Inorg. Chem. **1997,** *36,* 3253−3257

Effect of Conformational Constraints on Gated Electron Transfer Kinetics. 2. Copper(II/I) Complexes with Phenyl-Substituted [14]aneS$_4$ Ligands in Acetonitrile[1]

Brian C. Dunn,[2a] L. A. Ochrymowycz,[2b] and D. B. Rorabacher*,[2a]

Departments of Chemistry, Wayne State University, Detroit, Michigan 48202, and University of Wisconsin—Eau Claire, Eau Claire, Wisconsin 54701

Received July 9, 1996[⊗]

Kinetic studies have been conducted in acetonitrile on the electron-transfer reactions of five copper(II/I) complexes involving ligands in which either a benzene or a cyclohexane ring, or both, have been substituted into the ligand backbone of the 14-membered tetrathiamacrocycle [14]aneS$_4$. The specific ligands utilized in this work include 2,3-benzo-1,4,8,11-tetrathiacyclotetradecane (bz-[14]aneS$_4$), 2,3-*trans*-cyclohexano-1,4,8,11-tetrathiacyclotetradecane (*trans*-cyhx-[14]aneS$_4$), 2,3-benzo-9,10-*trans*-cyclohexano-1,4,8,11-tetrathiacyclotetradecane (bz,*trans*-cyhx-[14]aneS$_4$), 2,3-benzo-9,10-*cis*-cyclohexano-1,4,8,11-tetrathiacyclotetradecane (bz,*cis*-cyhx-[14]aneS$_4$), and 2,3-*cis*-9,10-*trans*-dicyclohexano-1,4,8,11-tetrathiacyclotetradecane (*cis*, *trans*-dicyhx-[14]aneS$_4$). Each $\mathrm{Cu^{II/I}L}$ system has been reacted with three separate reducing agents and three separate oxidizing agents to examine the effect of driving force upon the kinetic parameters. The Marcus relationship has been applied to each cross-reaction rate constant to estimate the apparent self-exchange rate constant, k_{11}, for each $\mathrm{Cu^{II/I}L}$ system. For all but one of the five systems, the k_{11} values obtained from the three reduction reactions are in virtual agreement with the corresponding value obtained for the oxidation reaction with the smallest driving force. As the driving force for $\mathrm{Cu^{I}L}$ oxidation increases, a smaller k_{11} value is calculated for each system. This behavior is consistent with our previously proposed dual-pathway square scheme mechanism in which a significant conformational change occurs as a separate step preceding electron transfer in the case of $\mathrm{Cu^{I}L}$ oxidation. Although direct observation of conformationally-gated electron transfer was not attained for any of the five systems included in the current work, limits for the rate constant for conformational change have been estimated from the conditions required to change the apparent pathway for the oxidation kinetics. These limits show that the $\mathrm{Cu^{I}L}$ complex involving a single phenyl substituent (bz-[14]aneS$_4$) exhibits a much slower conformational change than do any of the other systems included in this study. The implications of this observation are discussed.

Introduction

In earlier studies we have examined the electron-transfer kinetics of copper(II/I) complexes involving macrocyclic tetrathiaether ligands in their reactions with selected oxidizing and reducing agents.[3−6] As a general rule, the reaction kinetics have been shown to correspond to a dual-pathway square scheme mechanism in which conformational change occurs sequentially with the electron-transfer step. As illustrated in Figure 1, pathway A represents the preferred pathway—for all systems observed to date—wherein the major conformational change occurs in the $\mathrm{Cu^{I}L}$ species. Under appropriate conditions, the specific process involving conformational change (R → P) of the reductant can itself become the rate-limiting step during oxidation, leading to a condition designated as *gated* electron transfer.[7]

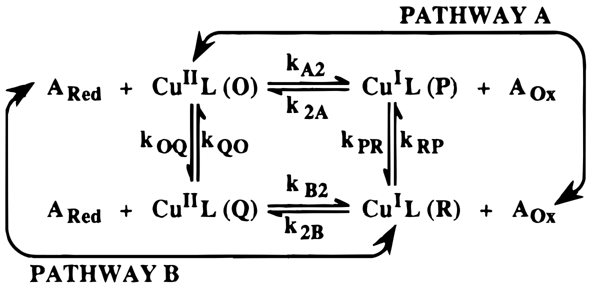

Figure 1. Dual-pathway square-scheme mechanism for $\mathrm{Cu^{II/I}L}$ electron-transfer reactions where A_{Red} and A_{Ox} represent the counter reductant and oxidant, respectively. Species $\mathrm{Cu^{II}L(O)}$ and $\mathrm{Cu^{I}L(R)}$ represent the thermodynamically stable species, while $\mathrm{Cu^{II}L(Q)}$ and $\mathrm{Cu^{I}L(P)}$ are metastable intermediates which are presumed to differ in conformation from the ground-state species. Previous work indicates that intermediate P is more stable than intermediate Q for the [14]aneS$_4$ series of ligands so that pathway A is generally preferred. However, under conditions where the rate constant for the R → P conformational change, k_{RP}, becomes rate limiting for pathway A, the reaction can be forced to switch to pathway B.

In recent work,[1] we examined the effect of incorporating either a *cis*- or *trans*-cyclohexane ring into the ligand backbone of our primary reference ligand, [14]aneS$_4$ (L0 in Figure 2), on the premise that this might be expected to alter the ability of the ligand to undergo conformational change from the tetrahedral coordination preferred by Cu(I) to the tetragonal or square pyramidal geometry preferred by Cu(II). For the preferred pathway A, the two cyclohexanediyl-substituted ligands resulted in $\mathrm{Cu^{II/I}L}$ self-exchange rate constants (k_{11A}) which differed by 30-fold, the *cis*-cyclohexanediyl derivative (L2) exhibiting a 6-fold increase—relative to the unsubstituted [14]aneS$_4$ complex—while the *trans* derivative (L3) yielded a 5-fold

---

[⊗] Abstract published in *Advance ACS Abstracts*, June 15, 1997.

(1) For paper 1 in this series, see: Salhi, C. A.; Yu, Q.; Heeg, M. J.; Villeneuve, N. M.; Juntunen, K. L.; Schroeder, R. R.; Ochrymowycz, L. A.; Rorabacher, D. B. *Inorg. Chem.* **1995**, *34*, 6053−6064.

(2) (a) Wayne State University. (b) University of Wisconsin—Eau Claire.

(3) Martin, M. J.; Endicott, J. F.; Ochrymowycz, L. A.; Rorabacher, D. B. *Inorg. Chem.* **1987**, *26*, 3012−3022.

(4) Meagher, N. E.; Juntunen, K. L.; Salhi, C. A.; Ochrymowycz, L. A.; Rorabacher, D. B., *J. Am. Chem. Soc.* **1992**, *114*, 10411−10420.

(5) Leggett, G. H.; Dunn, B. C.; Vande Linde, A. M. Q.; Ochrymowycz, L. A.; Rorabacher, D. B. *Inorg. Chem.* **1993**, *32*, 5911−5918.

(6) Meagher, N. E.; Juntunen, K. L.; Heeg, M. J.; Salhi, C. A.; Dunn, B. C.; Ochrymowycz, L. A.; Rorabacher, D. B. *Inorg. Chem.* **1994**, *33*, 670−679.

(7) Hoffman, B. M.; Ratner, M. A. *J. Am. Chem. Soc.* **1987**, *109*, 6237−6243.

S0020-1669(96)00793-8 CCC: $14.00

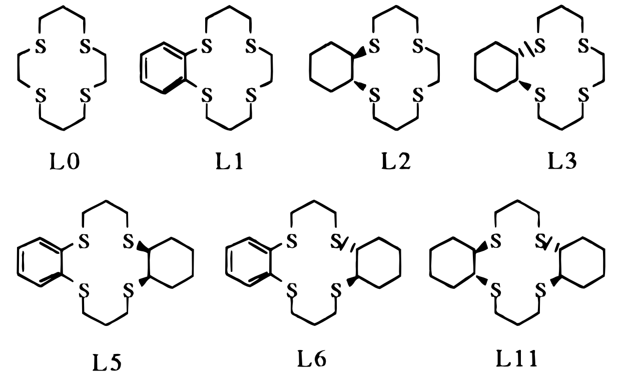

Figure 2. Ligands discussed in this work. Ligand numbers are correlated to ref 8.

Table 1. Formal Potentials and Stability Constants for Copper(II/I) Complexes with Substituted 14-Membered Cyclic Tetrathiaethers and the Visible Spectral Parameters of the Copper(II) Complexes in Acetonitrile at 25 °C with $\mu = 0.10$ (ClO_4^-)[a]

complexed ligand	E^f, V vs Fc[b]	log $K_{Cu^{II}L'}$	log $K_{Cu^{I}L'}$	λ_{max}, nm ($10^{-3}\epsilon$)	λ_{max}, nm ($10^{-3}\epsilon$)
L0	0.21	10.8	4.20	390 (8.52)	560 (2.0)
L1	0.46	7.8	5.43	384 (4.97)	580 (2.0)
L3	0.20	12.2	5.43	392 (11.5)	538 (2.0)
L5	0.38	9.2	5.48	391 (6.52)	562 (2.4)
L6	0.39	9.7	6.18	393 (6.19)	562 (2.5)
L11	0.140	13.3	5.46	394 (9.71)	548 (2.2)

[a] All data are from ref 8. [b] All potential values in acetonitrile are referenced to ferrocene for which the formal potential is assumed to be $E^f = 0.340$ V vs the normal hydrogen electrode (Koepp, H.-M.; Wendt, H.; Strehlow, H. *Z. Elektrochem.* **1960**, *64*, 483−491).

decrease. Surprisingly, however, neither derivative significantly altered the rate constant for conformational change, k_{RP} (Figure 1).

It was suspected that the substitution of a benzene ring into the macrocyclic ligand structure might cause greater changes in the electron-transfer and conformational rate constants due to its greater rigidity and the negative inductive effect of the benzene ring. Our attempts to include the corresponding phenyl derivative (L1) during the previous aqueous study were thwarted by the limited solubility of the phenyl-substituted ligand in aqueous solution as well as by the extreme weakness of the resulting $Cu^{II}L$ complex. However, independent thermodynamic studies on both the phenyl and cyclohexanediyl substituted [14]-aneS_4 ligands have revealed that the solubility of these ligands improves significantly in acetonitrile and the stability constants of the Cu(II) complexes increase by 6 orders of magnitude relative to aqueous values.[8] Thus, by using acetonitrile as a solvent, it is feasible to prepare both Cu(II) and Cu(I) complexes involving phenyl-substituted ligands.

As we have demonstrated in our previous studies, the investigation of a Cu(II/I) complex system, in terms of its conformance to a square scheme mechanism, is facilitated by the availability of a variety of oxidizing and reducing reagents. In a very timely review, Wherland[9] has summarized the available published data on the self-exchange rate constants for a number of metal complexes in acetonitrile which are suitable as oxidizing agents for our studies. Using the available literature data, we have recently generated self-exchange rate constants for additional reagents using selected cross reactions.[10] As part of the same work, we examined the electron-transfer cross-reaction kinetics of several counter oxidants and reductants reacting with $Cu^{II/I}$([14]aneS_4) in acetonitrile.[10] The results indicate that the self-exchange rate constant for this reference Cu(II/I) system is virtually identical in water and in acetonitrile, particularly after corrections are made for the differences in the solvent dielectric. This indicates that acetonitrile can readily be used for obtaining comparable data on the electron-transfer kinetics of Cu(II/I) systems which, due to limitations imposed by solubility and/or complex stability, cannot be studied directly in water.

In the current work, we have investigated the electron-transfer kinetics, in acetonitrile, of the Cu(II/I) complex formed with the phenyl derivative of [14]aneS_4 in which the benzene ring bridges the 2,3 positions (2,3-benzo-1,4,8,11-tetrathiacyclotetradecane—designated as ligand L1 in Figure 2). We have also restudied the Cu(II/I) system involving the corresponding *trans*-cyclohexanediyl derivative (2,3-*trans*-cyclohexano-1,4,8,11-tetrathiacyclotetradecane = L3) in acetonitrile for comparison to our earlier aqueous results. In addition, we have examined the effect of incorporating both a benzene ring bridging the 2,3 positions in [14]aneS_4 plus either a bridging *cis*-cyclohexane ring (2,3-benzo-9,10-*cis*-cyclohexano-1,4,8,11-tetrathiacyclotetradecane = L5) or *trans*-cyclohexane ring (2,3-benzo-9,10-*trans*-cyclohexano-1,4,8,11-tetrathiacyclotetradecane = L6) at the 9,10 positions. As a final comparison to these latter derivatives, we have also included the disubstituted [14]aneS_4 ligand involving a *cis*-cyclohexane ring at the 2,3 bridge and a *trans*-cyclohexane group at the 9,10 bridge (2,3-*cis*-9,10-*trans*-dicyclohexano-1,4,8,11-tetrathiacyclotetradecane = L11). The previously determined properties of these six $Cu^{II/I}L$ complexes are compared in Table 1.[11]

By applying the Marcus relationship[12] to the experimental cross-reaction rate constants, we have been able to generate the values of the apparent self-exchange rate constants for all five Cu(II/I) systems included in this work under varying conditions. These values then permit a thorough examination of the influence of phenyl substitution upon the kinetics of electron transfer in cyclic Cu(II/I)−tetrathiaether systems.

Experimental Section

Reagents. The acetonitrile utilized in this work was purchased from Fisher Scientific (HPLC grade) and was used as received. Karl Fischer titrations indicated that the water content did not exceed 0.017% w/w (about 7 mM) even after the bottle had been opened for 2−3 weeks. No attempt was made to dry the solvent since previous studies have shown that adding amounts of water up to 3% (w/w) had no effect upon the electron-transfer kinetics.[10]

The syntheses for all cyclic tetrathiaether ligands included in this work have already been described.[8] The determination of the stability constants for both the $Cu^{II}L$ and $Cu^{I}L$ complexes as well as the $Cu^{II/I}L$ formal potentials in acetonitrile with all five ligands have also been reported.[8] The sodium perchlorate used to control the ionic strength at $\mu = 0.10$ was prepared from $HClO_4$ and NaOH as previously noted[13] and then recrystallized from acetonitrile before use. Copper(II) perchlorate was prepared by the dropwise addition of $HClO_4$ to solid $CuCO_3$ until all the solid had dissolved. The resulting solution was boiled to reduce the volume and cooled in an ice bath to obtain crystalline $Cu(ClO_4)_2\cdot 6H_2O$ which was then collected on a Buchner funnel by vacuum filtration. (**Warning!** *Metal perchlorate salts are*

---

(8) Aronne, L.; Dunn, B. C.; Vyvyan, J. R.; Souvignier, C. W.; Mayer, M. J.; Howard, T. A.; Salhi, C. A.; Goldie, S. N.; Ochrymowycz, L. A.; Rorabacher, D. B. *Inorg. Chem.* **1995**, *34*, 357−369.

(9) Wherland, S. *Coord. Chem. Rev.* **1993**, *123*, 169−199.

(10) Dunn, B. C.; Ochrymowycz, L. A.; Rorabacher, D. B. *Inorg. Chem.* **1995**, *34*, 1954−1956.

(11) The numbers assigned to the various ligands in Figure 2 correspond to the numbering system used in the previous publication on the thermodynamic properties of the $Cu^{II/I}L$ systems: Reference 8.

(12) Marcus, R. A.; Sutin, N. *Biochim. Biophys. Acta* **1985**, *811*, 265−322.

(13) Cooper, T. H.; Mayer, M. J.; Leung, K.-H.; Ochrymowycz, L. A.; Rorabacher, D. B. *Inorg. Chem.* **1992**, *31*, 3796−3804.

Table 2. Formal Potentials, Electron Self-Exchange Rate Constants, and Spectral and Size Parameters for Reagents As Applied to Acetonitrile at 25 °C with $\mu = 0.10$ (ClO_4^-)

reagent	E^f, V vs Fc[a,b]	k_{22}, $M^{-1}\ s^{-1}$	$10^8 r$, cm	λ_{max}, nm ($10^{-3}\epsilon$)
Reductants				
$Co^{II}(bpy)_3$	−0.076	0.645[b]	7.0[c]	
$Ru^{II}(NH_3)_4bpy$	0.127	5.50×10^5 [b]	4.4[d]	295 (32)[e]
$Ru^{II}(NH_3)_5isn$	−0.012	4.71×10^5 [b]	3.8 [e]	478 (11.9)[f]
Oxidants				
$Mn^{III}(bpyO_2)_3$	0.442	80[g]	4.0[g]	362 (10)[h]
$Ni^{III}((14)aneS_4)$	0.591	3.3×10^3 [i]	3.6[j]	308 (11)[k]
$Fe^{III}(4,7\text{-}Me_2phen)_3$	0.538	2.7×10^7 [l]	6.6[d]	512 (14)[m]
$Fe^{III}(bpy)_3$	0.669	3.7×10^6 [l]	6.0[d]	522 (8.65)[m]

[a] All potential values in acetonitrile are referenced to ferrocene. [b] Reference 10. [c] Tsukahara, K.; Wilkins, R. G. *Inorg. Chem.* **1985**, *24*, 3399−3402. [d] Reference 3. [e] Brown, G. M.; Sutin, N. *J. Am. Chem. Soc.* **1979**, *101*, 883−892. [f] Shepard, R.; Taube, H. *Inorg. Chem.* **1973**, *12*, 1392−1401. [g] Macartney, D. H.; Thompson, D. W. *J. Chem. Res. Synop.* **1992**, 344−345. [h] Morrison, M. M.; Sawyer, D. T. *Inorg. Chem.* **1978**, *17*, 338−339. [i] Macartney, D. H.; Mak, S. *Can. J. Chem.* **1992**, *70*, 39−45. [j] Fairbank, M. G.; Norman, P. R.; McAuley, A. *Inorg. Chem.* **1985**, *24*, 2639−2644. [k] Zeigerson, E.; Ginzburg, G.; Schwartz, N.; Luz, Z.; Meyerstein, D. *J. Chem. Soc., Chem. Commun.* **1979**, 241−243. [l] Chan, M.-S.; Wahl, A. C. *J. Phys. Chem.* **1978**, *82*, 2542−2549. [m] Brandt, W. W.; Smith, G. F. *Anal. Chem.* **1949**, *21*, 1313−1319.

potentially explosive and should be handled with care; they should never be heated to dryness!) Stock solutions of $Cu(ClO_4)_2$ were prepared by dissolving the hydrated salt in acetonitrile and then adding water before titrating with a standard EDTA solution. At the Cu(II) concentration levels used for the kinetic experiments, the amount of water introduced from the hydrated salt was considered to be insignificant since small amounts of added water have previously been shown to have no effect upon the Cu(II/I) electron-transfer kinetics (*vide supra*). The Cu(I) perchlorate salt, $CuClO_4 \cdot 4CH_3CN$, was prepared by crystallization from acetonitrile using the method of Hathaway et al.[14] For standardization of $Cu(CH_3CN)_4^+$ solutions in acetonitrile, excess aqueous EDTA can be added with aeration (resulting in the immediate oxidation of Cu(I) to Cu(II)) followed by back-titration with aqueous Cu(II).

Solutions of $Cu^{II}L$ and $Cu^{I}L$ were prepared by mixing the appropriate copper salt with an excess amount of ligand. In preparing $Cu^{I}L$, the two constituent solutions were first purged with nitrogen before mixing.

All oxidizing and reducing counter reagents were prepared in acetonitrile as previously described.[10] The concentrations of the counter reagent solutions were generally determined spectrophotometrically. The formal potentials and major absorbance peaks for each reagent utilized are listed in Table 2.

Instrumentation. All kinetic measurements were made with a Durrum D-110 stopped-flow spectrophotometer equipped with a newly-modified flow system, designed and built by Tritech Scientific Ltd. of Winnipeg, Manitoba, Canada. This flow system contained all Teflon gaskets, avoiding the leakage problems inherent when using acetonitrile in the original rubber gasket system. The temperature was maintained at 25.0 ± 0.2 °C using a circulating water bath. The instrument was interfaced to an Insight 486 PC for data collection.

Results

Kinetic Measurements. As has been our practice in previous studies on $Cu^{II/I}L$ electron-transfer kinetics, both the reduction and oxidation kinetics were determined for each system using multiple counter reagents:

$$Cu^{II}L + A_{Red} \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} Cu^{I}L + A_{Ox} \tag{1}$$

All reactions were first order with respect to each reactant. For all five $Cu^{II}L$ complexes, the reduction kinetics were studied using $Co^{II}(bpy)_3$, $Ru^{II}(NH_3)_4bpy$, and $Ru^{II}(NH_3)_5isn$ as reducing agents.[15] However, the reaction of $Cu^{II}(L1)$ with the last reagent proved to be too fast to measure. For all $Cu^{I}L$ complexes except the L1 system, the reaction kinetics were studied using $Mn^{III}(bpyO_2)_3$, $Ni^{III}([14]aneN_4)$, and $Fe^{III}(4,7\text{-}Me_2phen)_3$ as oxidizing agents.[15] In the specific case of $Cu^{I}(L1)$, the latter two oxidizing agents were used along with $Fe^{III}(bpy)_3$.

Approximately twelve replicate kinetic runs were measured for each set of conditions with four or five different concentration levels being utilized. Slower reactions were generally run under pseudo-first-order conditions with either reactant in large excess. The resulting pseudo-first-order rate constants were in the range of 0.1−200 s^{-1}. Faster reactions—particularly for those with second-order rate constants in the range of 10^6 to $2 \times 10^7\ M^{-1}\ s^{-1}$—were studied using second-order conditions (i.e., neither reagent in notable excess).[16] For each set of reactants, the kinetics were studied under conditions where the reaction half-life was varied by at least 5-fold.

The resolved second-order rate constants for all 30 reactions included in this study are tabulated in Table 3 along with the corresponding data previously reported for $Cu^{II/I}([14]aneS_4)$ (i.e., $Cu^{II/I}(L0)$) in acetonitrile.[10] Standard deviations (relative to the last digit listed) are given in parentheses. In all cases, the oxidizing and reducing agents are listed in order of increasing driving force (i.e., increasing $K_{12}k_{22}$ products) so that the reaction rate constants tend to increase significantly proceeding down the column within each category.

Discussion

As in our earlier studies[3] the Marcus square root relationship was applied to all cross-reaction rate constants to permit the calculation of the apparent self-exchange rate constant, k_{11}, for each of the $Cu^{II/I}L$ systems. In the making of these calculations, the parameters utilized included the $Cu^{II/I}L$ potentials in Table 1 and the potentials, self-exchange rate constants, and ion size parameters for the counter reagents as listed in Table 2. For the $Cu^{II/I}L$ systems, a constant ion size parameter of 4.4×10^{-8} cm was utilized for simplicity.[17] The logarithmic k_{11} values obtained from the Marcus calculations are tabulated in Table 4. In all cases, both the reducing and oxidizing reagents are arranged in order of increasing driving force.

Comparison to Aqueous Values. In our earlier study on the electron-transfer kinetics of the $Cu^{II/I}([14]aneS_4)$ system in acetonitrile,[10] we noted that the calculated $k_{11(Red)}$ and the limiting $k_{11(Ox)}$ values for this system were 2- to 3-fold smaller than the corresponding values obtained earlier in aqueous solution.[4] When corrections were made to account for the electrostatic differences due to the difference in the solvent dielectric constants, the values for the two solvents were well within experimental error.

---

(14) Hathaway, B. J.; Holah, D. G.; Postlethwaite, J. D. *J. Chem. Soc.* **1961**, 3215−3218.

(15) Reagent abbreviations are as follows: bpy = 2,2′-bipyridine, isn = isonicotinamide, $bpyO_2$ = N,N′-dioxo-2,2′-bipyridine, $[14]aneN_4$ = 1,4,8,11-tetraazacyclotetradecane (cyclam), and $4,7\text{-}Me_2phen$ = 4,7-dimethyl-1,10-phenanthroline.

(16) In independent studies, we have shown that rapid second-order kinetics can be obtained using the stopped-flow method for reactions having rate constants as large as $10^8\ M^{-1}\ s^{-1}$ (Dunn, B. C.; Meagher, N. E.; Rorabacher, D. B. *J. Phys. Chem.* **1996**, *100*, 16925−16933). The modified stopped-flow instrument used in the current study actually has a slower filling time (ca. 10 ms) so that the upper limit on second-order rate constants is in the range of $3 \times 10^7\ M^{-1}\ s^{-1}$.

(17) Molecular models indicate that, on the basis of the criteria established earlier for estimating ion size parameters (see ref 3), the value will increase only to about 5×10^{-8} cm for the dicyclohexanediyl-substituted complexes. This will not result in a significant change in the calculations for k_{11}.

Table 3. Resolved Second-Order Rate Constants at 25 °C, $\mu = 0.10$ (ClO_4^-), in Acetonitrile for All Reactions Included in This Work

	k_{12} or k_{21} ($M^{-1}\ s^{-1}$) for cross reactions between counter reagent and $Cu^{II/I}L$[a]					
reagent	$Cu^{II/I}(L0)$[b]	$Cu^{II/I}(L1)$	$Cu^{II/I}(L3)$	$Cu^{II/I}(L5)$	$Cu^{II/I}(L6)$	$Cu^{II/I}(L11)$
			Reductants			
$Co^{II}(bpy)_3$	$5.7(2) \times 10^3$	$2.0(1) \times 10^5$	$1.1(1) \times 10^3$	$6.5(6) \times 10^4$	$5.0(1) \times 10^4$	$4.4(3) \times 10^3$
$Ru^{II}(NH_3)_4bpy$	$2.7(6) \times 10^5$	$7.0(5) \times 10^6$	$6.9(7) \times 10^4$	$2.9(6) \times 10^6$	$3.8(9) \times 10^6$	$9.3(3) \times 10^4$
$Ru^{II}(NH_3)_5isn$	$2.6(1) \times 10^6$	$> 3 \times 10^7$ [c]	$1.0(3) \times 10^6$	$1.8(3) \times 10^7$	$1.5(5) \times 10^7$	$1.1(1) \times 10^6$
			Oxidants			
$Mn^{III}(bpyO_2)_3$	$4.2(3) \times 10^4$		$2.3(1) \times 10^4$	$1.71(4) \times 10^3$	$2.86(9) \times 10^3$	$1.07(6) \times 10^5$
$Ni^{III}([14]aneN_4)$	$1.52(8) \times 10^5$	$3.4(2) \times 10^3$	$1.2(1) \times 10^6$	$9.0(2) \times 10^4$	$9.8(2) \times 10^4$	$6.7(7) \times 10^6$
$Fe^{III}(4,7\text{-}Me_2phen)_3$	$8.2(6) \times 10^5$	$5.6(4) \times 10^4$	$3.2(2) \times 10^6$	$2.8(1) \times 10^5$	$3.5(2) \times 10^5$	$5.1(3) \times 10^6$
$Fe^{III}(bpy)_3$	$2.2(1) \times 10^6$	$1.66(7) \times 10^5$				

[a] Values in parentheses refer to the standard deviation in terms of the last integer shown; thus, $1.66(7) \times 10^5$ represents $(1.66 \pm 0.07) \times 10^5$. [b] All data for the L0 system are from ref 10. [c] Reaction was too fast to measure; value shown is lower limit.

Table 4. Calculated Logarithmic Self-Exchange Rate Constants for Copper(II/I) Systems at 25 °C, $\mu = 0.10$, in Acetonitrile As Calculated from All Cross Reactions Included in This Work

	log k_{11} ($M^{-1}\ s^{-1}$) for $Cu^{II/I}L$					
reagent	$Cu^{II/I}(L0)$[a]	$Cu^{II/I}(L1)$	$Cu^{II/I}(L3)$	$Cu^{II/I}(L5)$	$Cu^{II/I}(L6)$	$Cu^{II/I}(L11)$
			Reductants			
$Co^{II}(bpy)_3$	3.24	2.90	1.83	2.81	2.74	3.85
$Ru^{II}(NH_3)_4bpy$	3.55	2.80	2.44	2.98	3.36	3.52
$Ru^{II}(NH_3)_5isn$	3.53		2.46	2.73	2.68	3.44
			Oxidants			
$Mn^{III}(bpyO_2)_3$	3.23		2.60	3.23	3.51	3.25
$Ni^{III}([14]aneN_4)$	0.63, 0.34	0.81	2.30	2.60	2.53	3.30
$Fe^{III}(4,7\text{-}Me_2phen)_3$	−1.02, −0.50	0.73	0.50	1.02	1.06	0.24
$Fe^{III}(bpy)_3$	−0.65	0.54				
		Estimated Limits for the Rate Constant for Conformational Change R → P				
log k_{RP} (s^{-1})	1.7[b]	≤ -0.5	≥ 2.3	≥ 2.2	≥ 2.2	≥ 2.2 (?)

[a] Reference 10. [b] Based on both cross-reaction and electrochemical studies in aqueous solution: (a) Reference 4. (b) Robandt, P. V.; Schroeder, R. R.; Rorabacher, D. B. *Inorg. Chem.* **1993**, *32*, 3957−3963.

The current results obtained in acetonitrile for the $Cu^{II/I}(L3)$ system (i.e., the *trans*-cyhx derivative) yield $k_{11(Red)}$ and $k_{11(Ox)}$ values which are similarly about 2- to 5-fold smaller than the values previously obtained in aqueous solution: log $k_{11(Red)} = 3.2$ and limiting log $k_{11(Ox)} \approx 1.0$.[1] Corrections for the solvent dielectric would again bring these values into reasonably close alignment. This observation adds additional veracity to our contention that, to a first approximation, the electron-transfer kinetic data for these $Cu^{II/I}L$ systems may be considered comparable in water and in acetonitrile—that is, specific solvation effects are not a significant factor for this class of Cu(II/I) complexes in these two solvents.

Only five additional Cu(II/I) electron-transfer studies have been reported previously in acetonitrile. Doine, Yano, and Swaddle[18] obtained a value of log $k_{11} = 3.7$ for the $Cu^{II/I}L_2$ complex formed with 2,9-dimethyl-1,10-phenanthroline as determined from NMR line-broadening measurements. A similar value was obtained by Swaddle and co-workers for the bis complex formed by copper(II)/I) with a substituted, conjugated dipyrrole ligand which is thought to be tetrahedral in both oxidation states.[19] Stanbury, Wilson, and co-workers[20−22] have studied three $Cu^{II/I}L$ systems involving acyclic ligands containing five unsaturated nitrogen donor atoms and obtained log k_{11} values in the range of 3.2−4.5, using both line-broadening and cross-reaction studies. All five of these previous values are equivalent to, or exceed, the range of k_{11} values we have found for the systems included in the current study. Although Stanbury and Wilson's systems appear to remain five-coordinate in both oxidation states, they have found some evidence for conformational change in at least one of their Cu^IL complexes.[23] The fact that all five studies cited above showed no evidence for a square scheme mechanism does not rule out the existence of such a scheme since these workers did not alter the driving force conditions by a significant amount.

General Mechanistic Behavior. For each specific $Cu^{II}L$ system, the self-exchange rate constants obtained with the three different reducing agents ($k_{11(Red)}$) are found to be consistent within the presumed limits of experimental error (Table 4). For all Cu^IL complexes except $Cu^I(L1)$, the *slowest* oxidation reactions yield calculated $k_{11(Ox)}$ values which are also in agreement with the values obtained for the corresponding $Cu^{II}L$ reductions. However, as the driving force of the Cu^IL oxidation reactions increases, the calculated $k_{11(Ox)}$ values are observed to decrease by 1.5 to 3 orders of magnitude, depending upon the specific system involved. This pattern of behavior is consistent with the dual-pathway mechanism shown in Figure 1 where the intermediate P is more stable (or less unstable) than intermediate Q. Thus, the $k_{11(Red)}$ values and the larger $k_{11(Ox)}$ values are presumed to be representative of pathway A, designated as $k_{11(A)}$, while the smaller $k_{11(Ox)}$ values represent the characteristic self-exchange rate constant for pathway B, $k_{11(B)}$.

The phenyl groups in L1, L5, and L6 might be expected to exhibit a significant negative inductive effect upon the proximal sulfur donor atoms as indicated by the much smaller $Cu^{II}L$

---

(18) Doine, H.; Yano, Y.; Swaddle, T. W. *Inorg. Chem.* **1989**, *28*, 2319−2322.

(19) Metelski, P. D.; Hinman, A. S.; Takagi, H. D.; Swaddle, T. W. *Can. J. Chem.* **1995**, *73*, 61−69.

(20) Goodwin, J. A.; Stanbury, D. M.; Wilson, L. J.; Eigenbrot, C. W.; Scheidt, W. R. *J. Am. Chem. Soc.* **1987**, *109*, 2979−2991.

(21) Goodwin, J. A.; Wilson, L. J.; Stanbury, D. M.; Scott, R. A. *Inorg. Chem.* **1989**, *28*, 42−50.

(22) Coggin, D. K.; Gonzalez, J. A.; Kook, A. M.; Bergman, C.; Brennan, T. D.; Scheidt, W. R.; Stanbury, D. M.; Wilson, L. J. *Inorg. Chem.* **1991**, *30*, 1125−1134.

(23) Coggin, D. K.; Gonzalez, J. A.; Kook, A. M.; Stanbury, D. M.; Wilson, L. J. *Inorg. Chem.* **1991**, *30*, 1115−1125.

stability constants previously determined for these complexes (Table 1). Yet all three of these systems exhibit $k_{11(A)}$ and $k_{11(B)}$ values which are nearly identical to those obtained for the L3 system, in which no phenyl group is present. The slight increase in the $k_{11(A)}$ value for the L11 system is reminiscent of the similar increase noted in our earlier aqueous system for the L2 system (i.e., the *cis*-cyclohexanediyl derivative).

On the basis of the lack of a discernible trend in the self-exchange rate constants as a function of the specific substituents involved, we conclude that the phenyl ring does not unduly influence any specific facet of the electron-transfer kinetics. The significant variation in electron-transfer kinetic parameters as noted for the cyclohexanediyl-substituted ligands L2, L3, and L11 suggest that the various ring substituents result in subtle differences in the ligand flexibility which do not follow an easily discernible trend.

Kinetics for Conformational Change. Since the $k_{11(A)}$ and $k_{11(B)}$ values do not differ by large orders of magnitude, the region in which conformational *gating* occurs should be reasonably narrow. This is presumed to account for the fact that, for the several systems included in this work, we were unable to obtain convincing evidence of limiting first-order kinetics as has been previously demonstrated for $\mathrm{Cu^{II/I}}$([14]aneS$_4$)[4] and its diol[6] and monocyclohexanediyl[1] derivatives in aqueous solution. In the absence of gated behavior, it is not possible to obtain quantitative values for the rate constant characteristic of the R → P conformational change, k_{RP} (see Figure 1). However, limiting estimates can be established.

The kinetic expression for the oxidation of a $\mathrm{Cu^IL}$ species conforming to the mechanism in Figure 1 has been developed previously:[6]

$$k_{21} = \frac{k_{2A}k_{RP}}{k_{2A}[\mathrm{A_{Ox}}] + k_{PR}} + k_{2B} \qquad (2)$$

Here the first term on the right represents reaction via pathway A and the k_{2B} term represents reaction via pathway B. For oxidation reactions in which both pathway B and the gated limit of pathway A are contributing to the observed kinetics, eq 2 can be written in the limiting form:[6]

$$k_{21} = \frac{k_{RP}}{[\mathrm{A_{Ox}}]} + k_{2B} \qquad (3)$$

Here k_{RP} represents the (gated) first-order rate constant for conformational change (see Figure 1). In the case of the $\mathrm{Cu^I}$(L1) oxidation with $\mathrm{Ni^{III}}$([14]aneN$_4$), the reaction appears to proceed entirely by pathway B with no evidence of a first-order "gated" contribution. This implies that $k_{21} \approx k_{2B}$, i.e., that $k_{2B} >> k_{RP}/[\mathrm{A_{Ox}}]$ or $k_{RP} << k_{2B}[\mathrm{A_{Ox}}]$. Multiplying the observed k_{21} value (3.4×10^3 M^{-1} s^{-1}; see Table 3) by the smallest Ni(III) concentration utilized in these studies (8.4×10^{-5} M) yields a maximum limiting value of $k_{RP} < 0.3$ s^{-1} (or log $k_{RP} < -0.5$; see Table 4).

For the other four $\mathrm{Cu^IL}$ complexes included in the current study, the cross-reaction data with $\mathrm{Ni^{III}}$([14]aneN$_4$) indicate that the reaction is proceeding entirely by pathway A. For systems in which k_{2B} is insignificant, we can apply the other limiting form of eq 2:[6]

$$\frac{1}{k_{21}} = \frac{[A_{\mathrm{Ox}}]}{k_{RP}} + \frac{K_{PR}}{k_{2A}} \qquad (4)$$

In this latter expression, the reciprocal of the first term on the right represents the gated first-order contribution while the second term represents the reciprocal value of k_{21} for pathway A in the absence of gating. For the systems involving L3, L5, L6, and L11, no evidence of gating was noted with the Ni(III) reagent. On the basis of this observation, we conclude that $K_{PR}/k_{2A} >> [\mathrm{A_{Ox}}]/k_{RP} << 1/k_{21}$ or $k_{RP} << k_{21}[\mathrm{A_{Ox}}]$. For both the $\mathrm{Cu^I}$(L5) and $\mathrm{Cu^I}$(L6) systems, a maximum Ni(III) concentration of 1.6×10^{-3} M was utilized in the kinetic studies which results in minimum k_{RP} estimates of about 150 s^{-1}. Although the oxidations of the L3 and L11 systems with the Ni(III) reagent were limited to lower reagent concentrations (due to the faster reactions involved),[16] similar minimum k_{RP} values are estimated.

As tabulated in the bottom row of Table 4, the limiting k_{RP} value for the $\mathrm{Cu^I}$(L1) species appears to be at least 500 times smaller than the values for the other four systems included in the current study. This implies that the presence of a single benzene ring severely retards the conformational change which is presumed to precede electron-transfer during oxidation.[7]

It is tempting to attribute this large effect on k_{RP} to the rigidity imposed upon the ligand by the unsaturated ring—the demonstration of which was the major motivation for the current study. However, it might then be expected that both the L5 and L6 systems, which incorporate both phenyl and cyclohexanediyl substituents into the macrocycle, would also exhibit slow conformational change. As noted by the data in the last row of Table 4, however, such is not the case. Our best current conjecture to explain this phenomenon is that, in these latter two systems, the effect of the rigidity of the benzene ring is compensated by the additional strain of the cyclohexane ring so that the ground state is raised in energy relative to the transition state encountered during the conformational conversion, thereby decreasing the energy barrier for R → P.

Acknowledgment. This work was supported by the National Science Foundation under Grant CHE-9218391. The authors wish to express their thanks to Dr. Cynthia Salhi for synthesizing some of the counter reagents utilized in this work.

IC960793J