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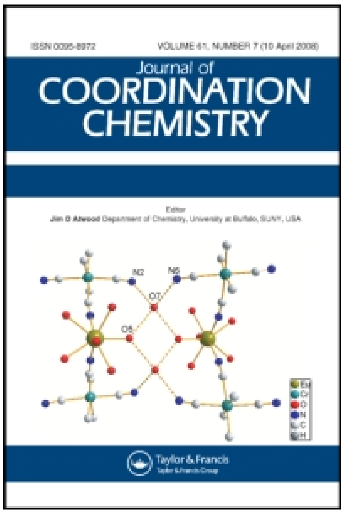

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SHORT COMMUNICATION

Electronic Effects on the rate of Oxidation of Substituted Phenanthroline Complexes of Copper(I) by Molecular Oxygen[1]

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Reactions of molecular oxygen with copper(I) complexes are of interest partly as a result of the observation that certain marine life utilize a copper based oxygen transport system, hemocyanin, and that copper has been proposed as an active site for the disproportionation of superoxide by the enzyme superoxide dismutase.[2,3] Additional interest arises from a general study of the mechanism of autoxidation of transition metal complexes. A limited number of studies have been made on the kinetics of autoxidation of various cuprous complexes.[4–13] We wish to report here on the influence of electronic effects on the autoxidation kinetics of a series of substituted phenanthroline complexes of copper(I). The ligands investigated are 5,6-dimethyl-,5-chloro-, 5-nitro-, and unsubstituted 1,10-phenanthroline.[14] Electron withdrawing or releasing substitutents were used at the 5 or the 5 and 6 positions to give maximum variation in electronic effects while keeping the ligand donor atom and stereochemistry constant. It is significant to note that the range of reactivity towards oxidation by molecular oxygen afforded by these substituted phenanthroline complexes is as wide as that reported in the literature for cuprous complexes with widely different ligand systems.

Complex stoichiometry, reaction stoichiometry and autoxidation kinetics in 2.5 M aqueous acetonitrile at 25°C were determined using apparatus and techniques described previously.[13] The substituted 1,10-phenanthroline complexes of copper(I) were generated *in situ* using tetra(acetonitrile)copper(I) perchlorate,[15] $Cu(CH_3CN)_4ClO_4$, as a cuprous ion source, thus precluding the necessity of using a copper(II) reducing agent. The aqueous acetonitrile solvent system served to enhance the low aqueous solubility of the phenanthroline ligands and also stabilized the copper(I) prior to phenanthroline complex formation.

Each substituted phenanthroline ligand was shown to form a 2:1 complex with copper(I) in 2.5 M acetonitrile by the method of continuous variations.[16] The stoichiometry of the reaction with molecular oxygen in 2.5 M aqueous acetonitrile at 25°C was determined using a polarographic oxygen electrode[17] to measure O_2 consumption, and found to be that shown in Eq. 1.

$$2Cu(X\text{-phen})_2^{+} + O_2 \xrightarrow{H^+} 2Cu(X\text{-phen})_2^{+2} + H_2O_2 \tag{1}$$

Additional evidence for this stoichiometry was obtained from data which show that the O_2 consumed was quantitatively regenerated upon titration of the H_2O_2 product with Ce(IV). Electronic spectra of the products also indicate complete conversion to $Cu(phen\text{-}X)_2^{+2}$. These data demonstrate that under the conditions of the kinetic experiments, oxidation of the parent cuprous complexes by the H_2O_2 produced in reaction [1] does not occur.

The kinetics of reaction [1] in 2.5 M acetonitrile at 25°C were investigated using stopped-flow spectrophotometry as described elsewhere.[13] Reaction progress was monitored at the wavelength maximum of each complex in the visible region of the spectrum: $(CH_3)_2$-phen ($\lambda = 420$ nm, $\epsilon = 1.3 \times 10^4$ M^{-1} cm^{-1}); phen ($\lambda = 435$ nm, $\epsilon = 6.2 \times 10^3$ M^{-1} cm^{-1}); Cl-phen ($\lambda = 450$ nm, $\epsilon = 5.2 \times 10^3$ M^{-1} cm^{-1}); NO_2-phen ($\lambda = 453$ nm, $\epsilon = 6.8 \times 10^3$ M^{-1} cm^{-1}) The rate law was determined over the pH range from 6.1 to 8.1

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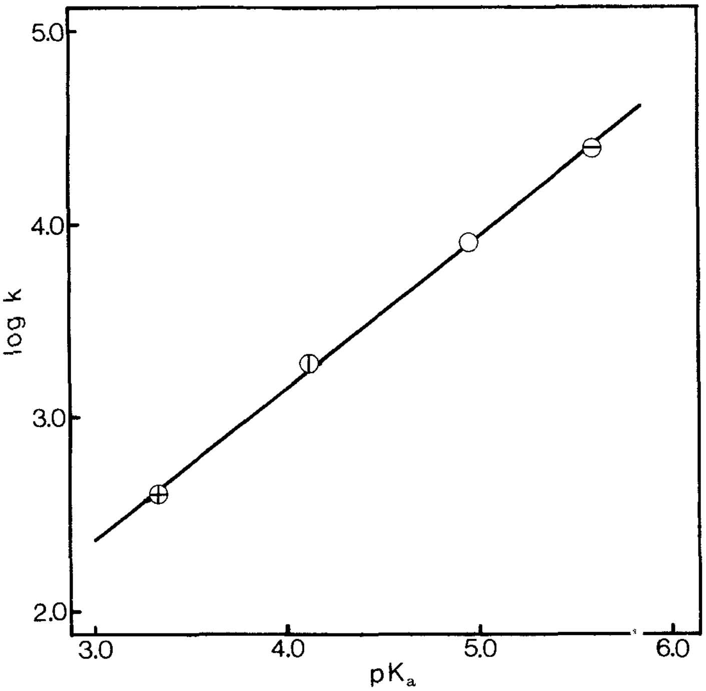

FIGURE 1 Log second-order rate constant, log k, for reaction [1] as a function of pK$_a$ of the conjugate acid of the free ligand X-phen: ⊖Cu((CH$_3$)$_2$-phen)$_2^+$; ○Cu(phen)$_2^+$; ⦶Cu(Cl-phen)$_2^+$; ⊕Cu(NO$_2$-phen)$_2^+$.

(phosphate buffer, I = 0.05 M) by the method of initial rates and found to be that shown in Eq. 2,

$$\frac{-d[\mathrm{Cu(X\text{-}phen)_2}^+]}{dt} = k[\mathrm{Cu(X\text{-}phen)_2}^+][\mathrm{O_2}] \quad (2)$$

where k = 2.4(±0.1) x 10^4 $M^{-1}sec^{-1}$, 8.2(±0.3) x 10^3 $M^{-1}sec^{-1}$, 1.9(±0.1) x 10^3 $M^{-1}sec^{-1}$ and 4.1(±0.1) x 10^2 $M^{-1}sec^{-1}$ for X-phen = $(CH_3)_2$-phen, phen,Cl-phen and NO_2-phen respectively.

There are two probable autoxidation mechanisms which are consistent with the observed rate law. The first mechanism involves a simultaneous two-electron reduction of O_2 to give H_2O_2 directly. When reaction [4] is rate limiting and

$$\mathrm{Cu(X\text{-}phen)_2}^+ + \mathrm{O_2} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} \mathrm{Cu(X\text{-}phen)_2O_2}^+ \quad (3)$$

$$\mathrm{Cu(X\text{-}phen)_2O_2}^+ + \mathrm{Cu(X\text{-}phen)_2}^+ \xrightarrow{k_4} 2\mathrm{Cu(X\text{-}phen)_2^{2+}} + \mathrm{O_2^{2-}} \quad (4)$$

$$\mathrm{O_2^{2-}} + 2\mathrm{H}^+ \longrightarrow \mathrm{H_2O_2} \quad (5)$$

the steady state assumption is applied to the concentration of the intermediate Cu(X-phen)$_2$O$_2^+$, the following rate expression is obtained.

$$\text{rate} = \frac{k_3k_4[\mathrm{Cu(X\text{-}phen)_2}^+]^2[\mathrm{O_2}]}{k_{-3} + k_4[\mathrm{Cu(X\text{-}phen)_2^+}]} \quad (6)$$

Under conditions where k_4 [Cu(X-phen)$_2^+$] $\gg k_{-3}$ equation [6] reduces to a form which is identical to that which is experimentally observed (equation [2]).

A second possible mechanism involves the stepwise reduction of O_2 by Cu(X-phen)$_2^+$. If reaction [7] represents the rate limiting step, then the

$$\mathrm{Cu(X\text{-}phen)_2^+} + \mathrm{O_2} \xrightarrow{k_7} \mathrm{Cu(X\text{-}phen)_2^{2+}} + \mathrm{O_2^-} \quad (7)$$

$$\mathrm{O_2} + \mathrm{H}^+ \longrightarrow \mathrm{HO_2} \quad (8)$$

$$\mathrm{Cu(X\text{-}phen)_2^+} + \mathrm{HO_2} \longrightarrow \mathrm{Cu(X\text{-}phen)_2^{2+}} + \mathrm{HO_2} \quad (9)$$

$$\mathrm{HO_2^-} + \mathrm{H}^+ \longrightarrow \mathrm{H_2O_2} \quad (10)$$

rate law for this mechanism is of the same form as that experimentally observed in equation [2]. The viability of this mechanism can be questioned, however, on thermodynamic grounds. The one electron reduction of O_2 to give O_2^- is an unfavorable process. If one uses the value −0.33 V for the O_2/O_2^- couple[18] and the formal potential values obtained in

50% dioxane for the $Cu^{II}(X\text{-phen})_2/Cu^{I}(X\text{-phen})_2$ couples, which vary from 0.25 V to 0.38 V[19], then log K_{eq} for reaction [7] is in the range −9.8 to −12.0. This results in calculated rate constants for the reverse of reaction [7] which are unreasonably high. One must bear in mind, however, that these calculations are based on formal potentials in 50% dioxane and a standard potential in water, which may not be strictly applicable to the aqueous acetonitrile solution used in this study.

Our results serve to demonstrate a strong influence on the autoxidation rates of copper(I) complexes by electron donating or withdrawing groups. The pK_a of the conjugate acid of the free ligand can be considered as a measure of sigma electron donor strength. These data indicate that a 10^2 fold increase in electron donor strength of the ligand results in an almost 10^2 fold increase in the second order autoxidation rate constant. This can be seen in Figure 1 which is a plot of the logarithm of the second-order rate constant for reaction [1] as a function of the pK_a[20] of the conjugate acid of the free ligand. The plot is linear with a slope of 0.8. James and Williams[19] have noted that sigma electron donor effects are important in stabilizing copper(II) while pi electron effects are important for copper(I). The linear correlation shown in Figure 1 suggests that these complexes exhibit a considerable degree of copper(II) character in the transition states of this series of reactions. A similar linear correlation may be obtained from a plot of the logarithm of the second-order rate constant for reaction [1] as a function of the formal potentials[19] for the $Cu^{II}(X\text{-phen})_2/Cu^{I}(X\text{-phen})_2$ couple in 50% dioxane.

One striking feature of the autoxidation kinetic data available in the literature for copper(I) complexes is the relatively small variation in second-order rate constants. Monodentate nitrogen donor,[8,9] polydentate nitrogen donor[10,11] and polydentate nitrogen-oxygen donor[10] ligand complexes of copper(I) have second-order autoxidation rate constants in the range from 10^2 to 10^4 $M^{-1} sec^{-1}$.[21] It is noteworthy that substituent variations on phenanthroline ligands in this study provide as wide a range of second order rate constants as variations in the entire ligand system. This suggests that electronic effects are as important as changes in coordination number, geometry, ligand donor atom and chelating ability.

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