

pendence of the observed rate on nucleophile concentration. With good axial ligands such as dialkylamines, the mechanism is a competitive two-path process involving concerted loss of axial ligand, nucleophilic attack at the $-\text{CH}_3$ group, and assistance by metal ion insertion. At least in the activated complex, then, the metal ion is withdrawing electron density from the $\text{N}-\text{CH}_3$ bond and the bonding would include metal ion-nitrogen atom coordination.

Poor axial ligands need not involve a second path in which the nucleophile acts as axial ligand as well as nucleophilic reactant. This is apparently the case when pyridine is employed. Cu^{2+} is apparently a better methyl cleavage promoter in *N*-methylpyridin than Zn^{2+} , since the cleavage using Zn^{2+} in neat pyridine (12.5 M) requires overnight reflux.²

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Registry No. $\text{CuNCH}_3\text{TPP}^+$, 57606-45-8; di-*n*-butylamine, 111-92-2; diethylamine, 109-89-7; pyridine, 110-86-1.

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Reactions of Copper Complexes. I. Reduction of (2,9-Dimethyl-1,10-phenanthroline)copper(II) Complexes by Thiocyanate and Thiourea in Aqueous Perchlorate Media and by Thiourea in Methanol

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The stoichiometry and kinetics of reduction of $\text{dmp}-\text{Cu}^{\text{II}}$ complexes (dmp = 2,9-dimethyl-1,10-phenanthroline) by SCN^- and thiourea in borate-buffered 0.1 M aqueous sodium perchlorate and by thiourea in methanol at 25.0 °C are reported. The major copper(I) product in all systems was shown to be $\text{Cu}(\text{dmp})_2^+$; the measured stoichiometry was consistent with the formation of thiocyanogen and formamidine disulfide, respectively, although these products could not be satisfactorily isolated and characterized. The kinetics of the reactions were followed in a stopped-flow apparatus by monitoring the appearance of $\text{Cu}(\text{dmp})_2^+$ in the wavelength range 315–600 nm. All reactions were first order in $[\text{Cu}^{\text{II}}]$ over the range $(0.5\text{--}5.0) \times 10^{-5}$ M and were not affected by variations of the monitoring wavelength, buffer concentration, or the presence of oxygen. The rate law for the reaction with excess SCN^- over the concentration ranges $[\text{dmp}]_{\text{T}} = (5.4\text{--}18.1) \times 10^{-5}$ M, $[\text{SCN}^-] = (1.0\text{--}11.3) \times 10^{-2}$ M, and $[\text{H}^+] = (0.68\text{--}94) \times 10^{-8}$ M is given by $d \ln [\text{Cu}^{\text{I}}]/dt = [\text{SCN}^-]/(B[\text{H}^+] + C)$, where $B = (1.02 \pm 0.02) \times 10^5$ s and $C = (1.40 \pm 0.03) \times 10^{-2}$ M s at 25.0 °C. Three mechanisms are consistent with the data. The first two involve the steady-state intermediacy of $\text{Cu}(\text{dmp})_2\text{OHSCN}$, which decomposes either to reactants or to primary redox products, while the third mechanism involves the rate-determining reaction of $\text{Cu}(\text{dmp})\text{SCNOH}$ with SCN^- . This third mechanism is analogous to that proposed for reduction by thiourea in buffered 0.1 M sodium perchlorate, the rate law for which is given by $d \ln [\text{Cu}^{\text{I}}]/dt = D[\text{tu}]_{\text{T}}^2/(E[\text{dmp}][\text{H}^+] + F[\text{tu}]_{\text{T}}[\text{H}^+] + [\text{tu}]_{\text{T}})$, where $D = 74.5 \pm 4.4$ M⁻¹ s⁻¹, $E = (2.86 \pm 0.29) \times 10^8$ M⁻¹, and $F = (2.91 \pm 0.29) \times 10^7$ M⁻¹ at 25.0 °C over a similar range of concentration conditions. The rate law for reduction by thiourea in methanol is given by $d \ln [\text{Cu}^{\text{I}}]/dt = G[\text{dmp}][\text{tu}]/([\text{dmp}] + H[\text{tu}] + J[\text{tu}]^2)$, where $G = (5.2 \pm 0.6) \times 10^3$ M⁻¹ s⁻¹, $H = (6 \pm 2) \times 10^{-2}$, and $J = 1.9 \pm 0.2$ M⁻¹ at 25.0 °C. This rate law is consistent with a mechanism involving rate-determining reaction between $\text{Cu}(\text{dmp})_2^+$ and tu, with the complexes $\text{Cu}(\text{dmp})\text{tu}^{2+}$ and $\text{Cu}(\text{dmp})(\text{tu})_2^{2+}$ oxidatively stable. It is tentatively concluded that the fastest reactions of the $\text{dmp}-\text{Cu}^{\text{II}}$ system are those which involve the production of $\text{Cu}(\text{dmp})_2^+$ as a primary product.

Introduction

Current interest in the reactions of copper complexes reflects the importance of the catalytic properties of copper species in many chemical^{2,3} and biochemical^{4,5} processes. Many of these processes involve one-electron redox cycles of the kind



The widespread operation of such catalytic cycles is often ascribed to the existence of unusual coordination environments of the metal or their facile attainment in the catalytic milieu.³⁻⁶

The mechanistic study of such processes is inevitably complicated by their cyclical nature.³ An approach to this problem is to cut the catalytic cycle by employing ligand systems which effectively deactivate one of the copper oxidation states. One such system involves the ligand 2,9-dimethyl-1,10-phenanthroline (dmp), which forms the thermodynamically stable⁷ and brightly colored⁸ $\text{Cu}(\text{dmp})_2^+$ moiety. Among the effects of this preferential stabilization is an increase in the reduction potential of the $\text{Cu}^{\text{II}}-\text{Cu}^{\text{I}}$ couple.²

In this paper we report on the kinetics and mechanisms of the reduction of $\text{dmp}-\text{Cu}^{\text{II}}$ complexes by thiocyanate and thiourea in aqueous sodium perchlorate at ionic strength 0.1 M. These studies were prompted by implications of the involvement of sulfur-containing ligands in biochemical redox

Table I. Equilibrium Data for Cu^{II} -dmp Complexes at 25.0 °C and Ionic Strength 0.1 M^a

Reaction	Constant
$\text{dmp} + \text{H}^+(\text{aq}) \rightleftharpoons \text{dmpH}^+(\text{aq})$	$7.4 \times 10^5 \text{ M}^{-1}$
$\text{Cu}^{2+}(\text{aq}) + \text{dmp} \rightleftharpoons \text{Cu}(\text{dmp})^{2+}(\text{aq})$	$1.6 \times 10^5 \text{ M}^{-1}$
$\text{Cu}(\text{dmp})^{2+}(\text{aq}) + \text{dmp} \rightleftharpoons \text{Cu}(\text{dmp})_2^{2+}(\text{aq})$	$6.1 \times 10^5 \text{ M}^{-1}$
$\text{Cu}^+(\text{aq}) + 2\text{dmp} \rightleftharpoons \text{Cu}(\text{dmp})_2^+(\text{aq})$	$1.3 \times 10^{19} \text{ M}^{-2}$

^a Data from ref 7.

systems which are catalyzed by copper.^{4,5} The reactions were monitored by observing the formation of $\text{Cu}(\text{dmp})_2^+$ in a stopped-flow apparatus at 25.0 °C in the presence of boric acid-sodium hydroxide buffer over a range of concentration conditions. Pertinent equilibrium constants of the Cu-dmp system are collected in Table I.

The kinetics of reduction of dmp- Cu^{II} complexes by thiourea in anhydrous methanol also is reported. The latter solvent system was chosen for study because the driving force for electron transfer is increased by the preferential stabilization of copper(I) species in solvents of low dielectric constant (ϵ_{MeOH} 32.6, ϵ_{water} 78.5).⁹ In addition, the poorer coordinating ability¹⁰ and much weaker basicity of methanol as compared to water provide means of investigating the effects of such parameters on the mechanism of reduction.

Experimental Section

Reagents. Triply distilled water was used throughout this work. Stock solutions of copper(II) were prepared from crystals of the perchlorate hexahydrate and were standardized by titration with EDTA (Fast Sulphon Black F indicator).¹¹ Sodium perchlorate solutions prepared by neutralization of sodium carbonate with perchloric acid were standardized gravimetrically. Ligand stock solutions were made up by weight from the solid hemihydrate which had been recrystallized from warm 20% v/v aqueous ethanol, and the concentrations were checked spectrophotometrically (ϵ_{270} $3.00 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$);¹² these solutions were stored in the dark.

Reagent grade thiourea was recrystallized from warm 20% v/v aqueous ethanol and its purity was checked by melting point determination (found 181.2 °C; lit. 180–182 °C) and by elemental analysis (by the University Microanalytical Laboratory). Reagent grade methanol (Fisons) was found to have properties which closely agreed with literature values and was used as supplied. Careful drying of the methanol had no effect on the kinetic results (see below).

All other chemicals were of reagent grade and were used as supplied.

Reactant and Product Characterization. Copper Oxidant. A concentrated solution of the copper(II) reactant was obtained by shaking 0.5 g (2.3 mmol) of dmp with 0.45 mmol of $\text{Cu}^{\text{II}}(\text{ClO}_4)_2$ in 50 ml of water; undissolved ligand was filtered off and an amorphous green precipitate was obtained on addition of 4 M sodium perchlorate solution. The precipitate was washed with cold water and dried to constant weight. The dry solid was purple. Complete elemental analysis of this solid (G. M. J. Powell, Microanalytical Laboratory, University of Kent, and Alfred Bernhardt Mikroanalytisches Laboratorium) showed it to be $[\text{Cu}(\text{dmp})_2](\text{ClO}_4)_2$.

Reaction Products with Thiocyanate. A crude sample of the copper-containing product of the reaction with thiocyanate was obtained by the addition of a solution of 0.5 g of dmp (in 10 ml of methanol) to an aqueous solution containing 0.45 mmol of $\text{Cu}^{\text{II}}(\text{ClO}_4)_2$ in the presence of excess sodium thiocyanate. An orange solid which precipitated was recrystallized from methanol giving deep red, diamond-shaped crystals. Complete elemental analysis and spectral measurements⁸ showed that this product was $[\text{Cu}(\text{dmp})_2]\text{ClO}_4$. At very large excesses of sodium thiocyanate a trace of insoluble CuSCN was also found as a product (see below). The stoichiometry of the reaction was investigated spectrophotometrically over the concentration ranges $[\text{Cu}^{\text{II}}]_0 = (0.5\text{--}20) \times 10^{-5} \text{ M}$ and $[\text{dmp}]_{\text{T}} = (0.5\text{--}16) \times 10^{-4} \text{ M}$ at $[\text{SCN}^-] = 1.5 \times 10^{-3} \text{ M}$ by monitoring absorbances at 454 nm, which is a wavelength of maximum absorbance for $\text{Cu}(\text{dmp})_2^+(\text{aq})$. The results were consistent with the information of a single product; the apparent extinction coefficient, ϵ , obtained from the slope of a linear plot of absorbance vs. $[\text{Cu}^{\text{II}}]_0$ was $(5.9 \pm 0.1) \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$, to be compared with $6.16 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ quoted⁸ for $\text{Cu}(\text{dmp})_2^+(\text{aq})$ and confirmed in our laboratory. Since the concentration of $\text{Cu}(\text{dmp})_2^+$ (ϵ_{454} $3.4 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$)⁸ calculated from the data of Table I was

far too small to be responsible for this difference under the experimental conditions, we ascribe the discrepancy to the presence of traces of thiocyanate-containing copper(I) species (see below) which have lower extinction coefficients than $\text{Cu}(\text{dmp})_2^+(\text{aq})$ at 454 nm. The kinetic data for this reaction (see below) suggest that such products may be formed at high concentrations of SCN^- .

The analytical identification of the oxidized thiocyanate product in this reaction was severely hampered by the low solubility of Cu^{II} -dmp and Cu^{I} -dmp complexes in aqueous media, and satisfactory analytical results could not be obtained. It has been shown that the corresponding reduction of $\text{Cu}^{2+}(\text{aq})$ by SCN^- produces copper(I) thiocyanate.¹³ The oxidized thiocyanate product in the latter reaction was identified as follows. Aqueous sodium thiocyanate (14 ml, 1 M) was added to 50 ml of 0.27 M aqueous copper(II) perchlorate in an Erlenmeyer flask and the mixture was stirred continuously at 25 °C for 45 min. The white copper(I) thiocyanate which had formed was removed by filtration and the filtrate was extracted with ether (two 50-ml portions). The combined ether extracts were dried over anhydrous MgSO_4 , filtered, and evaporated to half-volume, whereupon the solution became deep yellow and precipitated a small quantity of brick red material, which was filtered off, washed with ice-cold ether, and vacuum dried over CaCl_2 . Elemental carbon, nitrogen, and sulfur analysis showed that this solid was polythiocyanogen, $(\text{NCS})_n$.

The filtrate was cooled in an acetone- CO_2 slush bath, whereupon a pale yellow precipitate was formed. The precipitate was removed by filtration at -80 °C and vacuum dried over CaCl_2 at room temperature. Elemental analysis of the orange solid so obtained showed it to be $(\text{NCS})_n$.

Reaction Products with Thiourea. A crude, orange precipitate of the copper(I) product was obtained as described above from both solvent systems by allowing a copper(II) perchlorate solution containing a fivefold excess of dmp to react with a slight stoichiometric excess of thiourea. Recrystallization of this initial precipitate from anhydrous methanol gave deep red, diamond-shaped crystals which were shown by complete elemental analysis to be $[\text{Cu}(\text{dmp})_2]\text{ClO}_4$. Experiments with up to a fivefold excess of thiourea gave the same results.

The stoichiometry of the reactions was investigated quantitatively by spectrophotometric measurement of the $\text{Cu}(\text{dmp})_2^+(\text{aq})$ product formed at 25 °C within the following ranges: $[\text{dmp}]_{\text{T}} = (0.7\text{--}22) \times 10^{-4} \text{ M}$, $[\text{Cu}^{\text{II}}]_0 = (0.4\text{--}16) \times 10^{-5} \text{ M}$, and $[\text{thiourea}]_{\text{T}} = (2.0\text{--}200) \times 10^{-5} \text{ M}$. These experiments included conditions with either reagent in excess.

Kinetic Measurements. A pH meter (Radiometer 26), equipped with G202B glass and K901 reference electrodes, was used for pH measurements. The pH standards employed were 0.05 M potassium hydrogen phthalate (pH 4.002 ± 0.002), 0.05 M potassium monobasic phosphate-sodium hydroxide buffer (pH 7.00 ± 0.02), and sodium tetraborate (pH 9.180 ± 0.002) at 25.0 °C. The pH obtained on mixing equal volumes of the reactants in a thermostated cell was equated to that for the kinetic measurements.

The kinetics of reaction with thiocyanate and thiourea were investigated spectrophotometrically by monitoring the formation of the copper(I) product in a stopped-flow apparatus¹⁴ in the wavelength range 315–600 nm. The temperature was maintained at 25.0 ± 0.05 °C and in aqueous media the ionic strength was adjusted to 0.1 M with sodium perchlorate. A number of runs were made in a 1.0 M aqueous sodium perchlorate medium, but difficulties with precipitation of the products were encountered at this ionic strength. No attempt was made to maintain constant ionic strength or to buffer the system in the kinetic investigations in methanol. The concentration ranges employed were $[\text{Cu}^{\text{II}}]_0 = (0.5\text{--}5.0) \times 10^{-5} \text{ M}$, $[\text{dmp}]_{\text{T}} = (1.8\text{--}30.8) \times 10^{-5} \text{ M}$, $[\text{SCN}^-]_0 = (1.0\text{--}11.3) \times 10^{-2} \text{ M}$, $[\text{tu}]_{\text{T}} = (0.50\text{--}5.0) \times 10^{-2} \text{ M}$, $[\text{H}^+] = (0.68\text{--}94) \times 10^{-8} \text{ M}$, and $[\text{boric acid}]_{\text{T}} = (0.5\text{--}11.3) \times 10^{-3} \text{ M}$ in 0.1 M aqueous sodium perchlorate and $[\text{Cu}^{\text{II}}]_0 = (0.8\text{--}9.0) \times 10^{-5} \text{ M}$, $[\text{dmp}]_{\text{T}} = (0.6\text{--}5.0) \times 10^{-3} \text{ M}$, and $[\text{tu}]_{\text{T}} = (4.0\text{--}18.0) \times 10^{-2} \text{ M}$ in methanol. The copper concentration range was limited at the lower end by reproducible working conditions for the stopped-flow apparatus, and the upper limit was set by the solubility of the copper complexes involved in water and methanol, respectively. For studies in aqueous solution, the lowest boric acid concentration was the minimum concentration at which buffering was effective, while the highest concentration was that at which the contribution to the total ionic strength due to boric acid species could be neglected. The concentrations of the reductant were always sufficiently high to ensure negligible variation during a run. Under these conditions the ap-

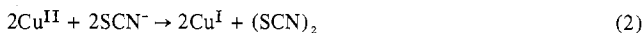
pearance of Cu^{I} was almost invariably first order (see below).

Solutions containing copper(II), ligand, and buffer ($\mu \approx 0$) were mixed with sodium thiocyanate or thiourea in aqueous sodium perchlorate ($\mu = 0.2 \text{ M}$) in the stopped-flow apparatus; mixing was complete within the time scale of the kinetic measurements. Each run was normally repeated four to six times and the rate constants obtained in replicate determinations generally agreed to within $\pm 5\%$. Small amounts of CuSCN were detected in the products when the thiocyanate concentration was greater than $12.0 \times 10^{-2} \text{ M}$ (see above). Nonexponential traces were obtained when the concentrations of H^+ and SCN^- were close to the lower limits quoted; rate constants were then determined from measurements of initial rates. Kinetic measurements were made difficult by the nonexponentiality of the traces at concentrations significantly below the limits quoted and rate constants were not determined.

The measured initial absorbance after mixing Cu^{II} -dmp solutions with thiocyanate in the stopped-flow apparatus showed variations which suggested that preequilibria involving thiocyanate-copper(II) species are involved in the subsequent redox reaction. However, the absorbances were small and the variations between them were too erratic to be useful in obtaining independent equilibrium data. A slight decrease in the initial absorbance of mixed reactants with increasing $[\text{tu}]_{\text{T}}$ and fixed $[\text{dmp}]_{\text{T}}$ was also noted in the reaction with thiourea but the variations were too small to be analytically useful.

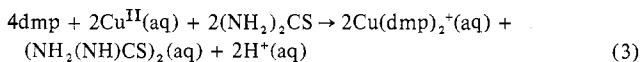
Results

Stoichiometry. The identification of $(\text{SCN})_2$ as the product of oxidation of SCN^- by $\text{Cu}^{2+}(\text{aq})$ and the quantitative establishment of $\text{Cu}(\text{dmp})_2^{2+}$ as the major reduced copper product in the reaction with $\text{Cu}(\text{dmp})_2^{2+}$ (which is a stronger oxidant than $\text{Cu}^{2+}(\text{aq})$) suggest that the stoichiometry of the reaction with thiocyanate is given by



with $\text{Cu}(\text{dmp})_2^{2+}(\text{aq})$ as the major copper(I) product. It should be noted that thiocyanogen also has been identified as a product of the oxidation of SCN^- by $\text{Co}^{\text{III}}(\text{aq})$ ¹⁵ and Fe^{III} (in acetonitrile),¹⁶ indicating that formation of $(\text{SCN})_2$ by dimerization of primary SCN radicals is sufficiently rapid to prevent their oxidation to other products even in systems which involve stronger metallic oxidants than $\text{Cu}(\text{dmp})_2^{2+}$.^{2,15,16}

The stoichiometric measurements with excess Cu^{II} or excess thiourea were consistent with the occurrence of the redox reaction



The postulated formamidine disulfide product could not be satisfactorily isolated and characterized because of the low solubility of Cu^{I} - and Cu^{II} -dmp species. However, the analytical identification of this product in the analogous reactions of thiourea with the strongly oxidizing species aquocerium(IV)⁷ and aquocobalt(III)¹⁸ makes this product assignment reasonable.

Kinetics of Reaction with Thiocyanate. Except under the particular reaction conditions noted above, plots of $\ln(A_{\infty} - A_t)$ vs. time, where A_t and A_{∞} are the absorbances at time t and at "infinite" time, respectively, were accurately linear for at least 4 half-lives and were independent of the initial copper(II) concentration, indicating that the reaction is first order in $[\text{Cu}^{\text{II}}]$. The few rate constants determined from initial rate measurements at low $[\text{H}^+]$ and $[\text{SCN}^-]$ and at high $[\text{H}^+]$ were also consistent with this conclusion. The observed first-order rate constant k_{obsd} was found to be independent of monitoring wavelength, indicating that photochemical activation could be neglected under the experimental conditions,⁸ and was also independent of the stoichiometric concentration of boric acid buffer and the presence of oxygen. The kinetic data are collected in Table II.¹⁹

The first-order rate constants increase linearly with $[\text{SCN}^-]$ in the range $[\text{SCN}^-] = (1.00\text{--}7.00) \times 10^{-2} \text{ M}$ at $[\text{H}^+] = (1.6$

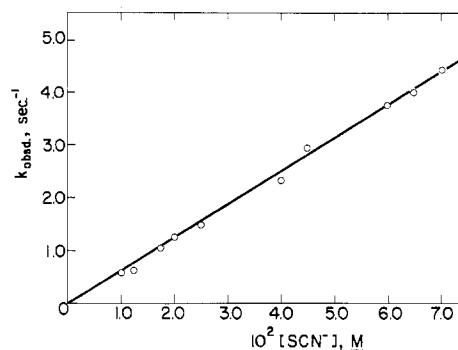


Figure 1. Plot of k_{obsd} vs. $[\text{SCN}^-]$ at $[\text{dmp}]_{\text{T}} = 1.54 \times 10^{-4} \text{ M}$, $[\text{Cu}^{\text{II}}] = 1.53 \times 10^{-5} \text{ M}$, $[\text{H}^+] = (1.6 \pm 0.1) \times 10^{-8} \text{ M}$, and $[\text{boric acid}]_{\text{T}} = 3.75 \times 10^{-3} \text{ M}$ at 25.0°C and ionic strength 0.1 M (NaClO_4).

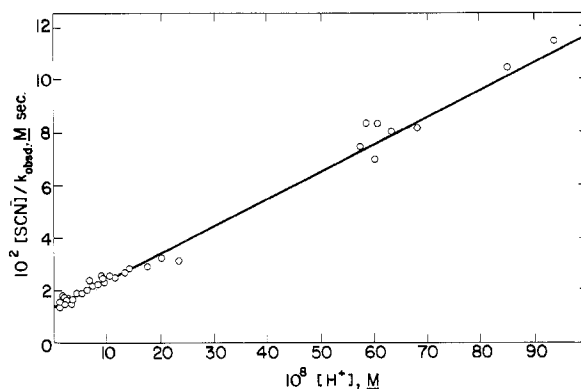


Figure 2. Plot of $[\text{SCN}^-]/k_{\text{obsd}}$ vs. $[\text{H}^+]$ for the data of Table II at 25.0°C and ionic strength 0.1 M (NaClO_4).

$\pm 0.1) \times 10^{-8} \text{ M}$ and $[\text{dmp}]_{\text{T}} = 1.54 \times 10^{-4} \text{ M}$ (Figure 1). Thus

$$k_{\text{obsd}} = A [\text{SCN}^-] \quad (4)$$

where A is an empirical rate parameter with units of $\text{M}^{-1} \text{ s}^{-1}$. A plot of $[\text{SCN}^-]/k_{\text{obsd}}$ vs. $[\text{H}^+]$ was found to be linear within experimental error, with a finite intercept suggesting that

$$1/A = B[\text{H}^+] + C \quad (5)$$

where B and C are the slope and intercept, respectively, of Figure 2. This result is consistent with a small or negligible effect of $[\text{dmp}]_{\text{T}}$ on A over the concentration ranges studied. A linear least-squares fit of the data in Figure 2 to eq 4 gave $B = (1.02 \pm 0.02) \times 10^5 \text{ s}$ and $C = (1.40 \pm 0.03) \times 10^{-2} \text{ M s}$ at 25.0°C . The calculated values from eq 4 are shown in Table II for comparison with k_{obsd} .

Kinetics of Reaction with Thiourea. Plots of $\ln(A_{\infty} - A_t)$ were linear for at least 90% of the reaction with thiourea in both solvent systems under all conditions where $[\text{tu}] \gg [\text{Cu}^{\text{II}}]_0$; the derived first-order rate constants, k_{obsd} , were independent of $[\text{Cu}^{\text{II}}]_0$ when all other reactant solution components were held at fixed concentration and were also unaffected by variation of the monitoring wavelength or by deoxygenation of reactant solutions before mixing. These results indicate that the reaction rate is first order in $[\text{Cu}^{\text{II}}]$ under the experimental conditions.

Reaction in Aqueous Sodium Perchlorate. Values for k_{obsd} obtained under various experimental conditions are collected in Table III.¹⁹ These data indicate that k_{obsd} is independent of the stoichiometric boric acid concentration over a ca. 10-fold range of $[\text{H}^+]$ at $[\text{dmp}]_{\text{T}} = 2.71 \times 10^{-4} \text{ M}$ and $[\text{tu}]_{\text{T}} = 2.50 \times 10^{-2} \text{ M}$ and that k_{obsd} is also independent of $[\text{dmp}]_{\text{T}}$ at $[\text{H}^+] = (1.83 \pm 0.08) \times 10^{-8} \text{ M}$ and $[\text{tu}]_{\text{T}} = 2.50 \times 10^{-2} \text{ M}$.

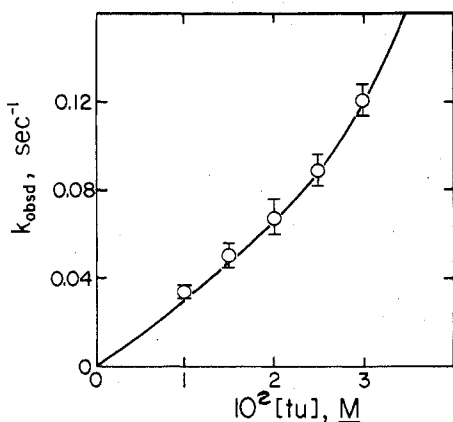


Figure 3. Plot of k_{obsd} vs. $[\text{tu}]$ for the reaction of Cu^{II} -dmp complexes with thiourea in 0.1 M aqueous sodium perchlorate at 25.0 °C under the following conditions: $[\text{Cu}^{\text{II}}]_0 = 1.53 \times 10^{-5}$ M, $[\text{dmp}]_{\text{T}} = 2.71 \times 10^{-4}$ M, $[\text{boric acid}]_{\text{T}} = 4.0 \times 10^{-3}$ M, and $[\text{H}^+] = 43.0 \times 10^{-8}$ M.

Although plots of k_{obsd} vs. $[\text{tu}]$ are linear with $[\text{H}^+] = 1.98 \times 10^{-8}$ and 3.78×10^{-8} M at $[\text{dmp}]_{\text{T}} = 2.71 \times 10^{-4}$ M, the corresponding plot at $[\text{H}^+] = 43.0 \times 10^{-8}$ M is curved upward (Figure 3), indicating a change in reaction order with respect to $[\text{tu}]$ on increasing the experimental acidity. Similarly, although a plot of $[\text{tu}]/k_{\text{obsd}}$ vs. $[\text{H}^+]$ is linear with a positive intercept at low or moderate acidity, the data obtained at low $[\text{tu}]$ with high $[\text{H}^+]$, including the data shown in Figure 3, do not fit this plot, indicating that k_{obsd} is not a simple function of $[\text{H}^+]$ at fixed $[\text{tu}]$ over the entire experimental acidity range.

The best, nonlinear least-squares fit of the data was obtained from the empirical expression

$$k_{\text{obsd}} = \frac{D[\text{tu}]_{\text{T}}^2}{E[\text{dmp}][\text{H}^+] + F[\text{tu}]_{\text{T}}[\text{H}^+] + [\text{tu}]_{\text{T}}} \quad (6)$$

where D , E , and F are empirical parameters with values of $(74.5 \pm 4.4) \text{ M}^{-1} \text{ s}^{-1}$, $(2.86 \pm 0.29) \times 10^8 \text{ M}^{-1}$, and $(2.91 \pm 0.29) \times 10^7 \text{ M}^{-1}$ at 25.0 °C and ionic strength 0.1 M. Estimates of the first-order rate constants calculated from eq 6 are included in Table III for comparison with k_{obsd} .

Reaction in Methanol. The kinetic data obtained for the reaction of Cu^{II} -dmp species with thiourea in methanol are collected in Table IV.¹⁹ Addition of water up to 11% v/v had no effect on the pseudo-first-order rate constant k_{obsd} at $[\text{Cu}^{\text{II}}]_0 = 8.84 \times 10^{-5}$ M, $[\text{dmp}]_{\text{T}} = 3.0 \times 10^{-3}$ M, and $[\text{tu}] = 6.25 \times 10^{-2}$ M. The data in Table IV exhibit the following dependences. (a) At $[\text{tu}] = 6.25 \times 10^{-2}$ M, k_{obsd} increases with $[\text{dmp}]_{\text{T}}$ but a plot of k_{obsd} vs. $[\text{dmp}]_{\text{T}}$ is curved. However, a plot of $1/k_{\text{obsd}}$ vs. $1/[\text{dmp}]_{\text{T}}$ is linear with a positive intercept (Figure 4). (b) k_{obsd} decreases with increasing $[\text{tu}]$ at fixed $[\text{dmp}]_{\text{T}} = 2.0 \times 10^{-3}$ and 3.0×10^{-3} M. Plots of k_{obsd} vs. $1/[\text{tu}]$ and $1/k_{\text{obsd}}$ vs. $[\text{tu}]$ were nonlinear under these conditions.

The best nonlinear least-squares fit of the data in methanol was obtained from the empirical expression

$$k_{\text{obsd}} = \frac{G[\text{dmp}][\text{tu}]}{[\text{dmp}] + H[\text{tu}] + J[\text{tu}]^2} \quad (7)$$

where G , H , and J are empirical parameters with values of $(5.2 \pm 0.6) \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$, $(6 \pm 2) \times 10^{-2}$, and $1.9 \pm 0.2 \text{ M}^{-1}$, respectively, at 25.0 °C. Rate constants calculated from eq 7 are included in Table IV for comparison with k_{obsd} .

Mechanisms

The concentrations of the various ligand and metal complex species under a given set of experimental conditions in the absence of SCN^- and thiourea may be calculated from the equilibrium data of Table I. These calculations indicate that

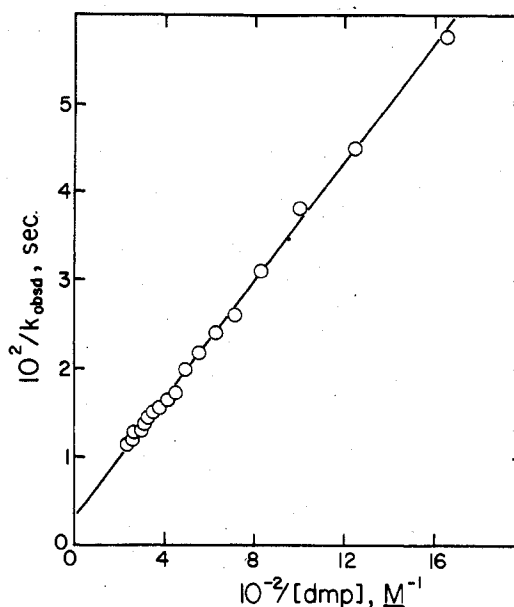
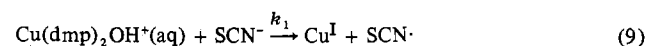
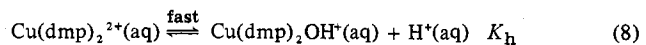


Figure 4. Plot of $1/k_{\text{obsd}}$ vs. $1/[\text{dmp}]$ for the reaction of Cu^{II} -dmp complexes with thiourea in methanol at 25.0 °C under the following conditions: $[\text{Cu}^{\text{II}}]_0 = 8.84 \times 10^{-5}$ M and $[\text{tu}] = 6.25 \times 10^{-2}$ M.

$\text{Cu}(\text{dmp})_2^{2+}(\text{aq})$ never accounts for more than 3% of the analytical copper(II) concentration even at the lowest $[\text{dmp}]$ employed in this work. Furthermore, there is no evidence in the literature to suggest that $\text{Cu}(\text{dmp})_3^{2+}(\text{aq})$ is ever stoichiometrically significant at the relatively low $[\text{dmp}]_{\text{T}}$ attainable in aqueous solution.

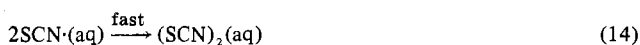
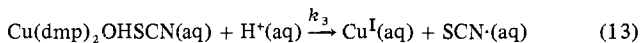
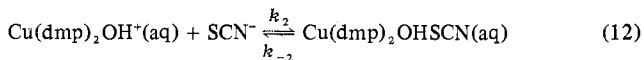
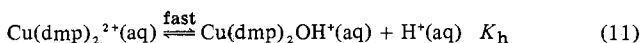
Reaction with Thiocyanate. The above considerations and empirical rate law 4 suggest that the mechanism of reduction of dmp- Cu^{II} complexes by thiocyanate involves the rate-determining reduction of $\text{Cu}(\text{dmp})_2^{2+}(\text{aq})$ species by SCN^- . However, while a mechanism comprising steps (8)–(10), with



(8) as a rapid preequilibrium and (9) as the rate-determining process, is consistent with all of the stoichiometric and kinetic observations, its predictions are not consistent with the equilibrium data in Table I.

Thus, the mechanism described by eq 8–10 predicts that empirical parameter A will be given by $A = k_1 K_{\text{h}} / ([\text{H}^+] + K_{\text{h}})$. Inversion of this relationship and comparison with eq 5 gives $B = 1/k_1 K_{\text{h}}$ and $C = 1/k_1$, corresponding to $k_1 = 72 \pm 2 \text{ M}^{-1} \text{ s}^{-1}$ and $K_{\text{h}} = (1.4 \pm 0.1) \times 10^{-7} \text{ M}$ at 25.0 °C. This simple mechanism can be rejected on the basis of its prediction of the acid-dissociation constant of $\text{Cu}(\text{dmp})_2^{2+}(\text{aq})$; if K_{h} were this large, then $\text{Cu}(\text{dmp})_2\text{OH}^+(\text{aq})$ would be a major stoichiometric copper(II) species and its presence would be reflected by an acid dependence of the equilibrium constants for the copper Cu^{II} -dmp system (Table I), which evidently is not observed.⁷

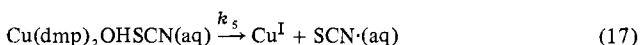
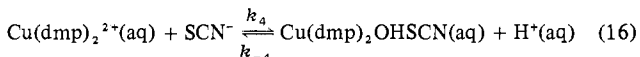
Although the increase in rate with decreasing acidity evidently points to the involvement of OH^- -dmp- Cu^{II} species in the rate-determining step(s), other mechanisms may be written which do not demand the existence of significant stoichiometric concentrations of $\text{Cu}(\text{dmp})_2\text{OH}^+(\text{aq})$ species. Thus, the mechanism shown in eq 11–14 accounts for the increase in rate with decreasing acidity. If the species $\text{Cu}(\text{dmp})_2\text{OHSCN}$ is assumed to be in a steady state, then this mechanism predicts that A is given by eq 15.



$$A = \frac{k_2 K_h k_3}{(k_{-2} + k_3 [\text{H}^+])(1 + K_h / [\text{H}^+])} \quad (15)$$

If $K_h / [\text{H}^+] \ll 1$, eq 15 may be inverted and compared with eq 5, where $B = 1/k_2 K_h = (1.02 \pm 0.02) \times 10^5 \text{ s}$ and $C = k_{-2}/k_2 k_3 K_h = (1.40 \pm 0.03) \times 10^{-2} \text{ M s}$, corresponding to $k_2 K_h = (9.8 \pm 0.2) \times 10^{-6} \text{ s}^{-1}$ and $k_{-2}/k_3 = (1.4 \pm 0.1) \times 10^{-7} \text{ M}$ at 25.0 °C. If $K_h / [\text{H}^+] < 0.1$ at the lowest acidity employed, then $K_h \leq 7 \times 10^{-10} \text{ M}$ and $k_2 \geq 1.4 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ at 25.0 °C for this mechanism.

A second mechanism consistent with the experimental observations and available equilibrium data for the $\text{dmp-Cu}^{\text{II}}$ system is given by eq 16–18. If $\text{Cu(dmp)}_2\text{OHSCN}(\text{aq})$ is



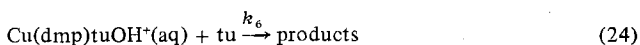
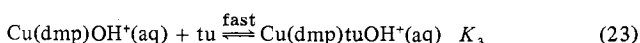
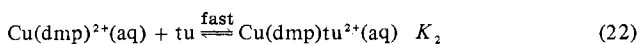
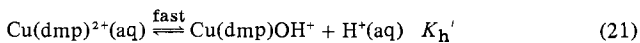
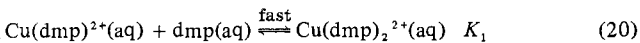
again assumed to be in a steady state, then parameter A is given by eq 19.

$$A = \frac{k_4 k_5}{k_5 + k_{-4} [\text{H}^+]} \quad (19)$$

Inversion of this equation and comparison with eq 5 gives $B = k_{-4}/k_4 k_5 = (1.02 \pm 0.02) \times 10^5 \text{ s}$ and $C = 1/k_4 = (1.40 \pm 0.03) \times 10^{-2} \text{ M s}$; thus, for this mechanism, $k_4 = (72 \pm 2) \text{ M}^{-1} \text{ s}^{-1}$ and $k_{-4}/k_5 = (7.3 \pm 0.2) \times 10^6 \text{ M}$ at 25.0 °C.

The mechanisms given in eq 11–14 and 16–18, respectively, differ only in the order in which a proton is lost to the solvent,²⁰ and either mechanism could be appropriate in this system. However, it is important to note that the latter alternative provides for a direct reaction between $\text{Cu(dmp)}_2^{2+}(\text{aq})$ and SCN^- ; i.e., both mechanisms require that primary products be formed from $\text{Cu(dmp)}_2\text{OHSCN}$. Although it is extremely unlikely that the respective steps governed by rate constants k_3 and k_{-4} are diffusion controlled, the assumption of $10^{10} \text{ M}^{-1} \text{ s}^{-1}$ as an upper limit for each of these parameters leads to an absolute upper limit of ca. $1 \times 10^3 \text{ s}^{-1}$ for k_{-2} or k_5 , respectively. A third possible mechanism for this reaction will be suggested after assignment of the thiourea data.

Reaction with Thiourea in Aqueous Solution. The kinetic data for reaction with thiourea are satisfactorily accounted for by eq 6, which includes a second-order term in $[\text{tu}]$ consistent with the mechanism given by eq 20–24. Here,



reaction 24 is assumed to be the rate-determining step which produces Cu(dmp)_2^{2+} (via rapid addition of dmp to the primary copper(I) product) and radical products analogous to those postulated in other redox systems involving the one-electron oxidation of thiourea.^{17,18}

The pseudo-first-order rate constant predicted by this mechanism is

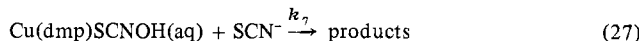
$$k_{\text{obsd}} = \frac{k_6 K_3 K_h' [\text{tu}]_{\text{T}}^2}{[\text{H}^+] + K_h' + K_1 [\text{dmp}] [\text{H}^+] + K_2 [\text{tu}]_{\text{T}} [\text{H}^+] + K_3 K_h' [\text{tu}]_{\text{T}}} \quad (25)$$

Neglect of the terms $[\text{H}^+]$ and K_h' in the denominator of eq 25 leads to an equation of the same form as eq 6, with $D = k_6 = (74.5 \pm 4.4) \text{ M}^{-1} \text{ s}^{-1}$, $E = K_1 / K_3 K_h' = (2.86 \pm 0.29) \times 10^8 \text{ M}^{-1}$, and $F = K_2 / K_3 K_h' = (2.91 \pm 0.29) \times 10^7 \text{ M}^{-1}$. The ratio $K_1 / K_2 = E / F$ is ca. 10 at 25.0 °C; combination of this result with the experimental estimate of K_1 (Table I) gives $K_2 \approx 6 \times 10^4 \text{ M}^{-1}$.

The mechanism proposed for the reaction with thiourea accounts for the curvature of the plots of k_{obsd} vs. $[\text{tu}]$ at high $[\text{H}^+]$. The highest $[\text{H}^+]$ in the thiourea study is $62.6 \times 10^{-8} \text{ M}$, while that in the corresponding SCN^- reaction is $94 \times 10^{-8} \text{ M}$. However, no evidence for a second-order $[\text{thiocyanate}]$ term in the empirical rate law for the latter reaction was obtained. Nevertheless, it is interesting to note that if the first term in the denominator of eq 6 is neglected, then empirical expression 26 is produced. This expression is of the same form

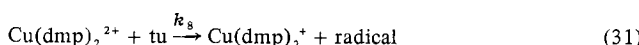
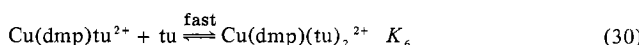
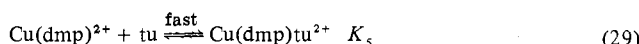
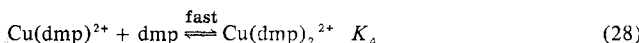
$$k_{\text{obsd}} = \frac{D [\text{tu}]_{\text{T}}}{F [\text{H}^+] + 1} \quad (26)$$

as eq 4, with $B = F / D$ and $C = 1 / D$. If a mechanism consisting of steps analogous to (20)–(24) is written with SCN^- replacing tu throughout, then neglect of the first three terms in the denominator of the analog of eq 25 leads to $B = K_2 / k_6 K_3 K_h'$ and $C = 1 / k_6$ for the reaction with SCN^- . Thus, this third alternative mechanism for reduction by SCN^- has $k_7 = 72 \pm 2 \text{ M}^{-1} \text{ s}^{-1}$ for the rate-determining step



and $K_2 / K_3 K_h' = B / C = (7.3 \pm 0.2) \times 10^6 \text{ M}$ for equilibria analogous to eq 21–23 in the thiocyanate system. The rate constant for the common rate-determining step in the thiourea system, k_6 , is remarkably similar to that governing step (27). In addition, the ratios $K_2 / K_3 K_h' = F$ and $K_2 / K_3 K_h' = B / C$ are of the same order of magnitude for thiourea and SCN^- as reductants, respectively.

Reaction in Methanol. The mechanism given by eq 28–32,



which is based on a consideration of the mechanism proposed above for the corresponding reaction in aqueous solution, is consistent with the experimental data. Here, step (31) is postulated to be rate determining and the rapid step (32) would satisfy the measured stoichiometry of the overall redox process, although we have no direct experimental evidence on this aspect of the reaction.

The expression for the pseudo-first-order rate constant predicted by this mechanism is given by eq 33. This ex-

$$k_{\text{obsd}} = \frac{k_3 K_4 [\text{dmp}] [\text{tu}]_{\text{T}}}{1 + K_4 [\text{dmp}] + K_5 [\text{tu}]_{\text{T}} + K_5 K_6 [\text{tu}]_{\text{T}}^2} \quad (33)$$

pression predicts that a plot of $1/k_{\text{obsd}}$ vs. $1/[\text{dmp}]$ will be linear at constant $[\text{tu}]$ and that the rate will decrease with

increasing [tu] at fixed [dmp], as observed. If the first term in the denominator of eq 33 is negligible, then rearrangement of eq 33 gives

$$\frac{1}{k_{\text{obsd}}} = \frac{K_5(1 + K_6[\text{tu}]_T)}{k_8 K_4 [\text{dmp}]} + \frac{1}{k_8 [\text{tu}]} \quad (34)$$

A value of $k_8 = (5.2 \pm 0.6) \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ was obtained by a linear least-squares fit of the data to eq 34 at fixed [tu]. Finally, eq 33 with neglect of the unit term in the denominator was rearranged to

$$k_{\text{obsd}} = \frac{k_8 [\text{dmp}][\text{tu}]}{[\text{dmp}] + K_5 [\text{tu}]_T / K_4 + K_5 K_6 [\text{tu}]_T^2 / K_4} \quad (35)$$

and fitted to the data by nonlinear least squares with k_8 fixed at $5.2 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$. Equation 35 is of the same form as eq 7, with $G = k_8 = 5.2 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$, $H = K_5 / K_4 = (6 \pm 2) \times 10^{-2}$, and $J = K_5 K_6 / K_4 = 1.9 \pm 0.2 \text{ M}^{-1}$. Thus $K_6 = J / H = 31 \pm 4 \text{ M}^{-1}$ at 25.0 °C.

Discussion

The three postulated mechanisms for reduction of $\text{dmp-Cu}^{\text{II}}$ species by thiocyanate are all consistent with the observed stoichiometry and kinetics of this system and with measured equilibrium data for oxidant species (Table I). These alternative mechanisms account for the increase in rate with decreasing acidity in terms of the involvement of inner-sphere hydroxide at the oxidant center, while not violating the requirement that all hydroxocopper(II) complexes are analytically insignificant under the experimental conditions.

The anticipated solvent exchange lability²¹ of $\text{Cu}(\text{dmp})_x^{2+}(\text{aq})$ species ($x = 1$ or 2) is manifested by the clear involvement of inner-sphere $\text{dmp-Cu}^{\text{II}}$ -reductant complexes in acceptable mechanisms for all the reactions of this study. The upward curvature in Figure 3 may also be present for the thiocyanate data in Figure 1, but we have been unable to test this possibility on increasing the thiocyanate concentration beyond the limits of this work because of the low solubilities of reactants and products at high $[\text{SCN}^-]$ in aqueous solutions. However, the assumption of similar mechanisms for reduction of $\text{Cu}(\text{dmp})_2^{2+}(\text{aq})$ by SCN^- (third mechanism) and thiourea in water offers an attractive alternative to the other two viable mechanisms for SCN^- oxidation, which both require the steady-state intermediacy of $\text{Cu}(\text{dmp})_2\text{OHSCN}(\text{aq})$.

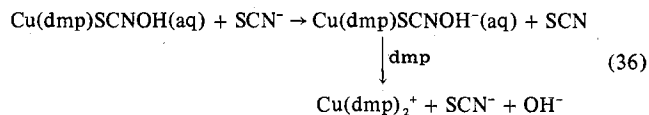
On balance, it seems preferable to accept similar mechanisms for SCN^- and tu reductions rather than to postulate a steady-state situation only in the SCN^- system, although this conclusion must, of course, be tentative in the absence of data for other reductants, particularly those which carry "soft" coordination sites (see below). The evidence for substantial stoichiometric concentrations of $\text{Cu}(\text{dmp})_x\text{tu}_n$ in water and methanol also tends to argue against a steady-state concentration of $\text{Cu}(\text{dmp})_2\text{SCNOH}$, since, on electrostatic considerations alone, SCN^- might be expected to form stronger complexes than does tu with a given cationic oxidant species.

Although similarity of the results may be circumstantial, it is notable that kinetic and thermodynamic parameters derived from the assumption of analogous mechanisms in aqueous solution are very similar. The lack of dependence of k_{obsd} on [dmp] is then accounted for by the absence of analytically significant concentrations of $\text{Cu}(\text{dmp})_2^{2+}$ under the experimental conditions because of the high thermodynamic stability of $\text{Cu}(\text{dmp})\text{tu}^{2+}(\text{aq})$ and $\text{Cu}(\text{dmp})\text{SCN}^+(\text{aq})$ complexes.

The large stability constant K_2 for the thiourea system is also implied by the predictions of an analogous mechanism for SCN^- oxidation, suggesting that similar complexes are formed with these two reductants despite the differences in their formal charges and geometries. Strong oxidant-re-

ductant complexes are also formed in methanol in the thiourea system. Since the $\text{Cu}(\text{dmp})_2^{2+}(\text{aq})$ system is evidently only weakly acidic and since complexes with the hard ligands H_2O_2 and HO_2^- have not been detected in reduction by hydrogen peroxide,²² we may tentatively conclude that $\text{Cu}(\text{dmp})_x^{2+}$ is a "soft" center and that similar mechanistic predictions in analogous reactions with SCN^- and thiourea are the result of bonding through sulfur. It is worth noting that the equilibrium constants for formation of $\text{M}(\text{DMG})_2\text{SCN}^-$ complexes (DMG = dimethylglyoxime) are much higher than the corresponding values for $\text{M}(\text{SCN})^+(\text{aq})$ when M is Co or Fe²³ and that strong thiocyanate complexes are formed by metalloporphyrins.²⁴

The great thermodynamic stability (Table I) and presumably rapid formation²¹ of $\text{Cu}(\text{dmp})_2^{2+}(\text{aq})$ would seem to ensure its appearance as the major product of reduction, although the nonexponentiality of reaction traces noted in the Experimental Section for SCN^- suggests that redistribution of ligand environments around copper such as in (36) may be



important processes under some reaction conditions. It is notable in this regard that direct reaction of $\text{Cu}(\text{dmp})_2^{2+}$ with tu in methanol is a very rapid process ($k_8 \approx 5 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$) in comparison to reactions involving production of mono-(dimethylphenanthroline)copper(I) primary products in the reaction with tu in aqueous solution ($k_6 = 74.5 \text{ M}^{-1} \text{ s}^{-1}$). A very rapid reaction between $\text{Cu}(\text{dmp})_2^{2+}(\text{aq})$ and HO_2^- has also been postulated in the reaction with hydrogen peroxide,²² pointing to the tentative conclusion that the most rapid reactions of $\text{Cu}(\text{dmp})_x^{2+}$ species are those which result in the direct formation of thermodynamically stable bis(dimethylphenanthroline)copper(I) primary products. This conclusion is mildly supported by the apparent oxidative stability of $\text{Cu}(\text{dmp})\text{tu}^{2+}$ and $\text{Cu}(\text{dmp})\text{tu}^{2+}$ species in methanol.

Finally, it should be noted that the ratio K_5/K_4 for thiourea in methanol is slightly smaller than the analogous ratio K_2/K_1 in water, indicating slight preferential stabilization of $\text{Cu}(\text{dmp})_2^{2+}$ over $\text{Cu}(\text{dmp})\text{tu}^{2+}$ in methanol. The small calculated value of K_6 in methanol suggests that an equilibrium corresponding to (30) would be observable only at very high [tu] in water.

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Registry No. $\text{Cu}(\text{dmp})_2^{2+}$, 14875-91-3; thiocyanate, 302-04-5; thiourea, 62-56-6.

Supplementary Material Available: Tables II-IV, listing kinetic data (7 pages). Ordering information is given on any current masthead page.

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Reactions of Copper Complexes. II. Reduction of Bis(2,9-dimethyl-1,10-phenanthroline)copper(II) Complexes by Hydrogen Peroxide in Aqueous Perchlorate Media¹

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The stoichiometry and kinetics of the reduction of Cu^{II}-dmp complexes (dmp is the bidentate ligand 2,9-dimethyl-1,10-phenanthroline) by hydrogen peroxide have been investigated in 0.1 M aqueous, borate-buffered sodium perchlorate in the pH range 6.6–8.6. The stoichiometry was determined to be $4\text{dmp} + 2\text{Cu}^{\text{II}} + \text{H}_2\text{O}_2 \rightarrow 2\text{Cu}(\text{dmp})_2^{2+} + \text{O}_2 + 2\text{H}^+$ by spectrophotometric measurements of the stable Cu(dmp)₂²⁺ product formed in the presence of either reactant in excess. The kinetics were investigated by the stopped-flow method by monitoring the appearance of Cu(dmp)₂²⁺(aq) within the concentration ranges $[\text{Cu}^{\text{II}}]_0 = (1.2\text{--}2.4) \times 10^{-5}$ M, $[\text{dmp}]_{\text{T}} = (1.8\text{--}36) \times 10^{-5}$ M, and $[\text{H}_2\text{O}_2]_{\text{T}} = (1.9\text{--}59.8) \times 10^{-3}$ M at ionic strength 0.1 M (NaClO₄) over the temperature range 25.0–45.0 °C. Under pseudo-first-order conditions, the rate is unaffected by buffer concentration and by the presence of oxygen. The reaction rate was first order in $[\text{Cu}^{\text{II}}]$ and $[\text{H}_2\text{O}_2]$, was inversely proportional to $[\text{H}^+]$, and reached a limiting rate at high $[\text{dmp}]$ at 25.0 °C. A mechanism is proposed which involves the rate-determining reduction of Cu(dmp)₂²⁺(aq) species by the acid-base pair H₂O₂–HO₂[•]. The consideration of mechanistic alternatives suggests that the high rate of reduction of copper(II) is explicable in terms of rate-determining electron transfer within bis(2,9-dimethyl-1,10-phenanthroline)peroxocopper(II) intermediate species present at very low concentrations. This would require little change of ligand geometry at the copper center. The results are related to observations in other copper–hydrogen peroxide catalytic systems.

Introduction

Current interest in the kinetics of copper ion catalyzed reactions of oxygen and hydrogen peroxide^{3–5} reflects the ability of the coordinated copper(II)–copper(I) couple to promote autoxidation in several important chemical and biological⁶ systems. In particular, the catalase-like activity of copper(II) complexes has been the subject of many investigations. We are interested in the mechanisms of the primary steps of reactions of this nature and have investigated the stoichiometry and kinetics of the reduction of copper(II) complexes of the bidentate ligand 2,9-dimethyl-1,10-phenanthroline (dmp) by a number of nonmetallic redox reagents. Copper(II) complexes of this ligand are particularly suitable for the study of such primary processes because of the thermodynamic and kinetic stability of the Cu^I(dmp)₂ product formed at neutral pH in the presence of excess ligand.¹ In addition, the ligand is practically nondegradable under the reaction conditions.

The results of a previously reported kinetic study¹ of the reduction of Cu^{II}-dmp complexes by SCN[−] and thiourea in aqueous sodium perchlorate were interpreted in terms of the existence of Cu(dmp)(reductant) and Cu(dmp)OH(reductant) species in rapid equilibrium *prior* to a rate-determining reaction of Cu(dmp)OH(reductant) with another reductant molecule. The lability and weakly oxidizing character of Cu(dmp)_x²⁺(aq) ($x = 1$ or 2) may be such as to favor greatly inner-sphere oxidation reactions of these species.

With the aim of providing a better understanding of copper(II)–copper(I) catalytic systems involving hydrogen peroxide, we have investigated the stoichiometry and kinetics of the reduction of copper(II) by hydrogen peroxide in the

presence of dmp over the pH range 6.6–8.6. The stoichiometry was investigated by standard analytical procedures and the kinetics were monitored by stopped-flow spectrophotometry in sodium hydroxide–boric acid buffers at ionic strength 0.1 M in the temperature range 25.0–45.0 °C.

Experimental Section

Reagents. The preparation and standardization of the copper, dmp, sodium perchlorate, and boric acid–sodium hydroxide buffer solutions were carried out as previously described.¹ A solution of cerium(IV) sulfate was standardized against sodium oxalate.⁷ Solutions of stabilizer-free hydrogen peroxide were then standardized against the cerium(IV) solution before each run; ferroin was used as the indicator. All other chemicals were of reagent grade and triply distilled water was used throughout.

Stoichiometry Measurements. A crude sample of the product of the reaction was obtained by the addition of a solution of 0.5 g of dmp (in 10 ml of methanol) to an aqueous solution containing 0.46 mmol of Cu^{II}(ClO₄)₂ in the presence of a slight excess of H₂O₂. The orange solid which rapidly formed was recrystallized from methanol giving deep red, diamond-shaped crystals. Complete elemental analysis of this substance (by the University Microanalytical Laboratory and by Alfred Bernhardt Mikroanalytisches Laboratorium, West Germany) showed it to be [Cu(dmp)₂]ClO₄.

The stoichiometry of the reaction was investigated by addition of aliquots of a standard copper(II) solution to a known excess of hydrogen peroxide in the presence of excess dmp. The concentration ranges employed were $[\text{Cu}^{\text{II}}]_0 = (0.4\text{--}16) \times 10^{-5}$ M, $[\text{dmp}]_{\text{T}} = (0.7\text{--}22) \times 10^{-4}$ M, and $[\text{H}_2\text{O}_2]_0 = 2.0 \times 10^{-3}$ M. The concentration of the Cu^I(dmp)₂ complex produced was measured spectrophotometrically ($\epsilon_{454} 6160$).^{1,8} A smaller number of measurements were made with $[\text{Cu}^{\text{II}}]_{\text{T}} = 1.60 \times 10^{-4}$ M, $[\text{dmp}]_{\text{T}} = 5.0 \times 10^{-4}$ M, and $[\text{H}_2\text{O}_2]_0 = (2.0\text{--}7.0) \times 10^{-5}$ M, employing matched 10- and 100-mm quartz cells as appropriate. Wehry et al.⁸ have detected significant