Inorg. Chem. **2007**, *46*, 1451–1458

Inorganic Chemistry

Article

Oxidation of Ferrocenes by Copper(II) in Aqueous Acetonitrile: Nitrate and Chloride Ion Effects

Japhet Irangu and Robert B. Jordan*

Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada T6G 2G2

Received September 27, 2006

The effect of nitrate and chloride ion on the rate of oxidation of ferrocene (Fc) and 1,1′-dimethylferrocene (DmFc) by Cu(II) has been studied in 95% and 80% acetonitrile/water solutions. The complex formation constants for Cu(II) with the same anions in the same media have been determined by spectrophotometry. Nitrate ion mildly inhibits the reaction, while chloride ion substantially increases the rate. The results have been analyzed in terms of the Marcus theory, and it is concluded that complexation increases the rate of self-exchange between the $\mathrm{Cu^{II}(X)}_n$ and $\mathrm{Cu^{I}(X)}_n$ species. In the case of nitrate, the latter effect is compensated for by a less favorable overall equilibrium constant, which results in mild inhibition.

Introduction

In a previous kinetic study,[1] the oxidation of ferrocene (Fc) and 1,1′-dimethylferrocene (DmFc) by copper(II) trifluoromethanesulfonate and perchlorate in varying compositions of aqueous acetonitrile (AN) was used to estimate the Cu(I/II) self-exchange rate constant. Recently, Fukuzumi and co-workers[2] have used a similar approach to estimate the self-exchange rates of several complexes of Cu(I/II) to optimize the performance of a dye-sensitized solar cell. As part of the earlier study, it was noted that copper(II) nitrate gave consistently slower rates than the other two salts. The present study is a more systematic examination of the effect of the nitrate ion on the kinetics in 80% and 95% AN, along with a parallel study of the effect of the chloride ion. In a generic form, the overall reaction is represented by eq 1.

$$\mathrm{Cu^{II}} + \mathrm{Fe(C_5H_4R)_2} \xrightarrow[\mathrm{An/H_2O}]{\mathrm{X^-}} \mathrm{Cu^{I}} + \mathrm{Fe(C_5H_4R)_2}^{+} \qquad (1)$$

Somewhat surprisingly, the two ions have opposite kinetic effects. The results have been analyzed to assess the effects on the rate of changes in $\Delta G°$ and the self-exchange rates of the $\mathrm{Cu^{I/II}(X)}_n$ systems. To speciate the Cu(II) and to calculate specific rate constants, a study of the complexation of Cu(II) by these two anions also is reported here.

There have been a number of studies of counterion effects on electron-transfer reactions. Numerous examples may be found in the review by Wherland[3] on nonaqueous systems and in the more recent comprehensive review by Swaddle.[4] The reaction studied here is related through the reductant and nonaqueous solvent to earlier work by Wherland and co-workers[5] on the following reaction:

$$\mathrm{Co^{III}(dmg)_3(BF_2)_2}^{+} + \mathrm{FeCp_2} \xrightarrow{\mathrm{X^-}} \mathrm{Co^{II}(dmg)_3(BF_2)_2} + \mathrm{FeCp_2}^{+} \qquad (2)$$

The kinetics were studied in solvents such as dichloromethane, acetone, and AN and with various anions, including nitrate and chloride. In all cases, the rate decreases with increasing anion concentration down to a limiting value and the effect was attributed to ion pairing with the cationic oxidant. However, the oxidant in the present study is substitutionally labile and may form inner-sphere complexes. From this perspective, this study is more related to that of Przystas and Sutin[6] on the reduction of several $\mathrm{Co^{III}(N)_6}^{3+}$ complexes by the labile reductants Cr(II) and V(II) in water with added $\mathrm{Cl^-}$ and $\mathrm{SCN^-}$. Catalysis by these ions was interpreted on the basis of the assumption that the reductant forms inner-sphere complexes with the added anions. However, it was later suggested by Lewis and co-workers,[7] based on the complexation study of Wrona,[8] that the dominant

---

* To whom correspondence should be addressed. E-mail: bob.jordan@ualberta.ca.

(1) Irangu, J.; Ferguson, M. J.; Jordan, R. B. *Inorg. Chem.* **2005**, *44*, 1619.

(2) Hattori, S.; Wada, Y.; Yanagida, S.; Fukuzumi, S. *J. Am. Chem. Soc.* **2005**, *127*, 9648.

(3) Wherland, S. *Coord. Chem. Rev.* **1993**, *123*, 169.

(4) Swaddle, T. W. *Chem. Rev.* **2005**, *105*, 2573.

(5) Pfeiffer, J.; Kirchner K.; Wherland, S. *Inorg. Chim. Acta* **2001**, *313*, 37 and references cited therein.

(6) Przystas, T. J.; Sutin, N. *J. Am. Chem. Soc.* **1973**, *95*, 5545.

(7) Lewis, N. A.; Purcell, W. L.; Taveras, D. V. *Inorg. Chem.* **1989**, *28*, 133. Lewis, N. A.; Ray, A. M. *Inorg. Chem.* **1984**, *23*, 3649.

10.1021/ic0618551 CCC: $37.00

equilibrium is ion-pair formation with the oxidant rather than substitution on Cr(II). It should be noted that the perchlorate ion, which is often present to control the ionic strength in kinetic studies, also forms ion pairs[9] and will attenuate the ion pairing with other anions present.

For reactions between an anion and a cation, the rate is expected to decrease with increasing ionic strength, although the effect may be attenuated by ion pairing. Sánchez and co-workers[10,11] have observed anomalous salt effects for two such systems when the oxidant is an anion; the rate constants increase with increasing ionic strength for the reaction of $Co(C_2O_2)_3^{3-} + Ru(NH_3)_5(pz)^{2+}$ and $Fe(CN)_6^{3-} + Ru(NH_3)_5(pz)^{2+}$ (pz = pyrazine). The authors interpreted this effect as being the result of competing ionic strength effects on ion-pair formation and the electron-transfer rate in the precursor complex.

For reaction (1) studied here, normal ionic strength effects are expected to be minimal because one reactant is neutral. This is consistent with the very modest effects of added salts on the $FeCp_2/FeCp_2^+$ electron-exchange reaction in AN found by Weaver and co-workers,[12] and our earlier study[1] in which no systematic effects of the ionic strength were observed with triflate and perchlorate anions. It also seems safe to assume that any anion effects will involve interactions with Cu^{2+} rather than Fc or DmFc.

Experimental Section

Materials. Acetonitrile (AN; Caledon, Fisher, or BDH), perchloric acid (Fisher), tetraethylammonium chloride (Et_4NCl; Sigma), copper(II) nitrate trihydrate (Allied Chemicals), sodium nitrate (ACP), and 1,1′-dimethylferrocene (DmFc; Alfa Inorganics) were used as received. Ferrocene (Fc; Strem Chemicals) was purified by sublimation. Tetraaquacopper(II) triflate was prepared as described previously.[1]

AN/Water Mixtures and Solutions. AN/water mixtures, given as percent by volume, and stock solutions of Cu(II) (nitrate or triflate) and of the Fc's were prepared as described previously.[1] The concentration of Cu(II) in the stock solutions was determined by iodimetry.[13] The concentrations of the stock solutions typically were $(4.0-5.0) \times 10^{-4}$ M for copper(II) triflate or nitrate and $(4.0-6.0) \times 10^{-3}$ M for Fc and DmFc for the kinetic measurements. The Cu(II) solutions contained either 0.101 or 0.202 mM $HClO_4$.

Complexation Measurements. Absorbance measurements were recorded on a Cary 219 spectrophotometer over the wavelength range 250−400 nm, with samples in either 2.00- or 5.00-cm-path-length cylindrical cells. In the spectral region finally used (250−280 nm), solutions of copper(II) triflate were found to have a molar extinction coefficient of ~2.2 M^{-1} cm^{-1}. Although of minor significance for the Cu(II) concentrations used (0.1−0.4 mM), this was taken into account in the analysis to determine the formation constants. The measurements were done at 22 ± 1 °C.

Essentially the same procedure was used for all of these measurements. A weighed amount of either $NaNO_3$ or Et_4NCl was added to a volumetric flask, and the stock solution of Cu(II) in the appropriate solvent mixture was added to the volume. The electronic spectrum of each solution was recorded, and the absorbance at the wavelength(s) of major change was recorded for each solution. In the spectral region of interest, the only significant chromophore, aside from the Cu(II) complexes, is the nitrate ion. To correct for its absorbance, the molar extinction coefficient (ϵ_X) of NO_3^- was determined from solutions of $NaNO_3$ under the conditions of the other measurements.

Kinetics Measurements. The kinetics were determined with a pseudo-first-order excess of Fc or DmFc except for a few runs with added Cl^- in 95% AN that were done with a pseudo-first-order excess of copper(II) triflate. The measurements were done on a Tritech Dynamic Instruments stopped-flow spectrophotometer at 25 °C as described previously.[1] The reactions were monitored at 616 nm, and the absorbance/time data were analyzed as described previously[1] to obtain the pseudo-first-order rate constants.

Results

The ultimate purpose of this study is to explore the effects of nitrate and chloride ions on the kinetics of reaction (1). To assist in the interpretation of the kinetic results, the extent of the interaction between solvated Cu(II) and these two ions was determined by spectrophotometric measurements. Preliminary observations showed that significant changes occur in the near-ultraviolet region of the spectrum when $NaNO_3$ or Et_4NCl is added to solutions of Cu(II) in 80% or 95% AN in water.

Determination of Complex Formation Constants. The analysis of the data to determine the formation constants followed standard procedures. For the general complexation reaction

$$\mathrm{Cu}^{2+} + n\mathrm{X}^- \underset{\mathrm{AN/H_2O}}{\overset{\beta n}{\rightleftharpoons}} \mathrm{Cu(X)}_n^{\,2-n} \tag{3}$$

the overall formation constant is defined as

$$\beta_n = [\mathrm{Cu(X)}_n]/[\mathrm{Cu}][\mathrm{X}]^n \tag{4}$$

where charges are omitted for generality. The total Cu(II) concentration is given by

$$[\mathrm{Cu}]_t = [\mathrm{Cu}] + [\mathrm{CuX}] + [\mathrm{CuX}_2] + [\mathrm{CuX}_3] + \ldots \tag{5}$$

which, after substitution from eq 4 and rearrangement, gives

$$[\mathrm{Cu}] = [\mathrm{Cu}]_t(1 + \beta_1[\mathrm{X}] + \beta_2[\mathrm{X}]^2 + \beta_3[\mathrm{X}]^3 + \ldots)^{-1} \tag{6}$$

and in general

$$[\mathrm{CuX}_n] = \beta_n[\mathrm{X}]^n[\mathrm{Cu}]_t(1 + \beta_1[\mathrm{X}] + \beta_2[\mathrm{X}]^2 + \beta_3[\mathrm{X}]^3 + \ldots)^{-1} \tag{7}$$

The total X concentration is given by

$$[\mathrm{X}]_t = [\mathrm{X}] + [\mathrm{CuX}] + 2[\mathrm{CuX}_2] + 3[\mathrm{CuX}_3] + \ldots \tag{8}$$

and substitution from eqs 6 and 7 gives

---

(8) Wrona, P. K. *Inorg. Chem.* **1984**, *23*, 1558.

(9) Yokoyama, H.; Kon, H. *J. Phys. Chem.* **1991**, *95*, 8956. Karmanova, E. G.; Pyartman, A. K.; Belousov, E. A. *Russ. J. Inorg. Chem. (Engl. Transl.)* **1987**, *32*, 1584.

(10) Muriel, F.; De La Vega, R.; Sánchez, F.; Jiminéz, R.; Prado-Gotor, R.; Pérez, F.; Pérez-Tejeda, P. *Int. J. Chem. Kinet.* **2005**, *37*, 81.

(11) Garcia-Fernandez, E.; Prado-Gotor, R.; Sánchez, F. *J. Phys. Chem. B* **2005**, *109*, 15087.

(12) Nielson, R. M.; McManis, G. E.; Safford, L. K.; Weaver, M. J. *J. Phys. Chem.* **1989**, *93*, 2152.

(13) Kolthoff, I. M.; Sandell, E. B.; Meehan, E. J.; Bruckenstein, S. *Quantitative Chemical Analysis*; Collier-MacMillan Canada Ltd.: Toronto, Ontario, Canada, 1969.

$$[X]_t = [X] + \frac{(\beta_1[X] + 2\beta_2[X]^2 + 3\beta_3[X]^3 + ...)[Cu]_t}{1 + \beta_1[X] + \beta_2[X]^2 + \beta_3[X]^3 + ...} \quad (9)$$

This expression can be rearranged to give a polynomial in [X] in terms of $[X]_t$, $[Cu]_t$, and β_n values. The polynomial will be second-, third-, or fourth-order, depending on whether the highest complex in the model is CuX, CuX_2, or CuX_3, respectively. Substitution of the value of [X] into eqs 6 and 7 gives values for [Cu] and $[CuX_n]$. The absorbance, as given by eq 10 where l is the path length of the cell, can be expressed in terms of known concentrations $[X]_t$ and $[Cu]_t$ and extinction coefficients ϵ_X and ϵ_0.

$$I_{obs} = \epsilon_X l[X] + \epsilon_0 l[Cu] + \epsilon_1 l[CuX] + \epsilon_2 l[CuX_2] + ... \quad (10)$$

Then the variation of I_{obs} with $[X]_t$ was fitted by least squares to determine the values of β_n and the other ϵ values. The experimental data for each system are tabulated in the Supporting Information, along with calculated values of I_{obs} obtained from the fitting. For the purpose of presenting the data, it is convenient to define a molar extinction coefficient for all $[Cu]_t$ values, ϵ_{Cu}, as

$$\epsilon_{Cu} = \frac{I_{obs} - \epsilon_X l[X]}{l[Cu]_t} = \frac{\epsilon_0 + \epsilon_1\beta_1[X] + \epsilon_2\beta_2[X]^2 + \epsilon_3\beta_3[X]^3 + ...}{1 + \beta_1[X] + \beta_2[X]^2 + \beta_3[X]^3 + ...} \quad (11)$$

Nitrate Ion Complexation. Under the conditions of the observations, the nitrate ion is a significant chromophore. In 95% AN at 280 nm, the values of ϵ_X (M^{-1} cm^{-1}) are 2.18 (0.101 mM $HClO_4$) and 2.28 (0.202 mM $HClO_4$); in 80% AN and 0.202 mM $HClO_4$, ϵ_X is 1.49 (270 nm) and 2.79 (280 nm). The system has been studied in 95% and 80% AN in a 5.00-cm-path-length cell. The variation of ϵ_{Cu} with $[NO_3^-]$ is shown in Figure 1. In 95% AN, the observations require the formation of $Cu(NO_3)^+$ and $Cu(NO_3)_2$ and show that the β values are insensitive to low concentrations of $HClO_4$. In 80% AN, complexation is substantially weaker, as can be seen from the shallower curves in Figure 1. The absorbance changes due to complexation also are much smaller, and two wavelengths and two different $[Cu]_t$ conditions have been used and combined in the least-squares fitting to obtain β_1. Only the formation of $Cu(NO_3)^+$ is required to fit the data in 80% AN. $[NO_3^-]_t$ and observed and calculated absorbances are tabulated in the Supporting Information. The β and ϵ values for both solvent compositions are summarized in Table 1 and were used to generate the calculated curves in Figure 1.

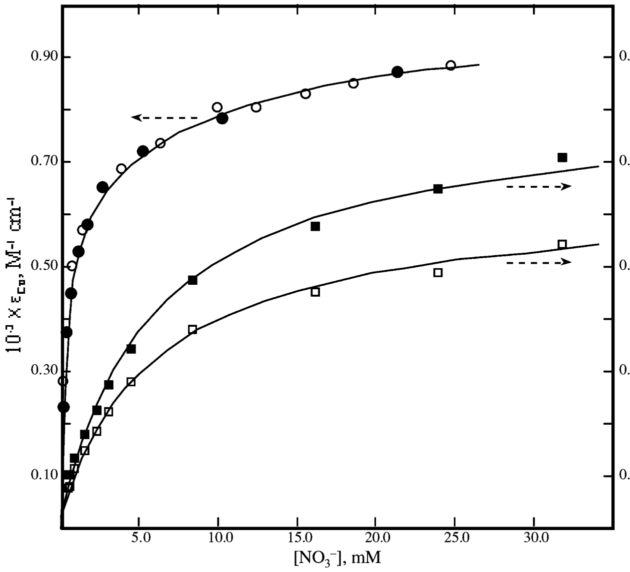


Figure 1. Dependence of ϵ_{Cu} on $[NO_3^-]$ for 95% AN with 0.101 mM $HClO_4$ (○) and 0.202 mM $HClO_4$ (●) and 80% AN with 0.101 mM $HClO_4$ at 270 nm (□) and 280 nm (■).

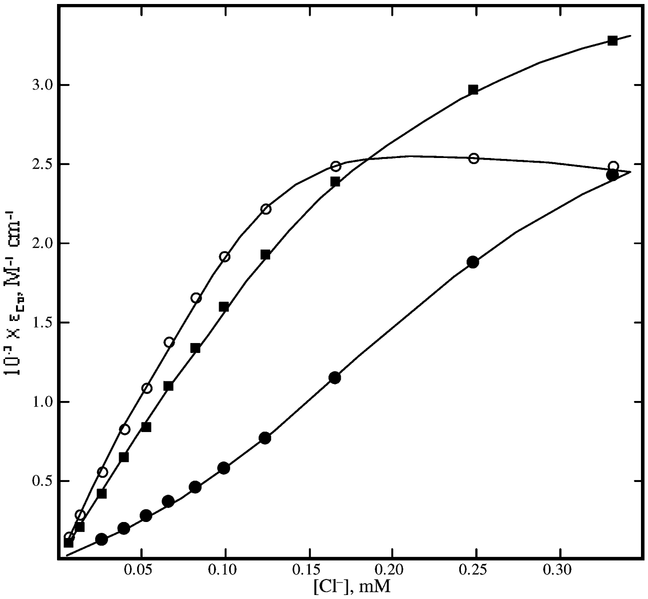


Figure 2. Dependence of ϵ_{Cu} on $[Cl^-]$ in 95% AN with 0.202 mM $HClO_4$ at 260 nm (○), 280 nm (■), and 300 nm (●).

Chloride Ion Complexation. Because chloride ion is not a chromophore, $\epsilon_X = 0$ in eq 11. Otherwise, the observations and treatment of data are analogous to those for the nitrate systems, except that a 2.00-cm-path-length cell was used because the ϵ values were larger, and it was possible to go to much higher concentrations of Cl^- in 80% AN because the anion had no absorbance. The observations in 95% and 80% AN are consistent with the formation of $Cu(Cl)^+$ and $Cu(Cl)_2$ complexes. The variation of ϵ_{Cu} with $[Cl^-]$ is shown in Figures 2 and 3, and the ϵ and β values are summarized in Table 2. The full data sets are tabulated in the Supporting Information.

There was one complication in 80% AN in that the kinetic results described below seem to require the formation of a tris complex, $Cu(Cl)_3^-$, although this was not required by the absorbance measurements. When $Cu(Cl)_3^-$ was included in the model, the overall fit was somewhat improved, but the value of β_3 was not defined, as indicated by its error limit in Table 2.

Kinetic Results. The rates of reaction (1) for both Fc and DmFc have been studied under pseudo-first-order conditions with [Fc] or [DmFc] $\gg$ $[Cu(II)]_t$. These conditions are opposite to those used previously[1] and open the possibility for autoxidation of Fc, catalyzed by Cu(II), as described by

Table 1. Summary of Complex Formation Constants (β) and Molar Extinction Coefficients (ϵ) for Complexation of Cu(II) by Nitrate Ion in Aqueous AN[a]

solvent % AN	β_1, M^{-1}	β_2, M^{-2}	ϵ_1, M^{-1} cm^{-1}	ϵ_2, M^{-1} cm^{-1}
95[b]	$(3.9 \pm 0.5) \times 10^3$	$(3.7 \pm 1.7) \times 10^5$	616 ± 32	993 ± 38
80[c]	$(1.66 \pm 0.07) \times 10^2$		63 ± 1[d] (81 ± 1.3)[e]	

[a] Determined at 22 ± 1 °C for total [NO_3^-] in the range of 0.2−30 mM. [b] Determined at 280 nm. [c] Determined from combined observations at 280 and 270 nm. [d] At 280 nm. [e] Value at 270 nm.

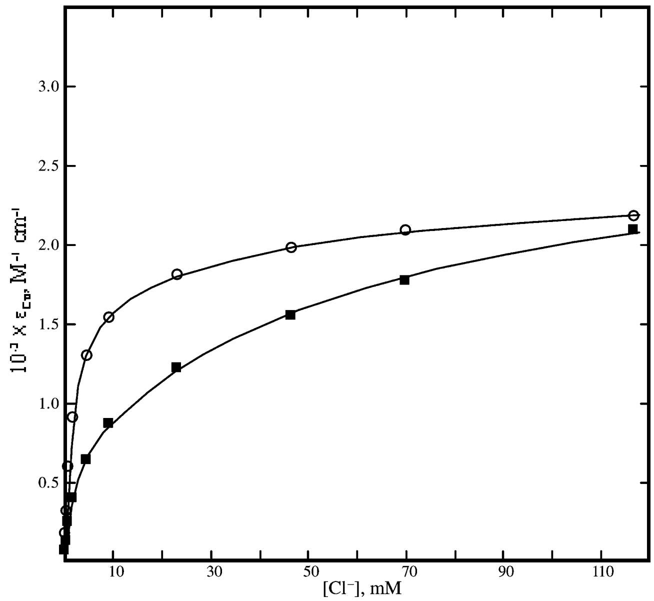


Figure 3. Dependence of ϵ_{Cu} on [Cl$^-$] in 80% AN with 0.202 mM $HClO_4$ at 254 nm (○) and 280 nm (■).

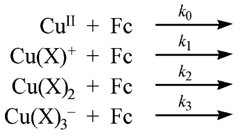
eq 12. Analogous chemistry has been reported by Fukuzumi

$$Cu^{II} + Fc \rightarrow Cu^{I} + Fc^{+}$$
$$2Cu^{I} + O_2 + 2H^{+} \rightarrow 2Cu^{II} + H_2O_2 \quad (12)$$

et al.[14] in benzonitrile with Co(III) complexes as oxidants. To assess the time scale of reaction (12), a solution containing 3.03 mM Fc and 1.01 mM copper(II) triflate in 95% AN was shaken in air and transferred to a 5.00-cm-path-length spectrophotometer cell. The spectrum from 500 to 700 nm remained invariant for 24 min, and the absorbance of 0.248 at 616 nm was in excellent agreement with the expected value of 0.250 if only 1.01 mM Fc^+ was produced. It was concluded that reaction (12) was slow enough so that the stopped-flow kinetic study could be done safely under aerobic conditions.

For the reaction in the presence of anions, the expected reaction pathways are outlined for Fc in Scheme 1, and the analogous pathways are expected for DmFc.

Scheme 1



For such a system, the rate is given by eq 13. After

$$-\frac{d[Cu^{II}]}{dt} = \frac{d[Fc^+]}{dt} = \{k_0[Cu^{II}] + k_1[Cu(X)^+] + k_2[Cu(X)_2] + k_3[Cu(X)_3^-]\}[Fc] \quad (13)$$

substitution for the concentrations of the various Cu(II) species in terms of [X] and β_n, one obtains

$$-\frac{d[Cu^{II}]}{dt} = \frac{d[Fc^+]}{dt} = \frac{k_0 + k_1\beta_1[X] + k_2\beta_2[X]^2 + k_3\beta_3[X]^3}{1 + \beta_1[X] + \beta_2[X]^2 + \beta_3[X]^3}[Cu^{II}][Fc] = k_{obs}[Cu^{II}] \quad (14)$$

where k_{obs} is the pseudo-first-order rate constant for constant [X] and [Fc] ≫ [Cu^{II}]. Then the second-order rate constant is given by

$$k_{2obs} = \frac{k_{obs}}{[Fc]} = \frac{k_0 + k_1\beta_1[X] + k_2\beta_2[X]^2 + k_3\beta_3[X]^3}{1 + \beta_1[X] + \beta_2[X]^2 + \beta_3[X]^3} \quad (15)$$

For the conditions of [Cu^{II}] ≫ [Fc], analogous relationships apply and $k_{2obs} = k_{obs}/[Cu^{II}]$. For consistency in fitting data for systems in which k_0 does not make a significant contribution, k_0 has been held constant for all of the fittings at average values from the earlier study.[1]

When Cu(II) is the deficient reagent, the range of concentrations is somewhat limited by the need to have enough Cu(II) to give a useable absorbance change while having [X] ≫ $[Cu^{II}]_t$ so that [X] does not increase as Cu^{II}-$(X)_n$ is consumed. In fact, the usual >10-fold excess of X was not always maintained, but because X is not consumed in the reaction, the usual pseudo-first-order constraint can be relaxed somewhat. Model calculations for these conditions indicate that [X] changes by <10% for the conditions reported. When Fc or DmFc is the deficient reagent, the variation of [X] during the reaction is not a problem unless $[Cu^{II}]_t \approx [X]_t$ and X is strongly complexed by Cu(I).

The kinetic results with added nitrate ion in 95% AN and [Fc] or [DmFc] ≫ $[Cu^{II}]_t$ are shown in Figure 4. For $[Cu^{II}]_t \approx 0.25$ mM, $[NO_3^-]_t$ must be >1 mM to maintain a constant anion concentration during the kinetic run. The rate constants from least-squares fits to eq 15 are summarized in Table 3 and produce the calculated curves in Figure 4.

For the results in 80% AN with $[Cu^{II}]_t$ ≫ [Fc], it is known[15] that Cu(I) is not significantly complexed by NO_3^- so that it is possible to work with $[Cu^{II}]_t \approx [NO_3^-]_t$. This system shows essentially no systematic change in k_{2obs} with

---

(14) Fukuzumi, S.; Okamoto, K.; Gros, C. P.; Guillard, R. *J. Am. Chem. Soc.* **2004**, *126*, 10441.

(15) Senne, J. K.; Kratochvil, B. *Anal. Chem.* **1971**, *43*, 79.

Table 2. Summary of the Results for Complexation of Cu(II) by Chloride Ion in Aqueous AN[a]

		$10^3\epsilon$, M^{-1} cm^{-1}					
solvent % AN	λ, nm	ϵ_1	ϵ_2	ϵ_3	β_1, M^{-1}	β_2, M^{-2}	β_3, M^{-3}
95[b]	260	2.91 ± 0.04	2.19 ± 0.07				
	280	2.28 ± 0.03	4.02 ± 0.2		$(3.6 \pm 0.8) \times 10^5$	$(4.5 \pm 2) \times 10^9$	
	300	0.674 ± 0.02	3.62 ± 0.3				
80[c]	254[d]	1.67 ± 0.03	2.50 ± 0.04		$(6.8 \pm 0.4) \times 10^2$	$(1.0 \pm 0.1) \times 10^4$	
	280[d]	0.708 ± 0.03	2.87 ± 0.09				
	254[e]	1.30 ± 0.1	2.03 ± 0.1	2.65 ± 0.1	$(1.0 \pm 0.2) \times 10^3$	$(8.9 \pm 5) \times 10^4$	$(4.0 \pm 4) \times 10^5$
	280[e]	0.496 ± 0.06	1.35 ± 0.2	3.83 ± 0.7			

[a] All solutions contain 0.202 mM $HClO_4$. [b] With $[Cu^{II}]_t = 0.1352$ mM. [c] With $[Cu^{II}]_t = 0.4006$ mM. [d] Values from a combined fitting of both wavelengths and a $Cu(Cl)^+/Cu(Cl)_2$ model. [e] Values from a combined fitting of both wavelengths and a $Cu(Cl)^+/Cu(Cl)_2/Cu(Cl)_3^-$ model.

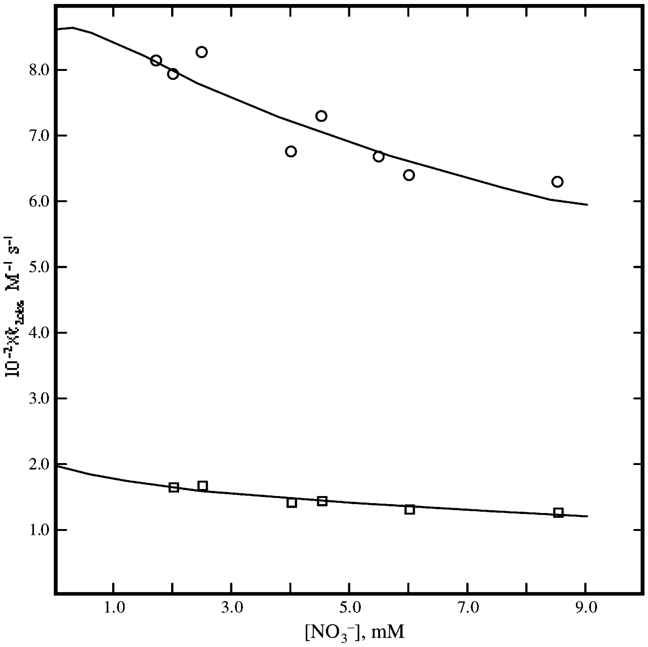


Figure 4. Dependence of k_{2obs} on $[NO_3^-]$ in 95% AN for Fc (□) and DmFc (○).

$[NO_3^-]$ between 5.05 and 30.0 mM. The average of seven values is 5.56 ± 0.3 M^{-1} s^{-1}, which indicates that k_0 and k_1 are essentially equal. A similar behavior is observed for DmFc, and the average of eight values of k_{2obs} is 28.3 ± 2.8 M^{-1} s^{-1}. Notwithstanding the limited variation in k_{2obs}, for consistency, least-squares values of k_1 also are given in Table 3. The full data sets are given in the Supporting Information.

The reaction of Fc with Cu(II) in the presence of chloride ion was studied in 95% AN with 2.5 mM $[Cu^{II}]_t$ and 0.24 mM Fc. Although Cu(I) is known to complex with Cl^-, the value of β_1 in 100% AN[15−17] is 5−10 times smaller than the value obtained here for Cu(II) in 95% AN. Because β_1 for CuCl decreases ~50-fold between pure AN and water,[18] it seems reasonable that it will also be at least 5−10 times smaller than β_1 for $CuCl^+$ in 95% AN. As a consequence of this, plus the much larger concentration of Cu(II), Cu(I) does not compete effectively at the low $[Cl^-]_t$ values, where it might cause the chloride ion available to Cu(II) to vary during the reaction. The results are shown in Figure 5, where it can be seen that k_{2obs} increases substantially as $[Cl^-]_t$ increases. The kinetic parameters are summarized in Table 4, and the full data set is given in the Supporting Information.

In 80% AN, the reactions of Fc and DmFc with Cu(II) have been studied with 0.20 mM $[Cu^{II}]_t$ and 2.5 mM [Fc] or [DmFc]. In this solvent, the competition of Cu(I) for Cl^- is more favorable than that in 95% AN because β_1 and β_2 for Cu(II) have decreased substantially, while β_1 for Cu(I) probably has not changed greatly, based on the values in water and 100% AN. The similar concentrations of Cu(I) and Cu(II) during the reaction also make Cu(I) more competitive. Model calculations indicate that a minimum concentration of Cl^- of ~2 mM is required to keep $[Cl^-]$ reasonably constant during the reaction. The values of k_{2obs} increase with increasing $[Cl^-]_t$, as shown in Figure 6.

As mentioned above, there is a problem of compatibility between the absorbance and kinetic measurements in 80% AN. The simplest model that fits the absorbances will not account for the steady increase in k_{2obs} for Fc when $[Cl^-]_t >$ ~30 mM. This is shown by the dashed curves in Figure 6, which are calculated on the basis that $CuCl_2$ is the highest complex formed. The problem is that the concentration of $CuCl_2$ is starting to level off at ~30 mM $[Cl^-]_t$ and cannot account for the increase in the rate at higher $[Cl^-]_t$. This higher concentration range was not accessible with DmFc because the rates became too fast to measure, but the effect also is detectable for this system, as shown in Figure 6. The nature of the deviation of the k_{2obs} values from the calculated dashed lines in Figure 6 suggests the presence of a $[Cl^-]^3$-dependent term in the rate law. This could be ascribed to the formation of a minor but highly reactive $CuCl_3^-$ species, in which case k_{2obs} would be given by eq 16. The absorbance

$$k_{2obs} = \frac{k_0 + k_1\beta_1[Cl^-] + k_2\beta_2[Cl^-]^2 + k_3\beta_3[Cl^-]^3}{1 + \beta_1[Cl^-] + \beta_2[Cl^-]^2 + \beta_3[Cl^-]^3} \qquad (16)$$

data do provide a fit to a three-complex model with β_1, β_2, and β_3 values of $(1.0 \pm 0.2) \times 10^3$, $(8.9 \pm 5) \times 10^4$, and $(4.0 \pm 4) \times 10^5$, respectively. It is understandable that β_2 is marginally defined and β_3 is not defined within its error limits because the simpler two-complex model provides an adequate fit of the data. The uncertainty in β_2 and β_3 causes a large uncertainty in the values of k_2 and k_3 because the kinetics primarily determine the $k_n\beta_n$ values in the numerator of eq 16. This uncertainty is not properly reflected in the error limits on these rate constants in Table 3, where the

---

(16) Manahan, S.; Iwamoto, R. T. *Inorg. Chem.* **1965**, *4*, 1409.
(17) Heerman, L. F.; Rechnitz, G. A. *Anal. Chem.* **1972**, *44*, 1655.
(18) Smith, R. M.; Martell, A. E.; Motekaitis, R. *NIST Critically Selected Stability Constants of Metal Complexes Database*, Version 2; NIST: Washington, DC, 1995.

Table 3. Summary of the Kinetic Results for Oxidation of Fc and DmFc by Various Cu(II) Species in Aqueous AN

			rate constant, k_n, M^{-1} s^{-1}			
solvent % AN	reductant	X^-	k_0	k_1	k_2	k_3
95	Fc	NO_3^-	1.92×10^2	$(1.80 \pm 0.07) \times 10^2$	43 ± 15	
95	DmFc	NO_3^-	8.26×10^2	$(8.9 \pm 0.4) \times 10^2$	$(2.3 \pm 0.9) \times 10^2$	
80	Fc	NO_3^-	6.2	5.2 ± 0.2		
80	DmFc	NO_3^-	27	27 ± 1		
95	Fc	Cl^-	1.92×10^2	$(4.6 \pm 0.1) \times 10^3$	$(1.70 \pm 0.04) \times 10^5$	
80	Fc	Cl^-	6.2	$(3.6 \pm 2) \times 10^2$	$(9.0 \pm 11) \times 10^2$	$(1.2 \pm 0.1) \times 10^5$
80	DmFc	Cl^-	27	$(5.9 \pm 0.9) \times 10^2$	$(6.6 \pm 0.5) \times 10^3$	$(3.0 \pm 0.07) \times 10^5$

Table 4. Summary of Stepwise Formation Constants for Cu(II) and Cu(I) with Nitrate and Chloride Ions in AN and Water and Mixtures

solvent	M/anion	K_1, M^{-1}	K_2, M^{-1}	K_3, M^{-1}	ref
H_2O	Cu^{II}/NO_3^-	3.2	0.13		18
80% AN	Cu^{II}/NO_3^-	1.7×10^3			this work
95% AN	Cu^{II}/NO_3^-	3.8×10^3	9.0×10^1		this work
AN	Cu^{I}/NO_3^-	≤ 5			15
H_2O	Cu^{II}/Cl^-	2.36	0.63	0.46	*a*
80% AN	Cu^{II}/Cl^{--}	1.0×10^3	90	(4)	this work
95% AN	Cu^{II}/Cl^-	3.6×10^5	1.2×10^4		this work
AN	Cu^{II}/Cl^-	4.9×10^9	8.9×10^7	8.7×10^4	*b*
AN	Cu^{II}/Cl^-	5.0×10^9	7.9×10^7	1.3×10^7	*c*
H_2O	Cu^{I}/Cl^-	1.3×10^3	2.1×10^2	0.2	18
AN	Cu^{I}/Cl^-	6.3×10^4	6.3×10^5		*d*
AN	Cu^{I}/Cl^-	7.9×10^4	7.9×10^5		*c*
AN	Cu^{I}/Cl^-	2.0×10^4	7.6×10^5		15

[a] Ramette, R. W. *Inorg. Chem.* **1986**, *25*, 2481. [b] Ishiguro, S.-I.; Jeliazkova, B. G.; Ohtaki, H. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 1749. [c] Manahan, S. E.; Iwamoto, R. T. *Inorg. Chem.* **1965**, *4*, 1409. [d] Heerman, L. F.; Rechnitz, G. A. *Anal. Chem.* **1972**, *44*, 1655.

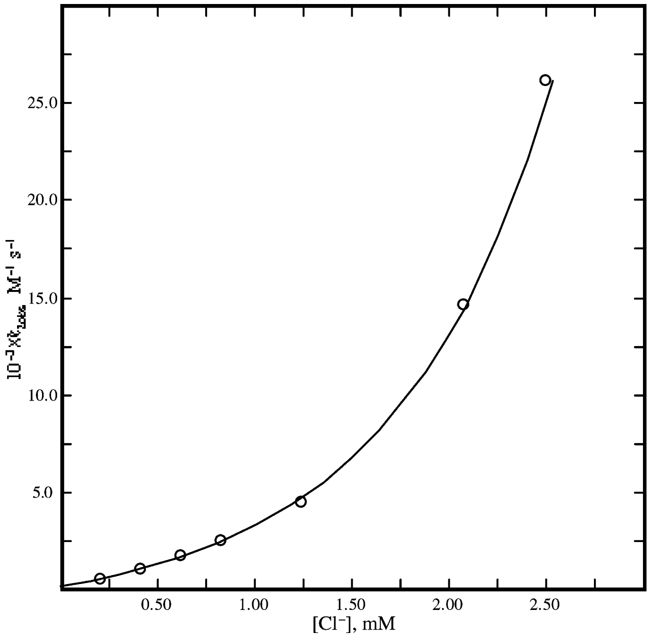


Figure 5. Dependence of k_{2obs} on $[Cl^-]$ in 95% AN for Fc.

limits are more a reflection of the quality of the fit and its sensitivity to the particular *k*. Clearly, the kinetics are dominated by the $k_3\beta_3$ term.

Discussion

It is generally more informative to discuss the formation constants in terms of the stepwise or successive values, $K_1 = \beta_1$ and otherwise $K_n = \beta_n/\beta_{n-1}$. The K_n values typically are in the order $K_1 > K_2 > K_3$, which is attributed to probability, charge, and steric effects, and the successive values normally decrease by a factor of 5−50 because of these effects. Significant deviations from this normal behavior may be attributed to changes in the spin-state or coordination geometry that accompany the complexation reaction. Values of K_n for Cu(II) and Cu(I) from this and previous relevant work are collected in Table 4. All of the results for Cu(II) in a particular solvent appear to follow the normal trends. The Cu^I/Cl^- system in pure AN shows an exception to the normal trend because $K_2 \gg K_1$, as confirmed by three studies. This may indicate a change in the geometry from a basic tetrahedral arrangement in $Cu(AN)_3Cl$ to trigonal in $Cu(AN)(Cl)_2^-$ or linear in $Cu(Cl)_2^-$.

The increase of the K_n values with an increase in the percent of AN seems typical of what one would expect for anion−cation interactions in solvents of decreasing dielectric constant; the values become larger as the percent of AN increases. However, the change between pure water and pure AN is much greater for the Cu^{II}/Cl^- system than for Cu^I/Cl^-. This may be associated with Cu(I) being more strongly solvated by AN than by water, while the opposite is the case for Cu(II). An indication of this comes from the fact that

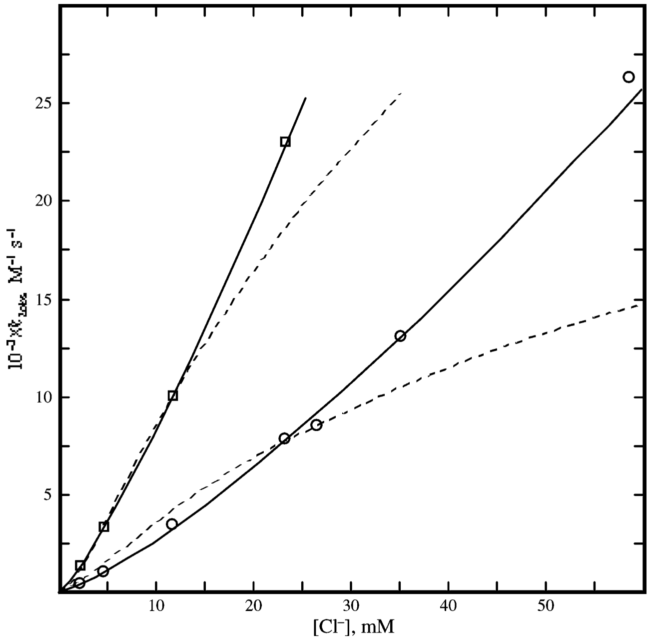


Figure 6. Dependence of k_{2obs} on $[Cl^-]$ in 80% AN for Fc (○) and DmFc (□). Dashed curves are calculated from a model with Cu^{2+}, $CuCl^+$, and $CuCl_2$. Solid curves also include $CuCl_3^-$.

Cu(I) disproportionates in water but is stabilized by the addition of modest amounts of AN.[19]

The kinetics of oxidation of Fc and DmFc by nitrate and chloride complexes of Cu(II) are unusual in that the nitrate system shows very modest changes in rate with increasing nitrate ion concentration, while the chloride ion greatly increases the reaction rate. It is generally believed that Fc's undergo oxidation by an outer-sphere mechanism so that it is appropriate to discuss the results in terms of the Marcus theory for such reactions. In its simplest form, the theory predicts that the rate constant, k_n, for such reactions is given by

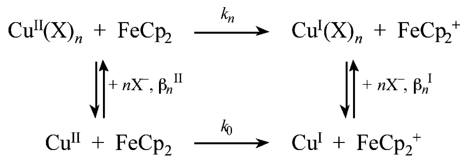
$$k_{\mathrm{n}} = (k_{\mathrm{ex}n} k_{22} K_{\mathrm{rx}n})^{1/2} \tag{17}$$

where $k_{\mathrm{ex}n}$ and k_{22} are the rate constants for electron exchange of the $\mathrm{Cu^{II}(X)}_n/\mathrm{Cu^{I}(X)}_n$ and $\mathrm{Fc^+/Fc}$ or $\mathrm{DmFc^+/DmFc}$ systems, respectively, and $K_{\mathrm{rx}n}$ is the equilibrium constant for the net reaction. This equation predicts that the ratio of the rate constants for oxidation of DmFc and Fc in a given solvent should be the same for all $\mathrm{Cu^{II}(X)}_n$ complexes and that DmFc should be the more reactive because of its more favorable reduction potential. From the previous study with perchlorate and trifluoromethanesulfonate anions,[1] the average ratio k_0(DmFc)/k_0(FC) is 4.4 ± 0.3 from 14 pairs of determinations in 80−97.5% AN. For the systems reported here, the results in Table 3 yield rate constant ratios k_n(DmFc)/k_n(FC) between 1.6 and 7.3, where the minimum and maximum values come from the poorly defined k_1 and k_2 in 80% AN; otherwise, the range is 2.5−5.3. Overall, the results are taken to be consistent with the simplest prediction of the Marcus theory.

Analogous rate constant ratios were used in the previously mentioned study by Przystas and Sutin.[6] They noted that the ratio $k_{\mathrm{NCS}}/k_{\mathrm{Cl}}$ was far from constant for a particular reductant reacting with a series of $\mathrm{Co(N)_6}^{3+}$ oxidants and concluded that variations in K_{rx} did not account for their observations. If one follows the suggestion of Lewis and co-workers[7] that the anion is associated with the oxidant, then $k_{\mathrm{NCS}}/k_{\mathrm{Cl}}$ should be the same for different reductants reacting with the same oxidant, but this also is not the case. It may be noted that ion pairing with a positively charged oxidant would be expected to decrease K_{rx} because of less ion pairing with the reduced product. This would explain the anion inhibition observed for reaction (2). This effect could be overcome if the self-exchange rate for the oxidant was catalyzed by anions. This is known to be the case for $\mathrm{Co^{II/III}(phen)_3}$.[20] In the absence of any kinetic saturation effect, one can deduce little about which reactant carries the anion into the transition state, and the orbital symmetry argument offered by Przystas and Sutin will be valid for either pathway.

It remains to be explained why the reaction is mildly retarded by a nitrate ion but accelerated by a chloride ion. Kinetic salt or ionic strength effects obviously will not provide an explanation for the opposite trends for the two anions and should be minimal because one of the reactants is uncharged. Marcus has discussed the kinetic effect when the counterion moves from the oxidant in the reactants to the oxidized product, but that seems unlikely for this reaction because $\mathrm{Cu^+}$ would appear to be a better Lewis acid than $\mathrm{Fc^+}$ or $\mathrm{DmFc^+}$. The systems may be considered in terms of eq 17 and Scheme 2. It is obvious that, if $\mathrm{X^-}$ complexes more strongly with Cu(I) than Cu(II), then $K_{\mathrm{rx}n}$ will be larger than that for the uncomplexed species. Conversely, if Cu(II) is more strongly complexed, then $K_{\mathrm{rx}n}$ will be smaller. The difference in $K_{\mathrm{rx}n}$ will be reflected in k_n through eq 17. The formation constants in Table 4 indicate that the nitrate ion is more strongly complexed by Cu(II) in AN-rich solutions, but the situation for the chloride ion is equivocal. However, changes in $k_{\mathrm{ex}n}$ also are possible and might reinforce or counteract the effect of K_n. To examine the relative effects of both of these factors, the ratio k_n/k_0 can be derived from eq 17, by noting that $K_{\mathrm{rx}n} = (\beta_n^{\mathrm{I}}/\beta_n^{\mathrm{II}})K_{\mathrm{rx}0}$. Because k_{22} is known to be rather independent of ionic strength changes,[12] the ratio k_n/k_0 from the two expressions based on eq 17 simplifies to

Scheme 2



$$\frac{k_n}{k_0} = \left(\frac{k_{\mathrm{ex}n}}{k_{\mathrm{ex}0}}\frac{\beta_n^{\mathrm{I}}}{\beta_n^{\mathrm{II}}}\right)^{1/2} \tag{18}$$

To estimate the effect of the anions on the self-exchange rate constants, the above expression can be rearranged to obtain

$$\frac{k_{\mathrm{ex}n}}{k_{\mathrm{ex}0}} = \frac{\beta_n{}^{\mathrm{II}}}{\beta_n{}^{\mathrm{I}}}\left(\frac{k_n}{k_0}\right)^2 \tag{19}$$

The k_n and β_n^{II} values are available from this study, but it is necessary to estimate β_n^{I} in order to complete the evaluation of $k_{\mathrm{ex}n}/k_{\mathrm{ex}0}$.

As shown in Table 4, only an upper limit of $\beta_1^{\mathrm{I}} \leq 5\ \mathrm{M^{-1}}$ is available for $\mathrm{NO_3}^-$, which gives lower limit estimates for $k_{\mathrm{ex}1}/k_{\mathrm{ex}0}$ of $\geq 7 \times 10^2$ and $\geq 9 \times 10^2$ from the Fc and DmFc systems, respectively. Because these are lower limits, it is clear that the self-exchange is faster in the presence of $\mathrm{NO_3}^-$, but for the net reaction, the effect is compensated for by $\beta_1^{\mathrm{I}}/\beta_1^{\mathrm{II}} \approx 1.3 \times 10^{-3}$ so that $k_1 \approx k_0$.

The data in Table 4 for the $\mathrm{Cu^I/Cl^-}$ system show that $\beta_1^{\mathrm{I}} = K_1^{\mathrm{I}}$ only decreases by a factor of ∼50 between pure AN and water, while K_2^{I} decreases by $\sim 10^3$. With the assumption that the K_n^{I} values are smaller in 95% AN than in pure AN, one can use the values in pure AN to estimate lower limits for $k_{\mathrm{ex}n}/k_{\mathrm{ex}0}$. For values of $K_1^{\mathrm{I}} \approx 6 \times 10^4\ \mathrm{M^{-1}}$ and $K_2^{\mathrm{I}} \approx 6 \times 10^5\ \mathrm{M^{-1}}$, one obtains $k_{\mathrm{ex}1}/k_{\mathrm{ex}0} \geq 3 \times 10^3$ and $k_{\mathrm{ex}2}/k_{\mathrm{ex}0} \geq 9 \times 10^4$ in 95% AN. The values of K_n^{I} used in these calculations give the ratios $\beta_1^{\mathrm{I}}/\beta_1^{\mathrm{II}}$ and $\beta_2^{\mathrm{I}}/\beta_2^{\mathrm{II}}$ as 0.17 and 8.3, respectively, and from eq 18, it can be seen that the

---

(19) Kamau, P.; Jordan, R. B. *Inorg. Chem.* **2001**, *40*, 3879.

(20) Warren, R. M. L.; Lappin, A. G.; Mehta, B. D.; Neumann, H. M. *Inorg. Chem.* **1990**, *29*, 4185.

acceleration due to Cl^- is primarily due to the more favorable k_{exn} for the $Cu^{I/II}(Cl)_n$ systems compared to the solvated $Cu^{I/II}(AN)_n$ system. It should be noted that, if the K_n^I values were smaller, as seems likely, then β_n^I/β_n^{II} would be smaller and the increase in k_{exn} would be an even more dominant factor.

In 80% AN, it is more difficult to estimate realistic limits for k_{exn}/k_{ex0}, in part because k_1 for Fc is poorly defined but also because β_2^I is almost certainly much less than that in pure AN and no β_3^I has been reported. Nevertheless, with the K_1^I value used above, the estimated values of k_{ex1}/k_{ex0} are ≥ 9 and ≥ 56 for Fc and DmFc, respectively. It is clear that β_1^I/β_1^{II} must be >60 because β_1^{II} in 80% AN has fallen to a value less than β_1^I in water and the latter is almost certainly larger in 80% AN. In this case, the values of k_{ex1}/k_{ex0} and β_1^I/β_1^{II} are both contributing to make $k_1/k_0 > 1$.

The overall picture that emerges is that complexation of Cu(II) by a nitrate or chloride ion causes the rate constant for self-exchange (k_{exn}) in the $Cu^{II}(X)_n/Cu^I(X)_n$ system to increase significantly relative to that for the solvated $Cu^{II}(AN)_n/Cu^I(AN)_n$ ions (k_{ex0}). In a previous study in AN/water mixtures,[1] the latter value has been estimated from a more complete version of the Marcus theory as $\sim 5 \times 10^{-9}$ M^{-1} s^{-1} at 25 °C, so that there is considerable scope for increase by complexation. Although the calculated increase in k_{exn} due to complexation makes the net reaction faster, the effect may be overcome by a decrease in K_n, as in the nitrate ion system reported here.

Supporting Information Available: Tables of the dependence of absorbance on the nitrate and chloride ion concentrations in various amounts of AN and of kinetic results. This material is available free of charge via the Internet at http://pubs.acs.org.

IC0618551