mV). Study of the Cu^I(polypyridyl)–$Co([14]aneN_4)(OH_2)O_2^{2+}$ reactions was complicated by the competition of the very rapid Cu(I)–O_2 reactions,[25] and the range of accessible concentrations was limited by the strong absorbancies and small solubilities. Our observations (Table SIV) permit us only to set upper limits for the rates of the $Co([14]aneN_4)(OH_2)O_2^{2+}$–$Cu^I$(polypyridyl) reactions (Table II).

The reactions of Cu^I–polypyridyl complexes with O_2 are rapid enough that, for large [Cu(I)], this reaction competes with the formation of $Co([14]aneN_4)(OH_2)O_2^{2+}$. Under such circumstances the rate law becomes very complex. Such complexities were found to be even more severe in our attempts to investigate the $Cu^+(aq)$, $Cu(im)_2^+$ and $Cu(CH_3CN)_2^+$ reactions with the cobalt–superoxo complex. For these copper(I) complexes we were unable to find concentration conditions where the copper(I) complex increased the decay rate of $Co([14]aneN_4)(OH_2)O_2^{2+}$ without greatly decreasing the amount of superoxo intermediate formed.

Finally, concentrations as large as 10^{-3} M of $Cu^{2+}(aq)$ Cu(histidinate)$^+$, $Cu(bpy)_2^{2+}$, and $Cu(bpy)^{2+}$ or 10^{-2} M $Hg^{2+}(aq)$ did not affect the $Co([14]aneN_4)(OH_2)O_2^{2+}$ decay rate.

Discussion

The simple electron-transfer reactions of the dioxygen ligand in $Co([14]aneN_4)(OH_2)O_2^{2+}$ are conveniently classified as outer sphere when the counterreagent substitution is slow compared to the rate of electron transfer: e.g.[5c,d]

$$Co([14]aneN_4)(OH_2)O_2^{2+} + Ru(NH_3)_6^{2+} \xrightarrow{H^+} Co([14]aneN_4)(OH_2)O_2H^{2+} + Ru(NH_3)_6^{3+}$$

When the reducing agent is sufficiently labile, and when the product stability is sufficiently great, adduct formation (of μ-peroxo complexes) usually dominates: e.g.[5]

$$Co([14]aneN_4)(OH_2)O_2^{2+} + Co^{II}(N_4) \rightarrow [H_2O([14]aneN_4)Co^{III}]\text{–}(O_2^{2-})\text{–}[Co^{III}(N_4)OH_2]$$

Depending on the stability of the Cu^{II}–(O_2^{2-}) bond, or on kinetic factors that discriminate between pathways, the reactions of Cu(II) complexes might react by means of either pathway.

Outer-Sphere Electron-Transfer Reactions of Cu(II)–Cu(I) Couples. Outer-sphere electron-transfer reaction rates can be interrelated by means of Marcus's square root relation[26]

$$k_{ab} = (k_{aa}k_{bb}K_{ab}f_{ab})^{1/2} \exp(-\Delta w) \qquad (1)$$

where $\log f_{ab} = -(\log K_{ab})^2/4 \log (k_{aa}k_{bb}/10^{22})$ and $\exp(-\Delta w)$ is a correction for differences in Coulombic work terms (designated w_{ij} for approach of the ith and jth species), provided the self-exchange and thermodynamic parameters are known. To facilitate such a comparison, we have investigated a few simple electron-transfer reactions of the copper complexes. While electron-transfer reactions of simple copper complexes have attracted considerable attention,[3,27-31] the apparent self-exchange rate constants extracted from eq 1 have spanned several orders of magnitude for some of the complexes, owing in part to failure to take account of the corrections for differences in Coulombic work terms in the cross and self-exchange reactions (these can be quite large for reactions unsymmetrical in charge type), and owing in part to variations in medium. There is an an additional concern[32] that self-exchange parameters inferred for Cu(II)–Cu(I) couples based on eq 1 may in principle be incorrect because the reactant and product potential energy surfaces must have very different slopes near the transition state. The apparent self-exchange parameters which we have extracted (Table I) fall within the range of literature values where these are reported.

It is clear that the polypyridyl–copper complexes are much more facile electron-transfer reagents than are the aquo, ethylene-, or chlorocopper complexes. However, since the apparent self-exchange rates of the polypyridyl complexes are 6–9 orders of magnitude slower than the diffusional limit, there is an appreciable barrier to outer-sphere electron transfer even for the polypyridyl complexes. This can be qualitatively associated with the structural differences between the Cu(II) and Cu(I) complexes. Thus, X-ray structural studies of nine bis(polypyridyl) complexes of Cu(II), differing in counterion and coordinated ligands, have been found to be approximately trigonal bipyrimidal with a monodentate ligand (e.g., H_2O, I^-, CN^-, etc.) occupying one of the equatorial coordination positions.[33-36] In contrast, the structures of $Cu(py)_4^+$[37] and three substituted-polypyridyl–copper(I) complexes[38-40] have been found to have distorted-tetrahedral coordination geom-

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etries. It is not unlikely that this structural difference persists in aqueous solution and that the reorganizational barrier associated with the large differences in $Cu^{II}-OH_2$ and $Cu^{I}-OH_2$ distances and the substantial differences in the dihedral angles of the polypyridyl ligands are the origins of the substantial reorganizational barrier. The variations in apparent self-exchange rate among these polypyridyl complexes roughly parallel the differences in size and may originate in the solvent reorganizational contribution.

There is much less structural information relating to the $Cu(C_2H_4)^{2+,+}$ and the $CuCl_3^{-,2-}$ couples. The complex $Cu(C_2H_4)(OH_2)_2ClO_4$ has been isolated, and some evidence has been found for a weak $Cu^{I}-(OClO_3^-)$ bond, consistent with a tetrahedral coordination environment.[14] However, X-ray structural studies of (pyrazolylborate)copper(I) complexes containing coordinated ethylene have demonstrated the existence of both trigonal and tetrahedral coordination geometries.[41] The $Cu(C_2H_4)^+$ species in aqueous solution can be expected to be tetrahedral (i.e., $Cu(OH_2)_3C_2H_4^+$), and oxidations of this species should yield five- or six-coordinate copper(II) species. Thus the small self-exchange rate inferred for these hydrated copper–ethylene complexes is consistent with the very small self-exchange rate inferred[3] for $Cu^{2+,+}$(aq).

While potassium and ammonium trichlorocuprates(I) in the solid state have been found to consist of chains of Cl^--bridged $CuCl_4$ tetrahedra,[42] the coordination geometry of monomeric species in aqueous solution has not been established. However, Raman studies of $Cu(CN)_3^{2-}$ indicated that this species is trigonal in aqueous solutions and that interactions of Cu(I) with axial solvent molecules did not give distinct Raman lines.[43] The preference of the tricyano complex for a trigonal structure has been attributed to π interactions,[43] and if correct, this feature makes $Cu(CN)_3^{2-}$ a poor model for $CuCl_3^{2-}$. Nevertheless, the large intrinsic barrier to electron transfer that is inferred for the $CuCl_3^{-,2-}$ couple can only be consistent with a large difference in the coordination geometries of the Cu(II) and Cu(I) complexes.

Inner-Sphere Reaction Pathways. Studies with cobalt ammines have indicated that, where possible, reductions by Cu^+(aq) show a preference for the inner-sphere reaction pathway.[27] In order to assess the intrinsic rate advantage of the inner-sphere pathway, one should compare the rate of an inner-sphere reaction to the rate of the equivalent outer-sphere process (i.e., an outer-sphere pathway for the same reactants, normalized so that the inner-sphere and outer-sphere pathways have the same free energy change[44]). This kind of rate comparison is most easily accomplished for reactions in which the transfer of a bridging ligand accompanies the electron-transfer process,[44] and for this reason we have investigated the $Co(Me_4[14]tetraeneN_4)Cl_2^+-CuCl_3^{2-}$ reaction. To avoid the problems involved in calculating outer-sphere rates for reactions of the $CuCl_3^{-,2-}$ couple, we consider the ratio of rates, $R(X)$, observed for the reductions of $Co(Me_4[14]tetraeneN_4)Cl_2^+$ (k^{Co}) and of $Ru(NH_3)_4phen^{3+}$ (k^{Ru}) by a "typical" outer-sphere reductant, $Ru(NH_3)_6^{2+}$ (X = Ru), and by $CuCl_3^{2-}$ (X = Cu). Thus $R(Ru) \simeq 10^{-2}$ [45-48] and $R(Cu) \simeq 7 \times 10^2$ (Table I). This suggests a very pronounced rate advantage for the innersphere reactions of $CuCl_3^{2-}$, with $(k^{IS}/k^{OS})_{\Delta G^\circ \to 0} \geq 10^4$. At present there is no justification for the quantitative transfer of information about the rate advantage of an inner-sphere pathway from reactions in which transfer of a bridging ligand accompanies electron transfer to reactions in which a metastable adduct is the immediate product of the oxidation–reduction process. There does seem to be a widespread belief that qualitatively similar factors should contribute to reactivity in these two classes of inner-sphere reactions.[49] Thus one might suspect purely kinetic factors (as distinguished from thermodynamic factors) to favor $Cu-O_2$ binding in copper(I) reductions of dioxygen moieties.

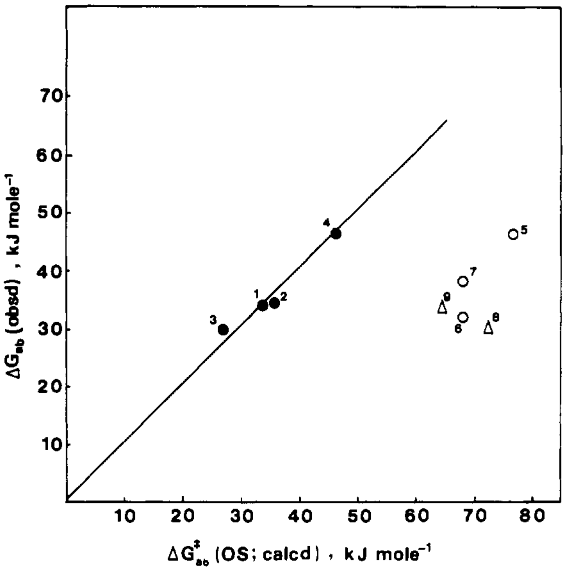

Figure 2. Comparison of observed and calculated rates of reaction between $Co([14]aneN_4)(OH_2)O_2^{2+}$ and several reductants, based on $k(\text{obsd}) = (2 \times 10^{11}) \exp(-\Delta G_{ab}(\text{obsd})/RT)$ and $\Delta G_{ab}^{\ddagger}$(OS,calcd) from eq 2. For the dioxygen moiety, $E^f = 0.3$ V and $k_{aa} = 10^3$ M^{-1} s^{-1} from ref 5d. Known outer-sphere reducing agents[5c,d] (closed circles): $Ru(NH_3)_6^{2+}$ (**1**); $V(OH_2)_6^{2+}$ (**2**); $Co(sep)^{2+}$ (**3**); $Ru(NH_3)_4phen^{2+}$ (**4**). Known inner-sphere reducing agents[5] (open circles): $Fe(OH_2)_6^{2+}$ (**5**); $Co([14]aneN_4)(OH_2)_2^{2+}$ (**6**); $Co([15]aneN_4)(OH_2)_2^{2+}$ (**7**). Copper(I) reductants (triangles): $CuCl_3^{2-}$ (**8**); $Cu(C_2H_4)^+$ (**9**).

Reactions of Cu(I) Complexes with Coordinated Dioxygen. In assessing the reactivity patterns of the $Co([14]aneN_4)(OH_2)O_2^{2+}-Cu(I)$ reactions, it is useful to refer the observed reaction rates to the outer-sphere limit. This could be conveniently accomplished by comparing the rate observed for each Cu(I) reductant to the outer-sphere rate calculated by using eq 1 and parameters in Table I and ref 5d. A more concise comparison is based on the logarithmic form of eq 1:

$$\Delta G_{ab}^{\ddagger}(\text{OS,calcd}) = w_{ab} - (w_{aa} + w_{bb})/2 + \tfrac{1}{2}(\Delta G_{aa}^{\ddagger} + \Delta G_{bb}^{\ddagger}) + \tfrac{1}{2}\Delta G_{ab}^{\circ} + (\Delta G_{ab}^{\circ})^2/8(\Delta G_{aa}^{\ddagger} + \Delta G_{bb}^{\ddagger} - w_{aa} - w_{bb}) \quad (2)$$

The observed values of $\Delta G_{ab}^{\ddagger}$ are compared in Figure 2 to the values of $\Delta G_{ab}^{\ddagger}$ calculated from eq 2. The reactions of $Fe(OH_2)_6^{2+}$, $Co([14]aneN_4)(OH_2)_2^{2+}$, and $Co([15]aneN_4)(OH_2)_2^{2+}$ with $Co([14]aneN_4)(OH_2)O_2^{2+}$ are known to form μ-peroxo adducts, and the rates of these reactions are much greater (i.e., $\Delta G_{ab}^{\ddagger}$(obsd) is much smaller) than expected for outer-sphere electron-transfer rates.[5] Comparable discrepancies between $\Delta G_{ab}^{\ddagger}$(obsd) and $\Delta G_{ab}^{\ddagger}$(OS,calcd) argue strongly for formation of a μ-peroxo adduct in the $Cu(C_2H_4)^+$ and $CuCl_3^{2-}$ reductions of $Co([14]aneN_4)(OH_2)O_2^{2+}$ (Figure 2). That $CuCl_3^{2-}$ is much more reactive toward the coordinated superoxide than is $CuCl_2^-$, despite the fact that the latter

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is a stronger reducing agent by about 0.1 V, also suggests a significant reorganizational component to the rate advantage for adduct formation with these copper complexes. This would be plausible in view of the observations on simpler electron-transfer reactions, but there is at present no way to assess the contribution to ΔG_{ab}^{*} that originates from the stability of the $Cu^{II}-(O_2^{2-})$ bond, a factor which appears to account for most of the difference between ΔG_{ab}^{*}(obsd) and ΔG_{ab}^{*}(OS,calcd) for the $Co^{II}(N_4)$ reductants.[5c,d]

The polypyridyl–copper(I) complexes may function principally as simple electron-transfer agents toward coordinated superoxide. For example, no reactions were observed for $Cu(bpy)_2^+$ even though the outer-sphere rate of electron transfer to the O_2^- moiety would have been only a little smaller than the rate limit dictated by the usable range of reagent concentrations. The apparent unimportance of the inner-sphere, or adduct formation, pathway for Cu^I(polypyridyl) complexes stands in marked contrast to the behavior of $Cu(C_2H_4)^+$ and $CuCl_3^{2-}$. A very small apparent rate advantage of the adduct formation pathway for the $Co([14]aneN_4)(OH_2)O_2^{2+}$–$Cu^I$(polypyridyl) reactions might originate from (a) a small inner-sphere reorganizational barrier to electron transfer in these systems (as manifested in the relatively large inferred self-exchange rates) so that there is no kinetic advantage to barrier reduction through adduct formation, (b) the possibility that the stability of the $Cu^{II}-(O_2^{2-})$ bond is not great enough to decrease by a significant amount the intrinsic barrier to electron transfer, and/or (c) relatively slow substitution into the Cu(polypyridyl) coordination sphere.

Conclusions

The observations reported in this study strongly suggest that the discrimination between the outer-sphere electron-transfer and the adduct formation pathways for the reactions of simple Cu(I) complexes with coordinated dioxygen is largely kinetic in origin and can be correlated with the size of the intrinsic reorganizational barriers to electron transfer. This variation in the discrimination between limiting reaction pathways is reminiscent of the O_2-bonding vs. electron transport functions proposed for various copper enzymes. The ability of a given copper system (complex or enzyme) to discriminate between mechanistically different reaction pathways (which are similar in the thermodynamic driving force) apparently depends on the magnitude of the first coordination sphere reorganization energy which accompanies the Cu(II)–Cu(I) electron exchange. Thus, relatively rigid coordination environments tend to result in relatively small intrinsic reorganizational barriers and favor the electron transport function. Relatively flexible coordination environments, and systems in which the Cu(II) and Cu(I) complexes have distinctly different coordination geometries, tend to have large intrinsic reorganizational barriers to simple electron transfer and to favor a concerted binding–redox process in reactions with dioxygen moieties.

Registry No. $Co([14]aneN_4)(OH_2)O_2^{2+}$, 83784-58-1; $Ru(NH_3)_4phen^{3+}$, 69799-62-8; $Co(Me_4[14]tetraeneN_4)Cl_2^+$, 43225-24-7; $Co(Me_6[14]$-4,11-diene$N_4)(OH_2)_2^{3+}$, 17815-30-4; $Co(bpy)_3^{3+}$, 19052-39-2; $Cu(phen)_2^+$, 17378-82-4; $Cu(2,9\text{-}Me_2phen)_2^{2+}$, 14875-91-3; $CuCl_2^-$, 15697-16-2; $Cu(CH_3CN)_2^+$, 22418-38-8; $Cu(Im)_2^+$, 27858-34-0; $CuCl_3^{2-}$, 29931-61-1; $Cu(C_2H_4)(H_2O)_2^+$, 92366-27-3; $Cu(tpy)(H_2O)^+$, 92366-28-4; $Cu(bpy)_2^+$, 36450-97-2; $Cu(4,4'\text{-}Me_2bpy)_2^+$, 92366-29-5.

Supplementary Material Available: Tables of kinetic parameters (12 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry,
University of New Brunswick, Fredericton, New Brunswick, Canada E3B 6E2

Solvent Effects on Redox Reactions. 1. Chromium(II) Reduction of Tris(pentane-2,4-dionato)cobalt(III) in Water/Dimethylformamide Solvent Mixtures

NITA A. LEWIS* and ANANDA M. RAY

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The Cr(II) reduction of $Co(ptdn)_3$ was studied in various dimethylformamide/water mixtures at $\mu = 1.00$ M (CH_3COOLi). The activation parameters were measured over a temperature range of 25–45 °C. Three pathways for reduction were observed—outer sphere, monobridged inner sphere, and dibridged inner sphere. Only the dibridged pathway showed an acid dependence. The outer-sphere and monobridged inner-sphere routes followed simple second-order kinetics whereas the dibridged path showed evidence for the presence of a binuclear intermediate. It was postulated that the dibridged transition state was stabilized by an organic solvent cage.

Introduction

Except for isotopic exchange reactions,[1-3] there have been few attempts to study the effect of solvent on electron-transfer reactions. The most comprehensive series of experiments was performed by Watts and co-workers.[4-9] This group studied the Fe(II) reductions of a series of $Co(NH_3)_5X^{2+}$ complexes where X = F^-, Cl^-, Br^-, and N_3^-, in dimethyl sulfoxide, dimethyl sulfoxide/water mixtures, and *N*,*N*-dimethylformamide. The reactions were investigated over a range of temperatures, ionic strengths, and acidities. Because of the lability of the Fe(III) products formed, the product criterion for establishing the mechanism of reduction (inner or outer sphere) could not be used. Watts and his co-workers interpreted their results in terms of an inner-sphere process in all cases using indirect methods.

A reductant that is capable of distinguishing between an inner- and an outer-sphere mechanism is Cr(II). When this reductant is used, the bridging ligand is captured in the first coordination sphere of the Cr(III) product if an inner-sphere pathway is operating, and the product is usually sufficiently robust that it can be purified by ion-exchange techniques and identified spectroscopically. In spite of the obvious advantages of using this reductant to establish the mechanism of electron transfer, few solvent studies have employed Cr(II) as a re-

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