

On In Situ Prepared Cu–Phenanthroline Complexes in Aqueous Alkaline Solutions and Their Use in the Catalytic Oxidation of Veratryl Alcohol

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The in situ prepared complex based on copper(II) sulfate and 1,10-phenanthroline (phen) and its performance in the catalytic oxidation of veratryl alcohol (3,4-dimethoxybenzyl alcohol) to veratraldehyde with O₂ in alkaline aqueous solutions have been studied. In aqueous solution, the structure of Cu–phen complexes varies with reaction conditions; by changing either the copper-to-ligand molar ratio or the pH, the amount of coordinated 1,10-phenanthroline and hydroxido ligands in the coordination sphere of copper can be altered in a controlled manner. The highest activities are achieved in the pH range 12.6–13.3, which correlates with the presence of the [Cu(phen)(OH)₂] species according to

complex distribution curves. According to the UV/Vis and EPR studies, the oxidation reaction is initiated by the reduction of [Cu(phen)(OH)₂] to Cu^I species by veratryl alcohol, which can be seen as a disappearance of the Cu²⁺ EPR signal and as a shift of the UV/Vis absorbance maximum from about 690 nm to the 410 and 525 nm regions. When molecular oxygen is added, the Cu^I species is readily oxidised back to Cu^{II} species, and the catalytic formation of aldehyde is initiated. On the basis of these observations, a mechanism for the catalytic oxidation is proposed.

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Introduction

Selective oxidation of alcohols to the corresponding aldehydes, ketones and acids finds its importance in the pharmaceutical industry as well as in the large-scale chemical industry. For further development of these applications towards more sustainable processes, the use of aqueous solutions and molecular oxygen as a cheap, easily available and environmentally friendly oxidant would be highly beneficial.^[1]

(Diimine)copper complexes with different polypyridyl ligands like 2,2'-bipyridine (bipy) and 1,10-phenanthroline (phen) have been studied as catalysts in the oxidation of primary alcohols since the 1970s.^[2,3] Because of their potency to activate molecular oxygen, various applications have been developed including (diimine)copper-catalysed DNA scission,^[4] oxidation reactions^[2,3] and pulp bleaching.^[5,6] Lately, highly active catalysts combining Cu–diimine complexes and TEMPO,^[7] DEADH₂ (= diethylhydrazine dicarboxylate) or DBADH₂ (= di-*tert*-butylhydrazine dicarboxylate)^[8] as co-activators have been reported for the oxidation of primary and secondary alcohols to corresponding aldehydes and ketones by air. In addition to the diimine-based catalysts, efficient copper phenoxyl radical catalysts have recently been introduced for the oxidation of alcohols.^[9,10]

We recently reported that various in situ prepared (diimine)copper complexes catalyse selective oxidation of veratryl alcohol in aqueous solutions.^[6,11] However, the alkaline reaction conditions needed for high catalytic activity together with the presence of paramagnetic Cu species reduce the choice of the analytical methods that can be used to elucidate the solution structures of the complexes and their catalytic reactions. By combining UV/Vis measurements with EPR spectroscopy, complementary pH and GC monitoring of the reaction, consistent information about the catalyst structure and the oxidation reaction were gathered. As a result of these measurements, we report herein the studies of the structure of an in situ prepared (phenanthroline)copper(II) complex under alkaline conditions and its use in the catalytic oxidation reaction.

Results and Discussion

The Nature of In Situ Prepared Cu^{II} Complexes

UV/Vis spectroscopy is a method that is widely used to investigate qualitative as well as quantitative changes in the coordination sphere of transition-metal complexes, and extensive studies on Cu^{II} species in aqueous media have been reported. In fact, the first visible spectra of (diimine)copper complexes were reported already in the 1950s^[12] followed by numerous studies elucidating the structures of these complexes and their spectroscopic properties.^[13a] Because of the available data and simple sample preparation, we

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Table 1. Main UV/Vis absorbances of selected Cu–phen complexes at a copper concentration of 0.01 M.

Molar ratio M/L	[OH [−]]/M	λ_{max} /nm	ϵ_{max} /M ^{−1} cm ^{−1}	Main species
CuSO ₄	–	800	12	[Cu(H ₂ O) ₆] ²⁺
1:1	–	710	12	[Cu(phen)] ²⁺ , Cu(phen)SO ₄ precipitates
1:2	–	720, ≈920	57	[Cu(phen) ₂] ²⁺
1:4	–	680	46	[Cu(phen) ₃] ²⁺
1:1	0.05	660	45	[Cu(phen)(OH)] ₂ ²⁺
1:2	0.01–0.05	690, ≈920	55	[Cu(phen) _{2–3}] ²⁺ , [Cu(phen)(OH) ₂]
1:2	0.1–0.5	690	44	[Cu(phen)(OH) ₂]
1:2	0.5–2.0	620–600	40–38	[Cu(OH) ₄] ^{2−}
1:4	0.05	690, ≈920	56	[Cu(phen) _{2–3}] ²⁺ , [Cu(phen)(OH) ₂]

found UV/Vis spectroscopy to be a useful method to investigate these efficient in situ prepared Cu–phenanthroline catalysts under alkaline conditions.

When reaction conditions are varied, the formation of different Cu–phen complexes in aqueous solutions is fast and reversible. In pure aqueous solution, copper(II) sulfate forms a light blue (aqua)copper complex, [Cu(H₂O)₆]²⁺ (Figure 1, species A), which has a wide absorbance maximum at the 800-nm region (Table 1). When one equivalent of the phenanthroline ligand is added, the absorbance is shifted to 710 nm and light blue Cu(phen)SO₄ precipitates. Addition of a second equivalent of the ligand dissolves this precipitate and forms a [Cu(phen)₂]²⁺ complex in which either a sulfate anion or water molecules complete the coordination sphere of copper. This solution has its main peak in the 720-nm region, while another peak/shoulder is observed at 920 nm (Figure 1, species B). When more than two equivalents of phenanthroline are added, a tris(chelated) [Cu(phen)₃]²⁺ complex (Figure 1, species C) becomes the major species in neutral solution, the absorbance maximum is shifted to 680 nm and the shoulder at 920 nm assigned to the [Cu(phen)₂]²⁺ complex disappears.

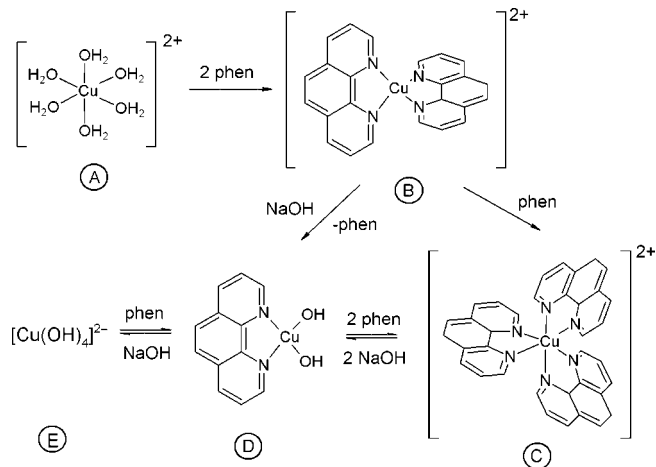


Figure 1. Formation of the catalytically active species D. The amount of coordinated phenanthroline and hydroxido ligands (marked as phen and NaOH) can be controlled by varying the concentration.

The Cu(phen)SO₄ precipitate can also be dissolved with an addition of sodium hydroxide (0.05 M), which leads to the formation of a dark blue solution with an absorbance maximum at around 660 nm. According to the distribution

plots, the [Cu(phen)(OH)]₂²⁺ dimer is the major component in this solution (Figure 2A). Similar spectra have previously been measured for isolated dihydroxido-bridged Cu–phen complexes.^[14] Apparently, in alkaline conditions, the system studied becomes dynamic, and as a result, the λ values are rather a sum of different species than those for one independent complex in the solution.

Addition of 0.05 M NaOH to the [Cu(phen)₂]²⁺ solution leads readily to the formation of the [Cu(phen)(OH)₂] complex, and the main absorbance maximum is shifted to a wavelength of 690 nm (Figure 2B and Figure 1, species D). Similarly, when OH[−] is added to a [Cu(phen)₃]²⁺ solution, the absorbance maximum is again shifted to 690 nm (Figure 1, species D), indicating the replacement of two phenanthroline ligands by hydroxido ligands and formation of the [Cu(phen)(OH)₂] species. Increasing the OH[−] concentration above 0.5 M shifts the absorbance maximum towards shorter wavelengths as the coordinated phenanthroline ligand is replaced by hydroxido ligands (Figure 1, species E, Figure 2). On the basis of the above results, it is obvious that, by varying hydroxide ion and ligand concentrations, the amount of coordinated phenanthroline and hydroxido ligands can be controlled. These observations are comparable with the studies of Garribba et al., in which they demonstrated by UV/Vis and EPR spectroscopic measurements how the structure of the (2,2′-bipyridine)copper complex changes in alkaline solutions.^[13a]

Our previous oxidation studies have revealed that the catalytic activity of these in situ prepared copper complexes is significantly dependent on the applied pH and the ligand concentration.^[6,11] The stability constant of a complex determines the optimum copper-to-ligand molar ratio at a chosen OH[−] concentration, and thus strongly coordinating phenanthroline has maximum activity at the copper/ligand molar ratio 1:5 at high pH (>12.6; 0.05 M NaOH). Under these optimised reaction conditions, the [Cu(phen)(OH)₂] complex is the predominant species (the absorbance maximum of the solution is at about 690 nm) and seems to be responsible for the catalytic activity (Figure 2C). When the copper/ligand molar ratio 1:2 is employed, OH[−] concentrations above 0.05 M shift the absorbance maximum towards shorter wavelengths as a result of complex decomposition and Cu(OH)₄^{2−} formation (Figure 2B). However, when the optimised copper/ligand molar ratio is applied, the absorption maximum at 690 nm remains until the OH[−] concentration exceeds 0.5 M. While the high pH is a prerequisite for

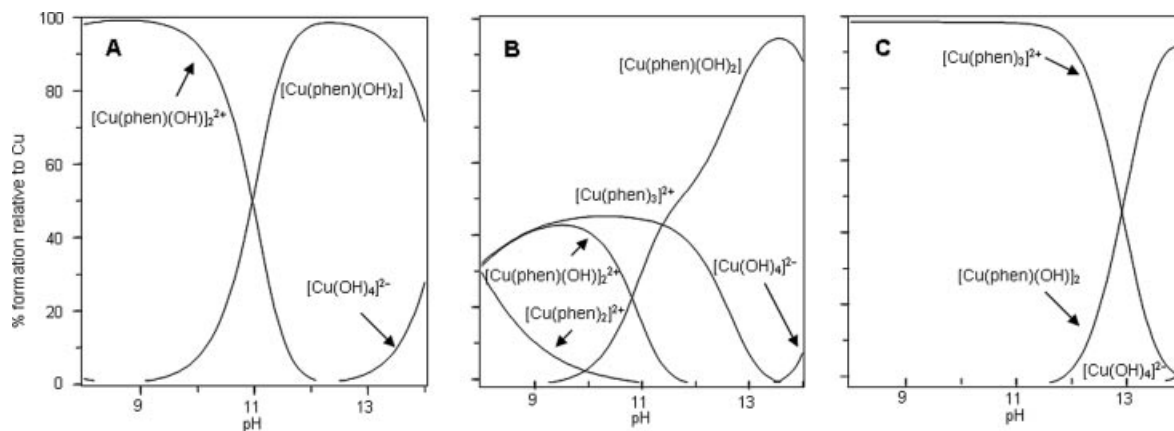


Figure 2. Complex distribution curves for (phenanthroline)copper complexes in alkaline water solutions. Calculated for $[Cu] = 0.01\text{ M}$, ionic strength = 0.1 M , Cu/phen = 1:1 (A), 1:2 (B) and 1:4 (C). See the Experimental Section for details.

the efficiency of the oxidation reaction, the role of the ligand excess is, according to these results, to protect the $[Cu(phen)(OH)_2]$ complex from the destructive coordination of a hydroxide ion.

Isolated $[Cu(phen)_2]^{2+}$ Complex

When the authentic catalyst solution is allowed to stand in an open vessel, the $Cu(phen)_2CO_3 \cdot 7H_2O$ complex crystallises out as a result of the slow evaporation of water. X-ray crystallographic analysis of the crystals revealed that the coordination polyhedron of the copper atom has a square pyramidal geometry as reported previously by van Eldik et al. (cell parameters are given in the Experimental Section).^[15] In the complex, the OH^- ligand is replaced by a carbonate anion as a consequence of CO_2 dissolution during the crystallisation procedure (Figure 3).

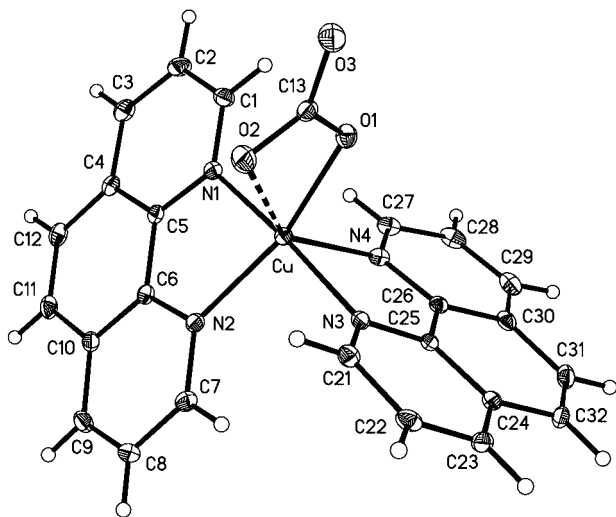


Figure 3. Solid-state structure of $Cu(phen)_2CO_3$ which crystallised out from the authentic catalyst solution kept in an open vessel.

The isolated $Cu(phen)_2CO_3$ complex behaves quite similarly to the in situ prepared catalyst upon variation of the reaction conditions. When the $Cu(phen)_2CO_3$ complex is

dissolved in water, an absorbance maximum appears in the visible spectrum at 680 nm , while addition of excess ligand (total M/L molar ratio 1:4) to the solution removes the carbonate anion from the coordination sphere of copper, and the λ_{max} of $[Cu(phen)_3]^{2+}$ appears. In alkaline solution (0.05 M), the absorbance maximum of the isolated complex is shifted to 690 nm , which indicates the formation of the $[Cu(phen)(OH)_2]$ complex. In highly basic conditions, the absorbance maximum is shifted to shorter wavelengths as the phenanthroline ligand is replaced by a hydroxide ion. Analogously, in oxidation experiments at $pH\ 12.6$, the addition of free ligand to the $Cu(phen)_2CO_3$ solution enhanced the catalytic activity.^[16]

Reaction Monitoring by pH and GC Analysis

The oxidation of veratryl alcohol with Cu–phen catalyst was monitored with parallel pH and GC analysis in order to determine any possible correlations between aldehyde formation and the consumption of hydroxide ions. In these reactions, an initial pH of 11.6 (0.005 M NaOH) was applied, as even modern pH electrodes seem to be too inaccurate for such a study at pH values higher than 12 . During the first 20 min of the reaction the pH decreases rapidly. This decrease is mainly related to the initiation of the catalytic reaction. In general, veratryl alcohol oxidation and OH^- consumption proceed parallel to one another (Figure 4); the actual molar ratio of these two species is around 10 . After 2 h , the pH is reduced to around 10 and the oxidation decelerates. The reaction rate can be increased again by the addition of $NaOH$ (marked in Figure 4). The high aldehyde/ OH^- ratio indicates that, after initiation, the catalytic oxidation reaction itself does not consume OH^- ions. A possible reason for the minor OH^- consumption during the reaction is the formation of a hydroperoxyl radical, which consumes base when forming the superoxide radical anion.^[17] Another reason for the decrease in pH is the formation of traces of veratric acid as detected by GC–MS.

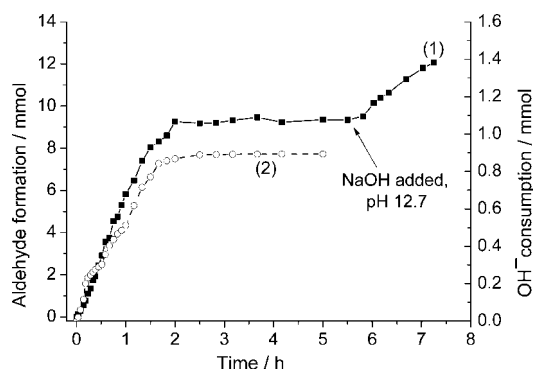


Figure 4. Rate of oxidation and total OH^- consumption in the Cu-phen-catalysed reaction: (1) formation of veratraldehyde and (2) consumption of OH^- ions. Reaction conditions: 80 °C, 10 bar O_2 , initial pH 11.6, Cu/veratryl alcohol molar ratio 1:500.

Visible Spectrum of Cu^{I} -phen

A copper(I) complex prepared from Cu_2O and phenanthroline gives a dark red solution in alkaline aqueous media under an argon atmosphere. In solution, the bis(phenanthroline)copper(I) should possess nearly regular D_{2d} symmetry.^[18,19] As a result of the presence of the low-energy π^* orbitals of the phenanthroline ligand, the complex exhibits strong metal-to-ligand charge-transfer absorption bands in the visible spectrum (Figure 5). The absorption involves the transfer of an electron from the d shell of the copper centre to π^* orbitals of the coordinated ligand. Solutions of the Cu^{I} -phen complex can be stored under argon, but are oxidised to $[\text{Cu}(\text{phen})(\text{OH})_2]$ by oxygen after a few minutes as the absorbances maxima at 405 and 535 nm disappear and that at 690 nm strengthens. This process is assisted by hydrogen peroxide formation; when a solution of the bis(phenanthroline)copper(I) complex was exposed to air, small amounts ($\approx 2 \text{ mg L}^{-1}$) of H_2O_2 were detected.^[20] In conclusion, changes in the oxidation state of copper can be determined in the visible region as Cu^{I} and Cu^{II} species have characteristic absorbances at different wavelengths.

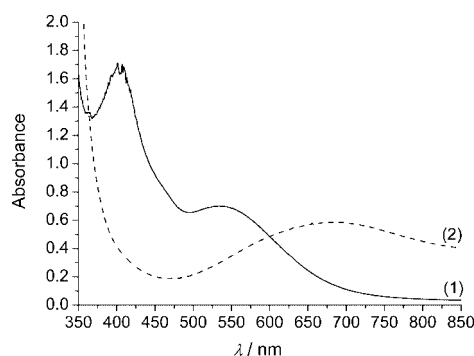


Figure 5. UV/Vis spectrum of $[\text{Cu}(\text{phen})_2]^+$ oxidation by O_2 : (1) the spectrum of the complex under an argon atmosphere, (2) the spectrum after O_2 bubbling. The Cu^{I} sample was diluted for the measurement. Conditions: 25 °C, $[\text{NaOH}]$ 0.05 M, $[\text{Cu}]$ 0.01 M.

Reaction Monitoring by UV/Vis Spectroscopy

UV/Vis spectroscopy turned out to be highly useful for monitoring the reaction. The addition of veratryl alcohol to an alkaline catalyst solution results in the formation of small absorption bands in the 410 and 525 nm regions, which indicates the presence of the Cu^{I} species. The reduction of Cu^{II} is seen more clearly when the reaction is carried out under an argon atmosphere (Figure 6, spectra 1–3); the absorbance maximum at 690 nm decreases while absorbances at 410 nm and 525 nm increase. Upon addition of oxygen, the characteristic absorbance maximum of the Cu^{II} species increases again (spectra 4–5).

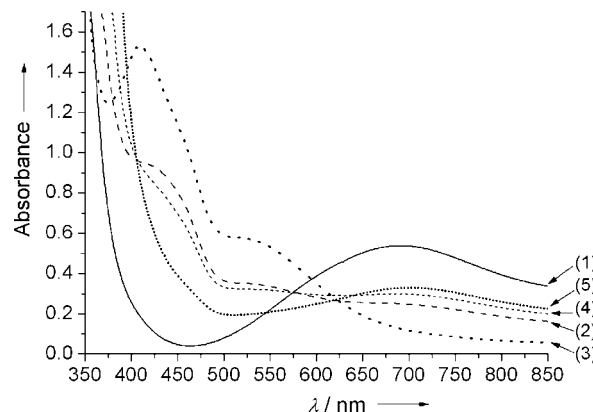


Figure 6. A UV/Vis spectrum of Cu^{II} reduction to Cu^{I} by alcohol under argon and reoxidation after oxygen addition. (1) Cu^{II} -phen complex under argon, (2) veratryl alcohol added, (3) 60 h under argon, (4) 1 h after O_2 addition, 18% aldehyde (5) 23 h, 93% aldehyde. Reaction conditions: 80 °C, 1 bar O_2 , pH 12.6, $[\text{Cu}]$ 0.01 M, Cu/veratryl alcohol molar ratio 1:20. The Cu^{I} samples were diluted for the measurement.

A small percentage of aldehyde (4%) can be detected when a 10 mol-% loading of Cu vs. alcohol is used under an argon atmosphere. In these conditions, the Cu/aldehyde ratio is 2.5, which indicates that two electrons are involved in veratryl alcohol oxidation. However, significant aldehyde formation only begins after the addition of oxygen. If Cu^{I} -phen (prepared from Cu_2O and phen) is used in the reaction in place of Cu^{II} -phen, no aldehyde is formed under an argon atmosphere. This shows that the alcohol is able to reduce copper(II) under anaerobic conditions, and the catalytic cycle begins when oxygen is added. If the reaction solution is degassed and set under an argon atmosphere again, the colour changes to dark brown, and the absorbances of Cu^{I} strengthen again.

Formation of the Cu^{I} species has also been observed in the oxidation of benzyl alcohol with $[\text{Cu}(\text{bipy})_2]^{2+}$ catalyst, but it was concluded that in acetonitrile solution the Cu^{I} species inhibits the oxidation while the actual catalysis proceeds via Cu^{III} intermediates.^[21] However, under the applied reaction conditions here, the reduction of Cu^{II} to Cu^{I} is a prerequisite for the formation of aldehyde, and during the reaction both Cu^{I} and Cu^{II} complexes are present. In this respect, the redox behaviour of the Cu species resembles that observed by Tretyakov et al. for the oxidation of propanol.^[3]

EPR Studies

The EPR spectrum of the in situ prepared Cu^{II}–phen complex in alkaline medium at room temperature is shown in Figure 7a. The typical four-line Cu hyperfine split signal (without sfhs from N atoms) with $g_{\parallel} = 2.33$, $g_{\perp} = 2.06$ and hfs constant $A_{\parallel} = 75$ G is in good agreement with previous reports for Cu^{II}–diamine tetragonal complexes with ground state $d_{x^2-y^2}$.^[13]

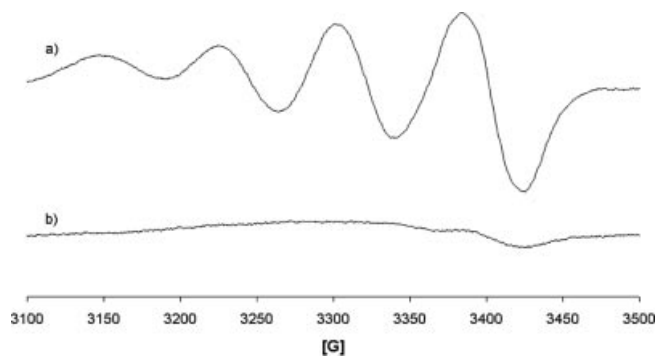


Figure 7. X-band EPR spectrum of the reduction of Cu^{II} to Cu^I by alcohol under nitrogen, (a) Cu^{II}–phen complex under nitrogen, (b) excess veratryl alcohol added. Reaction conditions: room temp., pH 12.6, [Cu] = 0.01 M, Cu/veratryl alcohol molar ratio ca. 1:200.

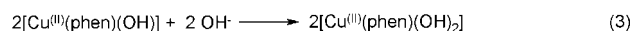
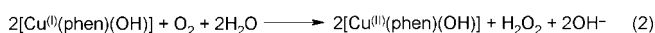
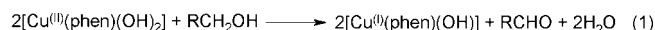
The addition of an excess of veratryl alcohol (alcohol/[Cu]: c.a. 200) to the Cu^{II}–phen complex solution in the absence of oxygen (nitrogen atmosphere) results in the disappearance of the Cu^{II} signal (Figure 7b). This suggests that alcohol can reduce the Cu^{II}–phen complex to an EPR-silent Cu^I (d^{10}) species. An identical solution of the Cu^{II}–phen complex in alkaline medium containing an excess of veratryl alcohol exposed to air under the same conditions exhibits no reduction of Cu^{II} to Cu^I. These EPR spectroscopic observations confirm the previous UV/Vis spectroscopic interpretations (see previous section).

Catalytically Active Species

The correlation between the catalytic activity and absorbance of the in situ prepared complex in alkaline aqueous solution indicates that high pH and the presence of the [Cu(phen)(OH)₂] complex are essential for catalytic activity. As demonstrated above, in the presence of hydroxide ions and veratryl alcohol, the [Cu^{II}(phen)(OH)₂] species is reduced by veratryl alcohol to [Cu^I(phen)(OH)] [Equation (1)]. Consequently, in the absence of oxygen, the formation of a small percentage of aldehyde is observed at low copper/alcohol ratios (1:10). In neutral or acidic solutions, neither catalyst reduction nor aldehyde formation was observed.

The Cu^I–phen complex formed is oxidised to Cu^{II}–phen species by oxygen as shown in Figure 5. In this process, hydrogen peroxide is formed even in the absence of veratryl alcohol [Equation (2)]. As shown in Figure 1 and Figure 2, the coordination sphere of the Cu^{II} complex is balanced by

a dynamic self-assembly process under alkaline conditions, and the formation of initial species, Cu^{II}(phen)(OH)₂ is feasible [Equation (3)].



On the basis of these results, a proposed mechanism for the Cu–phen-catalysed oxidation reaction is summarised in Figure 8. Unfortunately, direct spectroscopic evidence for the short-lived intermediates in the catalytic cycle is not available. Therefore, it can not be excluded that, under alkaline conditions, an alcohol molecule could also coordinate to the [Cu^I(phen)(OH)] complex to form a Cu^I–alkoxide complex, which converts alcohol to aldehyde via a copper(II) alkoxide peroxo species. Also in this pathway hydrogen peroxide is released, but Cu^I works as the actual catalyst. The formation of hydrogen peroxide with the catalyst but in the presence of alcohol has also been shown earlier.^[21] However, all of the experimental observations, such as the reduction of Cu^{II} by alcohol, the minor OH[−] consumption during the catalytic cycle, the oxidation of Cu^I by oxygen and the formation of hydrogen peroxide even in the absence of alcohol can be reasonably explained by the proposed mechanism in Figure 8. After all, the proposed catalytic cycle has similarities with a ping-pong mechanism proposed previously for galactose oxidase.^[22]

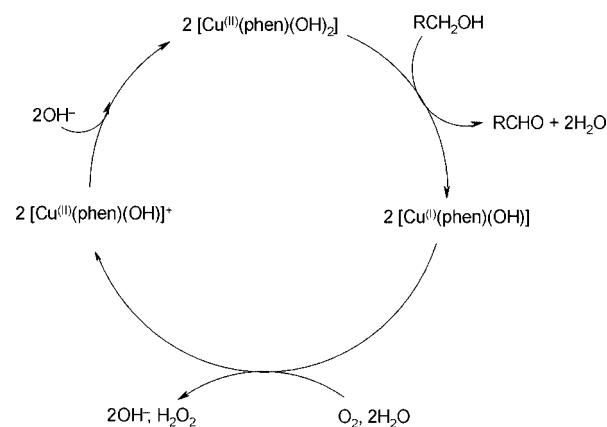


Figure 8. The proposed catalytic cycle for the oxidation of veratryl alcohol in alkaline media with the in situ prepared Cu–phen catalyst by using dioxygen as the end-oxidant.

Conclusions

In alkaline aqueous solution, in situ addition of copper sulfate to phenanthroline leads to the formation of various complexes by a self-assembly process depending on the OH[−] concentration and phenanthroline-to-copper molar ratio. The dynamic changes in the coordination sphere of the

catalyst upon variation of the reaction conditions were identified by UV/Vis spectroscopy and verified with the complex distribution curves. As the ligand concentration and pH are interdependent, under optimum reaction conditions the OH^- concentration needs to be adequate for efficient alcohol oxidation, and the phenanthroline concentration should be high enough to preserve the structure of the $[\text{Cu}(\text{phen})(\text{OH})_2]$ species, whose presence is essential for high catalytic activity.

Under alkaline conditions and in the presence of veratryl alcohol, $[\text{Cu}^{\text{II}}(\text{phen})(\text{OH})_2]$ is reduced to the $[\text{Cu}^{\text{I}}(\text{phen})(\text{OH})]$ species. When oxygen is added, the Cu^{I} species is readily oxidised back to the Cu^{II} species, and the catalytic formation of aldehyde is initiated. The catalytic reaction was further studied by combining pH and gas chromatographic monitoring with UV/Vis and EPR spectroscopy. On the basis of these results, a catalytic cycle for the oxidation of veratryl alcohol was proposed.

Experimental Section

Commercially available copper sulfate, 1,10-phenanthroline and veratryl alcohol (3,4-dimethoxybenzyl alcohol, 96%) were used without further purification. Deionised water and oxygen (AGA 99.5) were used for the reactions.

pH and Oxidation Monitoring

For the pH and gas chromatographic reaction monitoring, veratryl alcohol (4.0 mL, 27.5 mmol) and catalyst in a molar ratio of 1:500 (0.055 mmol) to veratryl alcohol were mixed in NaOH solution (200 mL). A copper/phenanthroline molar ratio of 1:2 was used. A 400-mL glass vessel with a magnetic stirring bar was fitted inside a 1-L steel autoclave, and the desired oxygen pressure (10 bar) and temperature (80 °C) were set. Samples were taken from the reactor and cooled to room temperature. The pH was measured, and a sample was prepared for GC analysis by a method described earlier (extraction with ethyl acetate) and analysed with GC/FID Agilent 6890N using an HP-5 30 m \times 320 μm \times 0.25 μm capillary column.^[11] After extraction, the aldehyde was the only product. However, if alcohol conversions were remarkably high, also a small amount of veratric acid (< 1%) was detected by HPLC analysis.

UV/Vis Spectroscopy

UV/Vis spectroscopic measurements were carried out with a HP 8453 spectrophotometer, and the data was analysed with UV/Vis ChemStation software. To see the changes in the visible region of the UV/Vis spectra, high catalyst concentrations (0.01 M) were used. For a usual reaction CuSO_4 (0.160 g, 1.0 mmol), 1,10-phenanthroline (0.3965 g, 2.0 mmol) and veratryl alcohol (2.9 mL, 20 mmol) were mixed in H_2O (100 mL). In the oxidation reactions monitored with UV/Vis spectroscopy, the oxygen atmosphere was maintained by using a balloon of oxygen. For the Cu^{I} species, the samples were diluted to 0.001–0.0015-M solutions (of copper) with degassed solvent. Complex distribution charts (Figure 2) were calculated by using the HySS program.^[23] Stability constants for the relevant species were obtained from the NIST Standard Reference Database 46.^[24]

EPR Spectroscopy

For an EPR experiment, a solution of Cu–phenanthroline complex (0.01 M) in NaOH (0.05 M) was prepared from CuSO_4 (0.016 g, 0.1 mmol) and 1,10-phenanthroline (0.0396 g, 0.2 mmol) in H_2O

(10 mL). To observe the decay of the Cu^{II} signal, veratryl alcohol (2.9 mL, 20 mmol) was mixed with the Cu–phenanthroline complex. Samples were degassed with flow of nitrogen gas (30 min) and contained in quartz capillary tubes.

X-band EPR spectra were measured with a Bruker ESP 300E spectrophotometer equipped with the Bruker NMR gaussmeter ER035 M and the Hewlett–Packard microwave frequency counter with 100-kHz field modulation and a microwave power of 20 mW at room temperature. The data obtained was analysed with Bruker WinEPR software.

Isolated $\text{Cu}(\text{phen})_2\text{CO}_3 \cdot 7\text{H}_2\text{O}$

Crystallisation of the Cu–phen complex was achieved by dissolving CuSO_4 (0.10 g, 0.63 mmol) and 1,10-phenanthroline (0.25 g, 1.26 mmol) in NaOH solution (0.05 M). Slow evaporation of water in room temperature yielded blue crystals of $\text{Cu}(\text{phen})_2\text{CO}_3 \cdot 7\text{H}_2\text{O}$. Crystal data for $\text{C}_{25}\text{H}_{30}\text{CuN}_4\text{O}_{10}$: $M_r = 610.07$, space group $P2_1/c$, $a = 9.87930(10)$, $b = 26.2067(3)$, $c = 10.49350(10)$ Å, $\beta = 105.8390(10)^\circ$, $V = 2613.66(5)$ Å³, $Z = 4$, $D_c = 1.550$ g cm^{−3}, $\mu(\text{Mo-K}\alpha) = 0.901$ mm^{−1}, $T = 120(2)$ K, 5984 reflections measured, R^2 refinement, $R_1 = 0.0555$, $wR_2 = 0.0856$, 4647 independent observed absorption-corrected reflections, 363 parameters.

Acknowledgments

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