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Tetrahedron
Tetrahedron 62 (2006) 9109–9114

Aerobic oxidation of primary alcohols under mild aqueous conditions promoted by a dinuclear copper(II) complex

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Received 12 May 2006; revised 23 June 2006; accepted 7 July 2006
Available online 1 August 2006

Abstract—A sugar-discriminating dinuclear copper(II) complex was investigated for its ability to promote aerobic oxidation of primary benzylic alcohols in the presence of TEMPO and base. The transformation of benzyl alcohol to benzaldehyde was chosen as exploratory model reaction. The constitution of the catalytically active species was deducted from isothermal titration calorimetry and kinetic experiments, and the catalytic reaction was characterized both in aqueous organic and aqueous solution. The dinuclear complex is found to selectively oxidize primary over secondary alcohols in aqueous solution at ambient temperature with a turnover rate of 9 h^{-1}. A mechanism for the catalytic cycle is proposed.

1. Introduction

Ecologically benign oxidations of alcohol groups have attracted much attention in recent years.[1–8] Catalysts for the oxidation of petrochemicals are required to have a very broad substrate scope that includes primary and secondary, aliphatic, benzylic, and allylic alcohols. On the other hand, catalysts designed for the transformation of biomolecules need to be able to selectively transform only one out of several different functional groups in the same molecule, ideally without protection of the remaining other groups. The development of a regioselective oxidation method to catalytically transform underivatized carbohydrates into hexose-6-carbaldehydes in aqueous solution is a long-term goal in this laboratory. Hexose-6-carbaldehydes are precursor compounds for unnatural carbohydrates that might evolve as new synthons for the preparation of glycosylated pharmaceuticals.[9]

Recently reported aerobic catalyst that promote oxidation of primary alcohols into aldehydes, while preventing overoxidation of this aldehyde into the corresponding carboxylic acid, use in situ prepared mixtures of Cu(II) salts and bipyridine ligands[10–13] or mononuclear Cu(I) phenanthroline complexes[14–17] in the presence of base and 2,2,6,6-tetramethylpiperidine-*N*-oxyl (TEMPO) as co-catalysts. Selectivity of mononuclear bipyridine copper(II) complexes toward oxidation of activated primary, but not secondary benzylic alcohols has been observed.[10,11] Oxidation of secondary benzylic and aliphatic alcohols into ketones is demonstrated for derivatized bipyridine copper(I) catalysts that are employed at elevated reaction temperature in the presence of excess of TEMPO.[18] The conversion of benzyl alcohol (**1**) into benzaldehyde (**2**) is usually used to establish oxidation ability of the catalyst toward primary alcohols due to the higher reactivity of the aromatic alcohols when compared to aliphatic alcohols, and the ease of detection by gas chromatographic analysis.[10–12,14–17]

A large variety of mono- and dinuclear copper(II) complexes with and without pyridine moieties in the backbone ligand were synthesized in this laboratory and investigated for their carbohydrate recognition properties.[19–22] All selected mononuclear complexes were incapable to promote oxidation of **1** into **2**, while the transformation is conveniently achieved with the dinuclear complex *N*,*N*-bis[(2-pyridylmethyl)-1,3-diaminopropan-2-olato] (μ-acetato) dicopper(II) perchlorate (Cu_2(bpdpo), **3**). Complex **3** was previously established to selectively discriminate between various carbohydrates depending on the number of hydroxyl groups of the sugar involved in coordination to **3**.[20,21] It is therefore postulated that if complex **3** is able to catalyze oxidation reactions in water, then it may be possible to use this complex for selective carbohydrate and glycoside oxidation.

To establish catalytic transformation ability of **3**, the aerobic oxidation of **1** into **2** was chosen as exploratory model study. The reaction is investigated on dependence of the concentrations of the co-catalysts TEMPO and base; the kinetic of the reaction is investigated in both aqueous organic and predominantly aqueous solutions at ambient temperature.

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0040–4020/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2006.07.025

In addition, the proposed catalytically active species is characterized and a mechanism for the reaction suggested. The results obtained are discussed below.

2. Results and discussion

2.1. Composition of the dinuclear copper(II) complex in alkaline solution

Spectrophotometric titration of the backbone ligand of the sugar-discriminating dinuclear copper(II) complex *N*,*N*-bis-[(2-pyridylmethyl)-1,3-diaminopropan-2-olato] (μ-acetato) dicopper(II) perchlorate (Cu_2(bpdpo), **3**) in the presence of 2-fold molar amounts of copper(II) ions with sodium hydroxide shows that the bridging acetate anion bound in the solid state is exchanged against two hydroxyl ions and two water molecules in alkaline aqueous solution (Scheme 1).[23,24] Two species, $[Cu_2(L_{-H})(OH)]^{2+}$ (**3a**) and $[Cu_2(L_{-H})(OH)_2]^{+}$ (**3b**), are observed in equilibrium depending upon the pH of the solution (Fig. 1).[20] A mononuclear species, $[Cu(L)]^{2+}$, is present below pH 8.

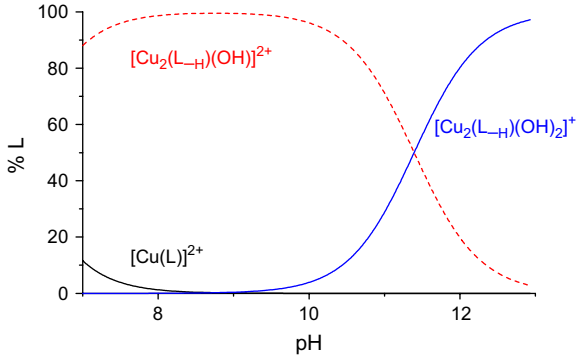


Figure 1. Distribution of species at pH 7–13 related to the binuclear copper(II) complex Cu_2(bpdpo) (**3**), calculated from measured UV–vis spectra in dependence of the pH.

2.2. Coordination of the TEMPO co-catalyst to the dinuclear copper(II) complex

Isothermal titration calorimetry was used to determine the interaction between the dinuclear copper(II) complex **3** and the TEMPO co-catalyst in aqueous alkaline acetonitrile (Fig. 2). Relating the titration data to a sequential binding model for four binding sites provide the best fit and reveal exothermic interaction of the first TEMPO molecule with one of the copper(II) centers with a rather low binding constant (K_1=320), while coordination of the second molecule of TEMPO is an endothermic process resulting in a strong TEMPO–**3**–TEMPO complex (K_2=9800). The interaction of the remaining two coordination sites of the Cu(II) core with TEMPO is exothermic, but results in weak TEMPO association only (K_3=400; K_4=14). The titration data reveal that the second molecule of TEMPO binds strongly to the dinuclear metal complex **3**, provided the first molecule of TEMPO is already weakly associated. This observation suggests that excess of TEMPO will enforce formation of a TEMPO–**3**–TEMPO complex in alkaline solution by replacement of coordinated water in **3b** (Chart 1). Further TEMPO coordination to **3b** is presumably slowed down as (a) replacement of hydroxyl ions is required, which coordinate stronger than water molecules, and (b) already coordinated TEMPO molecules provide steric hindrance to further association of TEMPO.

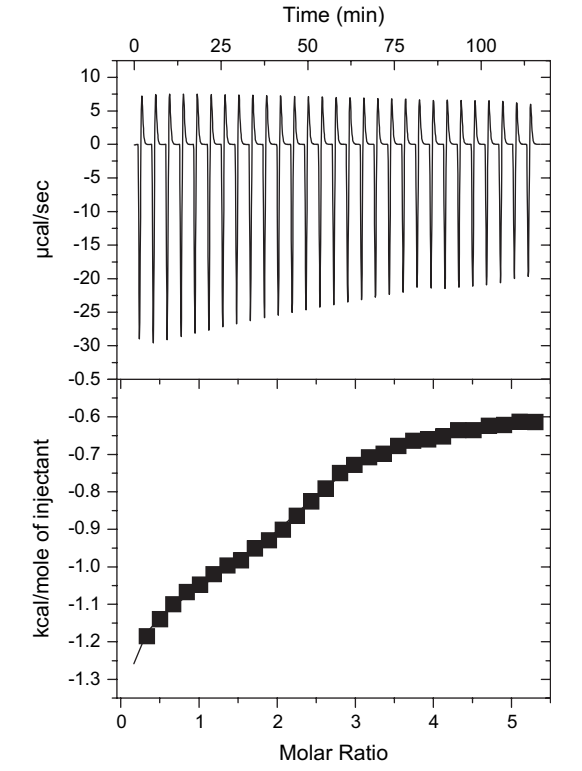
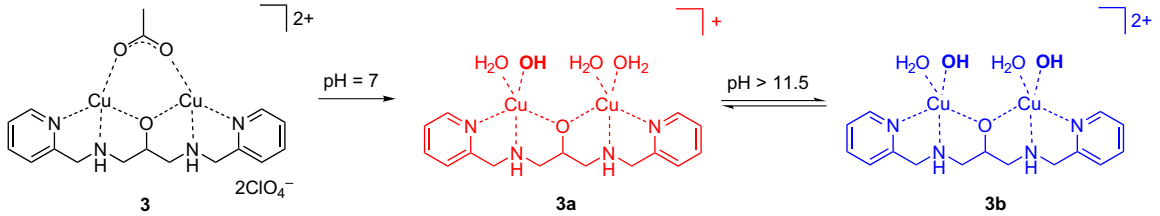


Figure 2. Isothermal titration of Cu_2(bpdpo) (**3**) with TEMPO in aqueous, alkaline acetonitrile (CH_3CN/H_2O=2/1) at 300 K. Fitting of the data was best using the sequential binding model for four sites; χ=61.5; K_1=322±28, ΔH_1=−3261±181 kcal mol^{-1}, ΔS_1=0.608 cal mol^{-1} K^{-1}; K_2=9.81E3±9.8E2, ΔH_2=877.9±192 kcal mol^{-1}, ΔS_2=21.2 cal mol^{-1} K^{-1}; K_3=393±35, ΔH_3=−1146±117 kcal mol^{-1}, ΔS_3=8.05 cal mol^{-1} K^{-1}; K_4=14.0±2.1, ΔH_4=−2.998E4±3.94E3 kcal mol^{-1}, ΔS_4=−94.6 cal mol^{-1} K^{-1}.



Scheme 1. Equilibria of the major species $[Cu_2(L_{-H})(OH)]^{2+}$ (**3a**) and $[Cu_2(L_{-H})(OH)_2]^{+}$ (**3b**) formed in alkaline water.

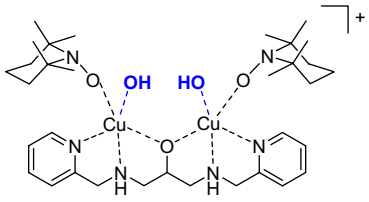
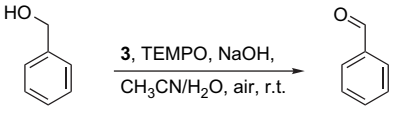


Chart 1. Suggested constitution of the catalytically active species derived from dinuclear copper(II) complex **3** and TEMPO.

2.3. Dependence of the catalytic activity of the dinuclear copper(II) complex on TEMPO and base as co-catalysts

The catalytic oxidation of benzyl alcohol **1** into benzaldehyde **2** was employed as exploratory model reaction to study the oxidation ability of **3** and was monitored by GC analysis (Scheme 2). All reactions were conducted under aerobic conditions at ambient temperature with 5 mol % of **3** with respect to the substrate concentration. Addition of TEMPO and base to a solution of **3** in presence of oxygen is required to detect any transformation, as has been established by appropriate control reactions (data not shown). Overoxidation of **2** into benzoic acid was not observed under the given conditions, which is in agreement with results for mononuclear copper(I) and copper(II) complexes reported by others earlier.[10,17]



Scheme 2. Oxidation of benzyl alcohol (**1**) into benzaldehyde (**2**) promoted by dinuclear copper(II) complex **3** in the presence of TEMPO and base.

According to the proposed structure of the dinuclear catalytically active species (Chart 1), the oxidation is expected to depend in a linear fashion on the concentration of the co-catalyst TEMPO. In order to verify this, product formation was determined by gas chromatography after withdrawing aliquots of the reaction mixture at defined time points and subsequent decomposition of the catalyst **3** with sodium sulfide (see Section 3). The molar ratios of complex **3** and TEMPO were varied in the presence of excess base (Fig. 3).

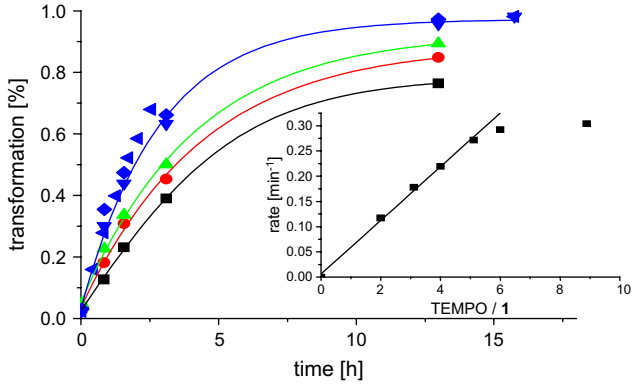


Figure 3. Oxidation of benzyl alcohol into benzaldehyde in the presence of **3** (4.5 mM) and excess base (80 mM) in CH_3CN/H_2O=2/1; the molar ratio between the copper(II) ions of **3** and TEMPO equals (a) 2:2 (■), (b) 2:3 (●), (c) 2:4 (▲), and (d) 2:5 (◀), 2:6 (▶), or 2:10 (◆). The inset shows a linear correlation between the initial rate and the TEMPO concentration for low co-catalyst concentrations.

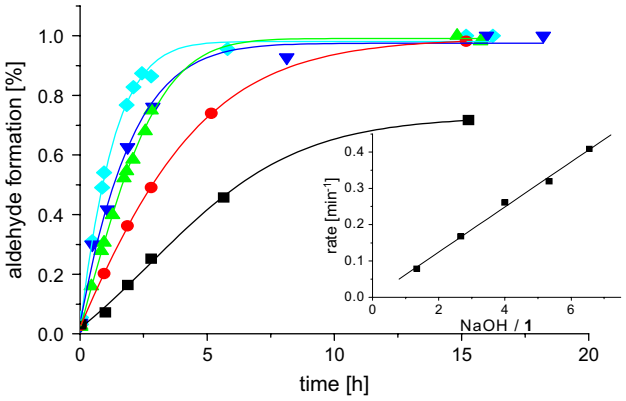


Figure 4. Oxidation of benzyl alcohol (90 mM) into benzaldehyde in the presence of **3** (4.5 mM) and excess TEMPO (18 mM) in CH_3CN/H_2O=2/1; the molar ratio between the copper(II) ions of **3** and NaOH equals (a) 2:1.3 (■), (b) 2:2.6 (●), (c) 2:4 (▲), (d) 2:5 (▼) and, (e) 2:6.7 (◆). The inset shows the linear correlation between the initial rate and the base concentration.

Increasing the TEMPO concentration by 2-fold doubles the initial rate acceleration of the oxidation, when the molar ratio between the copper(II) ions and TEMPO is kept below 2:5. Additional increase of the TEMPO concentration does not speed up the initial rate of the reaction further.

In the next experiment, the molar ratio of TEMPO to the dinuclear complex **3** was kept constant at 4:1, while the base concentration was varied. Linear dependence of the initial reaction rate of the oxidation on the base concentration is observed (Fig. 4). Using less than equimolar amounts of base compared to the amount of copper(II) ions in the metal complex core leads to incomplete substrate oxidation indicating that formation of the catalytically active species requires at least one hydroxyl ion per copper ion. Increasing the base concentration by 2-fold results in a linear increase of the initial rate of the oxidation suggesting that molar amounts of base with respect to **3** are involved in the catalytic turnover. Further, control experiments demonstrated that the reaction does not proceed in the absence of the dinuclear copper(II) complex, or if copper(II) acetate is used as a potential catalyst. The oxidation does also not proceed in pure acetonitrile indicating that water is required during the catalytic turnover.

Last, the initial rate of the aerobic oxidation of benzyl alcohol in the presence of **3** (4.5 mM), TEMPO (18 mM), and NaOH (18 mM) in aqueous organic solution (CH_3CN/H_2O=2/1) was determined (Fig. 5). The oxidation follows classical saturation kinetics and was fitted with Michaelis–Menten model for enzymatic reactions, giving a turnover rate (k_{cat}) of 0.64 min^{-1} (=38 h^{-1}) and a substrate affinity (K_m) of 340 mM. The initial rate of the reaction depends linearly on the catalyst concentration.

2.4. Selectivity for primary versus secondary benzylic alcohols, control reactions

Carbohydrates are multifunctional biomolecules containing primary and secondary alcohol groups. Protection and deprotection of hydroxyl groups that need to remain unchanged are therefore required prior to application of conventional oxidation methods. In the light of our postulate

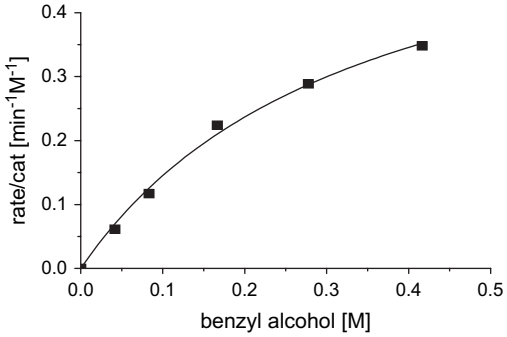


Figure 5. Initial rate plot of the aerobic oxidation of benzyl alcohol in the presence of **3** (4.5 mM), TEMPO (22 mM), and NaOH (18 mM) in aqueous acetonitrile (CH_3CN/H_2O=2/1) at ambient temperature. Initial rate data are plotted against concentrations of the substrate benzyl alcohol; k_{cat}=0.64 min^{-1} (=38 h^{-1}), K_m=340 mM.

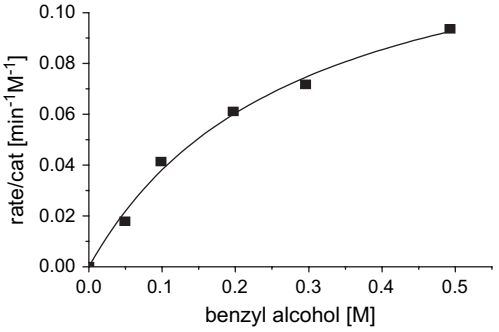


Figure 7. Initial rate plot of the aerobic oxidation of benzyl alcohol in the presence of **3** (4.5 mM) and TEMPO (22 mM) in aqueous NaOH (18 mM) containing 8% CH_3CN at ambient temperature. Initial rate data are plotted against increasing concentrations of the substrate benzyl alcohol; k_{cat}=0.15 min^{-1} (=9 h^{-1}), K_m=281 mM.

that dinuclear complex **3** may be able to selectively oxidize the primary hydroxyl group in carbohydrates, we investigated its ability to regioselectively oxidize a primary alcohol function over a secondary in a model substrate. For that purpose, we chose the oxidation of 1-phenylethanol into acetophenone under the same conditions as for the oxidation of benzyl alcohol.

The reaction was monitored by GC analysis. No evidence for oxidation of the activated secondary alcohol was found, even if the reaction was allowed to proceed for 15 h after which the oxidation of benzyl alcohol was completed (Fig. 6). This finding suggests that the hydrogen atom abstraction by TEMPO in the secondary alcohol might be hindered by the methyl group in 1-phenylethanol, i.e., the methyl group in 1-phenylethanol does not stabilize the forming TEMPOH species. In contrast, the formation of TEMPOH during benzyl alcohol oxidation can be stabilized through hydrogen bonds between TEMPOH and the aldehyde proton in benzaldehyde. A similar rationale for the observed selectivity was given by others previously.[10,11]

2.5. Oxidation in water

All experiments reported before were conducted in aqueous organic solvent (CH_3CN/H_2O=2/1). However, the most suitable reaction conditions for the transformation of biomolecules involve water as main solvent. Polar organic solvents, such as pyridine or DMF, dissolve carbohydrates, but are less attractive from both an economic and environmental viewpoint. The catalytic oxidation of benzyl alcohol into benzaldehyde was subsequently conducted in aqueous solution at pH 12.5. Due to the low solubility of TEMPO and high benzyl alcohol concentrations in water, even at alkaline pH, 8% acetonitrile are necessary in the reaction solution. The proceeding of the oxidation was monitored by GC analysis (Fig. 7).

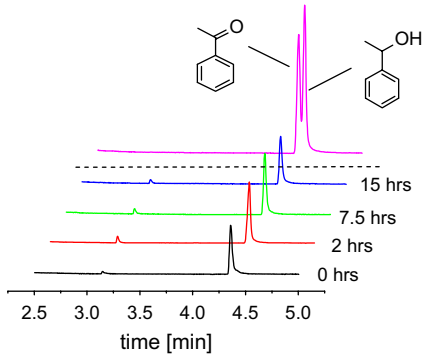


Figure 6. Gas chromatographic traces of sample aliquots of the putative catalytic oxidation of 1-phenylethanol (90 mM) into acetophenone for 0–15 h. The reaction was conducted in the presence of **3** (4.5 mM), TEMPO (18 mM), and NaOH (18 mM) in CH_3CN/H_2O=2/1 at ambient temperature; the trace in magenta refers to an equimolar mixture of commercially available 1-phenylethanol and acetophenone standards separated under the same conditions.

The oxidation follows classical saturation kinetics, and non-linear regression was applied to fit the data according to the Michaelis–Menten model, giving a turnover rate (k_{cat}) of 0.15 min^{-1} (9 h^{-1}) and a substrate affinity (K_m) of 281 mM. As the reaction does not proceed in the absence of **3** or when Cu(II) acetate is used instead of **3**, the self-promoted (k_{non}) and the potential metal ion-catalyzed oxidation of the substrate were not determined. The turnover rate of the catalytic benzyl alcohol oxidation by **3** in aqueous solution is only 4-fold slower than the same reaction in aqueous acetonitrile (see Fig. 5, k_{cat}=38 h^{-1}, K_m=340 mM).

Although our catalytic system promotes alcohol oxidation with a turnover in the same order of magnitude as the catalyst recently reported by Sheldon et al. (k_{cat}=14 h^{-1}),[10] it has several advantages for our intended purpose toward carbohydrate oxidation: (i) the system is able to work under mild, predominantly aqueous conditions, (ii) the dinuclear copper(II) complex **3** is structurally characterized in solution, (iii) the constitution of the most likely catalytically active species has been established, and (iv) complex **3** is able to differentiate between carbohydrates containing *cis*-diols and *cis*,*cis*-triols.[19–21] In the light of these results, we are encouraged to extend our investigations in further studies about the oxidation of carbohydrates.

2.6. Oxidation mechanism

Based on the determination of the catalytically active species and the observed catalytic turnover of benzyl alcohol into benzaldehyde, a mechanism for the catalytic cycle of the oxidation is proposed (Fig. 8). The dinuclear

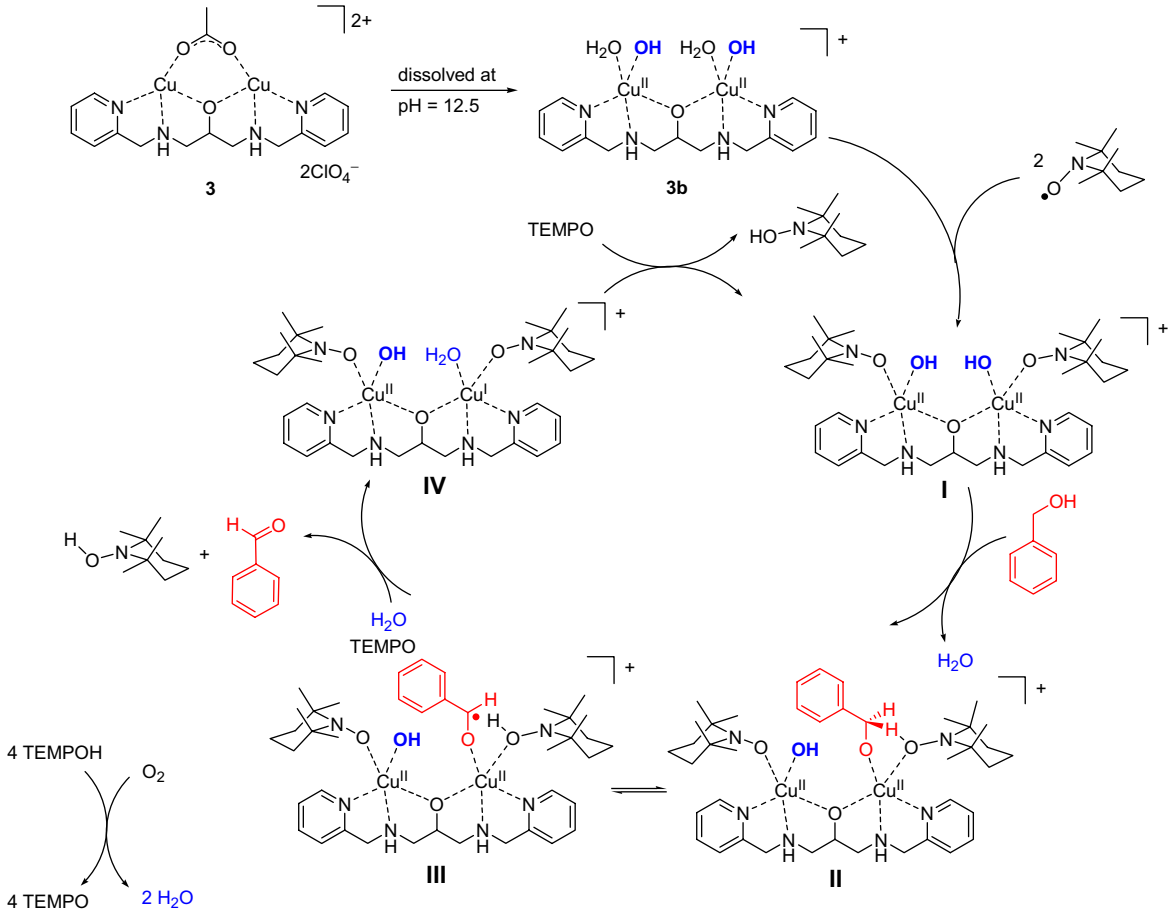


Figure 8. Proposed mechanism for the oxidation of benzyl alcohol into benzaldehyde by the dinuclear copper(II) complex **3**.

copper(II) complex **3** exchanges first the bridging acetate ion against two water molecules and two hydroxyl groups. Subsequently, TEMPO radicals replace the weakly coordinating water molecules (Fig. 8, species **I**). The substrate benzyl alcohol is then coordinated to one copper(II) center under displacement of one hydroxyl group (Fig. 8, species **II**). This is possible either by binding of the anion from the equilibrium of alcohol and alcoholate that exists in basic solution, or by deprotonation of the alcohol at the copper(II) center and release of water. Subsequent transfer of a hydrogen atom to TEMPO is followed by release of benzaldehyde under reduction of Cu(II) into Cu(I) and coordination of water (Fig. 8, species **III**). The formed TEMPOH is very likely weakly coordinated to **3** and as such easily displaced from the complex by another TEMPO radical (Fig. 8, species **IV**). Regeneration of the catalytically active species is then achieved by formal deprotonation of the coordinated water molecule by another molecule of TEMPO radical and oxidation of Cu(I) into Cu(II) (Fig. 8, species **I**). The two molecules of TEMPOH that are formed during the catalytic cycle are reoxidized by oxygen present in the reaction solution. Control experiments (data not shown) have demonstrated that in the absence of both oxygen or TEMPO no reaction is observed, indicating that oxygen is the regenerative agent for the TEMPO radical and not for the copper(II) complex **3**.

The proposed mechanism is in agreement with the finding that (a) only two molecules of TEMPO coordinate strongly to the transition metal complex (see Section 2.2), while (b) the catalytic transformation is linearly dependent on the TEMPO concentration as long as the molar ratio between **3** and TEMPO is less than 1:5. Further increase did not show a significant effect (see Fig. 3). The proposed mechanism furthermore reflects the observed linear dependence of the initial reaction rate on the hydroxide concentration (see Fig. 4).

In conclusion, a catalytic system based on a dinuclear copper(II) complex **3** has been developed that is able to oxidize primary benzylic alcohols catalytically at ambient temperature. Base and TEMPO are required as co-catalysts, water and oxygen are in addition necessary for the catalytic reaction. Our current efforts are directed toward the detailed investigation of the aerobic oxidation of unactivated aliphatic alcohols, including monosaccharides, in purely aqueous alkaline solution, utilizing the introduced system of dinuclear copper(II) complex **3** and TEMPO.

3. Experimental

3.1. General

All chemicals were purchased from Sigma–Aldrich and used without further purification. Nanopure water (18 MΩ) was used for all kinetic experiments described. The dinuclear copper complex **3** was prepared as described previously.[20,21]

3.2. Typical procedure for alcohol oxidation

Round bottom flasks (50 mL) were charged with the dinuclear copper(II) complex **3** (30 mg, 4.57 mmol) dissolved in 9 mL of alkaline aqueous acetonitrile each (CH_3CN/H_2O=2/1). The solutions turned from dark blue to yellow-green after vigorous stirring at ambient temperature for 45 min. Subsequently, 200 μL aliquots of a TEMPO stock solution in acetonitrile were added to adjust the total TEMPO concentration in the final reaction mixtures to 18 mM. The solutions were stirred for another 30 min to allow formation of the catalytically active species. Darkening of the yellow-green solutions to dark green is observed. Varying amounts of benzyl alcohol are then added to each flask via syringe, and the total volume of each solution is adjusted with the solvent mixture to a final volume of 10 mL yielding final substrate concentrations in the range from 50 to 450 mM. Sample aliquots (20 μL) of the reaction mixture were taken in 60 s intervals, diluted with 10 μL of a 1 M aqueous Na_2S solution and 100 μL acetonitrile, centrifuged to remove precipitated CuS and filtered. The supernatant was subjected to GC analysis. The same procedure was followed for the oxidation in water, except that alkaline water was used and benzyl alcohol was added as aliquots from a CH_3CN stock solution, so that the final amount of acetonitrile in water remained at 8% for all flasks.

3.3. Typical procedure for GC analysis

All oxidation experiments were monitored on a A14 gas chromatograph (Shimadzu) with AOC-20 autoinjector and flame ionization detector. Helium was used as carrier gas, a Rtx-1 capillary column (30 m×0.25 mm×0.25 μm) was used as stationary phase. Sample aliquots were treated prior to analysis as described above. GC analysis for all experiments was performed isocratic at 100 °C, 0.25 μL injection (1/100 split) at 200 °C and flame ionization detection at 220 °C. The retention of benzyl alcohol (**1**) allows baseline separation from benzaldehyde (**2**) under these conditions (R_f (**1**)=3.9 min; R_f (**2**)=3.0 min).

Acknowledgements

Partial support of this work by a grant in the Competitive Research Program, Auburn University, is gratefully acknowledged.

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