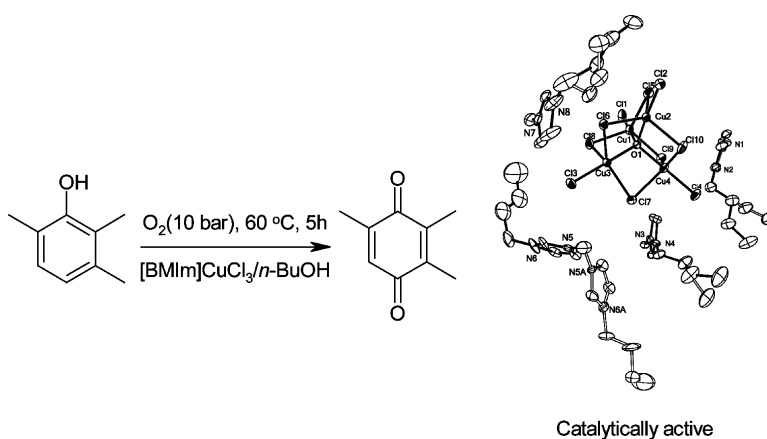


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Aerobic Oxidation of 2,3,6-Trimethylphenol to Trimethyl-1,4-benzoquinone with Copper(II) Chloride as Catalyst in Ionic Liquid and Structure of the Active Species

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In the industrial production of vitamin E, trimethyl-1,4-benzoquinone (TMQ) is a key intermediate. The current method for its production is para-sulfonation of 2,3,6-trimethylphenol (TMP) followed by oxidation of MnO₂. One-step oxidation of TMP to TMQ has been investigated using different oxidizing agents such as hydrogen peroxide,¹ and peroxy acids.² In this process, several catalysts such as iron complex³ and cobalt complex⁴ were attempted to increase the selectivity and yield and to decrease the amount of byproducts. Molecular oxygen as oxidant would be the most important method because it is environmentally friendly.

In a patent, the oxidation of alkyl-substituted phenols with a stoichiometric amount of copper(II) salt was carried out in an oxygen atmosphere (30 bar) in dimethylformamide.⁵ The corresponding *p*-benzoquinone was the major product. The oxidation of TMP afforded TMQ in acetone/water in yield of 80–87% at full conversion. BASF AG further developed this process over a catalyst containing copper(II) halide and in an alcohol/water two-phase medium.⁶ The yield of TMQ reached 98.5%. Abe's group proposed copper(II) as catalyst and lithium chloride as cocatalyst for the oxidation. In hexanol/water two-phase medium a yield of 97% at full conversion was obtained.⁷ A serious drawback of these methods is that almost or even more than a stoichiometric amount of catalyst is required for a complete and selective oxidation of TMP.

A great development of this catalytic oxidation was made by Takehira.⁸ He reduced the amount of catalyst to 10 mol % by applying nitrogen-containing organic compounds as cocatalysts. With the best cocatalyst, hydroxylamine hydrochloride, the yield of 92% was attained. But during the oxidation the cocatalyst, hydroxylamine hydrochloride was partly consumed. With 1 mol of hydroxylamine hydrochloride, about 20 mol of TMQ was produced. Baiker and co-workers made a progress in this direction.⁹ TMQ was obtained in up to 80% yield using only 1.5 wt % CuCl₂ catalyst under ambient conditions. Takaki succeeded in an efficient oxidation of TMP with polymer-supported copper catalysts.¹⁰ But it took a long time to complete the reaction. Xiao's group studied catalytic hydroxylation of TMP with hydrogen peroxide over copper hydroxyphosphate.¹¹ The selectivity for trimethylhydroquinone was reached when the reaction was carried out under N₂.

Since the first application of ionic liquid as a reaction medium,¹² there have been some reports about application of ionic liquids in the catalytic process.¹³ Song's work proved that oxidation can advantageously be realized in ionic liquid.¹⁴ The epoxidation of 2,2-dimethylchromen could clearly be accelerated with the addition of ionic liquid. Recently, Gree developed an aerobic oxidation of alcohols to the corresponding aldehydes and ketones in ionic liquid.¹⁵ However, the oxidation of phenols to quinones in ionic liquid is not known.

Table 1. Influence of the Amount of [BMIm]CuCl₂ on the Selectivity of TMQ

| entry ^a | 1 | 2 | 3 | 4 | 5 |
|--------------------------------|-----|----|----|----|-----|
| [BMIm]CuCl ₂ /mol % | 2.5 | 5 | 10 | 20 | 100 |
| selectivity ^b | 86 | 89 | 94 | 96 | 98 |

^a 2 mmol TMP, 2 mL of *n*-BuOH, 10 Bar O₂, 60 °C, 5 h. ^b Conversion is 100% in all of the experiments.

Table 2. Influence of the Proportion of CuCl₂ to [BMIm]Cl on the Selectivity of TMQ

| entry ^a | 1 | 2 | 3 | 4 | 5 | 6 |
|-----------------------------|-------|-----|-----|-----|-----|------|
| CuCl ₂ /[BMIm]Cl | 1:0.5 | 1:1 | 1:2 | 1:4 | 1:8 | 1:20 |
| selectivity ^b | 71 | 94 | 84 | 80 | 74 | 55 |

^a 2 mmol TMP, 2 mL of *n*-BuOH, 10 Bar O₂, 60 °C, 5 h. ^b Conversion 100% for entry 1–5; 90% for entry 6.

We herein describe a “green chemistry approach” with respect to the highly selective and environmentally friendly oxidation of TMP to TMQ with molecular oxygen as oxidant and a copper(II) chloride as catalyst in the ionic liquid medium of 1-butyl-3-methylimidazolium chloride ([BMIm]Cl). *n*-Butanol as cosolvent has a positive effect on the selectivity and activity. We found that the amount of copper(II) chloride catalyst can be substantially reduced in ionic liquid without a large decrease in the yield and selectivity. With the amount of copper(II) chloride in 2.5 mol %, a yield of 86% TMQ could still be attained.

The first results (Table 1) show that with a stoichiometric amount of copper(II) chloride a yield of 98% could be reached. With the decrease of the amount of copper(II) chloride dihydrate the yield gradually declines. When 2.5 mol % copper(II) chloride dihydrate was used in the experiment, a yield of 86% could still be reached. If the used amount of copper(II) chloride is constant at 10 mol % and we only change the amount of [BMIm]Cl, it can be found that the largest yield could be attained in the proportion (1:1) of copper(II) chloride dihydrate to [BMIm]Cl (Table 2). If we increase the amount of the ionic liquid, we get the lower yield and selectivity. In the proportion of 1:20 a selectivity of 55% could only be reached. In almost all of the experiments the conversion is 100%. Besides TMQ the other product is 2,2',3,3',5,5'-hexamethyl-4,4'-dihydroxybiphenyl. TMP is soluble in the ionic liquid in all of the experiments.

Red cubic crystals were obtained from the catalytic solution. X-ray structure shows that it is a 1-*n*-butyl-3-methylimidazolium oxotetracuprate (Figure 1). Four copper(II) ions form a tetrahedron core in the cluster compound and have an oxygen atom center. Moreover, there are six bridging Cl atoms and four end Cl atoms. Four disordered 1-*n*-butyl-3-methylimidazolium cations complete the asymmetric unit of the crystal structure as counterions of the tetrahedron. The similar structures were found in the literature.¹⁶ But this is the first time to isolate the catalytically active species

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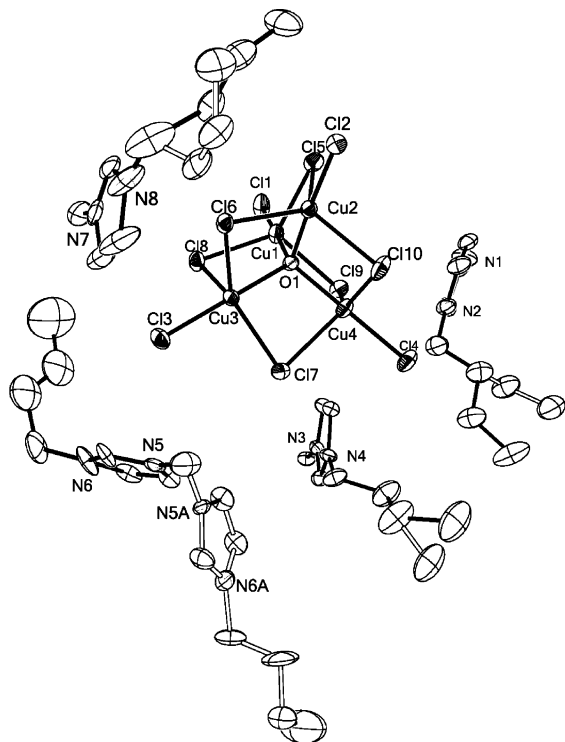
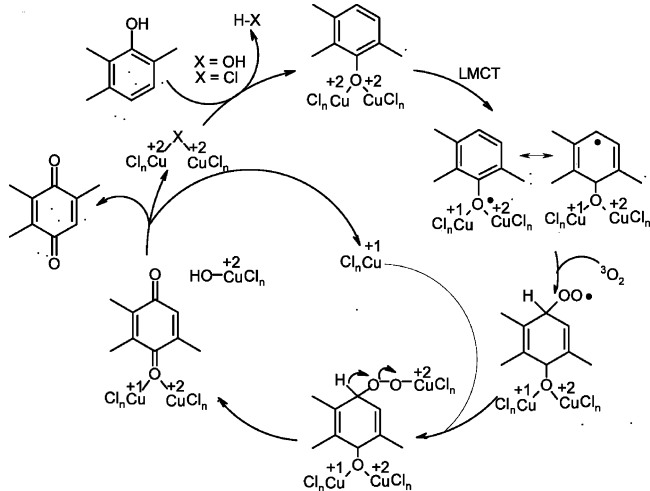


Figure 1. ORTEP view. Selected bond lengths [Å] and angles [deg]: Cu1–O1 1.919(6), Cu2–O1 1.917(6), Cu3–O1 1.937(6), Cu4–O1 1.913(6); Cu4–O1–Cu2 109.0(3), Cu4–O1–Cu1 111.7(3), Cu2–O1–Cu1 107.7(3), Cu4–O1–Cu3 110.4(3), Cu2–O1–Cu3 109.8(3), Cu1–O1–Cu3 108.2(3).

Scheme 1. Proposed Mechanism of the Aerobic Oxidation



from the original catalytic solution in the oxidation of phenol to quinone. We found that this oxotetracuprate has comparable catalytic activity to the original catalytic system.

In the proposed mechanism (Scheme 1), the $[\text{Cu}_4(\mu^4\text{-O})\text{Cl}_{10}]^{4-}$ as an active species plays a key role. At first the bridging Cl atom is substituted by phenol. Then, through spin delocalization a copper-bound phenolate radical ion is formed. After the attack by triplet oxygen at the para position, the peroxy radical is obtained. In the next step through the attack of Cu(I) species on the peroxy function group and the proton-mediated elimination the copper cluster can again be regenerated as an active electron acceptor. We consider that *n*-butanol as cosolvent is of benefit to the formation of the oxo-bridge.

In conclusion, the oxidation of TMP to TMQ with 2.5 mol % copper(II) chloride catalyst in ionic liquid [BMIm]Cl with *n*-butanol

as cosolvent affording 86% yield provides a new alternative to the copper(II) chloride-catalyzed aerobic oxidation. The advantage in this catalytic system is that only a catalytic amount of copper(II) chloride is necessary. A oxotetracuprate $[\text{Cu}_4(\mu^4\text{-O})\text{Cl}_{10}]^{4-}$ was isolated as an active species. We are currently investigating the scope of this system and the influence of some other reaction conditions on the selectivity and yield. The preliminary tests verified this catalytic system is also applicable for oxidation of 2-methylnaphthol. We also want to test the other ionic liquids as oxidation reaction medium.

In a typical procedure, a 60-mL thick glass autoclave was charged with the catalyst solution of copper(II) chloride in mixed medium of [BMIm]Cl and *n*-butanol. The autoclave was pressurized with oxygen (10 bar) and heated to 60 °C. After 5 h, the autoclave was cooled to the ambient temperature and depressurized. The conversions and yields were determined by GC using an AHRGC-5300 Capillary GC with column DB-5 without removal of the ionic liquid/Cu complex from the catalytic solution.

To isolate the oxotetracuprate, a mixture of TMP (2 mmol), $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.2 mmol), and 1-butyl-3-methylimidazolium chloride (0.2 mmol) in 2 mL of 1-butanol was stirred at 60 °C under 10 bar of O_2 for 5 h. The reaction solution was left to stand at room temperature for several days. Red cubic crystals were formed and separated by decantation and were washed with pentane. Yield: 51%. Elemental analysis (%) Calcd for $\text{C}_{32}\text{H}_{60}\text{Cl}_{10}\text{Cu}_4\text{N}_8\text{O}$: C, 25.53; H, 4.02; N, 7.44; Cl, 25.33; Cu, 37.68. Found: C, 25.95; H, 4.26; N, 7.34; Cl, 25.23; Cu, 37.28. Decomposition temperature 116 °C.

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Supporting Information Available: Crystallographic data collection and refinement parameters, position and thermal parameters, and bond distances and angles for the oxotetracuprate (CIF, PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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