

Kinetic Study of the Oxidation of Catechol by Aqueous Copper(II)

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The kinetics of the oxidation of catechol by aqueous copper(II) have been studied as a function of reactant concentrations at pH 6.4–7.2. To follow the reaction, a spectrophotometric method has been developed that circumvents the problem of precipitation of decomposition products of the initial *o*-quinone oxidation product. The rate law shows that the reactive species is the monocatecholate complex of Cu^{II}, and that this species undergoes rate-limiting intramolecular electron transfer with $k = 1.9 \times 10^{-5} \text{ s}^{-1}$ ($22 \pm 1 \text{ }^\circ\text{C}$, $\mu = 0.125 \text{ M NaClO}_4$). The results have allowed a reanalysis of previous work on the autoxidation in the aqueous Cu^{II}–catechol–dioxygen system, and comparisons to mechanisms of copper(II) oxidases.

Introduction

A number of copper-containing enzymes are known to act as oxidases and oxygenases toward catechol and its derivatives.¹ The oxygenases have provided some of the impetus for studies on the reaction of O₂ with Cu^I complexes and the formation of (Cu^{II})₂(O₂²⁻) derivatives,^{2–4} which may be the active oxidizing species in these systems. The copper amine oxidases also are relevant to this chemistry because they have the cofactor 2,4,5-trihydroxyphenylalanine. Dooley and co-workers⁵ identified a Cu^I–semiquinone valence tautomer in the latter system, and this type of tautomerism has been mimicked in several model systems.^{6,7} However, it is somewhat ironic that more recent studies by Klinman and co-workers⁸ have suggested that this species is not on

the major enzymatic reaction pathway, and that O₂ is binding to the enzyme at a nonmetal site. Evidence for this comes in part from metal-replacement experiments⁹ in which it was found that the Zn^{II} and Ni^{II} forms of the enzyme are not active, but the Co^{II} form has ~19% of the activity of the native enzyme toward oxidation of methylamine. The dependence of the rate on [O₂] follows the Michaelis–Menten equation, with k_{cat} being the same, within experimental error, for the native and Co^{II} forms of the enzyme. The difference in activity arises because K_{m} is 68 times larger for the Co^{II} form. For the oxidation of the semiquinone form of the cofactor by O₂, the rate increases in the order Cu-depleted \ll Co^{II} $<$ Zn^{II} $<$ Cu^{II}. In general, Klinman and co-workers^{8,9} have attributed these observations to structural and electrostatic effects of the metal on the binding site of the O₂ and the stability of the reduced O₂ species. The primary role of the metal is suggested to be the activation of the cofactor for oxidation.

The present study involves the kinetics of the simple anaerobic oxidation of catechol by aqueous copper(II). The results show the type of Cu^{II}–catechol interaction that can provide the activation necessary for the redox process. This reaction also provides a benchmark for assessing the effectiveness and probable reaction pathways for more complex

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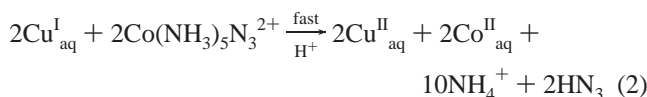
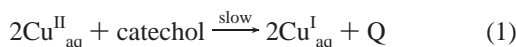
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catalytic systems. This is illustrated by a reanalysis of the autoxidation reaction, i.e., aqueous Cu^{II} + catechol + O_2 .

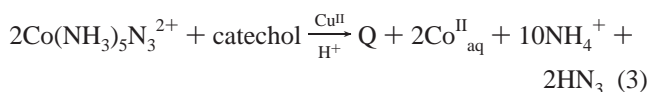
There probably are two reasons why the simple Cu^{II} –catechol reaction has not been studied previously. One is that the reaction does not appear to proceed at a finite rate under anaerobic conditions. The other problem is that catechol oxidation products are known to precipitate from near neutral aqueous solutions, so that normal spectrophotometric analysis is not possible. The present study circumvents these problems by using a cobalt(III) complex, $\text{Co}(\text{NH}_3)_5\text{N}_3^{2+}$, as a scavenger for aqueous copper(I) and by monitoring the production of cobalt(II) by standard analytical methods. The choice of scavenger is dictated in part by the fact that $\text{Co}(\text{NH}_3)_5\text{N}_3^{2+}$ does not react with catechol on the time scale of the copper(II) reaction, and that it yields an easily quantified product. The elucidation of the rate law has given the composition of the reactive copper(II) species and provided considerable insight into the more complex autoxidation mechanism.

Results

The reaction system under study can be summarized in eqs 1 and 2, without implying anything about the reactive species or intermediates, where Q is the *o*-quinone, which decomposes to insoluble products.



Then the overall reaction is given by eq 3. The reaction appears to be the copper(II)-catalyzed oxidation of catechol by the cobalt(III) complex and thus has a formal analogy to the autoxidation in which O_2 is the net oxidant.



Under the experimental conditions of $[\text{Co}(\text{NH}_3)_5\text{N}_3^{2+}] \ll [\text{catechol}]$, the concentrations of copper(II) and catechol remain essentially constant, so that the production of cobalt(II) is expected to have a simple linear dependence on time until the cobalt(III) is nearly consumed. As described in the Experimental Section, the procedure involves the periodic sampling of the reaction solution and spectrophotometric analysis for Co^{II} as the Co^{III} complex of 1-nitroso-2-hydroxynaphthalene-3,6-disulfonate (NRS). Some typical absorbance–time profiles are shown in Figure 1. The curves in Figure 1 are calculated from numerical solutions of the equations in the mechanism developed below.

The cobalt(II) concentration in the reaction mixture (2.0 mL aliquots diluted 12.5 times to 25.0 mL) is related to the absorbance (*A*) measured in a 1.0 cm cuvette by eq 4, where

$$[\text{Co}^{\text{II}}] = \frac{12.5A}{\epsilon l} \quad (4)$$

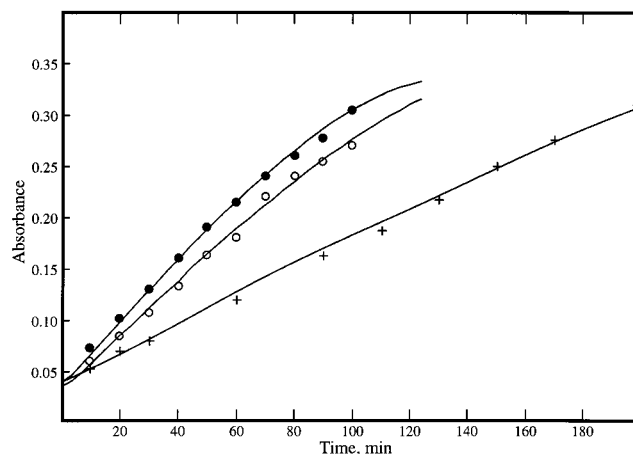


Figure 1. Variation of the absorbance of the Co^{III} (NRS) complex with time during the reaction of aqueous Cu^{II} (0.72 mM) with catechol (0.63 mM) in the presence of $(\text{NH}_3)_5\text{CoN}_3^{2+}$ (0.34 mM) at pH 6.8 (●), 7.0 (○), and 7.4 (+). The curves are calculated from a simulation of the system based on fourth-order Runge–Kutta numerical integration.

ϵ is the molar absorptivity of the Co^{III} –NRS complex ($1.48 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$). Since the rate of change of absorbance equals the slope (S , s^{-1}) of the linear region of the absorbance–time plot, then taking the derivative of both sides of eq 4 and substituting the numerical values gives the rate of production of cobalt(II) as eq 5. From the overall

$$\frac{d[\text{Co}^{\text{II}}]}{dt} = \frac{12.5}{\epsilon l} \frac{dA}{dt} = (8.446 \times 10^{-4})S \quad (5)$$

reaction stoichiometry, the rate of formation of cobalt(II), the rate of disappearance of catechol (H_2Cat), and S are related by eq 6. In general, the rate of disappearance of H_2Cat is expected to be some function of the concentrations of

$$\frac{1}{2} \frac{d[\text{Co}^{\text{II}}]}{dt} = - \frac{d[\text{H}_2\text{Cat}]}{dt} = (4.22 \times 10^{-4})S \quad (6)$$

Cu^{II} , H_2Cat , and H^+ as given generically by eq 7. In the kinetic study, these concentrations were varied systematically, and the changes in S were used to evaluate the rate law.

$$- \frac{d[\text{H}_2\text{Cat}]}{dt} = k[\text{Cu}^{\text{II}}]^m[\text{H}_2\text{Cat}]^n[\text{H}^+]^p = (4.22 \times 10^{-4})S \quad (7)$$

The kinetic results are summarized in Table 1. It is apparent for the first four runs at pH 6.4 and five runs at pH 7.0 that S has a first-order dependence on $[\text{Cu}^{\text{II}}]_{\text{tot}}$, since $S[\text{Cu}^{\text{II}}]_{\text{tot}}^{-1}$ is reasonably constant over the ~ 8 -fold change in $[\text{Cu}^{\text{II}}]_{\text{tot}}$. In the following 11 runs at pH 7.0, the $[\text{H}_2\text{Cat}]$ is varied by ~ 10 -fold and $S[\text{Cu}^{\text{II}}]_{\text{tot}}^{-1}$ decreases as $[\text{H}_2\text{Cat}]$ is increased. The final runs complete a pH variation study so that the pH range 6.4–7.4 has been covered. The $S[\text{Cu}^{\text{II}}]_{\text{tot}}^{-1}$ goes through a maximum in the pH 6.6–6.8 region and decreases substantially by pH 7.4.

An understanding of the above observations is possible when one recognizes that copper(II) is complexed by catechol under the experimental conditions to give $\text{Cu}(\text{Cat})$ and $\text{Cu}(\text{Cat})_2^{2-}$. The results qualitatively suggest that either Cu^{2+} or $\text{Cu}(\text{Cat})$ is the reactive species. Then increasing $[\text{H}_2\text{Cat}]$

Table 1. Kinetic Results for the Reaction of Aqueous Copper(II) with Catechol in 0.025 M HEPES Buffer and 0.125 M NaClO₄^a

| [Cu ^{II}] _{tot} , mM | [H ₂ Cat], mM | pH | 10 ⁵ S, s ⁻¹ | 10 ² S/[Cu ^{II}] _{tot} , M ⁻¹ s ⁻¹ | 10 ² S/[Cu(Cat)], M ⁻¹ s ⁻¹ |
|---|--------------------------|------|------------------------------------|--|--|
| 0.287 | 2.18 | 6.40 | 2.35 | 8.19 | 8.61 |
| 0.574 ^b | 2.18 | 6.40 | 4.72 | 8.22 | 8.80 |
| 0.718 ^c | 2.18 | 6.40 | 5.12 | 7.13 | 7.64 |
| 0.861 | 2.18 | 6.40 | 8.08 | 9.38 | 9.94 |
| 0.144 | 4.36 | 7.00 | 1.04 | 7.22 | 11.5 |
| 0.369 | 4.36 | 7.00 | 2.30 | 6.23 | 9.66 |
| 0.861 | 4.36 | 7.00 | 5.78 | 6.71 | 9.80 |
| 0.900 | 4.36 | 7.00 | 6.57 | 7.30 | 10.6 |
| 1.08 | 4.36 | 7.00 | 8.52 | 7.89 | 11.2 |
| 0.718 | 1.09 | 7.00 | 6.60 | 9.19 | 9.75 |
| 0.718 | 1.64 | 7.00 | 6.63 | 9.23 | 10.4 |
| 0.718 | 2.18 | 7.00 | 5.05 | 7.03 | 8.40 |
| 0.718 | 2.72 | 7.00 | 5.15 | 7.17 | 9.07 |
| 0.718 | 2.72 | 7.00 | 4.70 | 6.55 | 8.27 |
| 0.718 | 3.27 | 7.00 | 5.85 | 8.15 | 10.9 |
| 0.718 | 3.82 | 7.00 | 5.28 | 7.35 | 10.4 |
| 0.718 | 4.36 | 7.00 | 4.43 | 6.17 | 9.15 |
| 0.718 | 8.72 | 7.00 | 2.90 | 4.04 | 8.41 |
| 0.718 | 11.6 | 7.00 | 2.35 | 3.27 | 8.13 |
| 0.718 | 14.4 | 7.00 | 1.95 | 2.72 | 7.80 |
| 0.718 | 2.18 | 6.60 | 6.25 | 8.70 | 9.14 |
| 0.718 | 2.18 | 6.80 | 6.63 | 9.23 | 10.0 |
| 0.718 | 2.18 | 7.20 | 4.57 | 6.36 | 9.20 |
| 0.718 | 2.18 | 7.40 | 2.88 | 4.01 | 7.98 |

^a All runs are at ambient temperature (22 ± 1 °C) and contain 0.34 mM Co(NH₃)₅N₃²⁺ scavenger for Cu^I. ^b Average of two runs. ^c Average of three runs.

or pH could decrease the rate by converting Cu²⁺ to the less reactive Cu(Cat), or by converting Cu(Cat) to Cu(Cat)₂²⁻. A choice between these alternatives can be made by using the known formation constants for the system, as defined by eq 8, to determine the species whose concentrations

$$K_{f1} = \frac{[\text{Cu(Cat)}][\text{H}^+]^2}{[\text{Cu}^{2+}][\text{H}_2\text{Cat}]} \quad K_{f2} = \frac{[\text{Cu(Cat)}_2^{2-}][\text{H}^+]^2}{[\text{Cu(Cat)}][\text{H}_2\text{Cat}]} \quad (8)$$

change in a manner consistent with the kinetics. Several studies^{10,11} have given values for K_{f1} and K_{f2} which are in good agreement and indicate that they are only mildly sensitive to ionic strength and temperature. The values suggested by Smith et al.¹² have been used here ($\text{p}K_{f1} = -8.39$, $\text{p}K_{f2} = -11.33$, 25 °C, $\mu = 0.1$ M). The species concentrations were calculated with the assumptions that the total copper(II) and catechol concentrations are given by eqs 9 and 10,

$$[\text{Cu}]_{\text{tot}} = [\text{Cu}^{2+}] + [\text{Cu(Cat)}] + [\text{Cu(Cat)}_2^{2-}] \quad (9)$$

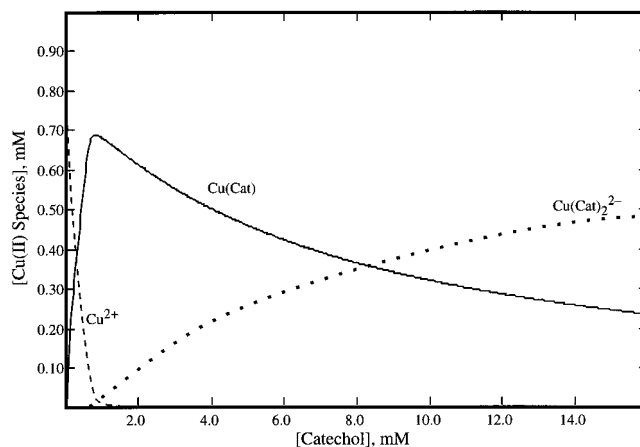
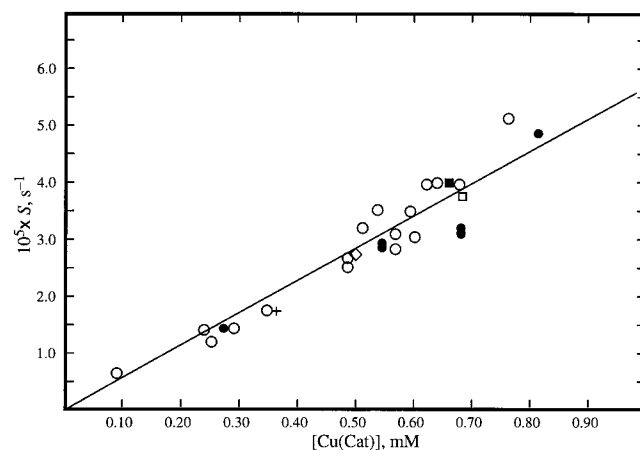
$$[\text{Cat}]_{\text{tot}} = [\text{H}_2\text{Cat}] + [\text{Cu(Cat)}] + 2[\text{Cu(Cat)}_2^{2-}] \quad (10)$$

respectively. Combination of these equations gives a cubic equation for uncomplexed [H₂Cat] in terms of K_{f1} , K_{f2} , [Cu]_{tot},

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**Figure 2.** Copper(II) species distribution for 0.72 mM total copper(II) at pH 7.0.**Figure 3.** Variation of the slope (S) from the kinetic runs with the concentration of the monocatecholate complex of copper(II) at various total catechol concentrations and pH 6.4 (●), 6.6 (□), 6.8 (■), 7.0 (○), 7.2 (◇), and 7.4 (+).

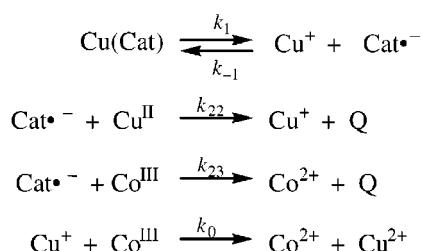
[Cat]_{tot}, and [H⁺], which was solved by the iterative, Newton method. Then the equilibrium concentration of Cu²⁺ was calculated from eq 11, and [Cu(Cat)] and [Cu(Cat)₂²⁻] were calculated from eq 8.

$$[\text{Cu}^{2+}] = \frac{[\text{Cu}]_{\text{tot}}[\text{H}^+]^4}{[\text{H}^+]^4 + K_{f1}[\text{H}^+]^2[\text{H}_2\text{Cat}] + K_{f1}K_{f2}[\text{H}_2\text{Cat}]^2} \quad (11)$$

The species distribution curve in Figure 2 shows that only the Cu(Cat) species shows a dependence on catechol concentration that is consistent with the observed dependence of the rate on catechol concentration at pH 7.0. An analogous pH distribution curve for the conditions of the pH dependence study also is consistent with Cu(Cat) as the reactive species, since significant amounts of Cu(Cat)₂²⁻ begin to form for pH > 6.8. Therefore, the rate is predicted to depend directly on [Cu(Cat)], and this is confirmed by the plot in Figure 3. Least-squares analysis gives $S = [(8.9 \pm 0.3) \times 10^{-2}][\text{Cu(Cat)}]$. This expression for S can be substituted into eq 7 to give the rate law as eq 12.

$$-\frac{d[\text{H}_2\text{Cat}]}{dt} = k[\text{Cu(Cat)}] = [(3.8 \pm 0.1) \times 10^{-5}][\text{Cu(Cat)}] \quad (12)$$

Scheme 1



This very simple rate law came as something of a surprise in view of earlier studies on the autoxidation reaction,¹¹ but more detailed comparisons will be made later. The rate law eliminates bimolecular rate-controlling electron transfer between Cu^{2+} and H_2Cat , or Cu^{2+} and Cu(Cat) . A mechanism consistent with the rate law is described in Scheme 1, where Co^{III} and Cu^{II} represent $\text{Co(NH}_3)_5\text{N}_3^{2+}$ and any copper(II) species, respectively, Q is the quinone, and the semiquinone radical anion ($\text{Cat}^{\bullet-}$) is taken to be fully deprotonated, since its $\text{p}K_a = 5$.¹³

This scheme predicts that the rate of formation of cobalt(II) is given by eq 13.

The steady-state concentration of $\text{Cat}^{\bullet-}$ is given by eq 14, where the last expression on the right

$$\frac{d[\text{Co}^{\text{II}}]}{dt} = k_0[\text{Co}^{\text{III}}][\text{Cu}^+] + k_{23}[\text{Co}^{\text{III}}][\text{Cat}^{\bullet-}] \quad (13)$$

$$[\text{Cat}^{\bullet-}] = \frac{k_1[\text{Cu(Cat)}]}{k_{-1}[\text{Cu}^+] + k_{22}[\text{Cu}^{\text{II}}] + k_{23}[\text{Co}^{\text{III}}]} = \frac{k_1[\text{Cu(Cat)}]}{k_{22}[\text{Cu}^{\text{II}}] + k_{23}[\text{Co}^{\text{III}}]} \quad (14)$$

has been simplified by the condition that $k_{-1}[\text{Cu}^+] \ll k_{22}[\text{Cu}^{\text{II}}] + k_{23}[\text{Co}^{\text{III}}]$. This should be true because all of the rate constants are expected to be at or near the diffusion-controlled limit (10^7 to $10^9 \text{ M}^{-1} \text{ s}^{-1}$), but the concentration of Cu^+ will be at a low, steady-state value, while the other species are in the 10^{-4} to 10^{-3} M range. The steady-state concentration of Cu^+ is given by eq 15, in which $[\text{Cat}^{\bullet-}]$ from eq 14 has been substituted to give the second expression in eq 15. This expression can be simplified by noting that

$$[\text{Cu}^+] = \frac{k_1[\text{Cu(Cat)}] + k_{22}[\text{Cu}^{\text{II}}][\text{Cat}^{\bullet-}]}{k_{-1}[\text{Cat}^{\bullet-}] + k_0[\text{Co}^{\text{III}}]} = \frac{k_1[\text{Cu(Cat)}](2k_{22}[\text{Cu}^{\text{II}}] + k_{23}[\text{Co}^{\text{III}}])}{k_1k_{-1}[\text{Cu(Cat)}] + k_0[\text{Co}^{\text{III}}](k_{22}[\text{Cu}^{\text{II}}] + k_{23}[\text{Co}^{\text{III}}])} \quad (15)$$

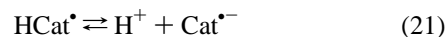
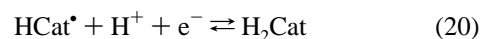
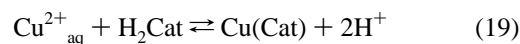
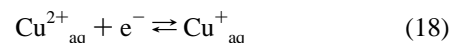
the results below show that $k_1 \ll k_0[\text{Co}^{\text{III}}]$, while the other rate constant times concentration factors in the denominator of eq 15 have similar magnitude. Therefore, $k_1k_{-1}[\text{Cu(Cat)}]$ will be small relative to the other terms in the denominator. Substitution from eq 14 and the simplified form of eq 15 into eq 13 gives eq 16 for the rate of production of cobalt-

$$\frac{d[\text{Co}^{\text{II}}]}{dt} = \frac{k_1[\text{Cu(Cat)}](2k_{22}[\text{Cu}^{\text{II}}] + k_{23}[\text{Co}^{\text{III}}])}{(k_{22}[\text{Cu}^{\text{II}}] + k_{23}[\text{Co}^{\text{III}}])} + \frac{k_1k_{23}[\text{Cu(Cat)}][\text{Co}^{\text{III}}]}{k_{22}[\text{Cu}^{\text{II}}] + k_{23}[\text{Co}^{\text{III}}]} \quad (16)$$

(II). If either $k_{22}[\text{Cu}^{\text{II}}] \gg k_{23}[\text{Co}^{\text{III}}]$ or $k_{23}[\text{Co}^{\text{III}}] \gg k_{22}[\text{Cu}^{\text{II}}]$, this equation simplifies to eq 17, which is consistent with the experimental rate law (eq 12). Comparison of eqs 12 and 17 shows that $k_1 = 1.9 \times 10^{-5} \text{ s}^{-1}$.

$$\frac{d[\text{Co}^{\text{II}}]}{dt} = 2k_1[\text{Cu(Cat)}] \quad (17)$$

One test of the proposal in Scheme 1 is to estimate the equilibrium constant $K_1 = k_1/k_{-1}$ and show that k_{-1} does not exceed the diffusion-controlled limit ($\sim 10^9 \text{ s}^{-1}$). Since copper(II) is a rather weak oxidizing agent, it is reasonable to expect that K_1 will be quite small, but the value of k_1 requires that $K_1 > 10^{-14}$. The magnitude of K_1 can be estimated from a combination of the thermodynamic information for reactions 18–21.



The values of $E^\circ_{18} = 0.15 \text{ V}$, $K_{19} = 4 \times 10^{-9} \text{ M}^{-1}$,^{10–12} and $K_{21} = 10^{-5} \text{ M}^{-1}$ ¹³ are reasonably well established, and only E°_{20} needs to be estimated. There are several ways to make this estimate. Mentasti et al.¹⁴ noted that, for 1,4-dihydroxybenzene systems, there is a difference of $\sim 0.38 \text{ V}$ between the two-electron reduction to the quinone and the one-electron reduction of the semiquinone and applied this to 1,2-dihydroxybenzene systems to obtain $E^\circ_{20} = E^\circ(\text{HCat}^{\bullet}/\text{H}_2\text{Cat}) + 0.38 = 1.17 \text{ V}$. Steenken and Neta¹⁵ obtained $E^\circ(\text{Cat}^{\bullet-}/\text{Cat}^{2-}) = 0.43 \text{ V}$, from measurements at pH 13.5, and this can be combined with K_{21} and the ionization constant of Hcat^- ($10^{-13.3} \text{ M}^{-1}$)¹² to obtain $E^\circ_{20} = 1.06 \text{ V}$. Kimura et al.¹⁶ used the oxidation kinetics of catechol in acidic solution and Marcus theory to estimate $E^\circ(\text{H}_2\text{Cat}^{\bullet+}/\text{H}_2\text{Cat}) = 1.10 \text{ V}$, and this can be combined with the acid dissociation constant of $\text{H}_2\text{Cat}^{\bullet+}$ ($\sim 10 \text{ M}^{-1}$)¹⁷ to obtain $E^\circ_{20} = 1.04 \text{ V}$. The fact that the last two estimates are derived from quite different approaches but are in good agreement suggests that it is reasonable to take $E^\circ_{20} \approx 1.05 \text{ V}$. Then one obtains $k_1/k_{-1} = 2 \times 10^{-12} \text{ M}$ and $k_{-1} = 1 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$. As expected, k_{-1} is large, but still well below the diffusion-controlled limit so that the reaction pathways in Scheme 1 are entirely viable.

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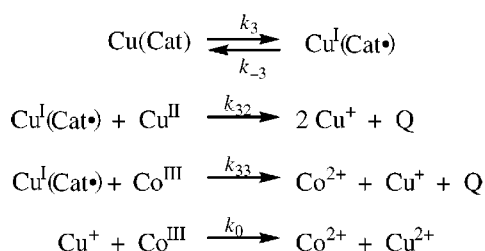
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Scheme 2



Some qualitative guidance as to reasonable magnitudes for k_{-1} , k_{22} , and k_{23} is available from previous studies. Meyerstein and co-workers¹⁸ found rate constants in the range of $(2-4) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ for the oxidation of aqueous Cu^{I} by several substituted aliphatic radicals. These are stronger oxidants than $\text{Cat}^{\cdot-}$, and give products with $\text{Cu}^{\text{II}}\text{-C}$ bonds, but provide some indication that a k_{-1} of $1 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ is not unexpected. Analogies to k_{22} may be drawn from the reactions of various radicals with aqueous Cu^{2+} which have rate constants in the range of $(0.5-1) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$.¹⁹ However, the oxidation of $\text{Cat}^{\cdot-}$ by $\text{Cu}^{2+}_{\text{aq}}$ is marginally spontaneous ($E \approx 0.03 \text{ V}$ at pH 7) and $[\text{Cu}^{2+}_{\text{aq}}] \approx 10^{-6} \text{ M}$, while the dominant species $\text{Cu}(\text{Cat})$ and $\text{Cu}(\text{Cat})_2^{2-}$ are even weaker oxidizing agents. The magnitude of k_{23} may be assessed from studies of the reduction of $\text{Co}(\text{NH}_3)_6^{3+}$, $\text{Co}(\text{NH}_3)_5\text{X}^{2+}$ ($\text{X} = \text{F}^-, \text{Cl}^-, \text{Br}^-$), and $\text{Co}^{\text{III}}(\text{N})_6^{3+}$ complexes by organic radicals for which the rate constants are in the range of 10^5 to $10^8 \text{ M}^{-1} \text{ s}^{-1}$.²⁰ From these observations, it seems probable that the condition $k_{23}[\text{Co}^{\text{III}}] \gg k_{22}[\text{Cu}^{\text{II}}]$ is applicable for the reduction of eq 16 to eq 17.

The above considerations predict that the simplification of eq 15 actually requires the condition that $k_1 k_{-1} [\text{Cu}(\text{Cat})] \ll k_0 k_{23} [\text{Co}^{\text{III}}]^2$. With rate constant values of 1.9×10^{-5} , 1×10^7 , 1.4×10^3 , and 10^5 , respectively, and typical concentrations of $[\text{Cu}(\text{Cat})] = 0.6 \text{ mM}$ and $[\text{Co}^{\text{III}}] = 0.3 \text{ mM}$, the first term in the inequality is ~ 100 times smaller than the second. Therefore, the simplification is justified for at least 90% of the reaction, if k_{23} is $\geq 10^5$.

Recent studies⁵⁻⁷ have identified valence-tautomer equilibria between $\text{L}_n\text{Cu}^{\text{II}}(\text{R-Cat})$ and $\text{L}_n\text{Cu}^{\text{I}}(\text{R-Cat}\cdot)$ species, where L is an ancillary ligand and R-Cat is a catechol derivative. This suggests the possibility that the mechanism in Scheme 1 might be modified to involve a $\text{Cu}^{\text{I}}(\text{Cat}\cdot)$ intermediate, as shown in Scheme 2.

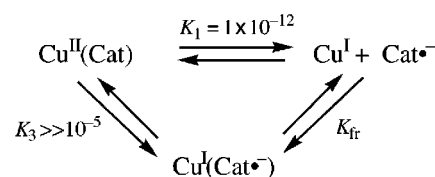
First of all it must be noted that this scheme will not produce the experimental rate law if the k_3/k_{-3} step is treated as a rapidly maintained equilibrium because all the subsequent steps are bimolecular and one of them must be rate-limiting. Therefore, the rate law has been developed using steady-state assumptions for $[\text{Cu}(\text{Cat}\cdot)]$ and $[\text{Cu}^+]$. The predicted rate of formation of Co^{2+} is given by eq 22. This

$$\frac{d[\text{Co}^{2+}]}{dt} = \frac{k_3[\text{Cu}(\text{Cat})](2k_{23}[\text{Cu}^{\text{II}}] + 2k_{33}[\text{Co}^{\text{III}}])}{k_{-3} + (k_{32}[\text{Cu}^{\text{II}}] + k_{33}[\text{Co}^{\text{III}}])} \quad (22)$$

(18) Navon, N.; Golub, G.; Cohen, H.; Meyerstein, D. *Organometallics* **1995**, *14*, 5670.

(19) Cohen, H.; Meyerstein, D. *J. Am. Chem. Soc.* **1972**, *94*, 6944.

Scheme 3



simplifies to the experimental rate law if $k_{-3} \ll k_{32}[\text{Cu}^{\text{II}}] + k_{33}[\text{Co}^{\text{III}}]$, in which case the experimental rate constant is k_3 . From the previous discussion, it is probable that $k_{33} \geq 10^5 \text{ M}^{-1} \text{ s}^{-1}$, and the experimental conditions have $[\text{Co}^{\text{III}}] \leq 0.3 \text{ mM}$, so that the inequality needed to simplify eq 22 requires that $k_{-3} \ll 30 \text{ s}^{-1}$. This can be combined with the experimental value of k_3 to calculate that $K_3 = k_3/k_{-3} \gg 10^{-5}$.

If the mechanism in Scheme 2 is viable, then the above magnitude of K_3 should be reasonable. One way to assess this is shown by the cycle in Scheme 3. The formation constant of the $\text{Cu}^{\text{I}}\text{-Cat}^{\cdot-}$ complex is given by $K_{\text{fr}} = K_3/K_1 \gg 10^7 \text{ M}^{-1}$. For conventional ligands, such as Cl^- , Br^- , NH_3 , and olefins, the analogous formation constants²¹ are $< 10^4 \text{ M}^{-1}$, and studies with simple catechols in our laboratory²² have failed to detect complexation ($K_{\text{f}} < 10^2$). Therefore, $K_{\text{fr}} \gg 10^7$ seems quite anomalous, unless there is something very special about the interaction of Cu^{I} with the catecholate radical. If the argument is reversed, and K_{fr} is taken to be $\leq 10^3 \text{ M}^{-1}$, then $K_3 \geq 10^{-9}$ and there will be insignificant amounts of the $\text{Cu}^{\text{I}}\text{-Cat}^{\cdot-}$ complex present in the system. The general conclusion from this analysis is that the $\text{Cu}^{\text{I}}\text{-semiquinone}$ complex is too unstable to be a significant intermediate in the aqueous copper(II)-catechol system.

However, a $\text{Cu}^{\text{I}}\text{-semiquinone}$ species has been identified⁴⁵ during the interaction of a copper amine oxidase and its cofactor 2,4,5-trihydroxyphenylalanine (TOPA). A major difference with the catechol system is that reduction of the semiquinone is $\sim 0.4 \text{ V}$ more favorable for TOPA,²³ and this makes $K_1 \approx 10^6$ times larger. Then, with a normal magnitude for K_{fr} , the value of K_3 would be $\sim 10^{-3}$ for TOPA. This estimate does not take into account that the $\text{Cu}^{\text{II}}/\text{Cu}^{\text{I}}$ reduction may be more favorable in the enzyme.^{23,24} These principles of increasing the oxidizability of the catechol derivative and the reducibility of the Cu^{II} have been exploited by Kaim and co-workers^{6a} to obtain measurable values of K_3 for a N,S-donor ancillary ligand and substituted catechol/semiquinone ligands in THF and toluene.

The results of the present study may provide some useful guidance for the autoxidation reaction, i.e., aqueous $\text{Cu}^{\text{II}} + \text{catechol} + \text{O}_2$. The two systems are analogous in that the O_2 has been replaced here by $\text{Co}(\text{NH}_3)_5\text{N}_3^{2+}$. This simplifies the situation by avoiding the possible complication of complexation of Cu^{I} by the oxidant, so that the differences between the two systems will reflect the effect of complex-

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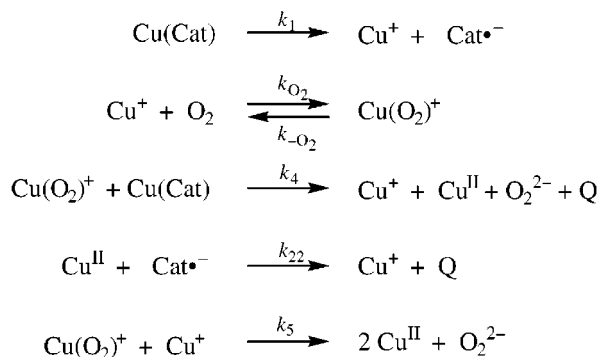
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Scheme 4



ation of Cu^{I} by O_2 . The autoxidation has been studied by Jameson and co-workers¹¹ under conditions similar to those used here. The major difference in the rate laws for the two systems is that the autoxidation is half-order in $[\text{O}_2]$ while the rate is independent of $[\text{Co}(\text{NH}_3)_5\text{N}_3^{2+}]$ in the present study. Jameson and co-workers also proposed that the $[\text{Cu}^{\text{II}}]$, pH, and [catechol] dependence of the rate indicated pathways involving the catecholate anion and the mono- and biscatecholate complexes of Cu^{II} , while only $\text{Cu}(\text{Cat})$ seems to be reactive when $\text{Co}(\text{NH}_3)_5\text{N}_3^{2+}$ is the oxidant. Before we address the latter difference, the mechanism in Scheme 4 is suggested to explain the $[\text{O}_2]^{1/2}$ dependence, while retaining some steps analogous to those in Scheme 1 and those proposed by Jameson.

For the sake of simplicity, the proton equilibria that convert $\text{Cat}^{\bullet-}$ to HCat^{\bullet} and O_2^{2-} to H_2O_2 have been omitted. The reaction of $\text{Cat}^{\bullet-}$ with Cu^{II} (k_{22}) has been retained as a termination step because Cu^{II} , in its various forms, is the dominant oxidant compared to other possibilities such as $\text{Cu}(\text{O}_2)^+$ or O_2 . Steady-state assumptions²⁵ for $[\text{Cat}^{\bullet-}]$, $[\text{Cu}(\text{O}_2)^+]$, and $[\text{Cu}^+]$ lead to a quadratic equation for $[\text{Cu}^+]$ of the general form of eq 23 (see the Supporting Information),

$$a[\text{Cu}^+]^2 - b[\text{Cu}^+] - c = 0 \quad (23)$$

where $a = k_{O_2}k_5[\text{O}_2]$, $b = k_1k_5[\text{Cu}(\text{Cat})]$, and $c = (k_{-O_2} + k_4[\text{Cu}(\text{Cat})])k_1[\text{Cu}(\text{Cat})]$. This equation can be solved for $[\text{Cu}^+]$ and the resultant substituted into the steady-state expressions to obtain equations for the concentrations of the other steady-state species in terms of known concentrations. However, this obviously will lead to complex equations, and only limiting-case roots of eq 23 will be considered further, to determine if Scheme 4 is capable of reproducing the $[\text{O}_2]^{1/2}$ dependence of the rate. Positive roots of eq 23 can be obtained if $b^2 \gg 4ac$, in which case $[\text{Cu}^+] = b/a$, or $4ac \gg b^2$, in which case $[\text{Cu}^+] = (c/a)^{1/2}$. The latter is the only situation that will lead to a half-order dependence on $[\text{O}_2]$.

With the assumption that $[\text{Cu}(\text{O}_2)^+]$ is small compared to $[\text{O}_2]$, then the rate of consumption of O_2 equals the rate of

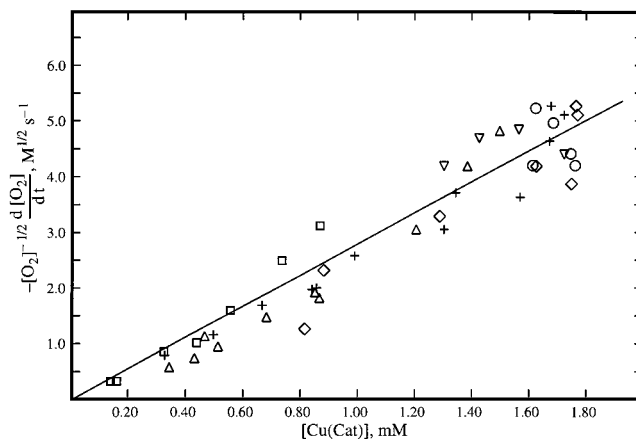


Figure 4. Variation of the rate of autoxidation for the aqueous Cu^{II} –catechol– O_2 system determined by Jameson and co-workers (ref 11) with the concentration of the monocatecholate complex of copper(II) at various total Cu^{II} and catechol concentrations and pH 4.6 (\square), 4.9 (Δ), 5.1 ($+$), 5.3 (\diamond), 5.5 (\circ), and 5.7 (∇).

production of O_2^{2-} (i.e., H_2O_2) and is given by eq 24.

$$-\frac{d[\text{O}_2]}{dt} = k_4[\text{Cu}(\text{Cat})][\text{Cu}(\text{O}_2)^+] + k_5[\text{Cu}^+][\text{Cu}(\text{O}_2)^+] \quad (24)$$

Substitution from the steady-state solutions (see the Supporting Information) gives eq 25. If the experimental rate has a first-order dependence on $[\text{Cu}(\text{Cat})]$, then this can be obtained from eq 25 if $k_4[\text{Cu}(\text{Cat})] \gg k_{-O_2}$. Then eq 25

$$-\frac{d[\text{O}_2]}{dt} = k_4 \left\{ \frac{k_1 k_{O_2}}{k_5} \right\}^{1/2} \frac{[\text{Cu}(\text{Cat})]^{3/2} [\text{O}_2]^{1/2}}{(k_{-O_2} + k_4[\text{Cu}(\text{Cat})])^{1/2}} + k_1[\text{Cu}(\text{Cat})] \quad (25)$$

simplifies to eq 26. This rate law predicts the half-order dependence on $[\text{O}_2]$ found by Jameson and co-workers if the first term is larger than the second (i.e., $(k_4 k_{O_2}/k_5)[\text{O}_2] \gg k_1^{1/2}$). However, it predicts a first-order dependence on

$$-\frac{d[\text{O}_2]}{dt} = \left\{ \frac{k_1 k_4 k_{O_2}}{k_5} \right\}^{1/2} [\text{Cu}(\text{Cat})][\text{O}_2]^{1/2} + k_1[\text{Cu}(\text{Cat})] \quad (26)$$

$[\text{Cu}(\text{Cat})]$ rather than the more complex dependence suggested by Jameson. To test this, the published tabulated data¹¹ on the pH dependence at various catechol concentrations and representative graphical data on the total Cu^{II} dependence have been analyzed according to the prediction of eq 26. The results²⁶ in Figure 4 show that a simple first-order dependence is reasonably consistent with these data and there are no systematic deviations that would be expected if higher order terms suggested by Jameson et al. were contributing. A least-squares analysis gives $(k_1 k_4 k_{O_2}/k_5)^{1/2} = (2.8 \pm 0.08) \times 10^{-2}$. The value of k_1 determined here and $k_{O_2} \approx 6 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ determined by Mi and Zuberbüler²⁷ allow one to calculate that $k_4/k_5 = 6.9 \times 10^{-6}$.

(25) In ref 11, it was assumed that the k_{O_2} , k_{-O_2} reaction was a rapid equilibrium and that the rates of initiation and termination were equal, while a standard steady-state treatment for a chain reaction has been used here, as in the following reference: Moore, J. W.; Pearson, R. G. *Kinetics and Mechanisms*; Wiley and Sons: New York, 1981; p 390. Pilling, M. J.; Seakins, P. W. *Reaction Kinetics*; Oxford University Press: New York, 1995; p 221.

(26) Least-squares analysis of 49 data points to the one-parameter model of eq 26 gave an insignificant 1.6% better standard error of the fit than the three-parameter model of ref 11, using the formation constants from ref 11 in both cases.

(27) Mi, L.; Zuberbüler, A. D. *Helv. Chim. Acta* **1991**, *74*, 1679.

It is possible to use the ratio k_4/k_5 to estimate k_4 . Karlin and co-workers³ have determined rate constants of $\sim 10^6 \text{ M}^{-1} \text{ s}^{-1}$ at 25 °C for several reactions of the type $\text{L}_n\text{Cu}^{\text{II}}(\text{O}_2^-) + \text{L}_n\text{Cu}^{\text{I}}(\text{NCR})$ that are analogous to k_5 . Since H_2O ligands are less strongly complexing than NCCH_3 toward Cu^{I} ,²¹ and provide less steric encumbrance than the ancillary L_n ligands, one might expect $\text{Cu}^{\text{I}}(\text{OH}_2)_m$ to have a larger rate constant than $\text{L}_n\text{Cu}^{\text{I}}(\text{NCR})$. Therefore, k_5 can be expected to be in the range of $>10^6$ to the diffusion-controlled limit of $\sim 10^9$. Then k_4 will be in the range of >6 to $6 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$.

With the numerical values determined, it is possible to test the assumption about the dominant term in eq 26, and those used to develop eq 26. The initial concentration range of O_2 ($\sim 0.3\text{--}1.3 \text{ mM}$) used by Jameson and co-workers¹¹ can be used to show that the first term in eq 26 is ~ 7 times greater than the second, even after 90% reaction at the lowest initial $[\text{O}_2]$. Therefore, the first term generally is dominant in eq 26. A critical assumption in the development is that $4ac \gg b^2$ in eq 23. After some rearrangement, it can be shown that this is equivalent to requiring that $4k_{\text{O}_2}[\text{O}_2] \gg k_1(k_4/k_5)$, and the numerical values show that the ratio of these terms is initially $\sim 2 \times 10^3$ at the lowest $[\text{O}_2]$. Therefore, this condition would be satisfied for 99% of the reaction.

It should be noted that Jameson and co-workers proposed a nonradical mechanism on the basis that acrylamide did not undergo polymerization when present during the autoxidation. However, Scheme 4 proposes a semiquinone intermediate ($\text{Cat}^{\cdot-}$). It seems possible that the acrylamide experiment was misleading because copper(II) species and H_2O_2 could serve as efficient terminators for the radical polymerization.

Conclusions

The results of this study show that aqueous copper(II) is capable of oxidizing catechol and that O_2 and its various complexes and reduced forms are not a necessary requirement. However, the latter do provide additional reaction pathways that accelerate the oxidation. The observation that the simple reactions proceed via the complex $\text{Cu}^{\text{II}}(\text{Cat})$ is consistent with the biological mechanisms which suggest that Cu^{II} activates the catechol for oxidation. The rate-controlling intramolecular electron transfer in the aqueous system is consistent with the observation by Dooley and co-workers⁵ of a Cu^{I} –radical valence tautomer in copper amine oxidase systems. However, the mechanism proposed here for the autoxidation does not require any direct reaction between the complexed catechol and O_2 that would be a simple precedent for the amine oxidase mechanism of Klinman and co-workers.^{8,9}

Experimental Section

Materials. All chemicals were of reagent grade and used as supplied. Azidopentaaminecobalt(III) nitrate was prepared by an adaptation of the synthesis of Linhard and Flygare²⁸ as described previously.²¹ Stock solutions of the cobalt(III) complex and the buffers HEPES and PIPES were prepared by dissolving a known mass of the solid in a known volume of water. The same method

was used for solutions of catechol, which were prepared daily. Stock solutions of copper(II) nitrate were prepared from $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and analyzed by reaction with excess KI and back-titration with standardized sodium thiosulfate. Solutions of NaClO_4 were standardized by titrating the H^+ released from Dowex X-8 cation-exchange resin by an aliquot of the solution.

Analytical Method. The analysis for cobalt(II) with NRS is based on the spectrophotometric detection of the cobalt(III) complex of NRS.²⁹ A sample from the reaction solution was added to a solution of phosphoric acid and NRS in a 25 mL volumetric flask. A solution of sodium acetate was added to adjust the pH, and oxidation of Co^{II} to Co^{III} occurs at this stage. Then hydrochloric acid was added to destroy the NRS complex of Cu^{II} , the solution was diluted to volume, and the absorbance was determined at 525 nm in a 1.00 cm path length cell on a Cary 219 spectrophotometer. A test for the effect of the final concentration of H_3PO_4 revealed that it should be $\leq 0.025 \text{ M}$, and 0.023 M was used. Previous studies suggest that the $\text{H}_3\text{PO}_4/\text{NaO}_2\text{C}_2\text{H}_3$ buffer should be at pH 5.5–6.5, and a final concentration of $\text{NaO}_2\text{C}_2\text{H}_3$ of 0.73 M was used, to give a pH of 5.9. Tests of the hydrochloric acid concentration (0.20–2.2 M) revealed that interference from other NRS complexes was essentially eliminated for $[\text{HCl}] > 1.0 \text{ M}$, and a final concentration of 1.86 M was used. For solutions containing 0.014 mM Co^{II} and Cu^{II} , it was found that the color of the Co^{III} –NRS complex was fully developed for NRS concentrations from 0.20 to 0.65 mM, and $[\text{NRS}] = 0.32 \text{ mM}$ in the final solution was routinely used. It also was determined that the absorbance of the Co^{III} –NRS complex was stable under these conditions for at least 24 h.

The absorbance was found to increase linearly with the Co^{III} concentration in the concentration range of 0.600×10^{-5} to $3.40 \times 10^{-5} \text{ M}$, and this was unaffected by up to $1.4 \times 10^{-4} \text{ M}$ Cu^{II} . In a 1.00 cm cuvette the absorbance is given by $A = 0.034 + (1.48 \times 10^4)[\text{Co}^{\text{III}}]$.

The solutions to be analyzed in the kinetic study will contain both $\text{Co}(\text{OH}_2)_6^{2+}$ and $\text{Co}(\text{NH}_3)_5\text{N}_3^{2+}$, and it is essential for this application that the Co^{III} complex does not undergo electron transfer with the Co^{II} –NRS complex, or that this reaction is not competitive with the air oxidation of the Co^{II} complex. Lalor³⁰ has observed that this reaction does occur with $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$ and $\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$, but not with $\text{Co}(\text{NH}_3)_5\text{NO}_2^{2+}$. Under anaerobic conditions, we have confirmed this observation for the first two complexes, and found that there is no reaction between $\text{Co}(\text{NH}_3)_5\text{N}_3^{2+}$ (0.16 mM) and Co^{II} (0.17 mM) in the presence of NRS (0.32 mM).

Kinetic Method. The apparatus consisted of two Erlenmeyer flasks closed by serum caps and connected in series by Teflon tubing. One flask was connected to an argon cylinder and the other to a three-way stopcock, which in turn was attached to Teflon tubing extending below the liquid surface of the second flask and to a 5.0 mL sampling syringe. The first flask contained the $\text{Co}(\text{NH}_3)_5\text{N}_3^{2+}$ and Cu^{II} in 20 mL of solution. The second flask contained the catechol in 30 mL of solution and a stirring bar. Both solutions also contained 0.025 M buffer (HEPES), adjusted to the required pH with aqueous HClO_4 or NaOH , and NaClO_4 to adjust the ionic strength. The tubing was adjusted so that both flasks and the sampling syringe could be deoxygenated by bubbling argon. The reaction was initiated by adjusting the connecting tubing so that the $\text{Co}^{\text{III}}/\text{Cu}^{\text{II}}$ solution was transferred by argon pressure into the catechol solution.

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Oxidation of Catechol by Aqueous Copper(II)

Periodically, 2.00 mL samples were withdrawn into the sampling syringe and then ejected into a 25.0 mL volumetric flask containing 5.0 mL of 0.115 M phosphoric acid. This served to quench the reaction. At the end of the run, each sample was treated with 3.0 mL of 2.65 mM NRS, 5.0 mL of 3.66 M sodium acetate, and 5.0 mL of 9.3 M hydrochloric acid. Each sample was diluted with water to 25.0 mL, and the absorbance at 525 nm was recorded in a 1.00 cm path length cuvette on a Cary 219 spectrophotometer.

Acknowledgment. We are pleased to acknowledge the Natural Sciences and Engineering Research Council of Canada for financial support.

Supporting Information Available: The detailed development of the rate law for Scheme 4, leading to eqs 23 and 26. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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