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Copper(II)-Catalyzed Oxidation of Catechol by Molecular Oxygen in Aqueous Solution

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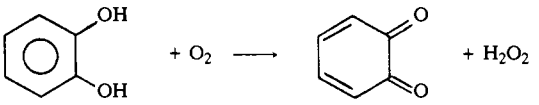
The oxidation of catechol by molecular oxygen in the presence of catalytic amounts of copper(II) ions has been followed by use of a Clark-type oxygen electrode and spectrophotometric methods at 25.0 °C and with the ionic strength maintained at 1.0 M (KNO_3). The overall stoichiometry of the reaction was established to be



Catechol (H_2A) o-Quinone (Q)

The rate of reaction was strictly of half-order in O_2 concentration but of no simple integral order with respect to either total copper(II) or total catechol concentration. However, the observed kinetic data were explicable in terms of a chain reaction involving the copper(I)-dioxygen species CuO_2^+, which reacts with the free ligand and its copper(II) complexes. The copper(I) is formed in the initiation step by the reaction of free copper(II) with the complex CuA, and the chain is terminated by bimolecular elimination of the activated dioxygen complex, with the formation of copper(II) and peroxide ion. This reaction scheme is shown to lead to the rate equation $-d[O_2]/dt = \{k_1'[HA^-] + k_2'[CuA] + k_3'[CuA_2^{2-}]\}\{[Cu^{2+}][CuA][O_2]\}^{1/2}$, with $k_1' = (3.15 \pm 0.15) \times 10^3$ $M^{-3/2}$ s^{-1}, $k_2' = (15.5 \pm 0.7)$ $M^{-3/2}$ s^{-1}, and $k_3' = (2.95 \pm 0.28) \times 10^2$ $M^{-3/2}$ s^{-1}.

Introduction

A kinetic investigation of the copper(II)-catalyzed autoxidation of catechol to *o*-quinone might provide a basis for a better understanding of related metalloenzyme-catalyzed in vivo reactions. One such enzyme is *tyrosinase*, which catalyzes the ortho-hydroxylation of phenols and the oxidation of catechols to *o*-quinones,[2] which includes the oxidative degradation of biologically active (*i.e.* hormone and neurotransmitter) catecholamines to the pigment melanin.[3,4] It was also considered that a study of the copper(II)-catalyzed oxidation of catechol by molecular oxygen would throw light on the way in which O_2 interacts with and is activated by copper complexes.[5-7]

Previously reported studies involving the autoxidation of catechols have been carried out mainly in nonaqueous solution with copper(I) or copper(II) as catalysts,[8] work in aqueous solution and involving copper(II) being confined to ligands such as ascorbate.[2,3,5-7] Although the precise details of the overall mechanism of the copper(II)-catalyzed transformation of catechol in aprotic media remain to be determined, the main features of the catalytic process seem to be the formation of a binuclear copper(II)-catecholate intermediate, followed by the transfer of two electrons from the aromatic ring to the two copper(II) centers, and then the irreversible reoxidation of the copper(I) species with oxygen to give the active copper-oxygen reagent.[8] With manganese(II) and cobalt(II) complexes as catalysts, however, the reversible formation of a substrate-catalyst-O_2 ternary complex was assumed in protic media.[9] As the stabilities of the copper(II) and copper(I) states are very much solvent-dependent, results obtained so far in aprotic media cannot simply be applied to aqueous solution.

This paper reports a study of the autoxidation of catechol to *o*-quinone by molecular oxygen in the presence of catalytic amounts of copper(II) in homogeneous aqueous solution.

Experimental Section

Materials. Catechol was a Reanal product of Puriss grade; it was further purified by low-pressure distillation in an argon atmosphere. The copper(II) stock solution was prepared from recrystallized $Cu(NO_3)_2 \cdot 3H_2O$ and the metal ion content was verified by gravimetric determination as the oxinate.

Kinetic Conditions. Measurements were performed at five different pH values in the range 4.60-5.50. At higher pH values the uncatalyzed reaction (without copper(II)) cannot be neglected. The catechol concentration spanned the range 0.02-0.20 M, and the copper(II) concentration spanned the range 4.0×10^{-4} to 2.0×10^{-3} M. Catechol solutions were made up daily at pH $\approx$ 2.5 to minimize oxidation during storage.

pH Titrations. Catechol concentrations were within the range 4.0×10^{-3} to 8.0×10^{-3} M and the metal ion:ligand ratios were 0:1, 1:1, 1:2, and 1:10. The titrations were performed with a KOH solution of known concentration (ca. 0.2 M) supplemented to 1.0 M ionic strength with KNO_3. Other experimental conditions have been described earlier.[10]

Oxygen-Sensitive Electrode Measurements. Pure oxygen or oxygen-nitrogen mixtures of known compositions were bubbled through an acidic solution of catechol and KNO_3 in the reaction cell until saturation was achieved. ($[O_2]$ of the solution samples saturated with the gas mixtures were determined in separate, blank experiments. In the case of pure oxygen it was found to be 1.3×10^{-3} M.) The cell was then closed to the atmosphere, and after a stable dioxygen concentration had established itself, catalyst (i.e. copper(II) solution) and concentrated base (KOH solution) were added rapidly. To obviate the use of buffers, which are often complexing agents in their own right, the pH was maintained by use of a pH-stat consisting of a Radiometer TTA60 titrator, an ABU13 buret, and a pHM64 pH-meter. Oxygen concentration was monitored with a Clark-type oxygen-sensitive electrode and recorded on a Radelkis OH814/1 potentiometric recorder.

Spectrophotometric Measurements. In some cases the oxidation reaction was followed spectrophotometrically by monitoring the formation of *o*-quinone. To achieve this, the sample solution was circulated in a closed system consisting of the reaction vessel and a flow-through quartz cell by means of a Verder-type leakage-free pump. The recording

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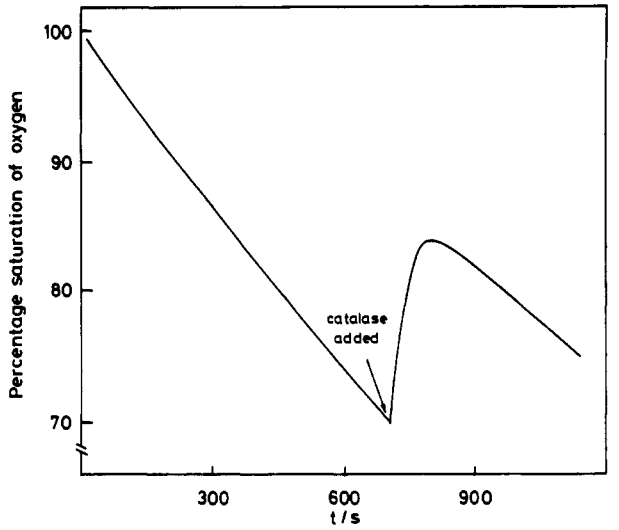


Figure 1. Effect of catalase on the time dependence of oxygen consumption: pH, 5.30; $[Cat]_0$, 0.15 M; $[Cu]_0$, 1.00×10^{-3} M.

Table I. Potentiometrically Determined Equilibrium Constants for the Copper(II)–Catechol System under Anaerobic Conditions at 25.0 °C and I = 1.0 M (KNO_3)

equilibrium		equilibrium constants: this work	ref 21
$H_2A \rightleftharpoons H^+ + HA^-$	pK_1	9.25 ± 0.01	9.23
$HA^- \rightleftharpoons H^+ + A^{2-}$	pK_2	13.0 ± 0.1	13.05
$Cu^{2+} + A^{2-} \rightleftharpoons CuA$	$\log \beta_1$	13.64 ± 0.01	13.60
$Cu^{2+} + 2A^{2-} \rightleftharpoons CuA_2^{2-}$	$\log \beta_2$	24.92 ± 0.01	24.92

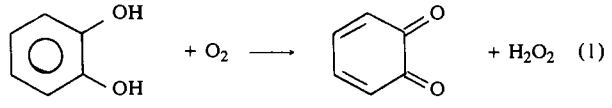
spectrophotometer was a Beckman Acta MIV double-beam instrument.

For both kinetic and thermodynamic work, experiments were carried out at 25.0 ± 0.1 °C, and the ionic strength was maintained at 1.0 M by the addition of KNO_3.

Results

Stoichiometry. The reactions between catechol and its derivatives and molecular oxygen in aqueous solution are extremely complicated, especially when metal ions are present. Fortunately, under the experimental conditions used, the early stage of the reaction, i.e. up to about 35% completion (ca. 10–15 min), was found to be stoichiometrically simple.

Formation of *o*-quinone could be followed spectrophotometrically via the absorption at 390 nm by making use of the molar absorbance of 1417 M^{-1} cm^{-1} reported by Waite.[11] When the disappearance of O_2 was followed in parallel with the formation of quinone, it was found that the rates were identical up to an oxygen consumption of about 35%. This suggested that molecular oxygen was reduced only to peroxide, and this was verified as follows: when a small amount of *catalase* was added to the reaction mixture after a short time, about 50% of the oxygen consumed up to that point was recovered (Figure 1). Hence, the overall stoichiometry is that given by (1).



(1)

Catechol (H_2A) o-Quinone (Q)

If the reaction is allowed to continue, various acidic and polymeric species, including a fine black powder, are obtained.[12-16]

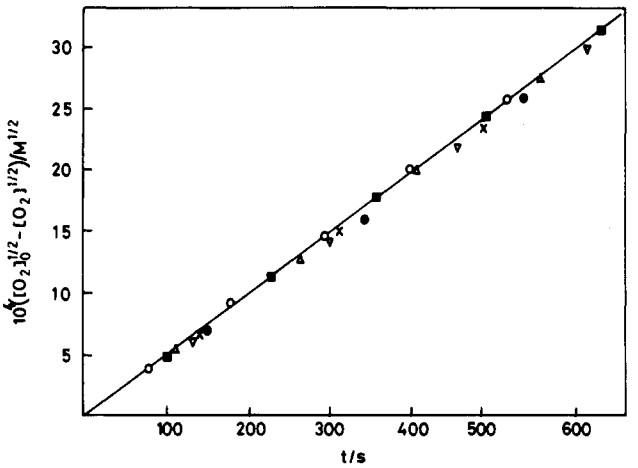


Figure 2. Verification of the reaction order with respect to oxygen (see text): pH, 5.50; $[Cat]_0$, 0.20 M; $[Cu]_0$, 4.00×10^{-4} M. Key: $[O_2]_0 \times 10^4$ M = 4.00 (○), 5.88 (■), 7.41 (△), 8.78 (▽), 10.27 (×), and 11.53 (●).

Table II. Typical Values of Rate Constants k_{obs} for the Rate of Consumption of Oxygen[a]

$[Cat]_0$, M	pH	$10^5 k_{obs}$, $M^{-1/2}$ s^{-1}	$[Cat]_0$, M	pH	$10^5 k_{obs}$, $M^{-1/2}$ s^{-1}
0.20	4.60	3.11	0.05	4.60	0.84
	4.90	4.82		4.90	1.80
	5.10	5.10		5.10	3.04
	5.30	5.28		5.30	4.20
	5.50	5.22		5.50	4.41
	5.70	4.20	0.02	4.60	0.31
0.15	4.60	2.48		4.90	1.12
	4.90	4.18		5.10	2.00
	5.10	4.64		5.30	3.29
	5.30	5.10		5.50	4.18
	5.50	4.95			
	5.70	4.69			
0.10	4.60	1.58			
	4.90	3.06			
	5.10	3.64			
	5.30	3.87			
	5.50	4.40			
	5.70	4.85			

[a] t = 25.0 °C; I = 1.0 M (KNO_3); $[Cu]_0 = 2.0 \times 10^{-3}$ M.

We confirmed this by bubbling oxygen through a reaction mixture for 30–40 min. The acidic product is most probably *cis,cis*-muconic acid[17] (formed by cleavage of the aromatic ring), and the precipitate contained ca. 21% copper (measured by atomic absorption). The latter is presumably a polynuclear condensation product of quinone and semiquinone fragments (the preparation and characterization of such complexes have been reported[18,19]).

Equilibrium Studies. The proton–catechol and copper(II)–catechol equilibria were reexamined under anaerobic conditions at an ionic strength of 1.0 M (KNO_3) by potentiometric titration. The pK_2 value characteristic of the dissociation of the very weakly acidic second phenolic hydroxy group was determined at 0.1 M ligand concentration as described in ref 20. The results are given in Table I, and it can be seen that the agreement with those published previously[21] is good.

Dependence of Rate on $[O_2]$. Pure oxygen and oxygen–nitrogen mixtures varying from 80% to 10% (v/v) oxygen were employed

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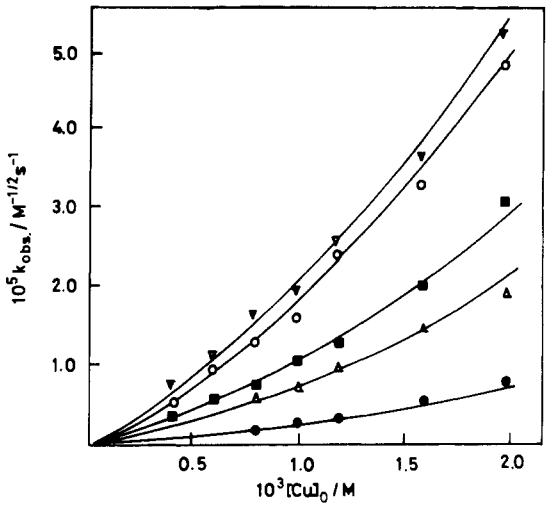


Figure 3. Dependence of k_{obs} on copper(II) concentration at various pH values and catechol concentrations: (▽) $[Cat]_0$ = 0.20 M, pH = 5.10; (○) $[Cat]_0$ = 0.20 M, pH = 4.90; (■) $[Cat]_0$ = 0.20 M, pH = 4.60; (△) $[Cat]_0$ = 0.05 M, pH = 4.90; (●) $[Cat]_0$ = 0.05 M, pH = 4.60.

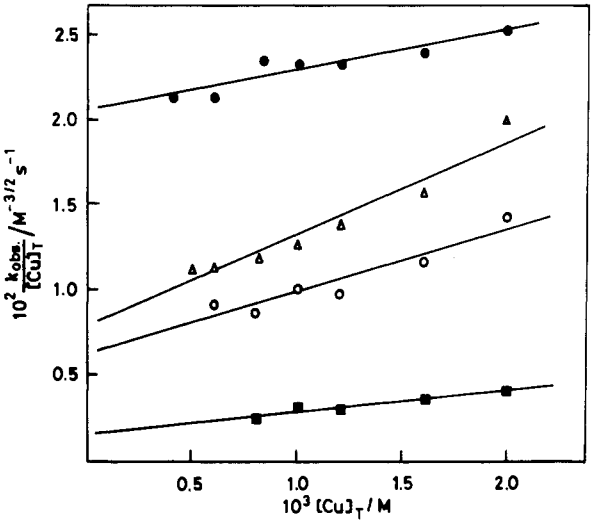


Figure 4. Dependence of $k_{obs}/[Cu]_T$ on $[Cu]_T$ at various pH values and catechol concentrations: (●) $[Cat]_0$ = 0.20 M, pH = 5.30; (○) $[Cat]_0$ = 0.20 M, pH = 4.60; (■) $[Cat]_0$ = 0.05 M, pH = 4.60; (△) $[Cat]_0$ = 0.05 M, pH = 5.30.

in these studies in a way described in the Experimental Section. The linearity of the $\{[O_2]_0^{1/2} - [O_2]^{1/2}\}$ vs t plot at constant $[H^+]$ and $[Cat]_0$ in Figure 2 shows clearly that the reaction is strictly of half-order in dioxygen, and some typical values of k_{obs} are listed in Table II.

$$-d[O_2]/dt = k_{obs}[O_2]^{1/2} \quad (2)$$

Dependence of Rate on $[Cu]_0$, $[Cat]_0$, and $[H^+]$. The dependence of the rate of reaction on the initial copper(II) concentration, $[Cu]_0$, is illustrated in Figures 3 and 4. The k_{obs} vs $[Cu]_0$ curves reveal a kinetic order of between one and two, the order varying with the concentrations of both the hydrogen ion and catechol. As the plots in Figure 3 pass through the origin, i.e. without an intercept, it can be stated that there is no measurable rate of oxidation in the absence of copper(II) ion. The plot of $k_{obs}/[Cu]_0$ vs $[Cu]_0$ is particularly revealing, since it shows that k_{obs} takes the form shown in (3) at constant $[H^+]$ and constant $[Cat]_0$.

$$k_{obs} = A[Cu]_0\{[Cu]_0 + B\} \quad (3)$$

Figure 5, in which the rate constant variation with pH is compared with the speciation, indicates that the rate is linked to the concentration of the monocatechol complex, [CuA], although not exclusively and/or not via a simple direct dependence.

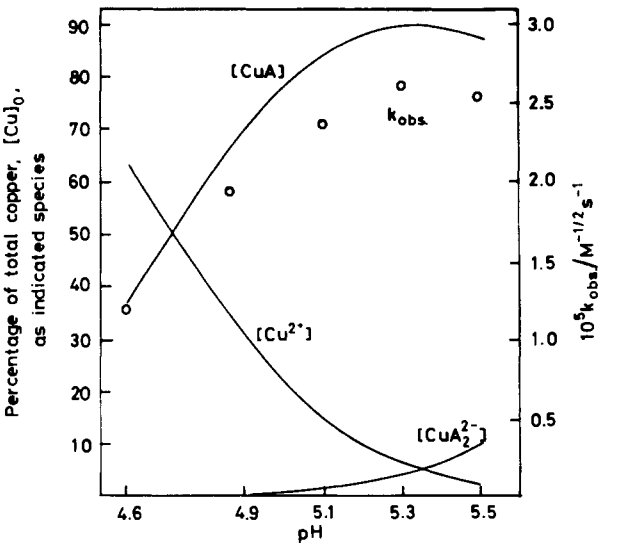


Figure 5. Concentration distribution (—) of the complexes formed in the copper(II)–catechol system, compared with the variation of the rate constants, k_{obs} (○) with pH: $[Cat]_0$, 0.15 M; $[Cu]_0$, 1.20×10^{-3} M.

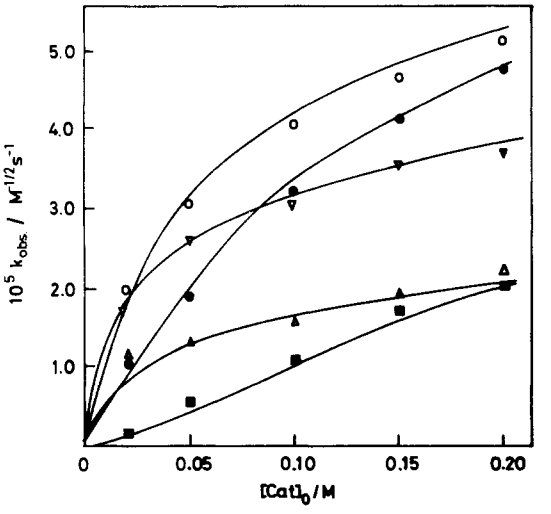


Figure 6. Dependence of k_{obs} on catechol concentration at various pH values and copper(II) concentrations: (○) $[Cu]_0 = 2.00 \times 10^{-3}$ M, pH = 5.10; (●) $[Cu]_0 = 2.00 \times 10^{-3}$ M, pH = 4.90; (▽) $[Cu]_0 = 1.60 \times 10^{-3}$ M, pH = 5.30; (■) $[Cu]_0 = 1.60 \times 10^{-3}$ M, pH = 4.60; (△) $[Cu]_0 = 1.20 \times 10^{-3}$ M, pH = 5.50.

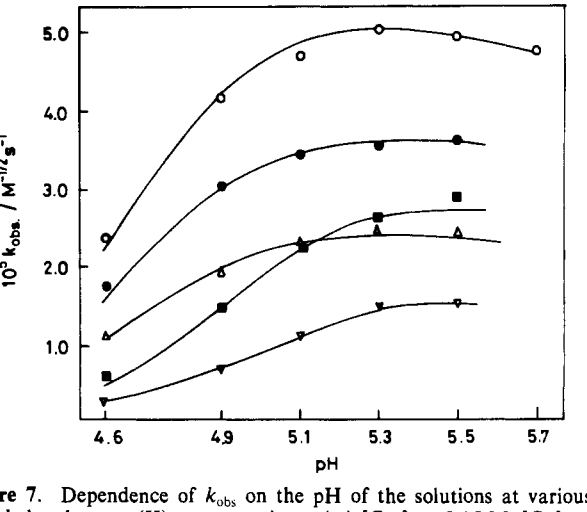


Figure 7. Dependence of k_{obs} on the pH of the solutions at various catechol and copper(II) concentrations: (○) $[Cat]_0$ = 0.15 M, $[Cu]_0 = 2.00 \times 10^{-3}$ M; (●) $[Cat]_0$ = 0.15 M, $[Cu]_0 = 1.60 \times 10^{-3}$ M; (△) $[Cat]_0$ = 0.15 M, $[Cu]_0 = 1.20 \times 10^{-3}$ M; (■) $[Cat]_0$ = 0.05 M, $[Cu]_0 = 1.60 \times 10^{-3}$ M; (▽) $[Cat]_0$ = 0.05 M, $[Cu]_0 = 1.00 \times 10^{-3}$ M.

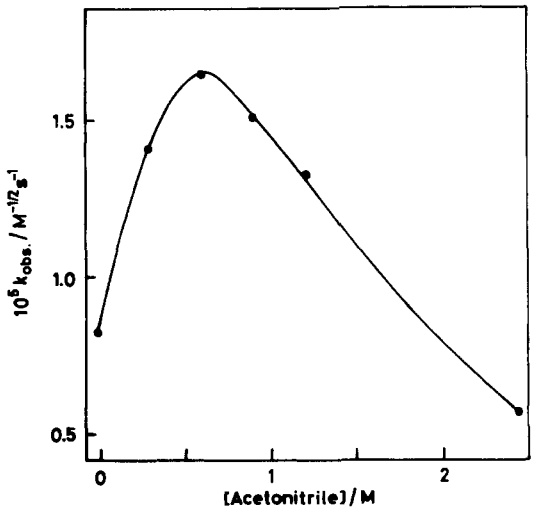
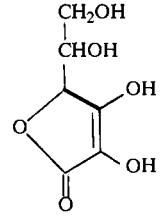


Figure 8. Dependence of k_{obs} on the concentration of acetonitrile; pH, 5.30; $[Cat]_0$, 0.15 M; $[Cu]_0$, 1.00×10^{-3} M.

Figure 6 illustates the effects of changes in the catechol concentration at various pH values, and Figure 7 those in the pH at various substrate concentrations. Both relationships exhibit a maximum or saturation character; this could be expected from the complex formation reactions between copper(II) and catechol.

Discussion

Mechanistic Features of the Reaction. (i) Free-Radical Participation. Among the copper(II)-catalyzed autoxidation reactions in water, that of ascorbic acid has been most widely studied.[5-7] Ascorbic acid (I) is a vicinal diol, and although it is not aromatic,



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its unsaturated character may result in some similarity to catechol as far as the role of the copper(II) catalyst is concerned. At least three mechanisms have been proposed for its copper(II)-catalyzed autoxidation. Jameson and Blackburn[22] assumed a radical chain mechanism involving an initial two-electron transfer to the oxygen and the formation of formally copper(III). Taqui Khan and Martell[23] proposed that the reaction took place in one-electron steps, again involving a chain mechanism. They proposed that the rate-determining step is electron transfer within the species $CuAHO_2^+$, and the copper(I) appearing in the second electron-transfer step is reoxidized in a fast reaction with superoxide radical (formed in the first step). Shtamm et al.[24] put forward a non-radical chain mechanism with the formation of CuO_2^+ in the chain-propagation steps, but in their mechanism this complex was formed in the irreversible rate-determining step, which seems highly improbable.[5]

The presence or not of free radicals is crucial, and this facet of the reaction between catechol, oxygen, and copper(II) was examined as follows: First, it was found that the addition of *superoxide dismutase* (which catalyzes the disproportionation of superoxide radical, O_2^-, to O_2 and peroxide) had no effect on the reaction. Second, acrylonitrile (a good radical scavenger) also had no observable effect on the process. Both of these observations argue strongly against the possibility of a free-radical mechanism.

(ii) Involvement of Copper(I). The intermediate formation of Cu(I) was detected spectrophotometrically via the formation of the colored Cu(I)–neocuproine complex (Cu(II) was found not to react with neocuproine). The effect of acetonitrile (which can stabilize the Cu(I) oxidation state) on the rate of the copper(II)–catalyzed autoxidation of catechol was also tested (Figure 8). Acetonitrile is known to inhibit the autoxidation of Cu(I) by coordination, forming practically inactive complexes.[25] This may be responsible for the decreased overall reaction rate at higher acetonitrile concentration. The slight increase in the reaction rate at low acetonitrile concentration is not simple to explain. However, a similar effect of acetonitrile was observed by Shtamm et al.[24] on the copper(II)-catalyzed autoxidation of ascorbic acid (which is also a chelating oxygen donor ligand). They suggested that the increase of the overall rate at low acetonitrile concentration was an effect of acetonitrile on the rate of Cu(I) initiation reaction via the formation of the transition complex Cu^{II}(An)–ascorbate. In this complex the electron transfer from ascorbate to Cu(II) was assumed to be more favored. We strongly feel that this explanation is applicable to the autoxidation of the chelate-forming oxygen donor catechol too.

Accordingly, the initiation step is almost certainly the production of copper(I) by the interaction of copper(II) with catechol. A difficulty here is that the possibility of carrying out potentiometric titrations in the absence of oxygen in order to establish stability constant data reveals that the redox equilibrium must lie well to the left (and this is confirmed by the redox potentials). The results obtained for the redox reactions of catechols with various copper(II) reagents under anaerobic conditions support this assumption.[8] A further difficulty is that the reaction does not appear to involve free-radical formation.

The Reaction Mechanism. If copper(I) is the effective oxygen carrier for this reaction, then two copper(II) species must be involved in the initiation reaction since there is no evidence for the intermediate formation of semiquinone. The concentration distribution curves of the complexes (Figure 5) combined with the observation that $[Cu^{2+}]$ falls with pH suggest that the participation of free Cu^{2+} is very likely, along with the species CuA. (Although the overall equilibrium constant of the initiation reaction is very low, the reverse reaction must be slow in comparison with any other route for the disappearance of Cu(I) and is therefore a minor route for the removal of copper (I).) Similar to what was assumed in aprotic media,[8] the initiation reaction may involve the formation of a dimeric species Cu_2A^{2+} in a fast preequilibrium, with internal electron transfer as the rate-determining step. The copper(I) ion formed in the initiation step should first react with molecular oxygen, as copper(I) is capable of only a very weak interaction with catechol. This process presumably involves the transfer of an electron from the metal ion to the oxygen molecule, as a result of which the copper–oxygen complex reacts more readily than copper(I) with catechol. Speier studied the copper(I)-catalyzed autoxidation of 3,5-di-*tert*-butylcatechol in dichloromethane and chloroform and suggested the formation of a dimeric species, $[Cu_2O_2]^{2+}$, in the rate-determining step.[26] He used the Cu(I)–pyridine–chloro complex as the catalyst. In aprotic media, these ligands stabilized the copper(I) state, and copper(II) appears only in the copper–oxygen complex. In aqueous solution under our experimental conditions, copper(I) cannot accumulate (and its accumulation cannot be the rate-determining step) because of its fast autoxidation.[6] Hence, when the Cu(I)–pyridine complex prepared by the method described by Rigo et al.[27] was added to an aqueous solution of catechol saturated with oxygen in the usual way, a rapid oxygen consumption started, and this can be ascribed to the autoxidation of Cu(I). The number of millimoles of oxygen consumed was about half of the amount of Cu(I); i.e., oxygen was reduced to peroxide. After the rapid decrease in oxygen concentration, the time dependence of the oxygen consumption fol-

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lowed the copper(II)-catalyzed pattern.

The CuO_2^+ moiety is formed in a reversible reaction with O_2 and oxidizes both free catechol and its copper(II) complexes. In the pH range studied, catechol is mainly present in the H_2A form. Due to the large excess of ligand, the concentration of the monoprotonated species HA^-, however, is comparable with those of the copper complexes, although it never exceeds $^1/_{10}$th of the total copper. The pH-dependence of the kinetic data suggested the involvement of the species HA^- rather than H_2A in the chain-propagation step.

The kinetic activity of species similar to $M(HA)O_2$, presumably the reactive intermediate formed in reaction 6, has been assumed in the reaction mechanisms of both the copper(II)-catalyzed autoxidation of ascorbic acid[23] and the manganese(II)- and cobalt(II)-catalyzed autoxidation of 3,5-di-*tert*-butylcatechol.[9] In a similar fashion reactions 7 and 8 suggest the intermediate formation of dicopper–catecholate–O_2 ternary complexes, which have been shown to play an important role in the copper(II)-catalyzed autoxidation of catechol and are assumed to be crucial in tyrosinase-catalyzed autoxidation reactions.[8]

Finally, in order for the overall reaction to be of half-order in $[O_2]$, we postulate that the termination step could well be the irreversible reoxidation reaction of Cu(I) with CuO_2^+. The final scheme thus becomes

initiation:

$$Cu^{2+} + CuA \underset{(k_{-1})}{\overset{k_1}{\rightleftharpoons}} 2Cu(I) + Q \quad (4)$$

chain propagation:

$$Cu(I) + O_2 \overset{K}{\rightleftharpoons} CuO_2^+ \quad (5)$$

$$CuO_2^+ + HA^- \xrightarrow{k_2} Cu(I) + HO_2^- + Q \quad (6)$$

$$CuO_2^+ + CuA \xrightarrow{k_3} Cu(I) + O_2^{2-} + Q + Cu^{2+} \quad (7)$$

$$CuO_2^+ + CuA_2^{2-} \xrightarrow{k_4} Cu(I) + O_2^{2-} + Q + CuA \quad (8)$$

termination:

$$CuO_2^+ + Cu(I) \xrightarrow{k_5} 2Cu^{2+} + O_2^{2-} \quad (9)$$

with the protonation reactions of peroxide ion taken to be fast.

Dioxygen is consumed by reactions 6–8; hence, if one makes use of 5, the rate expression is given by (10). Furthermore, for a linear chain reaction it is reasonable to assume that the rate of termination is equal to the rate of initiation, which gives (11).

$$-d[O_2]/dt = K[Cu(I)][O_2]\{k_2[HA^-] + k_3[CuA] + k_4[CuA_2^{2-}]\} \quad (10)$$

$$k_1[CuA][Cu^{2+}] = k_5K[Cu(I)]^2[O_2] \quad (11)$$

Substitution of [Cu(I)] from (11) into (10) gives

$$-d[O_2]/dt = \{k_1'[HA^-] + k_2'[CuA] + k_3'[CuA_2^{2-}]\}\{[Cu^{2+}][CuA][O_2]\}^{1/2} \quad (12)$$

in which $k_1' = k_2(k_1K/k_5)^{1/2}$, $k_2' = k_3(k_1K/k_5)^{1/2}$, and $k_3' = k_4(k_1K/k_5)^{1/2}$; i.e.

$$k_{obs} = \{k_1'[HA^-] + k_2'[CuA] + k_3'[CuA_2^{2-}]\}\{[Cu^{2+}][CuA]\}^{1/2} \quad (13)$$

If (13) is expressed in terms of total copper, $[Cu]_T = [Cu^{2+}] + [CuA] + [CuA_2^{2-}]$, and, over the pH range under consideration, total catechol, $[Cat]_T = [H_2A]$ (copper(II) catechol complexes are not considered since $[Cat]_0 \gg [Cu]_0$), then at constant [catechol] and constant pH we obtain a complicated expression which reduces to one identical to the experimentally obtained relationship (3).

Finally, the concentration terms in (13) can all be calculated from the thermodynamic data, and thus the three pseudo rate constants could be obtained from the experimental rate data by a least-squares curve-fitting program. The following values were extracted from the data in this manner:

$$k_1' = (3.15 \pm 0.15) \times 10^3\ M^{-3/2}\ s^{-1}$$

$$k_2' = 15.5 \pm 0.7\ M^{-3/2}\ s^{-1}$$

$$k_3' = (2.95 \pm 0.28) \times 10^2\ M^{-3/2}\ s^{-1}$$

The solid lines in Figures 3, 6, and 7 have been calculated on the basis of the above values and illustrate the goodness of the fit obtained. Due to the ambiguity in choosing the more reliable form of protonated catechols HA^- or H_2A involved in the chain-propagating steps (see above) the calculations were repeated by substituting the concentrations of H_2A instead HA^- into (13). In this way a $k_1'' = 0.16 \pm 0.02\ M^{-3/2}\ s^{-1}$ was obtained with a little poorer fit with the experimental data.

Conclusion

The proposed mechanism for the copper(II)-catalyzed autoxidation of catechol in weakly acidic aqueous solution agrees in many points with that obtained in aprotic media[8] and is essentially similar to the mechanism proposed for the copper(II)-catalyzed autoxidation of ascorbic acid by Shtamm et al.[24] The chain-carrier copper(I) is formed in a bimolecular reaction step and is reoxidized to copper(II) in a further bimolecular irreversible step. In the propagation steps, however, the activated copper–oxygen complex is formed in a reversible step, which is in agreement with the basic findings obtained for the autoxidation of copper(I)[5] and disagrees with the mechanism suggested by Shtamm et al.,[24] where the complex $Cu^IO_2^+$ is formed in the irreversible rate-determining step. The activated copper–oxygen complex then reacts with the free and complex bound ligands and generates the *o*-quinone product.

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