

## Electron-Transfer Reactions of Copper Complexes. 2. Kinetic Investigation of the Oxidation of Bis(1,10-phenanthroline)copper(I) by Tris(acetylacetonato)cobalt(III) and (Ethylenediaminetetraacetato)cobalt(III) in Aqueous and Micellar Sodium Dodecyl Sulfate Solution<sup>1</sup>

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The kinetics of the  $\text{Co}(\text{acac})_3$  and  $\text{Co}(\text{EDTA})^-$  oxidations of  $\text{Cu}(\text{phen})_2^+$  have been investigated in both aqueous and micellar sodium dodecyl sulfate solution. Rate data indicate that the bis-chelated form of  $\text{Cu}(\text{I})$  is the only reducing species in aqueous solution. The reaction rate is first order in both oxidant and reductant and reaches a limiting value at high phenanthroline concentrations. The following rate parameters have been obtained at pH 6 (cacodylate,  $\mu = 0.25$  M, excess phenanthroline): for  $\text{Co}(\text{acac})_3$ ,  $k_2 = 756 \pm 2 \text{ M}^{-1} \text{ s}^{-1}$ ,  $\Delta H^\ddagger = 8.0 \pm 0.5 \text{ kcal/mol}$ ,  $\Delta S^\ddagger = -19 \pm 1 \text{ eu}$ ; for  $\text{Co}(\text{EDTA})^-$ ,  $k_2 = 448 \pm 1 \text{ M}^{-1} \text{ s}^{-1}$ ,  $\Delta H^\ddagger = 7.5 \pm 0.5 \text{ kcal/mol}$ ,  $\Delta S^\ddagger = -21 \pm 1 \text{ eu}$ . In 0.1 M SDS solution both the mono- and bis(phenanthroline) forms of  $\text{Cu}(\text{I})$  are reducing species. The latter complex binds strongly to SDS micelles, resulting in 39- and 272-fold rate inhibitions for the  $\text{Co}(\text{acac})_3$  and  $\text{Co}(\text{EDTA})^-$  oxidations, respectively. Barriers to electron transfer arising from strong micellar association of the reductant are calculated for both oxidations.

### Introduction

A broad range of organic reactions have been investigated in micellar systems,<sup>2</sup> but there have been only a few relatively recent studies of transition-metal electron transfers in detergent media. We are continuing our investigations of micellar effects on the electron-transfer reactions of copper complexes.<sup>1</sup> Rate studies can provide information on how the redox event is affected by electrostatic and hydrophobic interactions between the micelle and the metal complexes. Important in their own right for mechanistic inorganic chemistry, these studies also have implications for physiological metalloprotein electron transfer which take place on membrane surfaces or at protein-substrate interfaces.

For a given reaction in detergent solution, observed rates depend on the extent of reagent association with the micellar aggregate.<sup>2</sup> In this study we are concerned with rate inhibitions that arise from both electrostatic and hydrophobic interactions. When one partner in the redox couple is micelle associated, electrostatic repulsion between the micelle surface and an aqueous reagent of like charge can slow the reaction considerably. For example, the rate of oxidation of micellar  $\text{Os}(\text{bpy})_3^{3+}$  by  $\text{Fe}(\text{CN})_6^{2-}$  is as much as 3 orders of magnitude slower than that in water.<sup>3,4</sup> Rate inhibition can occur when a neutral molecule is "buried" in the aggregate, as in the  $\text{IrCl}_6^{2-}$  reduction of micellar  $\text{Fe}(\text{phen})_2(\text{CN})_2$ .<sup>4</sup> Inhibition can occur even when the aqueous reagent is a small neutral molecule and the micellar reagent is likely to reside near the surface. Our previous study of the  $\text{H}_2\text{O}_2$  oxidation of  $\text{Cu}(\text{phen})_2^+$  in SDS shows a 20-fold inhibition relative to the reaction in aqueous solution, suggestive of some type of nonelectrostatic barrier to electron transfer, presumably arising from hydrophobic interactions between the reductant and the micelle.<sup>1</sup>

In this report we compare the aqueous and micellar oxidation of  $\text{Cu}(\text{phen})_2^+$  by two similar  $\text{Co}(\text{III})$  complexes,  $\text{Co}(\text{acac})_3$  and  $\text{Co}(\text{EDTA})^-$ . Any rate difference for the neutral oxidant should come from hydrophobic interactions between one or both of the redox reagents and the micelle, while for the anionic oxidant both electrostatic and hydrophobic interactions should be important.

### Experimental Section

**Reagents.** The synthesis and characterization of  $\text{Cu}(\text{phen})_2\text{HSO}_4$  as well as the anaerobic procedures and experimental techniques have been described previously.<sup>1</sup> The oxidants  $\text{Na}[\text{Co}(\text{EDTA})] \cdot 4\text{H}_2\text{O}$  and  $\text{Co}(\text{acac})_3$  were prepared according to published procedures.<sup>5,6</sup> Compound purity was checked by UV-visible<sup>7,8</sup> and IR spectroscopy<sup>9,10</sup> as well as by elemental analysis.

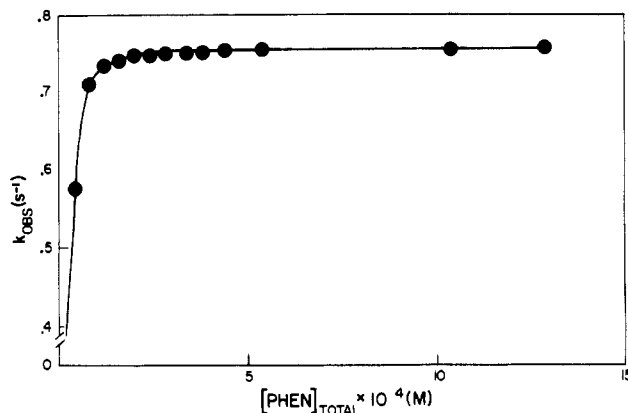
**Techniques.** Aqueous oxidant and reductant solutions were prepared by dissolving the appropriate amount of a given salt in cacodylate buffer (0.1 M, pH 6,  $\mu = 0.25$  M ( $\text{Na}_2\text{SO}_4$ )). The nonbinding buffer was chosen to avoid any possibility of anion complexation with  $\text{Cu}(\text{I})$ , although we have subsequently found the phosphate buffer is satisfactory at this pH. So that differential neutralization of micelle surface and changes in micellar size due to varying concentrations of counterion could be avoided, the total sodium ion concentration was maintained at 0.2 M in all detergent solutions ( $[\text{SDS}] = 0.1$  M,  $\mu = 0.2$  M). Reagent concentrations were checked from the absorbance of stock solutions:  $\text{Cu}(\text{phen})_2\text{HSO}_4$ ,  $E_{410} = 4100 \text{ M}^{-1} \text{ cm}^{-1}$  (aqueous, excess phen),  $E_{440} = 5700 \text{ M}^{-1} \text{ cm}^{-1}$  (micellar);<sup>11</sup>  $\text{Na}[\text{Co}(\text{EDTA})]$ ,  $E_{535} = 318 \text{ M}^{-1} \text{ cm}^{-1}$ ,  $E_{380} = 224 \text{ M}^{-1} \text{ cm}^{-1}$ ,<sup>7</sup> and  $\text{Co}(\text{acac})_3$ ,  $E_{595} = 133 \text{ M}^{-1} \text{ cm}^{-1}$ .<sup>8</sup> Solutions were used within 3-8 h of preparation.

For the aqueous reaction between  $\text{Cu}(\text{phen})_2^+$  and  $\text{Co}(\text{EDTA})^-$  a 1:1 stoichiometry was determined by monitoring the loss of  $\text{Co}(\text{III})$  at 535 nm caused by addition of reductant. Due to competing absorbance changes from the association of  $\text{Cu}(\text{I})$  with free ligand labilized by the formation of  $\text{Co}(\text{II})$ , it was not possible to determine stoichiometries for the  $\text{Co}(\text{acac})_3$  oxidations or the micellar  $\text{Co}(\text{EDTA})^-$  oxidation.

Proton NMR spectra were recorded on a JEOL FX-60 Pulse FT instrument at ambient temperatures. Solutions were freshly prepared in  $\text{D}_2\text{O}$ , and chemical shifts were measured relative to  $(\text{CH}_3)_4\text{Si}$ , contained in an internal capillary tube.

- (1) Part I: Ponganis, K. V.; de Araujo, M. A.; Hodges, H. L. *Inorg. Chem.* **1980**, *19*, 2704.
- (2) See the following references and the references cited therein: (a) Cordes, E. H.; Gitler, C. *Prog. Bioorg. Chem.* **1973**, *2*, 1. (b) Fendler, J. H.; Fendler, E. J. "Catalysis in Micellar and Macromolecular Systems"; Academic Press: New York, 1975. (c) Bunton, C. A. *Prog. Solid State Chem.* **1973**, *8*, 239. (d) Mittal, K. L., Ed. "Micellization, Solubilization and Microemulsions"; Plenum Press: New York, 1977; Vol 1 and 2. (e) Berezin, I. V.; Martinek, K.; Yatsimirskii, A. K. *Russian Chem. Rev. (Engl. Transl.)* **1973**, *42*, 787.
- (3) The following nomenclature will be used throughout this paper: SDS = sodium dodecyl sulfate, phen = 1,10-phenanthroline, bpy = 2,2'-bipyridyl, cmc = critical micelle concentration, EDTA = ethylenediaminetetraacetic acid, acac = acetylacetonate ion.
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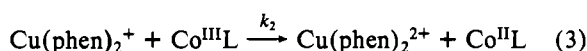
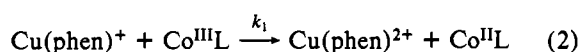
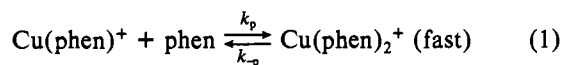
**Figure 1.** Plot of  $k_{\text{obsd}}$  as a function of  $[\text{phenanthroline}]_{\text{total}}$  for the oxidation of Cu(I) by  $\text{Co}(\text{acac})_3$  in aqueous solution:  $[\text{Cu}(\text{I})]_t = 2.0 \times 10^{-5} \text{ M}$ ,  $[\text{Co}(\text{III})] = 1.0 \times 10^{-3} \text{ M}$ , pH 6.0,  $\mu = 0.25 \text{ M}$ ,  $T = 25^\circ \text{C}$ .

**Kinetics.** Absorbance-time data were recorded on a Hewlett Packard Model 7004B X-Y Recorder, and traces were analyzed with a Scriptorgraphics Model HW-1-11 Digitizer and a Varian 620 L computer. All kinetic data were processed with standard computer programs.

Studies were done under pseudo-first-order conditions with Cu(I) as the limiting reagent. Reactions were monitored by following the loss of Cu(I) absorbance at 410 (aqueous) or 440 nm (micellar). Conditions for a typical kinetic experiment were as follows: aqueous  $[\text{Cu}(\text{phen})_2^+] = 2.0 \times 10^{-5} \text{ M}$ ,  $[\text{Co}(\text{acac})_3] = (0.25-1) \times 10^{-3} \text{ M}$ ,  $[\text{phen}] = 5 \times 10^{-4} \text{ M}$ ; micelle  $[\text{Cu}(\text{phen})_2^+] = 2 \times 10^{-5} \text{ M}$ ,  $[\text{Co}(\text{acac})_3] = (0.25-2.7) \times 10^{-3} \text{ M}$ ,  $[\text{SDS}] = 0.1 \text{ M}$ . Except for the experiment in Figure 3, all micellar studies were done under conditions where there was a 40–50-fold excess of micelles over Cu(I), ensuring no more than one metal complex per micelle. For all aqueous studies and those micellar studies done in the presence of excess phenanthroline, plots of  $\log(A - A_\infty)$  were linear for 90–95% of each reaction. For those micellar systems showing curvature in the log plots, data were successively analyzed with the assumption of two parallel first-order reactions.<sup>12</sup> In a typical biphasic analysis it was possible to fit 90% of the log data (ca. 75 points) to either the fast or the slow reaction phase. Since rate constants for the two phases only differed by a factor of 2 in some cases, a more detailed analysis was done on several data sets with a program which fit raw data to two exponential decays. Values of  $k_{\text{obsd}}$  did not differ by more than 10% for the two methods.

## Results

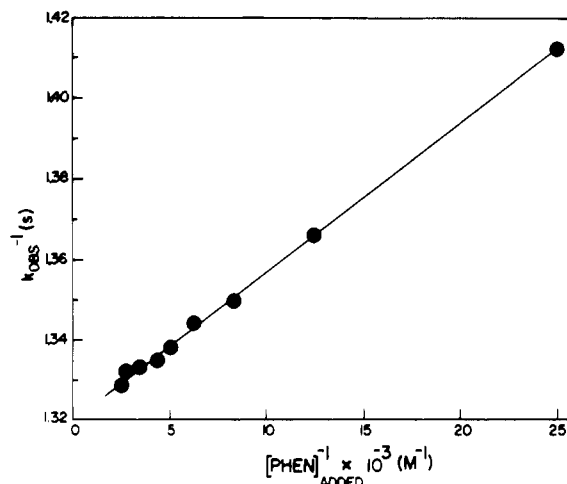
**Aqueous Chemistry. Oxidation by  $\text{Co}(\text{acac})_3$  and  $\text{Co}(\text{EDTA})^-$ .** The rate of Cu(I) oxidation by either  $\text{Co}(\text{acac})_3$  or  $\text{Co}(\text{EDTA})^-$  increases with increasing phenanthroline concentration until the total ligand:metal ratio is approximately 10:1, as shown in Figure 1 for  $\text{Co}(\text{acac})_3$ .<sup>13</sup> The kinetic behavior is consistent with two potentially oxidizable forms of Cu(I) in fast equilibrium:



where L indicates either acac or EDTA. Under pseudo-first-order conditions with excess oxidant and phenanthroline, the following theoretical rate expression is obtained.

$$k_{\text{obsd}} = [(k_2 k_p [\text{phen}] + k_1) / (1 + K_p [\text{phen}])] [\text{Co}(\text{III})] \quad (4)$$

A plot of  $1/k_{\text{obsd}}$  vs.  $1/[\text{phen}]$  should be linear if  $k_1 \ll$



**Figure 2.** Plot of  $1/k_{\text{obsd}}$  vs.  $1/[\text{phen}]$  added for the oxidation of Cu(I) by  $\text{Co}(\text{acac})_3$  in aqueous solution. Conditions are the same as those indicated in Figure 1.

$k_2 K_p [\text{phen}]$  (see below). If we initially approximate  $[\text{phen}]$  by  $[\text{phen}]_{\text{added}}$ , we obtain the linear double reciprocal plot shown in Figure 2. A rough value of  $K_p = 3.6 \times 10^5 \text{ M}^{-1}$  is obtained from the slope of this plot. The calculation of  $K_p$  is difficult because rate enhancement is dramatic at low ligand concentrations where the above approximation is not totally valid. With use of an iterative process where more accurate values of  $[\text{phen}]$  are calculated from  $[\text{phen}]_{\text{total}}$  and successively more accurate values of  $K_p$ , after five cycles  $K_p$  does not change and we obtain  $K_p = (3.04 \pm 0.05) \times 10^5 \text{ M}^{-1}$  and  $k_2 = 759 \pm 2 \text{ M}^{-1} \text{ s}^{-1}$  for the  $\text{Co}(\text{acac})_3$  oxidation. Similarly, for  $\text{Co}(\text{EDTA})^-$ ,  $K_p = (3.04 \pm 0.05) \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$  and  $k_2 = 449 \pm 4 \text{ M}^{-1} \text{ s}^{-1}$ . From the value of  $K_p$ , which is in excellent agreement with that of  $(3.1 \pm 0.2) \times 10^5 \text{ M}^{-1}$  obtained from an independent determination of  $k_p$  and  $k_{-p}$ ,<sup>11</sup> we calculate that the mono(phenanthroline)copper(I) represents only 1–10% of the total Cu(I) present over the range of phenanthroline concentrations in Figure 1. If this form were stoichiometrically insignificant but still kinetically important ( $k_1 \geq k_2 K_p [\text{phen}]$ ), the plot shown in Figure 2 would not be linear. Therefore, within experimental error, eq 2 must be a nonexistent pathway on the time scale of our experiments in aqueous solution.

Under pseudo-first-order conditions with excess phenanthroline and oxidant, values of  $k_{\text{obsd}}$  vary linearly with oxidant concentration for both Co(III) complexes.<sup>13</sup> Second-order rate constants from the oxidant dependence data are in excellent agreement with those obtained from the phenanthroline dependence studies:  $k_2 = 756 \pm 2 \text{ M}^{-1} \text{ s}^{-1}$  ( $\text{Co}(\text{acac})_3$ ) and  $k_2 = 448 \pm 1 \text{ M}^{-1} \text{ s}^{-1}$  ( $\text{Co}(\text{EDTA})^-$ ). Holwerda and co-workers have measured  $k_2 = 312 \text{ M}^{-1} \text{ s}^{-1}$  for the latter reaction at a higher ionic strength of 0.5 M.<sup>14</sup> Due to the low solubility of  $\text{Co}(\text{acac})_3$ , the concentration range of  $(0.25-1) \times 10^{-3} \text{ M}$  for this oxidant is considerably narrower than that for  $\text{Co}(\text{EDTA})^-$  [ $(0.25-25) \times 10^{-3} \text{ M}$ ]. For both oxidants, redox reactions are independent of pH over the range 5.8–7.8.

Eyring plots of the temperature dependence data<sup>13</sup> are linear over a 30 °C range. Resultant activation parameters are  $\Delta H^\ddagger = 8 \pm 0.5 \text{ kcal/mol}$  and  $\Delta S^\ddagger = -19 \pm 1 \text{ eu}$  for  $\text{Co}(\text{acac})_3$  and  $\Delta H^\ddagger = 7.5 \pm 0.5 \text{ kcal/mol}$  and  $\Delta S^\ddagger = -21 \pm 1 \text{ eu}$  for  $\text{Co}(\text{EDTA})^-$ . Aqueous rate parameters are listed in Table I.

**Micelle Chemistry. Reagent-Micelle Association.** We have previously established through changes in the visible spectrum of  $\text{Cu}(\text{phen})_2^+$  that there is strong association between this reductant and SDS micelles characterized by a binding constant,  $K/N = 10^4 \text{ M}^{-1}$ .<sup>1,11,15</sup> While  $\text{Co}(\text{EDTA})^-$  must be

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(13) See supplementary material for complete tabulation of kinetic data and additional data plots.

(14) Yoneda, G. S.; Blackmer, G. L.; Holwerda, R. A. *Inorg. Chem.* 1977, 16, 3376.

Table I. Rate Parameters for the Oxidation of  $\text{Cu}(\text{phen})_2^+$ 

	aqueous	micellar	$k_2^{\text{aq}}/k_2^{\text{mic}}$
<b>Co(acac)<sub>3</sub><sup>a</sup></b>			
$k_2,^b \text{ M}^{-1} \text{ s}^{-1}$	756 (2) <sup>c</sup>	19.2 (0.1) <sup>d</sup>	39:1
$\Delta H^\ddagger, \text{ kcal/mol}$	8 (0.5)	9.6 (0.5)	
$\Delta S^\ddagger, \text{ cal/(mol deg)}$	-19 (1)	-20 (1)	
<b>Co(EDTA)<sup>-a</sup></b>			
$k_2,^b \text{ M}^{-1} \text{ s}^{-1}$	488 (1) <sup>c</sup>	1.65 (0.1) <sup>d</sup>	272:1
$\Delta H^\ddagger, \text{ kcal/mol}$	7.5 (0.5)	10.5 (0.5)	
$\Delta S^\ddagger, \text{ cal/(mol deg)}$	-21 (1)	-22 (1)	
<b>H<sub>2</sub>O,<sup>e</sup></b>			
$k_2,^b \text{ M}^{-1} \text{ s}^{-1}$	3910 (60) <sup>f</sup>	204 (3) <sup>g</sup>	19:1
$\Delta H^\ddagger, \text{ kcal/mol}$	5.8 (0.4)	6.6 (0.4)	
$\Delta S^\ddagger, \text{ cal/(mol deg)}$	-24 (1)	-25 (1)	

<sup>a</sup> Conditions: pH 6.0 (cacodylate),  $[\text{Na}^+] = 0.2 \text{ M}$ ,  $\mu = 0.25$  (aqueous),  $\mu = 0.20$  (micellar),  $[\text{Cu(I)}]_t = (2.0\text{--}2.5) \times 10^{-5} \text{ M}$ .  
<sup>b</sup>  $T = 25^\circ \text{C}$ . <sup>c</sup>  $[\text{phen}] = 5 \times 10^{-4} \text{ M}$ . <sup>d</sup>  $[\text{SDS}] = 0.1 \text{ M}$ . <sup>e</sup> Data from ref 1: pH 5.8 (phosphate),  $\mu_t = 0.15 \text{ M}$ ,  $[\text{Cu(I)}]_t = (2.5\text{--}5) \times 10^{-5} \text{ M}$ . <sup>f</sup>  $[\text{phen}] = 10^{-3} \text{ M}$ . <sup>g</sup>  $[\text{SDS}] = 0.05 \text{ M}$ .

repelled by the anionic micelle surface, neutral  $\text{Co}(\text{acac})_3$  probably experiences some association since its solubility in 0.1 M SDS is increased approximately 3-fold relative to that in water. The UV-VIS spectrum of  $\text{Co}(\text{acac})_3$  is not sensitive to solvent polarity, so it is not possible to monitor micelle-induced spectral changes as it is for  $\text{Cu}(\text{phen})_2^+$ .<sup>11</sup> Shifts of <sup>1</sup>H NMR frequencies have been used to demonstrate binding of another Co(III) oxidant,  $\text{Co}(\text{phen})_3^{3+}$ , to SDS micelles.<sup>16</sup> We find the <sup>1</sup>H NMR chemical shifts for  $\text{Co}(\text{acac})_3$ , known to be sensitive to solvent polarity,<sup>17</sup> are identical in water and in 0.1 M SDS solution. This suggests that any micellar association of  $\text{Co}(\text{acac})_3$  is relatively weak and probably at the micelle-water interface.

**Detergent Rate Profile.** Electron-transfer rates were studied above the cmc over the range  $1.5 \times 10^{-3} \leq [\text{SDS}] \leq 0.1 \text{ M}$  in the presence of excess phenanthroline. Below the cmc,  $\text{Cu}(\text{phen})_2^+$  solutions are turbid due to the formation of an insoluble pre-micellar aggregate which disappears at higher detergent concentrations.<sup>1</sup> Under pseudo-first-order conditions with excess Co(III) and phenanthroline, micellar reactions are first order in Cu(I). As shown in Figure 3, the  $\text{Co}(\text{EDTA})^-$  rate drops by a factor of 3 over the range of detergent concentration studied, while the  $\text{Co}(\text{acac})_3$  rate remains unchanged. Both oxidations are slower than in aqueous solution, with an aqueous:micellar (0.1 M SDS) rate ratio of 39:1 for  $\text{Co}(\text{acac})_3$  and 272:1 for  $\text{Co}(\text{EDTA})^-$ . Subsequent micellar redox data were collected at 0.1 M SDS where  $\text{Co}(\text{EDTA})^-$  exhibits no rate variation with detergent concentration.

**Oxidation by  $\text{Co}(\text{acac})_3$ .** In 0.1 M SDS solution (no excess phenanthroline), the oxidation of Cu(I) is first order in  $\text{Co}(\text{acac})_3$  over a 10-fold range of oxidant. At the lowest oxidant concentrations the reaction is biphasic with a minor contribution (20–40%) from a slower reaction.<sup>13</sup> Addition of a 5-fold excess of phenanthroline over Cu(I) removes the minor phase, and the rate of the major phase is independent of phenanthroline concentration. This suggests that the minor and major phases represent oxidation of the mono- and bis(phenanthroline)copper(I) species, respectively, which are in slow equilibrium relative to the electron-transfer reactions. From the

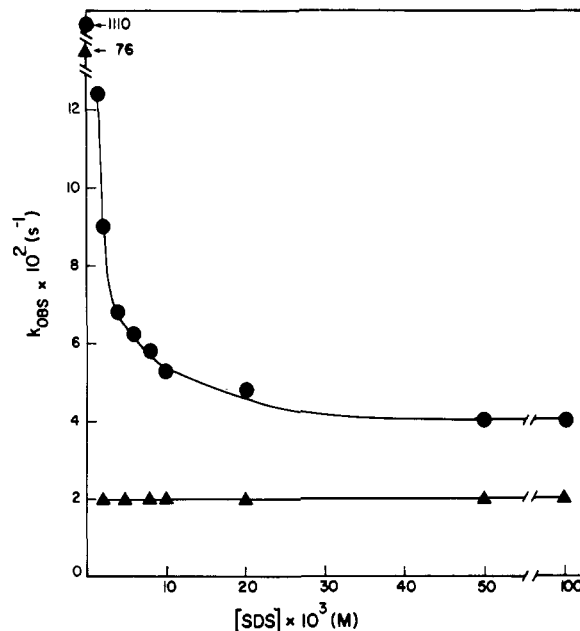


Figure 3. Plot of  $k_{\text{obs}}$  for the oxidation of Cu(I) as a function of  $[\text{SDS}]$ . ●  $[\text{Co}(\text{EDTA})^-] = 2.5 \times 10^{-2} \text{ M}$ ;  $[\text{Cu(I)}]_t = 2.5 \times 10^{-5} \text{ M}$ ;  $[\text{phen}] = 5.0 \times 10^{-3} \text{ M}$ . ▲  $[\text{Co}(\text{acac})_3] = 1.0 \times 10^{-3} \text{ M}$ ;  $[\text{Cu(I)}]_t = 2 \times 10^{-5} \text{ M}$ ;  $[\text{phen}] = 4.0 \times 10^{-4} \text{ M}$ . All studies were done at  $25^\circ \text{C}$ , pH 6, and  $[\text{Na}^+]_t = 0.2 \text{ M}$ .

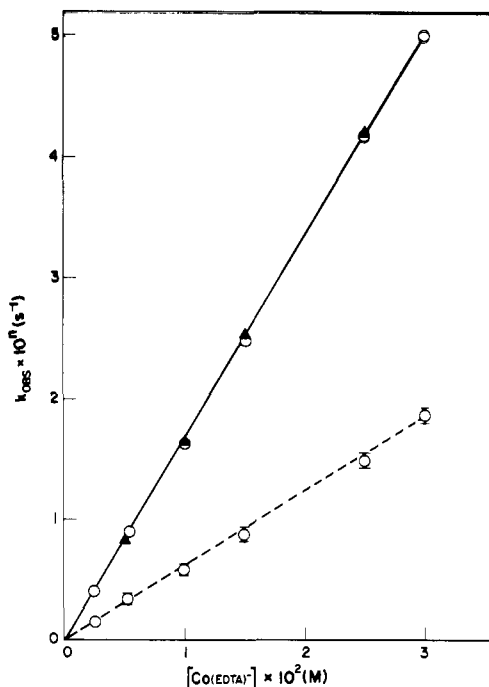


Figure 4. Plot of  $10^2 k_{\text{obs}}$  vs.  $[\text{Co}(\text{EDTA})^-]$  for the oxidation of Cu(I). Symbols: —, rate data for the major (slow) reaction phase,  $n = 2$ ; ---, rate data for the minor (fast) reaction phase,  $n = 1$ ; ○, points from biphasic data, no excess phenanthroline; ▲, points from monophasic data,  $[\text{phen}] = 5 \times 10^{-3} \text{ M}$ . For all studies,  $[\text{Cu(I)}]_t = 2.5 \times 10^{-5} \text{ M}$ ,  $[\text{SDS}] = 0.1 \text{ M}$ ,  $[\text{Na}^+] = 0.2 \text{ M}$ , pH = 6 (cacodylate), and  $T = 25^\circ \text{C}$ .

data, we calculate  $k_{2\text{M}} = 19.2 \pm 0.1 \text{ M}^{-1} \text{ s}^{-1}$ . (The notation is the same as that in eq 1–3 where the subscript M denotes a micellar reaction.) The rate constant for the minor reaction is approximately half this value.

Temperature-dependence data were obtained at two different SDS concentrations (0.05 and 0.1 M) in the presence of excess phenanthroline where the reaction is monophasic. Eyring plots are linear over a  $20^\circ \text{C}$  range, with activation parameters  $\Delta H^\ddagger = 9.6 \pm 0.1 \text{ kcal/mol}$  and  $\Delta S^\ddagger = 20 \pm 1 \text{ eu}$ .

(15) Because of the uncertainty in micellar size, reagent binding constants are typically expressed per detergent head group,  $K/N$ , where  $N$  is the number of detergent monomers per micelle. The true micellar binding constant would be obtained by multiplying this number by  $N$ , which for SDS, has a value of approximately 110 under the conditions of our experiments.<sup>23</sup>

(16) Ponganis, K. V.; de Araujo, M. A.; Hodges, H. L. *J. Am. Chem. Soc.*, in press.

(17) Smith, J. A. S.; Wilkins, E. J. *J. Chem. Soc. A* 1966, 1749.

Table II. Ionic Strength Dependence<sup>a</sup>

[Co(EDTA) <sup>-</sup> ], M	$\mu$ , M	$k_{\text{obsd}}$ , s <sup>-1</sup>
$2.5 \times 10^{-2}$	0.23	0.0417
	0.45	7.03
	0.68	12.1

<sup>a</sup> All studies done at pH 6.0, [cacodylate] = 0.1 M, [SDS] = 0.1 M, [Cu(I)]<sub>t</sub> =  $2.5 \times 10^{-5}$  M, [phen] =  $5 \times 10^{-9}$  M, and with the adjusting electrolyte Na<sub>2</sub>SO<sub>4</sub>.

Within experimental error, the concentration of SDS has no effect on these values.

**Oxidation by Co(EDTA)<sup>-</sup>.** In the presence of excess phenanthroline the Co(EDTA)<sup>-</sup> oxidation of Cu(I) in 0.1 M SDS solution exhibits monophasic kinetics and is first order in oxidant (Figure 4; triangles, solid line). The reaction is biphasic at low phenanthroline concentrations and at all but the highest Co(EDTA)<sup>-</sup> concentrations. Under these conditions, the major reaction (open circles, solid line) shows a dependence on Co(III) which is identical with that for the monophasic reaction when phenanthroline is in excess. The major reaction represents at least 75% of the total absorbance change. The minor phase (open circles, dashed line), which is the faster of the two reactions, also shows a linear dependence on oxidant. Addition of excess phenanthroline has no effect on the rate of either phase but does decrease the percent contribution of the minor phase from 25 to 0% as the added phenanthroline is increased from 0 to  $2.5 \times 10^{-4}$  M ([Cu(I)]<sub>t</sub> =  $2.5 \times 10^{-5}$  M, [Co(III)] =  $2.5 \times 10^{-2}$  M). Results are consistent with the oxidation of micellar Cu(phen)<sub>2</sub><sup>+</sup> (major species) and micellar Cu(phen)<sup>+</sup> (minor species), with second-order rate constants  $k_{2M} = 1.65 \pm 0.10 \text{ M}^{-1} \text{ s}^{-1}$  and  $k_{1M} = 5.8 \pm 0.3 \text{ M}^{-1} \text{ s}^{-1}$ , respectively.

Temperature-dependence data for the oxidation of Cu(phen)<sub>2</sub><sup>+</sup> were collected in the presence of excess phenanthroline at two different SDS concentrations. Eyring plots (not shown) are linear over a 20 °C range. Rate parameters are listed in Table I.

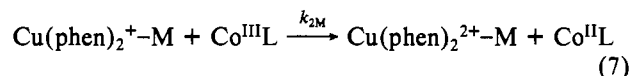
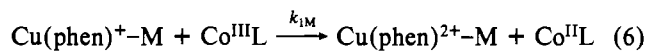
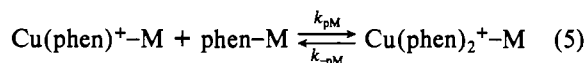
The oxidation of Cu(phen)<sub>2</sub><sup>+</sup> by Co(EDTA)<sup>-</sup> in SDS solution was studied at three different ionic strengths. As shown in Table II, the rate is increased substantially with increased salt concentration, consistent with a reaction involving two anionic species, one of which is highly charged.

## Discussion

Rate data for the Co(acac)<sub>3</sub> and Co(EDTA)<sup>-</sup> oxidations in aqueous solution indicate that Cu(phen)<sub>2</sub><sup>+</sup> is the only oxidizable form of Cu(I) on the time scale of our experiments. Because of the established outer-sphere reactivity of Co(EDTA)<sup>-</sup><sup>18</sup>, and the substitution inertness of Co(III) complexes in general, it is reasonable to assume that the reduction by Cu(phen)<sub>2</sub><sup>+</sup> is outer sphere with respect to both Co(III) oxidants used in this study. Since Cu(I) should increase its coordination number prior to electron transfer,<sup>19</sup> an inner-sphere pathway with respect to the substitution-labile Cu(I) center through the bridging carbonyl group in Co(EDTA)<sup>-</sup> is a possibility. Such a mechanism has been proposed for the Co(EDTA)<sup>-</sup> oxidation of aquo Cr<sup>2+</sup> and Fe<sup>2+</sup> species.<sup>20,21</sup> However, we have shown that the rate of the reaction of EDTA or acac with Cu(phen)<sub>2</sub><sup>+</sup> in aqueous solution is characterized by a first-order rate constant,  $k_{\text{obsd}} = 0.2 \text{ s}^{-1}$ , which is both independent of ligand concentration<sup>11</sup> and slower than the electron-transfer rate constants in this study. Since the complexation of Cu(I) by EDTA or acac is presumably preceded by dissociation of a phenanthroline ligand, an inner-sphere

electron-transfer pathway dissociation of phenanthroline can be ruled out. Furthermore, an inner-sphere associative pathway seems very unlikely since neither EDTA nor acac react with Cu(phen)<sub>2</sub><sup>+</sup> by this route. Therefore, we conclude that the electron-transfer reaction is outer sphere with respect to both Cu(I) and the Co(III) oxidants.

For micellar oxidations we can write a reaction scheme analogous to eq 1–3



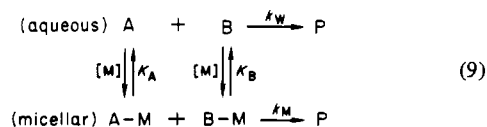
The overall rate law for the reaction in the micelle must contain terms for both Cu(phen)<sup>+</sup>-M and Cu(phen)<sub>2</sub><sup>+</sup>-M:

$$-d[\text{Cu(I)}]/dt = k_{2M}[\text{Co(III)}][\text{Cu(phen)}_2^+-\text{M}] + k_{1M}[\text{Co(III)}][\text{Cu(phen)}^+-\text{M}] \quad (8)$$

We assume that phenanthroline is micelle-associated and, for purposes of simplicity, that the Co<sup>III</sup>L species are not. The oxidant association will be treated in detail below. We have previously determined that the copper complex is almost exclusively in the bischelated form in micellar solution (no excess phenanthroline).<sup>11</sup> The two Cu(I) species can no longer be related by an equilibrium expression (as for the aqueous case) because the time scale for their interconversion is comparable to that for the oxidation of Cu(phen)<sup>+</sup>-M. Biphasic kinetics are observed until the contribution of the second term in the rate law becomes negligible, either because  $k_{2M}[\text{Co}^{\text{III}}\text{L}] \gg k_{-pM}$  (high Co<sup>III</sup>L) or because  $k_{pM}[\text{phen-M}] \gg k_{1M}[\text{Co}^{\text{III}}\text{L}]$  (high phenanthroline). To check that rate data are consistent with this scheme, we see that biphasic kinetics disappear once [Co(EDTA)<sup>-</sup>] >  $3 \times 10^{-2}$  M. Under these conditions,  $k_{2M}[\text{Co}^{\text{III}}\text{L}] = 0.051 \text{ s}^{-1}$ , which is more than 10 times greater than the value of  $0.002 \text{ s}^{-1}$  measured for  $k_{-pM}$ .<sup>11,22</sup>

In contrast to these results, the H<sub>2</sub>O<sub>2</sub> oxidation of micellar copper(I) phenanthroline is always monophasic, even in the absence of excess phenanthroline. This is consistent with our current work since the H<sub>2</sub>O<sub>2</sub> reaction is fast ( $1 \text{ s}^{-1} \leq k_{\text{obsd}} \leq 10 \text{ s}^{-1}$ ) and oxidation of Cu(phen)<sub>2</sub><sup>+</sup>-M is complete before any dissociation to the monochelated form can occur. Although the focus of our work is on the Cu(phen)<sub>2</sub><sup>+</sup> species, it is interesting to note that Cu(phen)<sup>+</sup> is oxidized faster than Cu(phen)<sub>2</sub><sup>+</sup> by Co(EDTA)<sup>-</sup>, while the reverse is true for Co(acac)<sub>3</sub>. This may be due to the fact that the monochelated form is reacting by a more facile inner-sphere route via a bridging carbonyl group on the EDTA ligand. For Co(acac)<sub>3</sub> no such bridge is available.

For a reaction between two reagents in detergent solution, we can write eq 9 where M and W refer to micellar and



(22) We have considered the possibility that the minor phase is due to complexation of Cu(I) with free acac (or EDTA) labilized from Co(II) produced in the electron-transfer reaction. Addition of these ligands to Cu(phen)<sub>2</sub><sup>+</sup> or Cu(phen)<sup>+</sup> is known to result in a color loss at 440 nm in SDS solution.<sup>11</sup> These reactions can be ruled out for several reasons. First, addition of excess acac(EDTA) to a reaction mixture which is biphasic has no effect on either the rates or percent contribution of the fast and slow phases. Furthermore, the reaction between acac(EDTA) and (phenanthroline)copper(I) or bis(phenanthroline)copper(I) are both independent of acac(EDTA) concentration. Since the minor phase shows a linear dependence on oxidant concentration, we attribute this to an electron-transfer process rather than to ligand association.

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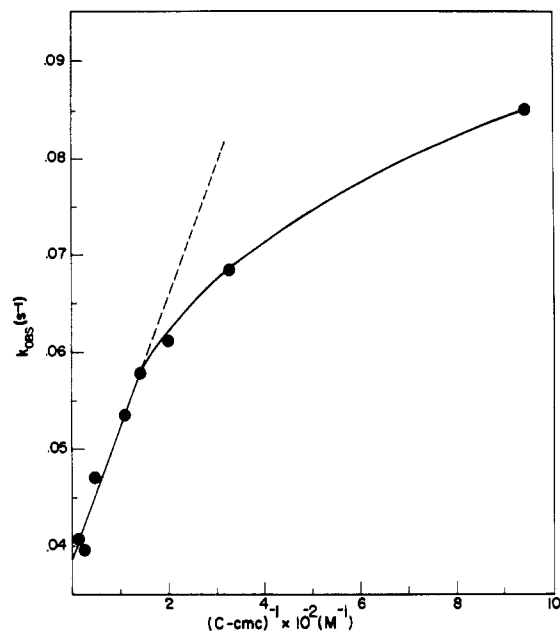


Figure 5. Plot of  $k_{\text{obsd}}$  vs.  $(C - \text{cmc})^{-1} \times 10^{-2} \text{ M}$  for the oxidation of  $\text{Cu}(\text{phen})_2^+$  by  $\text{Co}(\text{EDTA})^-$ . Conditions are the same as in Figure 4.

aqueous phase, respectively,  $K_A$  and  $K_B$  are the micellar binding constants for reagents A and B. The Berezin expression for a second-order rate constant considers all possible combinations of aqueous and micellar reactions:<sup>2c</sup>

$$k_{\text{exp}} = \frac{(k_M P_A P_B + k_M' P_A + k_M'' P_B) C \bar{V} + k_W (1 - C \bar{V})}{(1 + K_A C)(1 + K_B C)} \quad (10)$$

where  $C$  is the detergent concentration minus the cmc. The partition coefficient and the micellar binding constant are related by the equation  $K_A = (P_A - 1) \bar{V}$ , where  $\bar{V}$  is the partial molar volume of the surfactant monomer in the micelle. The rate constants  $k_M$  and  $k_W$  characterize reactions occurring exclusively in the micellar and aqueous phases, respectively, while  $k_M'$  is the rate constant for the reaction between A in the micellar phase and B in the bulk solution and  $k_M''$  is the rate constant for the reverse situation.

From a study of the reaction as a function of detergent concentration, certain micellar constants can be calculated if several simplifying assumptions are made. Our studies in Figure 3 were done in the presence of excess phenanthroline so only  $\text{Cu}(\text{phen})_2^+$  is a reducing species. At all SDS concentrations in this study, the volume fraction of the micelles is small, so  $(1 - C \bar{V}) \approx 1$ . The anionic oxidant,  $\text{Co}(\text{EDTA})^-$ , will be repelled by the micelle surface, so  $P_B = 0$  and eq 10 simplifies to eq 11. Since  $\text{Cu}(\text{phen})_2^+$  binds strongly to SDS

$$k_{\text{exp}} = k_M' K_A C + k_W / (1 + K_A C) \quad (11)$$

micelles,  $(1 + K_A C) \approx K_A C$ . This gives eq 12 and predicts

$$k_{\text{exp}} = k_M' + k_W / K_A C \quad (12)$$

an inverse linear relationship between  $k_{\text{exp}}$  and  $C$ . Such behavior is shown for the data plotted in Figure 5 at high detergent concentrations. Here the pseudo-first-order rate constant,  $k_{\text{obsd}} = k_{\text{exp}}[\text{Co}(\text{EDTA})^-]$  is plotted rather than  $k_{\text{exp}}$ . From the y intercept,  $k_M' = 1.56 \text{ M}^{-1} \text{ s}^{-1}$ , in excellent agreement with  $k_{2M} = 1.65 \text{ M}^{-1} \text{ s}^{-1}$  obtained from the  $\text{Co}(\text{EDTA})^-$  concentration dependence studies at  $[\text{SDS}] = 0.1 \text{ M}$ . A value of  $K_A = 8.5 \times 10^4 \text{ M}^{-1}$  is calculated from the slope of Figure 5 and the known value of  $k_W^{\text{obsd}}$  under our reaction conditions. This binding constant is 10-fold higher than that of  $(1.05 \pm 0.04) \times 10^4 \text{ M}^{-1}$  obtained from spectral studies.<sup>11</sup> The dis-

crepancy in the values of  $K_A$  and the curvature in Figure 5 at low detergent concentrations may be due to the ion pair formation between the detergent and the  $\text{Cu}(\text{I})$  complex near the cmc. This could affect the formation of "normal" micelles so that eq 12 would not be an accurate expression in this case. In these calculations we have assumed  $\text{cmc} = 0.94 \times 10^{-3} \text{ M}$ , determined for  $[\text{NaCl}] = 0.2 \text{ M}$ .<sup>23</sup> Even if this value is somewhat inaccurate for our reaction conditions, a slight variation in cmc will make little difference in either the slope or intercept of Figure 5. Recent studies in our lab using nonionic detergent (which does not precipitate  $\text{Cu}(\text{phen})_2^+$  at low detergent concentrations) show good correlation between spectral and kinetic determinations of  $K_A$ .<sup>24</sup> At this time we place more confidence in the value of  $K_A$  determined by spectral methods for binding of  $\text{Cu}(\text{phen})_2^+$  to SDS micelles.

It is not possible to gain much information about the SDS association of  $\text{Co}(\text{acac})_3$  from the rate profile data since  $k_{\text{obsd}}$  is independent of detergent concentration over the range of study. We assume there is some binding of this oxidant to the micelle since its solubility increases in SDS solution. A possible explanation of the kinetic behavior is to assume, in addition to  $K_A C \gg 1$  and  $(1 - C \bar{V}) \approx 1$ , that  $K_B C \ll 1$  and the contribution from the  $k_M''$  term is negligible. Equation 10 then reduces to eq 13 where  $\bar{k}_M = k_M / \bar{V}$ . This is analogous

$$k_{\text{exp}} = (\bar{k}_M K_B + k_M') + k_W / K_A C \quad (13)$$

to eq 12 for the  $\text{Co}(\text{EDTA})^-$  system with an additional term for the reaction of micellar bound oxidant and reductant. If the aqueous rate constant is not substantially larger than the sum of the micellar values, this expression reduces to eq 14

$$k_{\text{exp}} = k_M K_B + k_M' \quad (14)$$

when  $K_A$  and  $C$  are large enough. Thus, somewhat above the cmc there is little or no aqueous contribution for the reaction between  $\text{Cu}(\text{phen})_2^+$  and  $\text{Co}(\text{acac})_3$ . When this redox couple is studied at very low concentrations of nonionic detergent (not possible in SDS), there is a continuous decrease in rate, supporting the above interpretation.<sup>24</sup> The micellar rate constant is a sum of two terms, but we cannot assess their relative importance without a knowledge of  $K_B$ .

The 40-fold rate inhibition for the  $\text{Co}(\text{acac})_3$  oxidation of  $\text{Cu}(\text{phen})_2^+$  in SDS is surprisingly large for a reaction involving a neutral molecule. In Table I we have included the rate parameters for the  $\text{H}_2\text{O}_2$  oxidation of  $\text{Cu}(\text{phen})_2^+$ , and it is seen that SDS micelles cause a 20-fold inhibition of this reaction as well. We have previously suggested a possible increase in the  $\text{Cu}(\text{phen})_2^+$  reduction potential upon micelle association which would decrease the thermodynamic driving force of the reaction.<sup>1</sup> A similar proposal has been made to explain micellar rate inhibition of other electron-transfer reactions.<sup>25,26</sup> Recent electrochemical experiments have shown that the half-wave potentials of several metal complexes do increase upon association with SDS micelles.<sup>27</sup> Another possible reason for rate inhibition is a decreased accessibility of the micellar  $\text{Cu}(\text{I})$  site. This argument seems plausible in our case since micelles cause a 100-fold inhibition of the association of  $\text{Cu}(\text{phen})^+$  with phenanthroline, a system where a neutral molecule approaches a micellar  $\text{Cu}(\text{I})$  species and no change in redox potential is involved. This limited accessibility could arise from strong association between the phenanthroline ligands and one or more detergent tails or from ion pair formation between the detergent head groups and the

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Cu(phen)<sub>2</sub><sup>+</sup> complex. The former seems more likely since current studies in nonionic detergent show rate diminution for both the Co(EDTA)<sup>-</sup> and Co(acac)<sub>3</sub> systems. At this time, rate inhibition in SDS can be attributed to changes in both the reduction potential and the accessibility of the Cu(I) site, although the relative importance of these effects cannot be assessed without further study.

Micellar association of Cu(phen)<sub>2</sub><sup>+</sup> causes very little change in the activation parameters for the Co(acac)<sub>3</sub>, Co(EDTA)<sup>-</sup>, and H<sub>2</sub>O<sub>2</sub> oxidations (Table I). This suggests that the metal complex is located in the Stern "region",<sup>28</sup> and the environment is very aqueous-like.

It is of interest to make a rough assessment of the relative importance of the electrostatic and nonelectrostatic barriers to electron transfer in the Co(acac)<sub>3</sub> and Co(EDTA)<sup>-</sup> systems. For outer-sphere electron transfer, the free energy of activation can be separated into electrostatic and nonelectrostatic terms:<sup>29</sup>

$$\Delta G_{12}^* = \Delta G_{12}^{**} + w_{12} \quad (15)$$

Here  $\Delta G_{12}^*$  and  $\Delta G_{12}^{**}$  are the measured and corrected free energies of activation and  $w_{12}$  is the work involved in bringing two reagents together. The work term contains both electrostatic and nonelectrostatic contributions,<sup>29</sup> but at this stage we will consider only the former to be significant. In a micellar system we can further separate  $\Delta G_{12}^{**}$  into two parts:

$$\Delta G_{12}^{**} = \Delta G_{12}^{**a} + \Delta G_{12}^{**m} \quad (16)$$

where  $\Delta G_{12}^{**a}$  represents those standard nonelectrostatic contributions to the free energy which would be present in both aqueous and micellar solution and  $\Delta G_{12}^{**m}$  represents additional contributions coming exclusively from the presence of micelles. The latter term could include contributions arising from a change in redox potential as well as steric hindrance due to strong reagent-micelle association.

For the Co(acac)<sub>3</sub> reaction we have

$$\Delta G_{12}^* = \Delta G_{12}^{**a} + \Delta G_{12}^{**m} \quad (17)$$

since  $w_{12} = 0$  for a neutral molecule. Calculating  $\Delta G_{12}^*$  from the second-order rate constant in 0.1 M SDS ( $k_{2M} = 19.2 \text{ M}^{-1} \text{ s}^{-1}$ ) and  $\Delta G_{12}^{**a}$  from the aqueous second-order rate constant ( $k_2 = 756 \text{ M}^{-1} \text{ s}^{-1}$ ), we obtain  $\Delta G_{12}^{**m} = 2.2 \text{ kcal/mol}$  for the nonelectrostatic contribution to the free energy term in the micellar reaction.<sup>30</sup>

For the Co(EDTA)<sup>-</sup> reaction the work term is evaluated at 25 °C by the following expression:<sup>31</sup>

$$w = 2.1175 \left( \frac{e^{\kappa R_1}}{1 + \kappa R_1} + \frac{e^{\kappa R_2}}{1 + \kappa R_2} \right) \frac{Z_1 Z_2}{R_1 + R_2} \exp[-\kappa(R_1 + R_2)] \quad (18)$$

where  $Z$  is the reagent charge,  $R$  is the reagent radius,  $\kappa = \beta\mu^{1/2}$ ,  $\beta$  is a constant (0.329 Å), and  $\mu$  is the ionic strength. The radius of Co(EDTA)<sup>-</sup> is estimated at 4.7 Å from molecular models. With the assumption of a spherical shape, a radius of 22 Å has been calculated from density measurements for SDS micelles in 0.2 M NaCl.<sup>32,33</sup> The micelle surface is

known to be 50–70% neutralized.<sup>2b</sup> Taking an average value of 60% and  $N = 110$  in 0.2 M NaCl,<sup>23</sup> we estimate  $Z$  to be approximately  $-45 \pm 10$ . We can also estimate  $Z$  under our experimental conditions from ionic strength studies. The Marcus theory has been used successfully to calculate protein charges from electron-transfer rate data as a function of ionic strength.<sup>34</sup>

$$\ln k = \ln k_0 - 3.576 \left( \frac{e^{-\kappa R_1}}{1 + \kappa R_2} + \frac{e^{-\kappa R_2}}{1 + \kappa R_1} \right) \frac{Z_1 Z_2}{R_1 + R_2} \quad (19)$$

All quantities have been defined previously except  $k_0$ , which refers to the rate constant at infinite (not zero) ionic strength. Using this expression and the data given in Table II, we obtain  $Z = -47 \pm 18$ . This is an approximate value, but it is in surprisingly good agreement with that estimated above and suggests that association of Cu(phen)<sub>2</sub><sup>+</sup> does not dramatically alter the micelle size. From eq 17, with  $R = 22 \text{ Å}$  and  $Z = -47$  for the micelle, we calculate  $w_{12} = 0.5 \text{ kcal/mol}$  for the Co(EDTA)<sup>-</sup> oxidation of micellar Cu(phen)<sub>2</sub><sup>+</sup>. Calculating  $\Delta G_{12}^*$  and  $\Delta G_{12}^{**a}$  from the micellar and aqueous second-order rate constants, respectively, and combining eq 14 and 15, we obtain  $\Delta G_{12}^{**m} = 2.7 \text{ kcal/mol}$  as the nonelectrostatic contribution to the free energy term in the micellar Co(EDTA)<sup>-</sup> electron transfer. This number is somewhat larger than that obtained for the Co(acac)<sub>3</sub> reaction, but considering the approximate nature of the calculations, it is not appropriate to make further comparisons at this stage. It is worth noting that the nonelectrostatic barrier to electron transfer through the surface of SDS micelles in the Cu(phen)<sub>2</sub><sup>+</sup>-Co(EDTA)<sup>-</sup> system is about 4–5 times that of the electrostatic barrier.

Using relative Marcus theory, Gray and co-workers have found that calculated metalloprotein self-exchange electron-transfer rate constants decrease with decreasing kinetic accessibility of the metal center.<sup>31</sup> Although the micellar Cu(I) species is a dynamic aggregate and cannot duplicate the more rigid and specialized protein conformations, there are some basic similarities between the micellar Cu(I) complex and small Cu metalloproteins, especially those with kinetically accessible metal centers. It is interesting that strong hydrophobic interactions between the micelle and the Cu(I) complex apparently can create a barrier to electron transfer relative to the reaction in aqueous solution. As might be expected, this barrier is substantially smaller than that observed for copper proteins whose redox sites are many Å removed from the protein surface.

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**Supplementary Material Available:** Tables of experimental kinetic data and Figure 1S, plot of  $k_{\text{obsd}}$  as a function of [Co(acac)<sub>3</sub>] for the oxidation of Cu(phen)<sub>2</sub><sup>+</sup> in aqueous solution, Figure 2S, Eyring plot of rate data for oxidation of (Cu(phen)<sub>2</sub><sup>+</sup> by Co(acac)<sub>3</sub>, and Figure 3S, plot of  $k_{\text{obsd}}$  vs. [Co(acac)<sub>3</sub>] for the oxidation of Cu(I) (7 pages). Ordering information is given on any current masthead page.

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