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

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

Introduction

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

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

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

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

Experimental Section

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

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

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

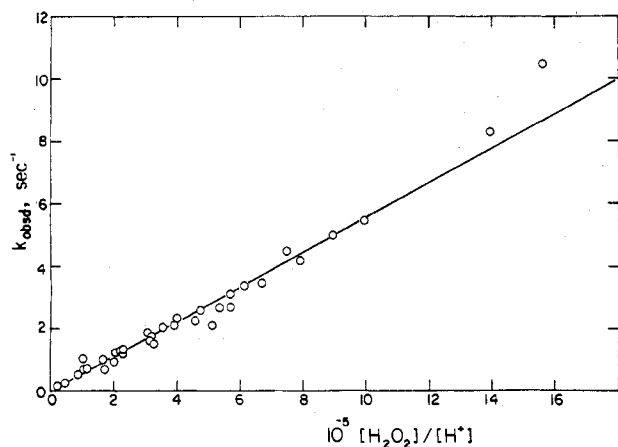


Figure 1. Plot of k_{obsd} vs. $[\text{H}_2\text{O}_2]/[\text{H}^+]$ under the following experimental conditions: $[\text{Cu}^{\text{II}}]_0 = 1.53 \times 10^{-5} \text{ M}$, $[\text{boric acid}]_T = 3.75 \times 10^{-3} \text{ M}$, $[\text{dmp}]_T = 2.57 \times 10^{-4} \text{ M}$.

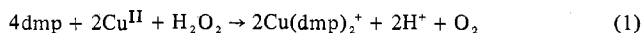
amounts of $\text{Cu}(\text{dmp})^+(\text{aq})$ in the photochemically induced reduction of $\text{Cu}(\text{dmp})_2^{2+}(\text{aq})$. Conversion to $\text{Cu}(\text{dmp})_2^{2+}(\text{aq})$ was quantitative, within experimental error, under our conditions.

Kinetic Measurements. The acidity of mixed reactant solutions was determined from pH measurements as described previously.¹ The reaction was investigated spectrophotometrically by monitoring the formation of the copper(I) product in a stopped-flow apparatus.¹ The temperature was maintained constant to within 0.05 °C for all runs, and the kinetic dependences were investigated at 25.0 °C. The ionic strength was adjusted to 0.1 M with sodium perchlorate. A number of runs were made in a 1.0 M sodium perchlorate medium, but difficulties with precipitation of the products were encountered at this ionic strength.¹ The concentration ranges employed were $[\text{Cu}^{\text{II}}]_0 = (1.2\text{--}2.4) \times 10^{-5} \text{ M}$, $[\text{dmp}]_T = (1.8\text{--}36) \times 10^{-5} \text{ M}$, and $[\text{H}_2\text{O}_2]_0 = (1.9\text{--}59.8) \times 10^{-3} \text{ M}$ with total boric acid concentration in the range $(0.4\text{--}4) \times 10^{-3} \text{ M}$. These concentration ranges are similar to those employed previously.¹ The concentrations of hydrogen peroxide were always sufficiently high to ensure negligible variation during a run. Under these conditions the appearance of Cu^{I} was almost invariably first order (see below).

Solutions containing copper(II), ligand, and buffer ($\mu \approx 0$) were mixed with hydrogen peroxide–sodium perchlorate solutions ($\mu = 0.2 \text{ M}$) in the stopped-flow apparatus; mixing was complete within the time scale of the kinetic measurements. Each run was normally repeated four to six times and the rate constants obtained in replicate determinations agreed to within $\pm 5\%$.

Results

The stoichiometric measurements with excess Cu^{II} or excess H_2O_2 were consistent with a redox reaction denoted by (1),



within an experimental uncertainty of $\pm 5\%$.

Kinetics. Kinetic data for the redox reaction under pseudo-first-order conditions are collected in Table I.⁹ The first-order rate constant k_{obsd} was independent of the concentrations of dissolved oxygen and of boric acid in the system. Variation of the monitoring wavelength in the range 315–580 nm also had no effect on the kinetics, indicating the absence of any photochemical activation under the experimental conditions.⁸ Most of the kinetic data were obtained at 454 nm. The kinetic traces at $[\text{dmp}]_T < 1.0 \times 10^{-4} \text{ M}$ were nonexponential, and only initial rates are reported; precipitation occurred with $[\text{dmp}]_T/[\text{Cu}^{\text{II}}]_T < 1.0$, vitiating kinetic analysis.

The reaction rate is accurately first order in $[\text{H}_2\text{O}_2]$ at fixed acidity and high $[\text{dmp}]_T$, indicating the absence of stoichiometrically important metal–peroxo species (see Discussion). A plot of k_{obsd} vs. $[\text{H}_2\text{O}_2]/[\text{H}^+]$ was found to be linear at high $[\text{dmp}]_T$ (Figure 1), suggesting an empirical form

$$k_{\text{obsd}} = A [\text{H}_2\text{O}_2]/[\text{H}^+] \quad (2)$$

where A is an empirical rate parameter with units of s^{-1} .

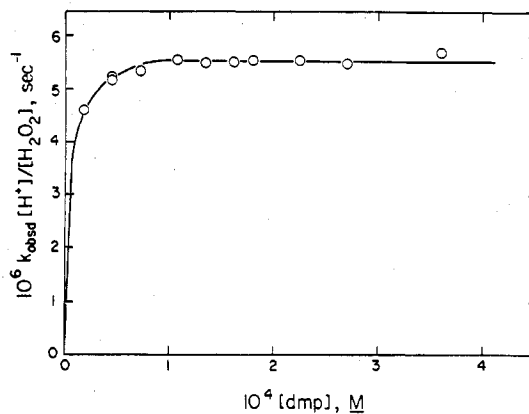


Figure 2. Plot of $k_{\text{obsd}}[\text{H}^+]/[\text{H}_2\text{O}_2]$ vs. $[\text{dmp}]_T$. The experimental conditions are $[\text{Cu}^{\text{II}}]_0 = 1.53 \times 10^{-5} \text{ M}$, $[\text{boric acid}]_T = 3.75 \times 10^{-3} \text{ M}$ at 25.0 °C.

Kinetic measurements at $[\text{dmp}]_T/[\text{Cu}^{\text{II}}] > 1$ indicated that A is $[\text{dmp}]_T$ dependent, reaching a limiting value at $[\text{dmp}]_T > 1.0 \times 10^{-4} \text{ M}$ (Figure 2). This dependence can be accounted for by an expression of the form

$$k_{\text{obsd}} = B [\text{H}_2\text{O}_2] [\text{dmp}] / [\text{H}^+] (1 + C [\text{dmp}]) \quad (3)$$

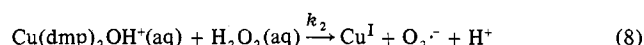
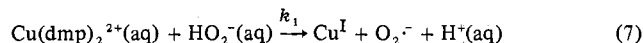
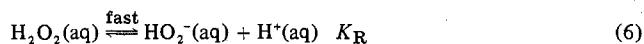
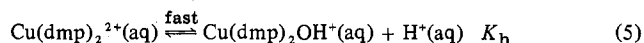
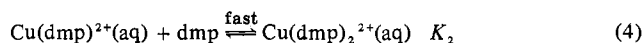
which reduces to eq 2, with $A = B/C$, at high $[\text{dmp}]$.

A $[\text{dmp}]$ dependence of this type indicates that the rate-determining step involves $\text{Cu}(\text{dmp})_2^{2+}(\text{aq})$, which is the major stoichiometric copper(II) species at high $[\text{dmp}]$.¹ It will be noted from Table I that the $[\text{hydrogen peroxide}]$, $[\text{acid}]$, and temperature dependences were investigated under conditions where the first-order rate constant is independent of $[\text{dmp}]_T$ (see below).

Mechanism

Since the reaction is first order in $[\text{H}_2\text{O}_2]$, it appears that peroxocopper(II) species are not stoichiometrically important under the reaction conditions; with this assumption, the equilibrium data cited previously¹ can be used to show that $\text{Cu}(\text{dmp})_2^{2+}(\text{aq})$ accounts for no more than 5% of the stoichiometric copper(II) concentrations over the $[\text{dmp}]_T$ studied.

A knowledge of the prevailing equilibria in this system suggests the mechanism of eq 4–9 for the reaction.¹⁰ Here,



steps (7) and (8) are postulated to be rate determining, O_2^- is a radical species, and reactions 4–6 are assumed to be in rapid equilibrium; it also seems reasonable to assume that step (9) will be much more rapid than (7) and (8)¹¹ and that rapid equilibration of Cu^{I} product species will lead to $\text{Cu}(\text{dmp})_2^{2+}$ in the presence of excess dmp .¹

The rate law predicted by this mechanism, with $[\text{H}_2\text{O}_2] = [\text{H}_2\text{O}_2]_T$ over the acidity range studied,^{11,12} is given by

$$(1/2)k_{\text{obsd}} = \frac{(k_1 K_R + k_2 K_h) K_2 [\text{dmp}] [\text{H}_2\text{O}_2]}{[\text{H}^+] (1 + K_2 [\text{dmp}]) + K_2 K_h [\text{dmp}]} \quad (10)$$

Equation 10 would account for the observed kinetic dependences if $K_2 K_h [\text{dmp}] \ll [\text{H}^+] (1 + K_2 [\text{dmp}])$, which is reasonable if equilibrium 5 is relatively unimportant under the

experimental conditions (Table I of ref 1); with this assumption eq 10 reduces to

$$(1/2)k_{\text{obsd}} = \frac{(k_1 K_R + k_2 K_h) K_2 [\text{dmp}] [\text{H}_2\text{O}_2]}{[\text{H}^+](1 + K_2 [\text{dmp}])} \quad (11)$$

At high [dmp] eq 11 may be compared with eq 2, with $A = 2(k_1 K_R + k_2 K_h)$, and, at lower [dmp], eq 11 may be compared with eq 3, where $B = 2K_2(k_1 K_R + k_2 K_h)$ and $C = K_2$. These expressions for A and B reflect the kinetic indistinguishability of reactions 7 and 8.¹¹

The data in Table I at 25.0 °C were fitted to eq 3 by means of a nonlinear least-squares program¹⁴ with $C = K_2$ fixed at the literature¹⁵ value of $6.1 \times 10^5 \text{ M}^{-1}$. This gave $A = 2(k_1 K_R + k_2 K_h) = (5.43 \pm 0.07) \times 10^{-6} \text{ sec}^{-1}$ at 25.0 °C. The calculated rate constants from this fit of the data are shown in the last column of Table I.⁹

Attempts to obtain an independent estimate of K_h by pH titration at $[\text{Cu}^{\text{II}}]_{\text{T}} \approx 3 \times 10^{-3} \text{ M}$ were vitiated by precipitation,¹⁶ which also gave rise to irreproducible kinetic data at lower acidities than those cited in Table I. Plots of $\log(k_{\text{obsd}}[\text{H}^+]/2[\text{H}_2\text{O}_2])$ vs. $1/T$ from the data of Table I are linear at high [dmp] over the temperature range investigated. The parameters ΔH^{\ddagger}_A and ΔS^{\ddagger}_A , which are the empirical activation parameters referring to the temperature dependence of A , were obtained from a nonlinear least-squares fit of the data to eq 2 with T as an independent variable.¹⁸ This treatment gave $\Delta H^{\ddagger}_A = 11.0 \pm 0.1 \text{ kcal mol}^{-1}$ and $\Delta S^{\ddagger}_A = -47 \pm 3 \text{ cal deg}^{-1} \text{ mol}^{-1}$ at 25.0 °C and ionic strength 0.1 M.

Discussion

Much of the recent work on the copper ion catalyzed decomposition of hydrogen peroxide has been restricted to the measurement of initial rates of oxygen evolution.³⁻⁵ Although this approach has given important information on the overall mechanisms for the systems studied, it has not been possible to obtain a detailed mechanism for the elementary steps of these reactions. A major complication in the previous studies is the rapid rate of oxidation of the copper(I) intermediate (detected by adding biquinoline^{4d,4e}) which, of course, completes the catalytic cycle. In addition, the reaction rate is often affected by the nature and concentration of the buffer medium, leading to considerable mechanistic uncertainty.

The stoichiometry and kinetics of the present system are much simpler than are those of previously studied reactions involving copper(II) reduction. This is because the rate of peroxide oxidation of the copper(I) species is negligible on the millisecond-second time scale. The nature of this system is such that it is possible to work under conditions where the total copper(II) concentration is essentially that of the actual copper(II) reactant, and thus only one copper(I) species is produced. Moreover, we were unable to detect any involvement of the borate buffer in the mechanism, in contrast to the complicated situation in other copper(II) systems.^{3,4,19}

Analytical and spectral investigations²⁰ of the green solid hydrates $[\text{Cu}(\text{dmp})_2](\text{ClO}_4)_{2-x}\text{H}_2\text{O}$ suggest that there is at least one water molecule in the inner coordination sphere of $\text{Cu}(\text{dmp})_2^{2+}(\text{aq})$. Since the spectra of these solid hydrates closely resemble those of $\text{Cu}(\text{dmp})_2^{2+}(\text{aq})$ in aqueous solution, it seems reasonable to assume that at least one labile water molecule²¹ is coordinated in $\text{Cu}(\text{dmp})_2^{2+}(\text{aq})$, as has been inferred from the photoredox behavior of this species.⁸

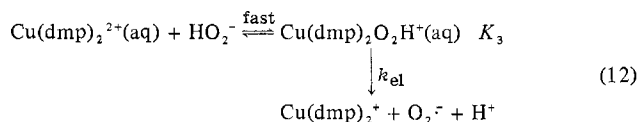
The experimental difficulties which we have encountered in attempting to obtain K_h by titration suggest that a kinetic approach to the verification of this parameter would be appropriate. A suitable system presumably would involve a substitution or redox reaction with a ligand which is not involved in significant acid-base equilibria, e.g., Cl^- , Br^- , or I^- . Our previous work¹ with thiocyanate and thiourea as reductants in aqueous perchlorate solution has shown that K_h

cannot be obtained from the kinetic data for such systems because of the considerable thermodynamic stability of $\text{dmp-Cu}^{\text{II}}$ -reductant complexes. The assumption that $K_2 K_h [\text{dmp}] \leq 0.1[\text{H}^+](1 + K_2 [\text{dmp}])$ in the present system may be used to obtain an upper limit for K_h at high [dmp] and the lowest experimental $[\text{H}^+]$, where $K_h \leq 0.1[\text{H}^+]$. The result obtained is $K_h \leq 4 \times 10^{-10} \text{ M}$ at 25.0 °C.²²

An unequivocal choice between the kinetically indistinguishable processes 7 and 8 is not possible in the absence of other thermodynamic and kinetic data. If (8) is the sole rate-determining process in this system, then, with the above estimate of K_h , $k_2 \geq 7 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ at 25.0 °C. On the other hand, if reduction occurs entirely through processes 7 and 9,^{3,4} then, with $K_R = 2.24 \times 10^{-12} \text{ M}$, $\Delta H_R = 8.2 \text{ kcal mol}^{-1}$, and $\Delta S_R = -26 \text{ cal deg}^{-1} \text{ mol}^{-1}$,¹² we obtain $k_1 = 1.2 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$, $\Delta H^{\ddagger}_1 = 2.9 \text{ kcal mol}^{-1}$, and $\Delta S^{\ddagger}_1 = -21 \text{ cal deg}^{-1} \text{ mol}^{-1}$ at 25.0 °C.

If the rate-determining step in the reduction of copper(II) bis complexes with imidazole (Im), ethylenediamine (en), and 1,3-diaminopropane (dap) by H_2O_2 is also assumed to involve reaction with HO_2^- , then the following second-order rate constants ($\text{M}^{-1} \text{ s}^{-1}$) may be derived:^{4f} $\text{Cu}(\text{Im})_2^{2+}(\text{aq})$, 5.3×10^2 ; $\text{Cu}(\text{en})_2^{2+}(\text{aq})$, 7.0×10^2 ; $\text{Cu}(\text{dap})_2^{2+}(\text{aq})$, 1.0×10^3 . Comparison of these data with k_1 indicates that the reaction of $\text{Cu}(\text{dmp})_2^{2+}(\text{aq})$ with HO_2^- is very rapid.

The enthalpy of activation for electron transfer resulting from the above interpretation is unusually low and could be accounted for in terms of a rapid reactant preequilibrium which has a negative enthalpy change, followed by rate-determining electron transfer, eq 12. The observed first-order



dependence of the reaction rate on $[\text{H}_2\text{O}_2]$ imposes an upper limit of $K_3 \leq 7 \times 10^6 \text{ M}^{-1}$ for reaction 12.²³ Thus, an inner-sphere redox process could conceivably take place within an intermediate, but analytically insignificant, peroxo complex; in this case $k_1 = K_3 k_{\text{el}}$, $\Delta H^{\ddagger}_1 = \Delta H_3 + \Delta H^{\ddagger}_{\text{el}}$ and $\Delta S^{\ddagger}_1 = \Delta S_3 + \Delta S^{\ddagger}_{\text{el}}$, where the subscript "el" refers to kinetic parameters for electron transfer. This tentative assumption of an inner-sphere mechanism for peroxide oxidation is reasonable in view of the weakly oxidizing character of the $\text{Cu}(\text{dmp})_2^{2+}(\text{aq})$ - $\text{Cu}(\text{dmp})_2^+(\text{aq})$ couple ($E^\circ = -0.59 \text{ V}$).²⁴

The above considerations do not, of course, resolve the kinetic indistinguishability between steps (7) and (8), but they do clearly indicate that the reduction of $\text{Cu}(\text{dmp})_2^{2+}(\text{aq})$ species is very facile, presumably because little change of copper stereochemistry is necessary in the overall activation process for electron transfer. It should be noted in this regard that reduction of $\text{Cu}(\text{dmp})_2^{2+}$ by thiourea in methanol is also rapid (rate constant $5.2 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ at 25.0 °C¹) while the corresponding reaction of $\text{Cu}(\text{dmp})\text{tuOH}^+(\text{aq})$ with tu in aqueous solution is much slower (rate constant $74.5 \text{ M}^{-1} \text{ s}^{-1}$ at 25.0 °C¹). It is also evident that the decrease in rate constant with decreasing [dmp] is understandable in terms of an increase in the proportion of mono(dimethylphenanthroline)copper(II) species but that these species do not give rise to a detectable kinetic term in the rate law at low [dmp].

On the basis of these comparisons, we feel that the previous arguments³⁻⁵ for high catalytic activity based on the assumption that only copper(II) species with less than three coordinated nitrogen atoms are active should be extended to include any situation where the copper reactant and product stereochemistries are, or can be made to be, closely similar. The main requirement for efficient catalytic activity would seem to be related to the rate with which the copper(II) and

copper(I) coordination spheres can be made to resemble each other on each side of the catalytic cycle. This requires alternating matching reduction (oxidation step) and increase (reduction step) of coordination numbers and would be facilitated by rapid loss and gain of weakly bound ligands such as H₂O, Cl⁻, etc. Catalytic efficiency is then a function of the relationship between the thermodynamic and kinetic properties of the two metal centers in a particular ligand environment, and the ease of electron transfer in the oxidation and reduction components of the catalytic cycle may be influenced by the involvement of coordinated peroxide. Although "simple" redox steps are consistent with the behavior of the Cu^{II}-dmp system, there is no compelling evidence to suggest that this is general for other copper-ligand catalysts involving smaller overall free energy changes in the catalytic components.³⁻⁵

In their study of the kinetics of the decomposition of hydrogen peroxide catalyzed by copper(II) complexes of the bidentate ligand 2,2'-bipyridyl, Sigel et al.^{4b} found that the rate constant calculated on the assumption that only 1:1 complexes are active was smaller than that observed when measurements were made with large excesses of bipyridyl. This observation is easily interpreted if it is assumed that bis(bipyridyl)copper complexes are also kinetically important.

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Registry No. Cu(dmp)₂²⁺, 14875-91-3; H₂O₂, 7722-84-1.

Supplementary Material Available: Table I, giving experimental and calculated kinetic data (2 pages). Ordering information is given on any current masthead page.

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- (23) A first-order dependence on [H₂O₂] will be observed if 1 ≫ *K*₃[HO₂⁻]. Putting *K*₃[HO₂⁻] = *K*₃*K*_R[H₂O₂]/[H⁺] ≤ 0.1 at [H₂O₂] = 6.0 × 10⁻² M and [H⁺] = 8.6 × 10⁻⁸ M from the data in Table I gives the upper limit quoted.
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