Thus, the influence of solvation upon the charge-transfer spectra affects the positions, but roughly not the intensities, of the band maxima. Nothing can be said about the modification of the d–d transition bands, when changing from $H_2O$ to DMF solvent, as the spectrophotometric study of the aqueous solutions was not made over 800 nm.


## Summary

The spectrophotometric analysis of the copper(II) chloride in dimethylformamide solutions and the numerical treatment of optical densities from the ultraviolet, visible, and near-infrared regions show accurately the presence of four absorbing species: the free copper(II) ion and the three mono-, tri-, and tetrachloro complexes. The absence of $CuCl_2$ can be attributed to auto complex formation, due to the similar coordinating properties of the solvent and the ligand.

The overall stability constants are found to be much higher than in aqueous solutions: $\log \beta_1 = 3.76 \pm 0.13$; $\log \beta_3 = 9.78 \pm 0.18$; $\log \beta_4 = 10.78 \pm 0.17$.

The charge-transfer bands of the individual calculated spectra have maxima at 268 nm for $CuCl^+$, at 300, 385, and 440 nm for $CuCl_3^-$, and at 296 and 411 nm for $CuCl_4^{2-}$. Their broad d–d transition bands are centered at 870 nm for $CuCl^+$, at 1100 nm for $CuCl_3^-$, and at 1200 nm for $CuCl_4^{2-}$. This quantitative information about the d–d bands is, to our knowledge, given for the first time for chlorocuprates in solution. It enables the structural conclusion that, in DMF, $CuCl^+$ probably is the square-planar ion $CuCl(DMF)_3^+$ and that $CuCl_3^-$ and $CuCl_4^{2-}$ are flattened tetrahedrons with one molecule of DMF coordinated to copper in the $CuCl_3(DMF)^-$ ion of $D_{2d}$ symmetry.


**Acknowledgment.** We thank Dr. J. Thomann, Ingénieur at the Computer Center of The Nuclear Research Center of the CNRS at Strasbourg, for his gracious help in the numerical analysis necessary to build up our new computer program, used for the treatment of spectrophotometric data.

**Registry No.** $CuCl(DMF)_3^+$, 73824-84-7; $CuCl_3(DMF)^-$, 73824-85-8; $CuCl_4^{2-}$, 44000-59-1.

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# Electron-Transfer Reactions of Copper Complexes. 1. A Kinetic Investigation of the Oxidation of Bis(1,10-phenanthroline)copper(I) by Hydrogen Peroxide in Aqueous and Sodium Dodecyl Sulfate Solution

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*Received October 12, 1979*

The kinetics and stoichiometry of the hydrogen peroxide oxidation of Cu(I) to Cu(II) have been investigated for the bis(1,10-phenanthroline) complex in both aqueous and micellar sodium dodecyl sulfate solution. At pH 5.8 (phosphate buffer, $\mu_{tot} = 0.15$ M) the Cu(I):$H_2O_2$ stoichiometry is 2:1. Under pseudo-first-order conditions the reaction rate is first order in oxidant and reductant, is zero order in hydrogen ion ($5.8 \leq pH \leq 7.8$), and reaches a limiting value at high phenanthroline concentrations. The following rate parameters are obtained in the presence of excess ligand: $k_2 = (3.91 \pm 0.06) \times 10^3$ $M^{-1}$ $s^{-1}$, $\Delta H^{\ddagger} = 5.8 \pm 0.4$ kcal/mol, and $\Delta S^{\ddagger} = -24 \pm 1$ eu. Carrying out the reaction in 0.05 M sodium dodecyl sulfate changes the Cu(I):$H_2O_2$ stoichiometry to 1:1, removes the phenanthroline dependence, and slows the reaction 20-fold. A mechanism involving electron transfer by OH radicals is proposed. The implications of the relatively modest micelle effects are discussed. Comparisons are made between metal–micelle complexes and redox metalloproteins with kinetically accessible active sites.

## Introduction

Although there have been many investigations of organic reactions in detergent media,[1] there have been very few reports on micelle effects on electron-transfer reactions involving metal systems. These few include studies of inner- and outer-sphere redox reactions on polyelectrolyte[2,3] and micellar surfaces[4,5] as well as micellar photoredox reactions.[6] In this paper we report a kinetic study of the influence of sodium dodecyl sulfate (SDS) micelles on the rate of Cu(I) oxidation in aqueous solution.[7] Rate studies in surfactant media can provide mechanistic details about electrostatic and hydrophobic influences on not only inorganic redox reactions but also biological electron transfers which take place on membrane surfaces or at protein–substrate interfaces.

A better understanding of electron transfer in copper and iron metalloproteins has come from a study of their reactions with inorganic redox reagents.[8] Useful insights have resulted from comparing the protein–inorganic electron-transfer processes to those that occur between two inorganic complexes.

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(7) The following nomenclature will be used throughout this paper: phen = 1,10-phenanthroline; dmp = 2,9-dimethyl-1,10-phenanthroline; bpy = 2,2′-bipyridyl; SDS = sodium dodecyl sulfate, cmc = critical micelle concentration.
(8) See the following references and the references cited therein: (a) L. E. Bennett, *Prog. Inorg. Chem.*, **18**, 1 (1973); (b) S. Wherland and H. B. Gray in "Biological Aspects of Inorganic Chemistry", A. W. Addison, W. R. Cullen, D. Dolphin, and B. R. James, Eds., Wiley, New York, 1977, p 289; (c) N. Sutin, *Inorg. Biochem.*, **2**, Chapter 19 (1973).

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Unfortunately, there has been very little work on the oxidation mechanisms of inorganic Cu(I) because of its instability in aqueous solution. Unless studies are done at very low pH or in the presence of aromatic chelates, the Cu(I) disproportionates to Cu(II) and Cu(0). In addition, most Cu(I) complexes are very sensitive to oxidation by $O_2$, and those that are stable are often relatively insoluble. Our system involves the oxidation of $Cu(phen)_2^+$ by hydrogen peroxide at pH 6. An advantage of the micellar system is that it slows down the rate of $O_2$ oxidation and increases the solubility of the Cu(I) salt.

Many of the electron-transfer studies in surfactant or polyelectrolyte media have involved redox reagents of like charge which compete for binding sites on an oppositely charged surface. From our own work we find that such competition can make interpretation of kinetic data ambiguous.[9] In order to characterize micellar effects on electron-transfer reactions in the most straightforward way, we have thus chosen to study a system where one reagent, hydrogen peroxide, is uncharged.

## Experimental Section

**Chemicals.** Reagent grade chemicals and deionized, distilled water were used throughout. Sodium dodecyl sulfate (99%), purchased from British Drug House, was used for all kinetic and spectral studies without further purification. All solutions were used within 12–16 h of preparation.

The $Cu(phen)_2HSO_4$ complex was synthesized by using the procedure of Jardine et al.,[10] by substituting bisulfate for nitrate as the counterion. Anal. Calcd for $Cu(phen)_2HSO_4$: C, 55.33; H, 3.29; S, 6.14; Cu, 12.19. Found: C, 55.26; H, 3.52; S, 5.85; Cu, 11.92. An infrared spectrum of the product (KBr pellet) showed absorptions characteristic of ligand and copper–nitrogen vibrations.[11] In addition, there was a strong absorption at 1250 $cm^{-1}$, characteristic of a bisulfate group.[12]

**Techniques.** Since aqueous $Cu(phen)_2^+$ is extremely oxygen sensitive, scrupulous anaerobic techniques were used for all transfers. Solutions were degassed by using argon passed through two chromous scrubbing towers to remove oxidizing impurities. Transfers were made with Hamilton gastight syringes fitted with Teflon needles. Typically, Cu(I) solutions were prepared by transferring a weighed amount of $Cu(phen)_2HSO_4$ to a serum bottle fitted with a rubber septum. After the bottle was degassed, a known volume of buffer was added. Aliquots of this stock solution were then transferred with a gastight syringe to the detergent solution used for spectral or kinetic studies. Argon was bubbled slowly through detergent solutions to avoid frothing. Care was taken to exclude halide ions which gave marked spectral changes indicative of an alteration in the Cu(I) coordination.

Hydrogen peroxide solutions were prepared in a similar fashion. To avoid trace-metal contamination, we washed glassware with metal-free soap and transferred all solutions with the use of Teflon fittings. Peroxide concentrations were usually determined by iodometric techniques,[13] although a titanyl sulfate method[14] was used for certain spectral determinations (see below).

Unless otherwise indicated, all kinetic and spectral work was done in phosphate buffer (0.10 M, pH 5.8, $\mu_{tot}$ = 0.15 M [$Na_2SO_4$]). To avoid differential neutralization of the micelle surface and changes in micelle size due to varying concentrations of counterion,[1a] we maintained the total sodium ion concentration at 0.15 M in all detergent solutions.

The spectra of all copper solutions were measured under an argon atmosphere on a Cary 14 UV–vis spectrophotometer using anaerobic 1-cm quartz cells. Stoichiometry experiments were done by monitoring the loss of Cu(I) absorbance at either 410 (aqueous) or 440 nm (micellar) caused by the addition of aliquots of peroxide. Copper(II) phenanthroline has no absorption in this region. Attempts to oxidize Cu(II) by $Na_2IrCl_6$ and $H_2O_2$ were monitored by determining oxidant concentrations under the following conditions: $[Cu(phen)_2^+] = 10^{-4}$ M; $[phen] = 2 \times 10^{-3}$ M; $[IrCl_6^{2-}] = 2 \times 10^{-4}$ M or $[H_2O_2] = 0.05$ M. Iridium concentrations were measured at $\lambda_{max}$ 488 nm ($\epsilon$ 4050 $M^{-1}$ $cm^{-1}$); $H_2O_2$ concentrations were determined by titanyl sulfate analysis.[14] The $H_2O_2$ oxidation of phenanthroline was monitored at $\lambda_{max}$ 263 nm ($\epsilon$ $2.8 \times 10^4$ $M^{-1}$ $cm^{-1}$) with $[phen] = 2 \times 10^{-5}$ M and $[H_2O_2] = 5 \times 10^{-2}$ M.

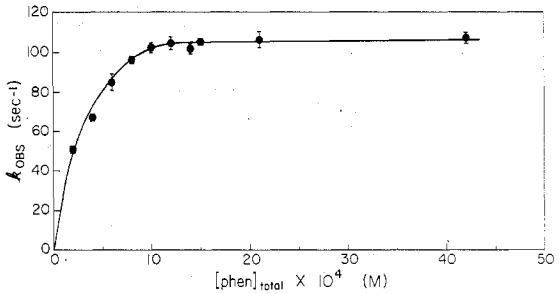


**Figure 1.** Plot of $k_{obsd}$ as a function of $[phenanthroline]_{tot}$ for the oxidation of Cu(I) by hydrogen peroxide in aqueous solution at pH 5.8 ($[Cu(I)] = 10^{-4}$ M, $[H_2O_2] = 2.5 \times 10^{-2}$ M, $\mu$ = 0.15 M). All studies were done at 25 °C in phosphate buffer.

**Kinetics.** A Durrum Model D-110 stopped-flow spectrophotometer was used for all kinetic measurements. Solutions were introduced into the drive syringes by using anaerobic glass vessels fitted with three-way Teflon valves. Conditions for a typical kinetic run for the aqueous solutions were $[Cu(phen)_2^+] = 5.0 \times 10^{-5}$ M, $[H_2O_2]$ = 0.0005–0.05 M, and $[phen] = 10^{-3}$ M and for the micellar solution were $[Cu(phen)_2^+] = 2.5 \times 10^{-5}$ M, $[H_2O_2]$ = 0.0005–0.05 M, and [SDS] = 0.05 M. Kinetic data were obtained by monitoring the loss of the Cu(I) peak. Absorbance–time data were recorded either on a nine-track tape or as photographs of traces from a Tektronix Model 5B10N oscilloscope. In the former case signals were collected by a home-built data acquisition system (DAS) interfaced to the stopped-flow apparatus. All kinetic plots and analyses were done on a PDP-11 computer using standard kinetic programs. Plots of log $(A - A_\infty)$ vs. time were linear for 90–95% of each reaction. The reported values of each $k_{obsd}$ are an average of at least three to four independent runs.

## Results

**Aqueous Chemistry.** Stoichiometry measurements using either excess Cu(I) or excess $H_2O_2$ are consistent with reaction 1.

$$2Cu(I) + H_2O_2 \xrightarrow{phen} 2Cu(II) + 2OH^- \qquad (1)$$

Both monovalent and divalent copper species can catalyze the hydrogen peroxide oxidation of organic molecules.[15,16] In the absence of copper we observe a very slow reaction between phenanthroline and peroxide, as evidenced by the appearance of a yellow solution ($k = 4 \times 10^{-9}$ $M^{-1}$ $s^{-1}$, initial rates). Over a 6-day period of monitoring $H_2O_2$ in a solution of copper(II) phenanthroline there was no observable loss of peroxide. Since the reaction between $H_2O_2$ and Cu(I) results in a colorless solution with no evidence of phenanthroline decomposition, we conclude that on the time scale of our stoichiometric and kinetic measurements (following section) there are no additional reactions competing with the oxidation of Cu(I).

**Kinetics.** The oxidation of $Cu(phen)_2HSO_4$ was studied under pseudo-first-order conditions by using an excess of hydrogen peroxide. The reaction is first order in Cu(I) as evidenced by the exponential relationship between absorbance change and time. Consistent with the existence of both the mono- and bis(phenanthroline)copper(I) species,[17] rate acceleration is observed with increasing phenanthroline con-

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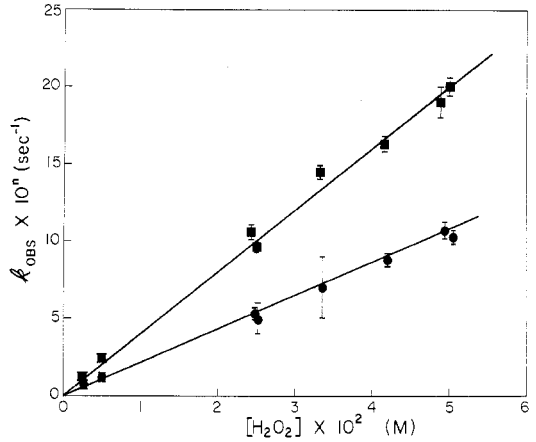


**Figure 2.** Plot of $k_{obsd} \times 10^{-1}$ as a function of $[H_2O_2]$ for the oxidation of $Cu(phen)_2^+$ by hydrogen peroxide in aqueous solution at pH 5.8, ■ ($[Cu(phen)_2^+] = 5.0 \times 10^{-5}$ M, [phen] = $10^{-3}$ M, $\mu$ = 0.15 M), and plot of $k_{obsd}$ as a function of $[H_2O_2]$ for the same reaction in sodium dodecyl sulfate solution, ● ($[Cu(phen)_2^+] = 2.5 \times 10^{-5}$ M, [SDS] = $5 \times 10^{-2}$ M, $[Na^+]$ = 0.15 M). All studies were done at 25 °C in phosphate buffer.

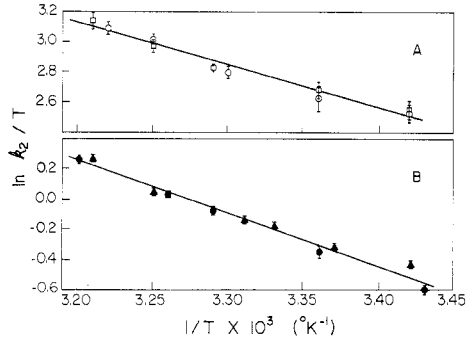


**Figure 3.** Eyring plot of rate data for oxidation of $Cu(phen)_2^+$ by hydrogen peroxide: (A) aqueous ($[Cu(phen)_2^+] = 5.0 \times 10^{-5}$ M, [phen] = $10^{-3}$ M, $\mu$ = 0.15 M, $[H_2O_2] = 1.25 \times 10^{-2}$ M (□), $[H_2O_2] = 2.5 \times 10^{-2}$ M (○)); (B) micellar ($[Cu(phen)_2^+] = 2.5 \times 10^{-5}$ M, $[H_2O_2] = 5.0 \times 10^{-2}$ M, $[Na^+]$ = 0.15 M, [SDS] = $5.0 \times 10^{-2}$ M (▲), [SDS] = $10^{-1}$ M (●)). All studies were done at pH 5.8 (phosphate).

centration until the ligand:metal molar ratio is approximately 10:1 (Figure 1). All aqueous data were obtained at a ligand:metal ratio of 20:1. The reaction is independent of pH ($5.8 \leq$ pH $\leq 7.8$) and ionic strength (0.02 M $\leq \mu \leq$ 0.15 M), suggesting that the fully protonated $H_2O_2$ molecules are the oxidizing species. These data can be fit to the empirical rate expression (2) which, except for the lack of an $[H^+]$ term, has

$$k_{obsd} = \frac{A[H_2O_2][phen]}{1 + B[phen]} \quad (2)$$

the same form as that observed for the $H_2O_2$ reduction of $Cu(dmp)_2^{2+}$.[18]

The reaction shows a first-order dependence on peroxide (Figure 2). At high ligand concentrations the value of the limiting second-order rate constant, obtained from a least-squares fit of the data in Figure 2, is $A/B = (3.90 \pm 0.06) \times 10^3$ $M^{-1}$ $s^{-1}$. An Eyring plot of the temperature-dependence data is linear over a 20 °C range (Figure 3A). Activation parameters are $\Delta H^{\ddagger} = 5.8 \pm 0.4$ kcal/mol and $\Delta S^{\ddagger} = -24 \pm 1$ eu.

Several experiments were performed to determine if the reaction involves a Cu(III) or an OH radical intermediate. The redox reaction was monitored at 350 nm where copper-

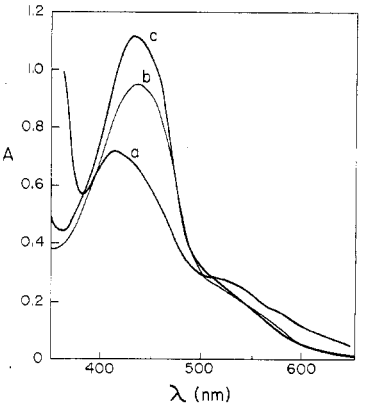


**Figure 4.** Visible spectra of $Cu(phen)_2^+$ in various aqueous solutions: a, $1.6 \times 10^{-2}$ M phenanthroline; b, 0.05 M SDS; c, 50% *tert*-butyl alcohol. All spectra were recorded at ambient temperatures under the following conditions: $[Cu(phen)_2^+] = 1.75 \times 10^{-4}$ M and pH 5.8 (phosphate).

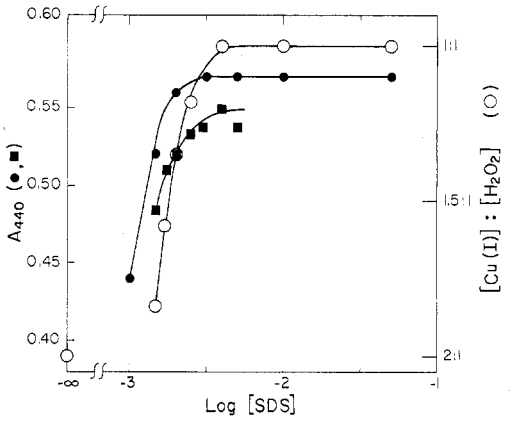


**Figure 5.** (■, ●) Variation of $Cu(phen)_2^+$ absorbance at 440 nm as a function of log [SDS]: ■, pH 5.8 (phosphate, $[Na^+]$ = 0.15 M); ●, pH 6.0 (cacodylate, $[Na^+]$ = 0.2 M). (○) Variation of $[Cu(phen)_2^+]:[H_2O_2]$ stoichiometry as a function of log [SDS]: pH 5.8 (phosphate, $[Na^+]$ = 0.15 M). All spectral data were measured at ambient temperatures; in each experiment, $[Cu(phen)_2^+] = 10^{-4}$ M.

(III) peptides exhibit a strong absorbance.[19,20] There was no evidence for a transient Cu(III) species. Attempts to oxidize the Cu(II) complex with either $IrCl_6^{2-}$ or $H_2O_2$ (in the absence of Cu(I)) were unsuccessful. Addition of ethanol, a known radical scavenger, changes the Cu(I):$H_2O_2$ stoichiometry from 2:1 to 1:1 over the range 1 M $\leq$ EtOH $\leq$ 10 M. Carrying out the oxidation in the presence of an OH radical trap, *N*,*N*-dimethyl-*p*-nitrosoaniline,[21] results in complete decolorization of the trap molecule. However, this result is inconclusive since control experiments showed some reaction with Cu(I) in the absence of peroxide.

**Micelle Chemistry.** The degree of solute–micelle association can be estimated by monitoring any accompanying absorbance change. The dominant peak in the visible spectrum of $Cu(phen)_2^+$ (Figure 4, curve a) has been assigned to a metal to ligand charge-transfer band.[22] In organic solvents such as *tert*-butyl alcohol (curve c), $\lambda_{max}$ is both red shifted and more intense than it is in aqueous solution. Since the spectrum of $Cu(phen)_2^+$ in SDS (curve b) above the cmc is similar to that in *tert*-butyl alcohol, this can be taken as evidence for a metal

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environment less polar than that in aqueous solution and, hence, for some type of micellar association.

A plot of copper(I) phenanthroline absorbance at 440 nm vs. log [SDS] in both phosphate and cacodylate buffers is shown in Figure 5. The onset of micelle formation at [SDS] $\cong 1.5 \times 10^{-3}$ M (phosphate; $[Na^+] = 0.15$ M) or at [SDS] $\cong 1.0 \times 10^{-3}$ M (cacodylate; $[Na^+] = 0.2$ M) is intermediate between literature cmc values of $2.3 \times 10^{-3}$ ($[Na^+] = 0.05$ M) and $0.94 \times 10^{-3}$ M ($[Na^+] = 0.2$ M).[1a] Solutions are turbid at detergent concentrations less than the cmc, a phenomenon also observed by other works in metal ion–SDS systems.[6] This can be attributed to ion-pair formation between the metal and several detergent head groups, resulting in an insoluble aggregate which has hydrophobic tails pointing toward the bulk solution.

The spectral data are consistent with equilibrium 3, where

$$Cu(phen)_{1,2}^+ + M \overset{K_M}{\rightleftharpoons} Cu(phen)_2^+\text{–}M \quad (3)$$

$Cu(phen)_{1,2}^+$ includes both the mono- and bischelated forms of Cu(I) in aqueous solution, $Cu(phen)_2^+$–M represents the bischelated micellar complex (the presence of only the bis complex is inferred from kinetic data; see below), M is the micelle, and $K_M$ is a measure of the metal complex–micelle association. The value of $K_M$ per detergent head group is given by

$$K/N = [Cu(phen)_2^+\text{–}M]/[Cu(phen)_{1,2}^+][CD - cmc] \quad (4)$$

where

$$[M] = [CD - cmc]/N \quad (5)$$

$N$ is the aggregation number, and CD is the total detergent concentration. By estimating the concentrations of the Cu(I) species from the limiting and measured absorbances in Figure 5, we obtain an approximate value of $K/N = (9 \pm 1) \times 10^3$ $M^{-1}$ in both phosphate ($[Na^+] = 0.15$ M) and cacodylate ($[Na^+] = 0.2$ M) buffers.

Stoichiometry measurements monitoring either oxidant or reductant in SDS solution indicate a Cu(I):$H_2O_2$ ratio of 1:1, unlike the 2:1 ratio found in aqueous solution. Changes in the reaction stoichiometry were measured as a function of detergent concentration. As seen in Figure 5, the stoichiometry changes parallel the onset of $Cu(phen)_2^+$–micelle association determined by independent spectral measurements. Control experiments showed no reaction between SDS and peroxide.

**Kinetics.** The hydrogen peroxide oxidation of $Cu(phen)_2HSO_4$ was studied in 0.05 M SDS solution (pH 5.8, phosphate buffer, $[Na^+] = 0.15$ M, $[Cu(I)] = 2.5 \times 10^{-5}$ M). From eq 5 we calculate the concentration of the micelles to be $(5\text{–}10) \times 10^{-4}$ M (cmc $\cong 1.5 \times 10^{-3}$ M; $50 < N < 100$). The 20–40-fold excess of micelles over copper insures that there is no more than one metal complex per micelle.

Rate data indicate a first-order dependence on Cu(I). Unlike the aqueous case, the addition of excess phenanthroline has no effect on either the visible spectrum of the Cu(I) solution or the rate of the oxidation by hydrogen peroxide. Therefore, in SDS solution the mono(phenanthroline)copper(I) species is stoichiometrically insignificant. The oxidation is independent of pH ($5.8 \leq pH \leq 7.8$). As shown in Figure 2, the reaction is first order in oxidant over a 100-fold concentration range, and for any given peroxide concentration, it is 20 times slower than that in aqueous solution. Assuming a simple second-order rate law, we calculate a rate constant $k = (2.04 \pm 0.03) \times 10^2$ $M^{-1}$ $s^{-1}$.

In many micellar reactions rate contributions from both the aqueous and micellar phases result in a variation of $k_{obsd}$ at low detergent concentrations. In our system $k_{obsd}$ remains constant ($1.5 \times 10^{-3}$ M $\leq$ [SDS] $\leq$ 0.1 M), and therefore kinetic data characterize the micellar reaction only. It was not possible to make kinetic measurements at lower detergent concentrations since solutions were turbid (see above).

Temperature-dependence data were obtained at two different SDS concentrations, 0.05 M and 0.1 M. The Eyring plot (Figure 3B) is linear over a 20 °C range. The activation parameters, averaged from the two determinations, are $\Delta H^\ddagger = 6.6 \pm 0.4$ kcal/mol and $\Delta S^\ddagger = -25 \pm 1$ eu. Within experimental error, the concentration of SDS has no effect on these values.

## Discussion

**Aqueous Chemistry.** From stoichiometric and kinetic data, mechanism (6)–(8) is proposed for the oxidation of Cu(I) by

$$Cu(phen)^+ + phen \overset{K_1}{\rightleftharpoons} Cu(phen)_2^+ \quad \text{(fast)} \quad (6)$$

$$Cu(phen)_2^+ + H_2O_2 \xrightarrow{k_2} Cu(phen)_2^{2+} + OH + OH^- \quad (7)$$

$$Cu(phen)_2^+ + OH \xrightarrow{k_3} Cu(phen)_2^{2+} + OH^- \quad \text{(fast)} \quad (8)$$

$H_2O_2$ in aqueous solution. The predicted rate law for the rate-determining step, (7), is

$$-d[Cu(I)]/dt = k_{obsd}[Cu(I)]_{tot} \quad (9)$$

where

$$k_{obsd} = K_1k_2[H_2O_2][phen]/(1 + K_1[phen]) \quad (10)$$

All kinetic data are consistent with bis(phenanthroline)copper(I) as the reducing species. From separate experiments monitoring the equilibrium in eq 6 we calculate a value of $3 \times 10^5$ $M^{-1}$ for $K_1$ (eq 9). Therefore, the mono(phenanthroline)copper(II) species accounts for less than 1% of the total Cu(I) under the conditions of our aqueous kinetic studies.

The $H_2O_2$ oxidation of transition-metal ions is generally believed to proceed by a radical mechanism[23] as shown in eq 7 and 8, rather than by an initial two-electron transfer. Most redox reactions involving Cu(I) are one-electron processes, although Cu(III) has been proposed as an intermediate in several reactions. These include the $H_2O_2$ oxidation of CuCl in acid solution[24] and the $O_2$ oxidation of galactose by the enzyme galactose oxidase.[25] Although we cannot rule out a Cu(III) intermediate, our results are most consistent with a radical mechanism for two reasons. First, the phenanthroline ligands are too bulky to allow a formation of a square-planar species, the presumed geometry for $d^8$ Cu(III) complexes. Second, a radical mechanism is supported by the change in reaction stoichiometry upon addition of SDS since this surfactant is known to react with OH radicals.[6] This is similar to the $H_2O_2$ oxidation of certain Co(II) macrocycles where the unexpected 1:1 stoichiometry has been explained by OH scavenging of H atoms from the ligand.[26] The change in Cu(I):$H_2O_2$ stoichiometry in aqueous solution caused by the addition of ethanol cannot be considered proof of either mechanism since the alcohol reacts rapidly with both OH and Cu(III).[27,28]

(23) There have been numerous studies of the peroxide oxidation of transition-metal species, both aquo and complexed. For example, see the following works and references cited therein: (a) R. E. James and F. Sicillio, *J. Phys. Chem.*, **74**, 1166 (1970); (b) C. Walling and S. Kato, *J. Am. Chem. Soc.*, **93**, 4275 (1971); (c) P. B. Chock, R. B. K. Dewar, J. Halpern, and L. Y. Wong, *ibid.*, **91**, 82 (1969); (d) G. Davies, N. Sutin, and K. O. Watkins, *ibid.*, **92**, 1892 (1970).
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Our conclusions disagree with those of Gorbunova and coworkers, who claim a Cu(III) intermediate is involved in the $H_2O_2$ oxidation of $Cu(bpy)_2^+$.[21] Their main argument is that calculated rate constants for the reaction between the intermediate and added alcohol are always two orders of magnitude smaller than the measured alcohol–radical rate constants. It is unlikely that the situation is this straightforward. In the analogous Fenton reagent system ($Fe^{2+}$, $H_2O_2$, organic substrate) there are numerous side reactions involving secondary radicals which affect the overall reaction stoichiometry.[29] The Cu system is likely to be at least as complex, and additional reactions of secondary radicals must be considered before rate constants are calculated from stoichiometry changes.

An inner-sphere mechanism is likely for the $H_2O_2$ oxidation of $Cu(phen)_2^+$ since the complex is tetrahedral[22,30] and a change to the preferred Cu(II) coordination of 5 or 6[31,32] would occur prior to electron transfer. Augustin and Yandell have suggested that the greatest barrier to Cu(I,II) electron transfer comes from changing the coordination number of the two copper oxidation states.[33] This being the case, we might expect that oxidations of Cu(I) complexes would have similar activation enthalpies, regardless of whether the reaction is inner sphere or outer sphere. Although there is limited data for comparison, the activation enthalpy obtained in our study ($\Delta H^\ddagger$ = 5.8 kcal/mol, pH 5.8) is similar to values for both the inner-sphere oxidation of $Cu^+$ by several substituted cobalt(III)–pentaamine complexes ($\Delta H^\ddagger$ = 3.9–5.4 kcal/mol, pH <1)[34,35] as well as the outer-sphere oxidation of $Cu(phen)_2^+$ by $Co(EDTA)^-$ ($\Delta H^\ddagger$ = 6.1 kcal/mol, pH 6.0).[36] In the $[Co(en)_2(SCH_2CO_2)]^+$ oxidation of $Cu^+$, where an intramolecular electron transfer is proposed to be the rate-limiting step, the activation enthalpy ($\Delta H^\ddagger$ = 21 kcal/mol, pH 1)[37] is considerably higher than the values reported above.

Davies has suggested the possibility of an analytically insignificant but kinetically important metal–peroxo complex in the $H_2O_2$ reduction of Cu(II)–dmp.[18] From the observed first-order dependence on peroxide, an upper limit of $K = 6 \times 10^6$ $M^{-1}$ is calculated for the formation of such a complex. Doing a similar treatment for our system

$$Cu(phen)_2^+ + H_2O_2 \overset{K_2}{\rightleftharpoons} Cu(phen)_2{\cdot}H_2O_2^+ \quad (11)$$

$$Cu(phen)_2{\cdot}H_2O_2^+ \xrightarrow{k_4} Cu(phen)_2OH^+ + OH \quad (12)$$

we calculate $K_2 \leq 2$ $M^{-1}$.[38] This value, 6 orders of magnitude lower than that for the Cu(II)–dmp species, is consistent with the fact that Cu(I) has little tendency to increase its coordination number.

**Micelle Chemistry.** Association of $Cu(phen)_2^+$ with anionic SDS micelles is indicated by both a bathochromic shift and a decrease in the rate of oxidation by hydrogen peroxide upon addition of detergent to a solution of the copper complex. The value of the micellar association constant, $K/N = 9 \times 10^3$ $M^{-1}$ ($[Na^+]$ = 0.15–0.2 M), is similar to $K/N = 4 \times 10^3$ $M^{-1}$ ($[Na^+]$ = 0.5 M) reported for binding of $Fe(phen)_2(CN)_2$ to SDS micelles.[5,39] Both spectral and kinetic data indicate a strong hydrophobic association in the latter complex. Nothing definitive can be said about the location of the metal complex in the micelle. Nonetheless, the 1+ charge, the hydrophobic ligand, and the high association constant all suggest strong electrostatic and hydrophobic solute association, presumably near the anionic micelle surface. With the use of the terminology recently proposed by Menger, the copper complex would be located in the Stern "region"[40] surrounded by hydrocarbon tails, head groups, counterions, and solvent. The immediate environment would have a polarity approximately equal to that of methanol, rather than that of pure hydrocarbon in the center. Thus, it is not surprising that our aqueous and micellar rate constants only differ by essentially one order of magnitude.

Although the micelle rate inhibition is not dramatic, we still find it difficult to explain the 20-fold inhibition by SDS. In some reactions, where electrostatic factors can be ruled out, rate inhibition has been attributed to the micelle pulling the solute molecule inside and making it kinetically less accessible.[5] Considering the likelihood that the cationic copper complex is located in the Stern "region", it seems improbable that micellar association could hinder approach of a neutral peroxide molecule.

We can account for the observed rate effects if the reduction potential of $Cu(phen)_2^+$ is changed upon forming a micelle complex. Decreasing solvent polarity is known to increase the reduction potential of cationic metal complexes and in this case it would result in a smaller thermodynamic driving force for the reaction. If no other factors are considered, a 20-fold increase in reaction rate would require a 0.16-V drop in $\Delta E^\circ_{ox} - \Delta E^\circ_{red}$. Experimental data are consistent with such an interpretation: in aqueous solution at pH 7 the reduction potential of the $Cu(phen)_2^{2+/1+}$ couple is 0.174 V; in 50% dioxane–water it is 0.296 V.[17] The extent of this effect must await studies on the redox potential of the Cu(I)–micelle species.

It is also possible that rate inhibition arises from ion pair formation between the Cu(I) complex and an anionic head group, resulting in hindered approach of the peroxide molecule. Such an interpretation is supported by the probable existence of ion pairs at SDS concentrations below the cmc, where solutions are turbid. At higher SDS concentrations the Cu(I)–detergent complex would be solubilized without necessarily disrupting the electrostatic interaction. Parallel experiments in a nonionic detergent system, now in progress, should help resolve this question.

The activation parameters for the aqueous and micellar systems are very similar. The 20-fold rate inhibition requires an 1.8 kcal/mol increase in $\Delta G^\ddagger$, which is observed within our experimental error. Bunton was cautioned against attaching too much significance to values of activation parameters for reactions in detergent solution because of potential artifacts arising from the micelles.[1c] Nonetheless, at two different detergent concentrations, the activation parameters are the same within experimental error and are remarkably close to the aqueous values as well. This would support Menger's claim that medium effects do not dramatically alter reactions taking place in the Stern "region".[40]

Micelle formation parallels the change in reaction stoichiometry exactly (Figure 5). The concentration of SDS necessary to cause this change is over 3 orders of magnitude smaller than that required for ethanol. Therefore, we conclude that the stoichiometry change comes from the association of micelles with the Cu(I) complex, rather than from the presence of scavenger molecules distributed homogeneously in solution. Once generated within the micelle (or at the surface) the OH

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radical reacts with a detergent molecule before it can diffuse away to oxidize another Cu(I).

Structural similarities between aqueous micelles and globular proteins have prompted the investigation of micelle systems as possible enzyme models.[1b] In general, micelle-associated species are poor models for enzymes because the dynamic equilibrium between monomer and aggregate does not allow duplication of critical protein–substrate interactions. Several iron and copper metalloproteins have kinetically accessible active sites which seem to transfer electrons as if they were simple transition-metal species.[8b] In these cases, where there appears to be no unique polypeptide contribution to the redox event, a metal–micelle complex may well mimic some of the features of the protein. Although we must exercise caution in drawing parallels between micelle and protein systems, the similarity in our aqueous and detergent rate data support Gray's arguments that metalloproteins with kinetically accessible sites should transfer electrons like simple inorganic complexes.[8b]

Studies with charged oxidants now in progress in our lab show, like this work, that aqueous and detergent rate constants usually agree within a factor of 10. This suggests that the metal center in the micelle is kinetically accessible and there is only a modest effect arising from association with amphipathic molecules.

**Acknowledgment** is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, to the Research Corp., and to the Faculty Research Committee, University of California, Santa Cruz, for support of this research. M.A.d.A. was supported by a fellowship from the Conselho Nacional de Desenvolvimento Cientifico e Tecnológico-CNPq-Brasil.

**Registry No.** $Cu(phen)_2^+$, 17378-82-4; $H_2O_2$, 7722-84-1; $Cu(phen)_2HSO_4$, 73697-83-3.

**Supplementary Material Available:** A table, giving experimental kinetic data (3 pages). Ordering information is given on any current masthead page.

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# Parametric Correlation of Formation Constants in Aqueous Solution. 2. Ligands with Large Donor Atoms

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*Received December 6, 1979*

The equation $\log K_1 = C_A^{aq}C_B^{aq} + E_A^{aq}E_B^{aq} - D_AD_B$ is used to correlate the formation constants in water of 266 different complexes involving 31 different Lewis acids with 16 different unidentate bases. The $C$ and $E$ parameters of each acid A and base B are identified with their tendency to undergo ionic or covalent bonding. The $D$ parameters are identified with desolvation effects, brought about by both steric hindrance to solvation and also alteration of the strength of solvation at specific sites. The latter effect is envisaged as operating through an alteration of the tendency of the acid to undergo ionic bonding by attachment of very covalent donor atoms, thereby weakening the bonds to the remaining coordinated water molecules. Correlations of the $C_B^{aq}$ parameters with the structural trans effect on infrared stretching frequencies and coupling constants in the NMR spectra are used to support the steric interpretation of the $D$ parameters, while analyses of gas-phase proton basicities are used to support the specific solvation interpretation. The hardness of the methyl carbonium ion in water is estimated.

In the first paper in this series[1] it was shown that the formation constants of the fluoride, hydroxide, and ammonia complexes of Lewis acids in aqueous solution could be correlated by eq 1. This equation is similar to that developed

$$\log K_1 = E_A^{aq}E_B^{aq} + C_A^{aq}C_B^{aq} \quad (1)$$

by Drago and co-workers[2] for the correlation of heats of adduct formation in solvents of low dielectric constant. $E$ and $C$ represent the tendency toward ionic and covalent bonding of Lewis acid A and base B. We have used $E^{aq}$ and $C^{aq}$ to avoid confusion with Drago's $E$ and $C$ parameters, which are not interchangeable with our own.

It was shown[1] that, for ligands with second- or third-row donor atoms, eq 1 was incapable of adequate correlation, and the deviations from the predictions of eq 1 were interpreted as being caused by steric hindrance to solvation. In this paper we consider this aspect further and discuss means of modifying eq 1 so as to predict correctly the formation constants of all unidentate ligands.

## LFER Diagrams

There is a distinct pattern in the behavior of formation constants that has led, for example, to the classification of Ahrland, Chatt, and Davies[3] into a- and b-type metal ions and Pearson's classification into hard and soft acids and bases.[4] At the same time, this pattern has led to many attempts at numerical correlation using four-parameter equations similar to eq 1, as in the pioneering work of Edwards.[5] This pattern can be illustrated conveniently in the LFER diagrams that we have developed.[1,6] In Figures 1–3 of the first paper in this series[1] we showed the LFER diagrams of log $K_1$ for $Ag^I$, $Bi^{III}$, and $Fe^{III}$ plotted against log $K_1$ for $Hg^{II}$ as a standard reference acid. In Figure 1 here is shown the LFER diagram for $Cd^{II}$. It is typical of such diagrams in that the relative positions of the ligands on the diagram are what we should expect if our standard reference acid $Hg^{II}$ has a greater tendency to covalent bonding, or is softer, than $Cd^{II}$. If all LFER diagrams were as "well-behaved" as Figure 1 (it is actually not completely "well-behaved", as will be seen in the following discussion), a four-parameter equation such as eq 1 would be adequate for the correlation of formation constants of all unidentate ligands. The problem is illustrated by a

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