Inorg. Chem. **1995,** *34,* 1083–1089

Dynamics of the Coordination Equilibria in Solutions Containing Copper(II), Copper(I), and 2,9-Dimethyl-1,10-phenanthroline and Their Effect on the Reduction of O_2 by Cu(I)

Yabin Lei and Fred C. Anson*

Arthur Amos Noyes Laboratories, Division of Chemistry and Chemical Engineering,[†]
California Institute of Technology, Pasadena California 91125

Received August 18, 1994[⊗]

The rates of establishment of coordination equilibria in solutions containing 2,9-dimethyl-1,10-phenanthroline (DMP) and Cu(II) when the latter is reduced to Cu(I) at electrodes were measured by means of cyclic voltammetry. Formal potentials for the $Cu(DMP)^{2+/+}$ and $Cu(DMP)_2^{2+/+}$ couples were evaluated (0.08 and 0.35 V vs SCE, respectively) from which the equilibrium constants for the formation of the $Cu(DMP)^+$ and $Cu(DMP)_2^+$ complexes were calculated (6.7×10^8 M^{-1} and 1.5×10^{10} M^{-2}, respectively). $Cu(DMP)_2^+$ is not oxidized by O_2, but $Cu(DMP)^+$, generated by addition of Cu^{2+} to solutions of $Cu(DMP)_2^+$, is oxidized by O_2. A rate law is presented that accounts for the observed second-order dependences of the reaction rate on $[Cu^{2+}]$, $[Cu(DMP)^{2+}]$, and $[Cu(DMP)_2^+]^{-1}$. The stoichiometric reduction of O_2 by $Cu(DMP)^+$ in solution is contrasted with the catalytic reduction of O_2 by the same complex adsorbed on graphite electrodes.

The complexes of Cu(II) and Cu(I) with 1,10-phenanthroline and related ligands are strongly adsorbed on graphite electrodes, where they provide catalytic pathways for the electroreduction of O_2. In recent studies directed at establishing the mechanisms of the catalytic cycles, the electrochemical behavior of several complexes of Cu(II) and Cu(I) were examined in the presence and absence of O_2.[1-3] Coordination equilibria on the electrode surface were found to control the catalytic activity of the adsorbed complexes: Those with one coordinated phenanthroline ligand were more active than those with two coordinated ligands.[1-4] This difference in reactivity was attributed to the more negative formal potential of the Cu(II)/Cu(I) couple of the singly ligated metal and to the need for an open coordination site on the Cu(I) complexes to provide an inner-sphere pathway for the electron transfer reaction.[1,2,4]

A complex of particular interest was formed by the coordination of Cu^{2+} to 2,9-dimethyl-1,10-phenanthroline (DMP) adsorbed on the surface of graphite electrodes. Separated responses corresponding to the $[Cu(DMP)_2^{2+/+}]_{ads}$ and $[Cu(DMP)^{2+/+}]_{ads}$ couples were obtained by appropriate manipulation of the concentration of Cu^{2+} in the solutions to which the electrode surfaces were exposed.[2,4] Catalytic electroreduction of O_2 and H_2O_2 occurred at the potential of the $[Cu(DMP)^{2+/+}]_{ads}$ couple but not at the more positive potential of the $[Cu(DMP)_2^{2+/+}]_{ads}$ couple. In the present study we sought to compare the catalytic behavior of the adsorbed complexes with that of their counterparts in solution. Salts of $Cu(DMP)_2^+$ were synthesized and used to prepare stable solutions of this complex. The $Cu(DMP)_2^+$ complex was partially converted to $Cu(DMP)^+$ by the addition of excess Cu^{2+} to its solutions, and the kinetics of the reduction of O_2 in such solutions were measured. The generation of $Cu(DMP)_2^+$ and $Cu(DMP)^+$ by electrochemical reduction of the corresponding Cu(II) complexes was also examined and provided evidence that the rate of establishment of coordination equilibrium among the various complexes was measurable. However, the coordination equilibria proceed sufficiently rapidly that the rate of the homogeneous reduction of O_2 is limited by the rate of the electron transfer step. The kinetic and electrochemical measurements and our interpretation of them are summarized in this report.

Experimental Section

Materials. 2,9-Dimethyl-1,10-phenanthroline (DMP) from Aldrich was recrystallized from acetone to obtain a white solid. Reagent grade $CuSO_4 \cdot 2H_2O$ was used as received. Solutions of the $Cu(DMP)^{2+}$ and $Cu(DMP)_2^{2+}$ complexes were prepared for cyclic voltammetric experiments by mixing the two reactants in aqueous buffer solutions. The buffer contained 0.04 mol/L each of acetic, phosphoric, and boric acids and was adjusted to pH 5.2 with NaOH. $[Cu(DMP)_2]_2SO_4$ was prepared by a literature procedure.[5] Solutions were prepared from laboratory deionized water that was further purified by passage through a purification train (Millipore).

Apparatus and Procedures. The conventional electrochemical cells and instrumentation have been previously described.[1a] Glassy carbon rather than pyrolytic graphite electrodes were employed to minimize the adsorption of the complexes on the electrode surfaces. The electrodes were polished to a mirror finish with 0.05 μm alumina and sonicated in pure water for 10 min before each experiment. Electrodes with areas of 0.86 and 0.07 cm^2 were employed. Potentials were measured and are quoted with respect to a saturated calomel electrode (SCE). Experiments were conducted at the ambient laboratory temperature (22 ± 1 °C). Spectral measurements were made with a HP 8450A spectrophotometer. Because of the limited solubility of the complexes in the presence of ClO_4^- or $CF_3SO_3^-$, kinetic measurements on the reactions of O_2 with Cu(I) complexes were carried out in 0.125 M Na_2SO_4 buffered at pH 5.2 with 0.05 M acetate. (A few runs conducted in 0.025 M acetate produced rates that were about 20% slower.)

Results and Discussion

Speciation. In previous studies of the complexation of Cu^{2+} and Cu^+ by 2,9-dimethyl-1,10-phenanthroline[6] (DMP) the following equilibria and equilibrium constants were reported:

---

* Author to whom correspondence should be addressed.

[†] Contribution No. 8973.

[⊗] Abstract published in *Advance ACS Abstracts,* February 1, 1995.

(1) (a) Zhang, J.-J.; Anson, F. C. *J. Electroanal. Chem. Interfacial Electrochem.* **1992**, *341*, 232. (b) *ibid.*, **1993**, *348*, 81.

(2) Zhang, J.-J.; Anson, F. C. *Electrochim. Acta*, **1993**, *38*, 2423.

(3) Sugiyama, K.; Aoki, K. *J. Electroanal. Chem. Interfacial Electrochem.* **1989**, *262*, 211.

(4) Lei, Y.; Anson, F. C. *Inorg. Chem.* **1994**, *33*, 5003.

(5) McMillin, D. R.; Buckner, M. T.; Ahn, B. T. *Inorg. Chem.* **1977**, *16*, 943.

(6) James, B. R.; Williams, R. J. P. *J. Chem. Soc.* **1961**, 2007.

0020-1669/95/1334-1083$09.00/0

$$Cu^{2+} + DMP \rightleftharpoons Cu(DMP)^{2+} \qquad K_1 = 1.3 \times 10^6\ M^{-1} \quad (1)$$

$$Cu(DMP)^{2+} + DMP \rightleftharpoons Cu(DMP)_2^{\ 2+} \qquad K_2 = 4 \times 10^5\ M^{-1} \quad (2)$$

$$Cu^+ + DMP = Cu(DMP)^+ \qquad K_3 \quad (3)$$

$$Cu(DMP)^+ + DMP = Cu(DMP)_2^{\ +} \qquad K_4 \quad (4)$$

No values for K_3 or K_4 had been reported prior to this study, but a value for their product has been estimated:[6]

$$Cu^+ + 2DMP = Cu(DMP)_2^{\ +} \qquad K_3K_4 = 10^{19}\ M^{-2} \quad (5)$$

On the basis of the reported values of K_1 and K_2, one calculates that it should be possible to prepare solutions containing appreciable concentrations of both $Cu(DMP)^{2+}$ and $Cu(DMP)_2^{2+}$ by appropriate adjustment of the concentration of the DMP ligand. However, the lack of a value for K_3 or K_4 prevents the corresponding calculation for solutions containing Cu^+ and DMP. One of the objectives of this study was to obtain estimates of these two equilibrium constants.

Cyclic Voltammetry. Complexes of Cu^{2+} and Cu^+ with the DMP ligand adsorb strongly on graphite electrodes.[2] In order to obtain voltammetric responses that were as free as possible of contributions from adsorbed complexes, highly polished glassy carbon electrodes were employed in the present study. In contrast to graphite electrodes, these glassy carbon electrodes did not exhibit a response from adsorbed complexes when they were transferred from solutions of the complexes to pure supporting electrolyte solutions.

In Figure 1 are shown cyclic voltammograms recorded with solutions of Cu^{2+} containing an excess or an equimolar quantity of the DMP ligand. The voltammogram in Figure 1A corresponds to a solution containing only $Cu(DMP)_2^{2+}$. The fraction of the Cu(II) present as $Cu(DMP)^{2+}$ in this solution is calculated to be less than 1% using the values of K_1 and K_2 given above. The voltammetric response consists of a single reversible couple with a formal potential of 0.35 V. This formal potential matches that in previous reports[4] where the response was assigned to the half-reaction

$$Cu(DMP)_2^{\ 2+} + e = Cu(DMP)_2^{\ +} \qquad E_6^{\ f} = 0.35\ V \quad (6)$$

The formal potential of 0.35 V agrees with the value that can be calculated from the reported values of K_1, K_2, and K_3K_4[6] and the potential of the Cu^{2+}/Cu^+ couple (−0.08 V vs SCE[7]). (The potential quoted is a standard potential uncorrected for any effects arising from differences in ionic strength.)

A different voltammetric response is obtained with solutions that contain equimolar quantities of Cu^{2+} and DMP. As shown in Figure 1B, two cathodic peaks are present but only one anodic peak. The first cathodic peak and the anodic peak appear at the same potentials as the single cathodic and anodic peaks in Figure 1A, and it is reasonable to assign them to half-reaction 6. The peak current of the first cathodic peak is smaller in Figure 1B than in Figure 1A because only part of the Cu(II) present is reduced at 0.35 V. Additional Cu(II) is reduced near 0.1 V, where a second cathodic peak appears, but the sum of the two cathodic peak currents in Figure 1B is considerably smaller than the peak current in Figure 1A. Thus, a substantial portion of the Cu(II) present in the solution used to record Figure 1B, which has the stoichiometric composition corresponding to $Cu(DMP)^{2+}$, is not reduced at potentials positive of 0 V. The single anodic peak near 0.4 V in Figure 1B is larger than either cathodic peak. Apparently the products of the reductions at both 0.35 and 0.1 V are oxidized at the same potential.

In Figure 1C is shown the voltammogram which results if the direction of the potential scan is reversed before the second cathodic wave is encountered. A smaller anodic peak current is obtained, but the peak potential is at the same potential as that of the larger anodic peak in Figure 1B.

The behavior shown in Figure 1B,C suggests that the cathodic peak near 0.1 V in Figure 1B arises from half-reaction 7 which is followed immediately by reaction 8. As a result, the single

$$Cu(DMP)^{2+} + e \rightleftharpoons Cu(DMP)^+ \qquad E_7^{\ f} \quad (7)$$

$$Cu(DMP)^+ + Cu(DMP)^{2+} \rightleftharpoons Cu(DMP)_2^{\ +} + Cu^{2+} \qquad K_8 \quad (8)$$

anodic peak near 0.4 V corresponds to the reverse direction of half-reaction 6. The smaller cathodic peak currents in Figure 1B are the result of the conversion, via reaction 8, of a portion of the $Cu(DMP)^{2+}$ present in the solution into noncomplexed Cu^{2+} cations which are not reduced (to Cu metal) until −0.2 V.

This account of the voltammetric responses in Figure 1 requires that the rate of establishment of the coordination equilibrium of reaction 9 be slower, and that of reaction 8 be

$$2Cu(DMP)^{2+} = Cu(DMP)_2^{\ 2+} + Cu^{2+} \qquad K_9 \quad (9)$$

faster, than the cyclic voltammetric time scale employed in Figure 1, which was ca. 4 s. If the equilibrium of reaction 9 responded more rapidly to the reductive consumption of $Cu(DMP)_2^{2+}$ at 0.35 V, half of the Cu(II) present would be reduced to $Cu(DMP)_2^+$ at the electrode surface (as the other half was converted to Cu^{2+}) and there would be no cathodic (or anodic) peak near 0.1 V.

To inspect the rate of response of equilibria 8 and 9 to changes in the concentrations of the $Cu(DMP)_2^{2+}$ and $Cu(DMP)^{2+}$ complexes at the electrode surface, cyclic voltammograms for solutions containing equimolar quantities of Cu^{2+} and DMP were recorded at widely different potential scan rates. The results are shown in Figure 2. At a scan rate of 500 mV s^{-1} the ratio of the second to the first cathodic peak current is larger than it is at 25 mV s^{-1} (Figure 2A,B). At 2500 mV s^{-1} the ratio of cathodic peak currents is about the same as at 500 mV s^{-1} but a prominent anodic peak appears near 0.1 V where none was apparent at the lower scan rates. A summary of the scan rate dependence of the first cathodic peak current in voltammograms like those in Figure 2 is shown in Figure 3A. The measured peak current at each scan rate was normalized by dividing it by the peak current obtained in an otherwise identical solution of $Cu(DMP)_2^{2+}$ where there was no evidence of kinetic complications associated with slow attainment of coordination equilibria. The pattern of behavior shown in Figures 2 and 3A is consistent with the slowly established coordination equilibria suggested above: At low scan rates the first cathodic peak is enhanced by the conversion of $Cu(DMP)^{2+}$ into $Cu(DMP)_2^{2+}$ and Cu^{2+} during the time required to record the voltammogram, while at scan rates of 1000 mV s^{-1} and greater this conversion does not have time to occur and the cathodic peak currents provide a measure of the equilibrium concentrations of $Cu(DMP)_2^{2+}$ and $Cu(DMP)^{2+}$ in the bulk of the solution. In our previous study of the $Cu(DMP)_2^{2+}$ and $Cu(DMP)^{2+}$ complexes adsorbed on the surface of graphite electrodes, stable cyclic

---

(7) *Standard Potentials in Aqueous Solution*; Bard, A. J., Parsons, R., Jordan, J., Eds.; M. Dekker, Inc.: New York, 1985.

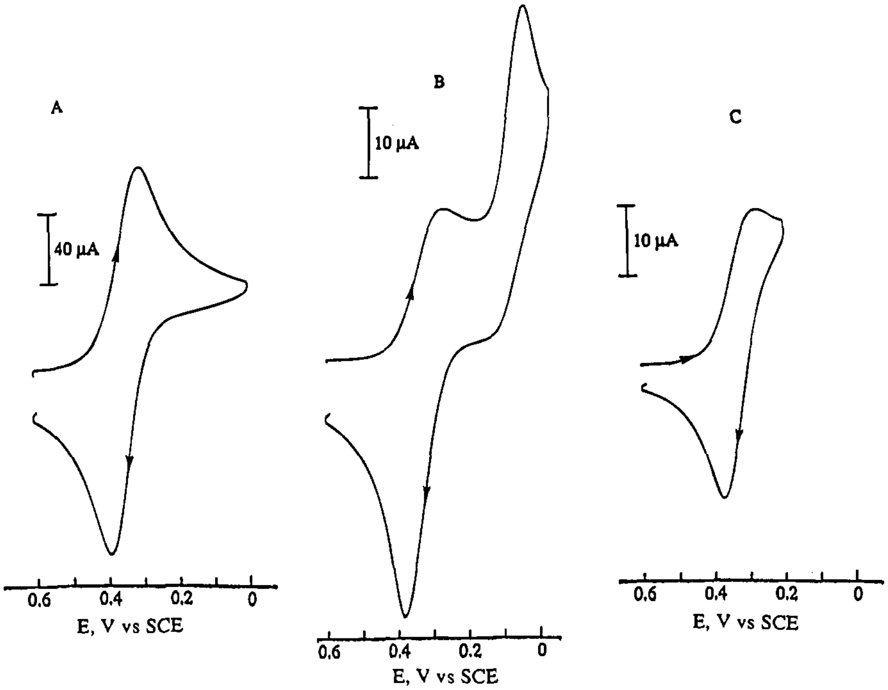

Figure 1. Cyclic voltammograms recorded with solutions containing 2 mM Cu^{2+} plus (A) 4.7 mM DMP and (B) 2 mM DMP. (C) Repeat of (B) with the direction of the potential scan reversed at 0.2 V instead of 0 V. Supporting electrolyte: 0.05 M buffer; pH 5.2. A polished glassy carbon electrode (0.86 cm^2) was used. Potential scan rate = 50 mV s^{-1}.

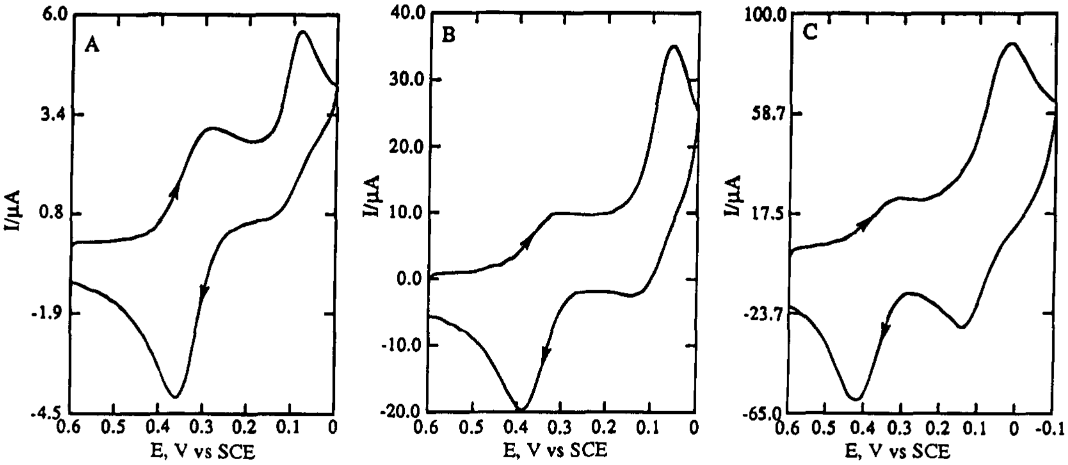

Figure 2. Cyclic voltammogram for a solution containing 2 mM Cu^{2+} and 2 mM DMP recorded at potential scan rates of (A) 25, (B) 500, and (C) 2500 mV s^{-1}. A smaller glassy carbon electrode (0.07 cm^2) was employed. Other conditions were as in Figure 1.

voltammetric responses were obtained for both the $[Cu(DMP)_2{}^{2+/+}]_{ads}$ and $[Cu(DMP)^{2+/+}]_{ads}$ couples, even at scan rates as low as 50 mV s^{-1}.[2] Evidently, and not surprisingly, the rate of establishment of the coordination equilibria when the complexes are adsorbed is considerably smaller than when the complexes are dissolved in solution.

The anodic peak near 0.1 V in Figure 2C seems clearly to correspond to the reverse of half-reaction 7. When sufficiently large scan rates are employed, the reverse of reaction 7 can compete successfully with reaction 8 and the redox couple near 0.1 V becomes reversible. The average of the anodic and cathodic peak potentials for voltammograms such as the one in Figure 2C provides a reasonable estimate of the previously unreported formal potential for half-reaction 7. The value obtained is $E_7{}^f = 0.08$ V vs SCE.

Rotating-Disk Voltammetry. The type of behavior shown in Figures 1–3 was also observed at rotating graphite disk electrodes. Current–potential curves recorded with solutions of $Cu(DMP)_2{}^{2+}$ or $Cu(DMP)^{2+}$ are shown in Figure 4A,B, respectively. The single wave in Figure 4A matches the single cathodic peak in Figure 1A, and the cathodic waves in Figure 4B match those in Figures 1B and 2. In Figure 3B is shown the dependence of the normalized plateau currents of the first wave in Figure 4B on the electrode rotation rate. As in Figure 3A, the normalized current reaches a value that is independent of the rotation rate above ca. 1000 rpm. The limiting values of normalized currents in Figures 3A,B are the same, namely 0.17. This value can be used to estimate the equilibrium constant for reaction 9. The value obtained is $K_9 = 7.9 \times 10^{-2}$, which corresponds to the dissociation of about 22% of $Cu(DMP)^{2+}$ into $Cu(DMP)_2{}^{2+}$ and Cu^{2+} at equilibrium. Reaction 9 consists of reaction 1 in reverse plus reaction 2. Thus, K_9 should be equal to K_2/K_1, or 0.3, which corresponds to the dissociation of about 26% of $Cu(DMP)^{2+}$. The difference between these two values of K_9 probably reflects differences between the reported values of K_1 and K_2 and those applicable to the supporting electrolyte employed in this study. To check on a reviewer's concern that the ligand equilibration rates might be affected by the presence of the anions in the buffer employed, measurements

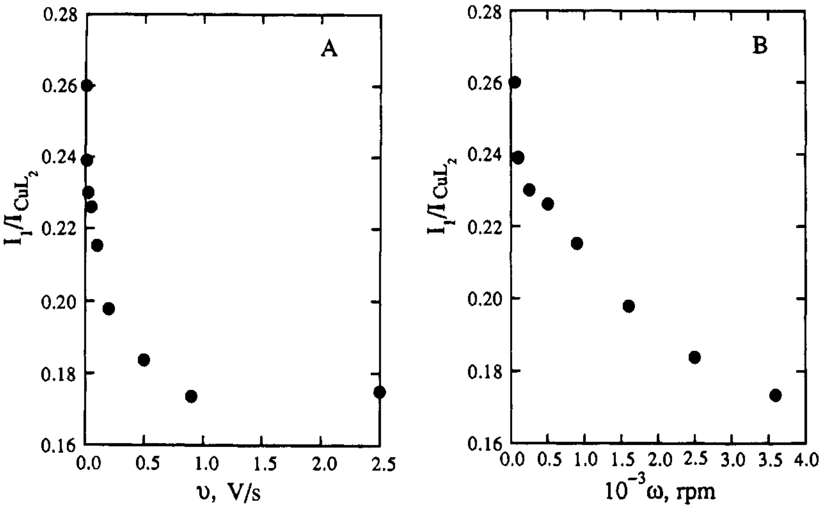

Figure 3. (A) Scan rate dependence of normalized peak currents for the first cathodic peak in voltammograms obtained with a solution containing 1 mM Cu^{2+} and 1 mM DMP. The ordinate is the ratio of the measured peak current to that obtained in a solution containing 1 mM Cu^{2+} and 2.3 mM DMP. (B) Corresponding rotation rate dependence of the normalized plateau currents of the first cathodic wave of rotating-disk voltammograms such as those in Figure 4B.

were also conducted using half the concentration of buffer. The results were essentially the same.

Digital Simulation. The somewhat sluggish coordination equilibria that are responsible for the observed voltammetric behavior comprise a mechanistic scheme with consequences that can be examined by means of digital simulation. Scheme 1 summarizes the reactions and half-reactions that have been proposed to control the cyclic voltammetric responses.

Scheme 1

$$\mathrm{Cu(DMP)_2}^{2+} + \mathrm{e} \rightleftharpoons \mathrm{Cu(DMP)_2}^{+} \qquad E_6^{\mathrm{f}} = 0.35\ \mathrm{V} \qquad (6)$$

$$\mathrm{Cu(DMP)}^{2+} + \mathrm{e} \rightleftharpoons \mathrm{Cu(DMP)}^{+} \qquad E_7^{\mathrm{f}} = 0.08\ \mathrm{V} \qquad (7)$$

$$\mathrm{Cu(DMP)}^{+} + \mathrm{Cu(DMP)}^{2+} \underset{k_{-8}}{\overset{k_8}{\rightleftharpoons}} \mathrm{Cu(DMP)_2}^{+} + \mathrm{Cu}^{2+} \qquad K_8 = 3 \times 10^3 \qquad (8)$$

$$2\mathrm{Cu(DMP)}^{2+} \underset{k_{-9}}{\overset{k_9}{\rightleftharpoons}} \mathrm{Cu(DMP)_2}^{2+} + \mathrm{Cu}^{2+} \qquad K_9 = 7.9 \times 10^{-2} \qquad (9)$$

The methods by which the values of E_6^{f}, E_7^{f}, and K_9 were obtained have been described. K_8 was calculated from these three measured parameters. To simulate cyclic voltammograms based on Scheme 1 it was only necessary to select values for k_8 and k_9, the forward rate constants governing the coordination equilibria of reactions 8 and 9 in Scheme 1. (Heterogeneous rate constants for half-reactions 6 and 7 would also be required in principle, but the lack of dependence of peak separations on scan rate allowed high values (>1 cm s^{-1}) to be assigned to both of these rate constants, which rendered them unimportant in the simulated voltammograms.) The parameters listed in Scheme 1 and trial values of k_8 and k_9 were employed with the commercially available Digisim program of Rudolph et al.[8] to obtain simulated voltammograms which were compared with their experimental counterparts. The values of the two rate constants were varied to obtain the best fit to the experimental voltammograms. The resulting values were $k_8 = 1.1 \times 10^4$ M^{-1} s^{-1} and $k_9 = 5 \times 10^2$ M^{-1} s^{-1}. The simulated voltammograms obtained with this set of parameters are compared with experimental voltammograms recorded at two scan rates in Figure 5. (Scan rates above 1 V s^{-1} were avoided in the simulations because the experimental voltammograms recorded at higher scan rates were exhalted by the apparent adsorption of $\mathrm{Cu(DMP)_2}^{+}$ on the electrode surface.) The agreement is reasonable and lends support to the proposal that the voltammetric responses are controlled by the half-reactions and coupled equilibria given in Scheme 1.

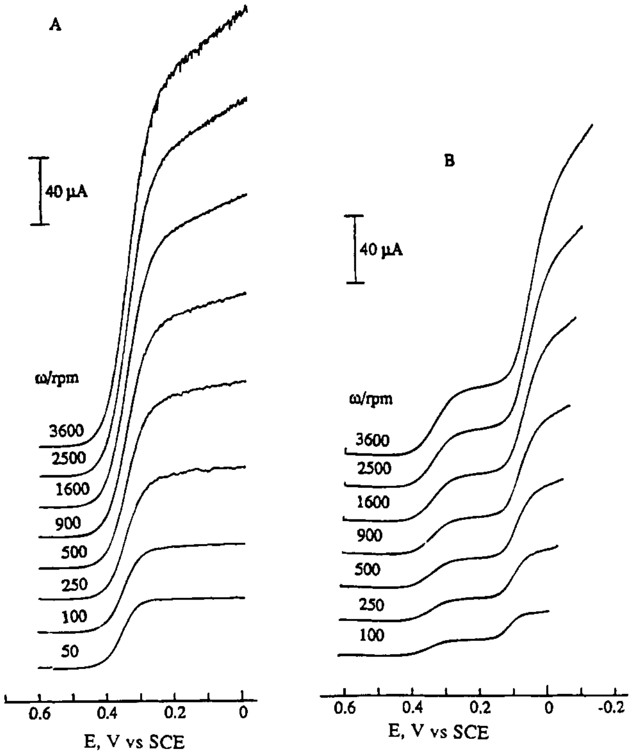

Figure 4. Rotating-disk voltammetry with solutions of $\mathrm{Cu(DMP)}^{2+}$ and $\mathrm{Cu(DMP)_2}^{2+}$. (A) Current–potential curves recorded with a solution containing 1 mM Cu^{2+}, 2.3 mM DMP, and 0.05 M buffer; pH 5.2. Electrode rotation rates are listed by each curve. The electrode potential was scanned at 10 mV s^{-1}. (B) Repeat of (A) with a solution containing 1 mM Cu^{2+} and 1 mM DMP.

Coordination Equilibrium Constants. The data obtained in this study did not include those needed to allow estimates of the equilibrium constants for reactions 1–4 to be calculated.

---

[8] Rudolph, M.; Reddy, D. R.; Feldberg, S. W. *Anal. Chem.* **1994**, *66*, 589A.

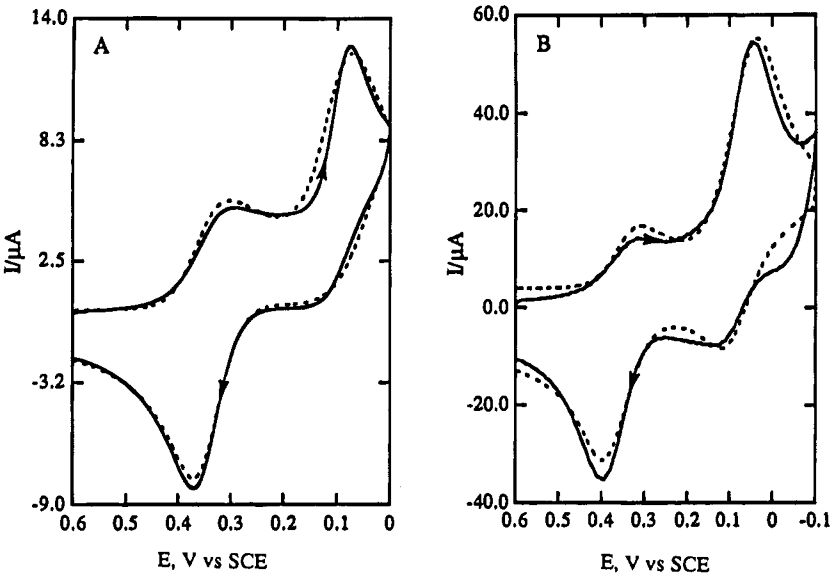

Figure 5. Comparison of simulated cyclic voltammograms (- - -) with those obtained experimentally (—) for a solution containing 1 mM Cu^{2+} and 1 mM DMP. Potential scan rate: (A) 100 mV s^{-1}; (B) 1000 mV s^{-1}. Other conditions were as in Figure 1. The simulation was based on the mechanism shown in Scheme 1 using the equilibrium parameters given in Scheme 1 plus $k_8 = 1.1 \times 10^4\ M^{-1}\ s^{-1}$, $k_9 = 5 \times 10^2\ M^{-1}\ s^{-1}$, a diffusion coefficient of $5 \times 10^{-6}\ cm^2\ s^{-1}$ for $Cu(DMP)_2^{2+}$ and $Cu(DMP)^{2+}$ and $6 \times 10^{-6}\ cm^2\ s^{-1}$ for $Cu(DMP)_2^+$, $Cu(DMP)^+$, and Cu^{2+}, and heterogeneous rate constants for half-reactions 6 and 7 of 1 cm s^{-1}.

However, the formal potentials of half-reactions 6 and 7 can be combined with that of half-reaction 10 to calculate the ratios

$$Cu^{2+} + e = Cu^+ \qquad E_{10}^f = -0.08\ V \qquad (10)$$

K_1/K_3 and K_2/K_4. The values calculated in this way are $K_1/K_3 = 1.9 \times 10^{-3}$ and $K_2/K_4 = 2.7 \times 10^{-5}$. The previously measured values of K_1, K_2, and K_3K_4 (see reactions 1, 2, and 5) can be combined to give $K_1K_2/K_3K_4 = 5.2 \times 10^{-8}$. The corresponding ratio calculated from the measurements made in this study is $K_1K_2/K_3K_4 = 5.1 \times 10^{-8}$. The good agreement with the previously reported data supports the values obtained in this study, including the previously unavailable value of E_7^f. With this value of E_7^f in hand, it is possible to calculate individual values for K_3 and K_4 using the known values of K_1, K_3K_4, and E_{10}^f. The result is $K_3 = 6.7 \times 10^8\ M^{-1}$ and $K_4 = 1.5 \times 10^{10}\ M^{-1}$. The fact that K_4 is larger than K_3 is consistent with the observed tendency for solutions of $Cu(DMP)^{2+}$ to be reduced to $Cu(DMP)_2^+$ (and Cu^{2+}) instead of to $Cu(DMP)^+$.

Reaction of $Cu(DMP)_2^+$ and $Cu(DMP)^+$ with O_2. Air-saturated, aqueous solutions of $Cu(DMP)_2^+$ are stable toward oxidation, especially in the presence of excess ligand. Indeed, pure salts of $Cu(DMP)_2^+$ can be isolated from air-saturated solutions.[5,9] It was shown previously that the $[Cu(DMP)^+]_{ads}$ complex, but not the $[Cu(DMP)_2^+]_{ads}$ complex, is an active catalyst for the electroreduction of O_2,[2,4] and we anticipated that the $Cu(DMP)^+$ complex in solution might also exhibit reactivity toward the reduction of O_2. However, the relative values of K_3 and K_4 make it impossible to prepare solutions in which $Cu(DMP)^+$ is the dominant species present: reduction (with ascorbate) of solutions containing equimolar quantities of Cu^{2+} and DMP produces solutions containing essentially equimolar quantities of $Cu(DMP)_2^+$ and Cu^{2+} with only ca. 2% of the Cu(I) present as $Cu(DMP)^+$ if K_8 is taken as 3×10^3. Nevertheless, such solutions are reactive toward the reduction of O_2 and the rate of the reduction is enhanced by the further addition of Cu^{2+} to the solutions.

The kinetics of the oxidation of $Cu(DMP)^+$ by O_2 were followed by monitoring the absorbance of the $Cu(DMP)_2^+$ complex with which $Cu(DMP)^+$ is in equilibrium. The former complex has an absorbance maximum at 454 nm with a molar extinction measured as $7.1 \times 10^3\ cm^{-1}\ M^{-1}$. (Previously reported values range from $6.1 \times 10^3\ M^{-1}\ cm^{-1}$ [9] to $7.5 \times 10^3\ M^{-1}\ cm^{-1}$ [10].) The absorbance of $Cu(DMP)^+$ at this wavelength is apparently much weaker and was assumed to be negligible in the kinetic analysis. This assumption seemed justified not only because a previous study demonstrated very weak absorbance of the $Cu(DMP)^+$ complex at 454 nm in acetonitrile[11] but also because under the conditions employed in the kinetic runs the predominant form of the Cu(I) complex was always $Cu(DMP)_2^+$, which was converted to $Cu(DMP)^+$ via equilibrium 8 as the $Cu(DMP)^+$ was oxidized to $Cu(DMP)^{2+}$ by O_2.

The disappearance of $Cu(DMP)_2^+$ was measured in solutions containing much larger concentrations of O_2, Cu^{2+} and $Cu(DMP)^{2+}$. The rate of the decrease in the concentration of $Cu(DMP)_2^+$ exhibited second-order kinetics as shown in Figure 6A. The rate constant obtained from the slope of the line in Figure 6A, k_{obs}, was linearly dependent on $[O_2]$ (Figure 6B), on $[Cu^{2+}]^2$ (Figure 6C), and on $[Cu(DMP)^{2+}]^{-2}$ (Figure 6D). In separate experiments we found that the combination of $Cu(DMP)_2^+$ plus Cu^{2+} also reduced H_2O_2 to H_2O. In dioxygen-free solutions that were otherwise identical to those utilized in monitoring the consumption of $Cu(DMP)_2^+$ by O_2, the addition of H_2O_2 at concentrations comparable to those that were generated during the reduction of O_2, e.g., 10 μM, resulted in a more rapid disappearance of $Cu(DMP)_2^+$ than was observed in the presence of much larger concentrations of O_2. Thus, the $Cu(DMP)_2^+-Cu^{2+}$ system apparently accomplishes the complete reduction of O_2 to H_2O. The overall reaction is

$$4Cu(DMP)_2^+ + 4Cu^{2+} + O_2 + 4H^+ \rightarrow 8Cu(DMP)^{2+} + 2H_2O \qquad (11)$$

The behavior of the system is consistent with the mechanism depicted in Scheme 2, in which one $Cu(DMP)^+$ complex

---

(9) Davis, G.; Higgins, R.; Loose, D. J. *Inorg. Chem.* **1976**, *15*, 700.

(10) Goldstein, S.; Czapski, G. *Inorg. Chem.* **1985**, *24*, 1087.

(11) Atkins, C. E.; Park, S. E.; Blaszak, J. A.; McMillin, D. R. *Inorg. Chem.* **1984**, *23*, 569.

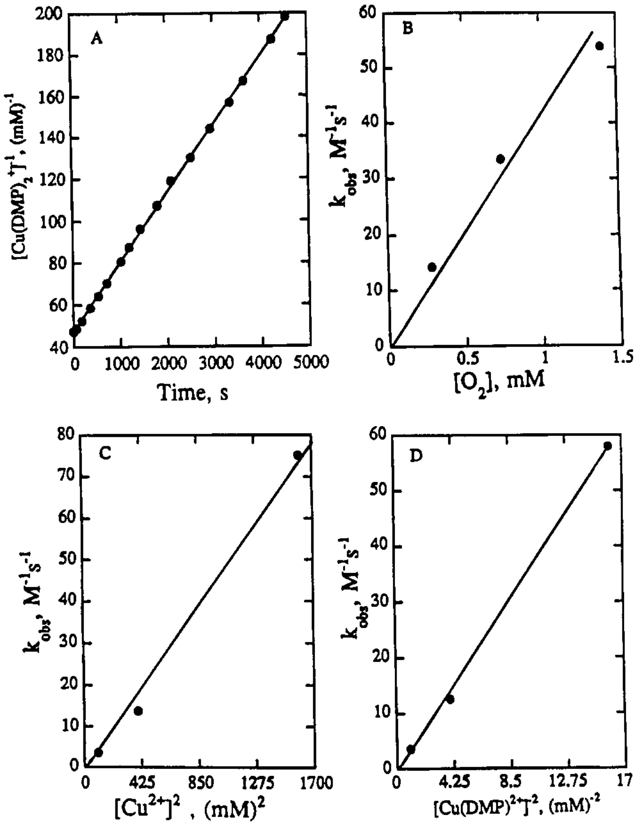

Figure 6. (A) Second-order kinetic plot of $[Cu(DMP)_2^+]^{-1}$ vs time during the oxidation of $Cu(DMP)^+$ by O_2. Solution composition: $[Cu^{2+}] = 20$ mM, $[Cu(DMP)^{2+}] = 1$ mM, $[O_2] = 0.7$ mM, initial concentration of $Cu(DMP)_2^+ = 20$ μM. Supporting electrolyte: 0.125 M Na_2SO_4 + 0.05 M acetate buffer at pH 5.2. (B) Dependence of the slopes of plots such as the one in (A), i.e., k_{obs}, on the concentration of O_2. Other concentrations were as in (A). (C) Variation in k_{obs} with $[Cu^{2+}]^2$. Other concentrations: $[O_2] = 0.28$ mM, $[Cu(DMP)^{2+}] = 1$ mM. (D) Variation in k_{obs} with $[Cu(DMP)^{2+}]^{-2}$. Other concentrations: $[O_2] = 0.28$ mM, $[Cu^{2+}] = 10$ mM. In (B)–(D) the lines were obtained from least-squares fits to $y = mx$.

activates the O_2 molecule by coordinating to it and additional $Cu(DMP)^+$ molecules provide the electrons required to reduce the coordinated O_2, ultimately to H_2O.

Scheme 2

$$Cu(DMP)_2^+ + Cu^{2+} \underset{k_{-12}}{\overset{k_{12}}{\rightleftharpoons}} Cu(DMP)^+ + Cu(DMP)^{2+} \qquad K_{12} = K_8^{-1} \quad (12)$$

$$Cu(DMP)^+ + O_2 \underset{k_{-13}}{\overset{k_{13}}{\rightleftharpoons}} [Cu(DMP)O_2]^+ \qquad K_{13} \quad (13)$$

$$Cu(DMP)^+ + [Cu(DMP)O_2]^+ \xrightarrow[+2H^+]{k_{14}} H_2O_2 + 2Cu(DMP)^{2+} \quad (14)$$

$$2Cu(DMP)_2^+ + 2Cu^{2+} + H_2O_2 \xrightarrow[2H^+]{fast} 4Cu(DMP)^{2+} + 2H_2O \quad (15)$$

The observed rate of disappearance of $Cu(DMP)_2^+$ in the presence of O_2 and Cu^{2+} was much slower than the rate at which equilibrium 12 is maintained as deduced from the digital simulation procedure described above. For example, with the experimental conditions employed, the pseudo-first-order rate constant for the forward direction of reaction 12 is 0.1 s^{-1}. Neither the rate nor equilibrium constants for reaction 13 are known. However, the rate constant for the forward direction of reaction 13 when the $Cu(DMP)^+$ complex is adsorbed on graphite electrodes was estimated previously[4] as 10^4 M^{-1} s^{-1}, which would correspond to a pseudo-first-order rate constant of 2.8 s^{-1} for reaction 13 in an air-saturated solution ($[O_2] = 0.28$ mM). These two pseudo-first-order rate constants are both sufficiently large to ensure that reactions 12 and 13 remain at equilibrium during the rather slow homogeneous reaction between O_2 and $Cu(DMP)^+$ in the experiments involved in Figure 6. The rate law corresponding to equilibrium for reactions 12 and 13 with reaction 14 as the rate limiting step is given in eq 16. This rate law accounts for the observed

$$-\frac{d[Cu(DMP)_2^+]}{dt} = \frac{4k_{14}K_{12}^2K_{13}[Cu(DMP)_2^+]^2[Cu^{2+}]^2[O_2]}{[Cu(DMP)^{2+}]^2} = k_{obs}[Cu(DMP)_2^+]^2 \quad (16)$$

dependences of the reaction rate on all three copper-containing reactants as well as the first-order dependence on $[O_2]$.

The observation that only the $Cu(DMP)^+$ complex is able to reduce the $[Cu(DMP)O_2]^+$ adduct in Scheme 2 is presumably the result of the significantly more negative formal potential of the $Cu(DMP)^{2+/+}$ couple compared with the $Cu(DMP)_2^{2+/+}$ couple.

The form of the rate law in eq 16 effectively eliminates an outer-sphere pathway for the reaction of $Cu(DMP)^+$ with O_2 because the O_2^- that would be formed in the first step of such a mechanism would not persist long enough to be further reduced in a subsequent rate-determining step as required by the observed second-order dependence on $Cu(DMP)^+$. The value of K_{12} obtained from the electrochemical measurements described above, $K_{12} = 3.3 \times 10^{-4}$, was used to calculate the product $k_{14}K_{13}$ from the slopes of the plots in Figure 6B–D. The average resulting value of $k_{14}K_{13}$ was 3×10^8 M^{-2} s^{-1}. This value is similar to those reported by Goldstein and Czapski[12] (2.2×10^8 M^{-2} s^{-1} [10] and 2.9×10^8 M^{-2} s^{-1} [12] after correction of typographical errors in the units) for the reduction of O_2 by $Cu(phen)_2^+$ by a reaction mechanism equivalent to reactions 13 and 14 of Scheme 2 involving a five-coordinate $[Cu(phen)_2O_2]^+$ adduct.[10,12,13] Steric factors might cause the analog of reaction 13 to have a smaller equilibrium constant in the case of $Cu(phen)_2^+$, but the more negative formal potential of the $Cu(phen)_2^{2+/+}$ couple (−0.05 V vs 0.08 V for $Cu(DMP)^{2+/+}$) could compensate for this effect and lead to the observed comparable value of the analog of $k_{14}K_{13}$.

Comparison of the Homogeneous and Heterogeneous Reduction of O_2 in the Presence of $Cu(DMP)_2^+$. The lack of reactivity of $Cu(DMP)_2^+$ toward O_2 in solution observed in the present and previous studies[9,10,12] matches the behavior reported when the complex is adsorbed on graphite electrodes.[2,4] The ready reaction between $Cu(DMP)^+$ and O_2 in solution described in the present study also parallels the behavior of this complex in the adsorbed state.[2,4] However, the rate laws that describe the kinetics in the two cases are quite different: When the $Cu(DMP)^+$ complex is generated in the presence of O_2 from $Cu(DMP)^{2+}$ adsorbed on the surface of graphite electrodes, the catalytic electroreduction of O_2 ensues at a rate that exhibits a

---

(12) Goldstein, S.; Czapski, G. *J. Am. Chem. Soc.* **1983**, *105*, 7276.

(13) Goldstein, S.; Czapski, G.; Eldik, R. V.; Cohen, H.; Meyerstein, D. *J. Phys. Chem.* **1991**, *95*, 1282.

first-order dependence on the quantity of $Cu(DMP)^+$ present on the electrode surface.[2] The O_2 is reduced directly to H_2O in a four-electron step, and the catalytic reduction current is limited by the rate of formation of a $[Cu(DMP)O_2]_{ads}^+$ adduct. The electrons consumed in the reduction of each O_2 molecule in the $[Cu(DMP)O_2]_{ads}^+$ adduct are supplied by the electrode. The adsorbed $Cu(DMP)^+$ complex functions as a catalyst by coordinative activation of the O_2 molecules so that they undergo electroreduction at more positive potentials than is possible on bare graphite surfaces.[2,4]

By contrast, when the $Cu(DMP)^+$ complex engages in the stoichiometric reduction of O_2 in homogeneous solution, all of the necessary electrons are supplied by $Cu(DMP)^+$ complexes and second-order kinetics are observed. In addition, because the reactive $Cu(DMP)^+$ complex must be generated from the dominant, unreactive $Cu(DMP)_2^+$ complex, the kinetics exhibit a second-order dependence on Cu^{2+} and a second-order inhibition by $Cu(DMP)^{2+}$ (eq 16).

At graphite electrodes on which $Cu(DMP)^+$ is adsorbed, the catalytic reduction of H_2O_2 by $Cu(DMP)^+$ proceeds much more slowly than does the reduction of O_2,[2] while the stoichiometric reduction of H_2O_2 by $Cu(DMP)^+$ in solution is more rapid than the reduction of O_2. However, the rates being measured in the two types of kinetic experiments correspond to such different circumstances that there is little reason to expect the results to be similar. The reduction rates at rotating disk electrodes are measured with the electrode maintained at potentials on the plateau of the current–potential curves where the currents exhibit no potential dependence. Thus, electron transfer *per se* is not the current-limiting step (if it were, the currents would be potential-dependent), so it is the rate of a purely chemical step, such as the coordination of O_2 or H_2O_2 molecules to the $Cu(DMP)^+$ adsorbed on the electrode surface, that is measured when the electroreductions of O_2 and H_2O_2 are examined.

By contrast, when the reductions are carried out in homogeneous solution, the energies of the reducing electrons are not continuously variable as they are at an electrode surface. Instead, the energy is determined by the redox potential of the reductant ($Cu(DMP)^+$) and it is significantly lower than the electron energies at potentials on the plateau of the current–potential curve for the electrogeneration of the reductant from its oxidized precursor ($Cu(DMP)^{2+}$). Activation of the substrate by coordination to the reductant may also be required in the case of homogeneous reductions, in which case the reaction rates observed can involve control by both coordination kinetics and electron transfer kinetics. The observation that adsorbed $Cu(DMP)^+$ catalyzes the electroreduction of O_2 to H_2O at a higher rate than it catalyzes the electroreduction of H_2O_2 to H_2O indicates that all four electrons are delivered to O_2 molecules coordinated to the adsorbed $Cu(DMP)^+$ complex before the partially reduced dioxygen dissociates from the Cu(I) center. The relative rates of the electroreduction of H_2O_2 and O_2 can be interpreted as measures of the relative rates of entry of the two substrate molecules to the coordination sphere of the adsorbed catalyst. The opposite order of reactivities for the same two substrates during their homogeneous reductions by $Cu(DMP)^+$ could reflect differences in both their relative rates of coordination to $Cu(DMP)^+$ in solution and the relative rates of electron transfer from a second $Cu(DMP)^+$ complex to the coordinated, activated substrate.

Conclusions

The high stability and corresponding low reactivity of the $Cu(DMP)_2^+$ complex toward the reduction of O_2 (and H_2O_2) can be circumvented by the addition of Cu^{2+} to convert a small portion of the complex to its more strongly reducing and reactive $Cu(DMP)^+$ form. The coordination equilibria involved in this conversion proceed at easily measurable rates that are, nevertheless, sufficiently rapid not to limit the rates of reduction of O_2 or H_2O_2 under the experimental conditions employed. The results of the electrochemical measurements used to evaluate the kinetics of the coordination reactions also allowed values to be determined for the heretofore unreported formal potential of the $Cu(DMP)^{2+/+}$ couple and the individual formation constants for the $Cu(DMP)^+$ and $Cu(DMP)_2^+$ complexes.

Acknowledgment. This work was supported by the National Science Foundation and ONR/DARPA.

IC940974Q