Aerobic oxidation of phenol to quinone with copper chloride as catalyst in ionic liquid

Hongjian Sun [a,*], Xiaoyan Li [a], Jörg Sundermeyer [b]

[a] *School of Chemistry and Chemical Engineering, Shandong University, Shanda Nanlu 27, 250100 Jinan, PR China*
[b] *Fachbereich Chemie der Philipps, Universität Marburg, Hans-Meerwein-Strasse, 35032 Marburg, Germany*

Abstract

Aerobic oxidation of 2,3,6-trimethyl-phenol to trimethyl-1,4-benzoquinone with 2.5 mol% copper(II) chloride as catalyst in ionic liquid 1-*n*-butyl-3-methyl-imidazolium chloride, [BMIm]Cl, with *n*-butanol as co-solvent affording 86% yield provides a new alternative to the copper(II) chloride catalysed aerobic oxidation. The advantage of this catalytic system is that only a catalytic amount of copper(II) chloride is necessary. This catalytic system is also applicable for oxidation of 2-methyl-1-naphthol to 2-methyl-1,4-naphthoquinone. This catalytic reaction was systematically investigated under different conditions.
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1. Introduction

Recently we have reported that copper(II) chloride as catalyst revealed a high activity and selectivity in the oxidation of 2,3,6-trimethyl-phenol (TMP) to trimethyl-1,4-benzoquinone (TMQ) with dioxygen as oxidant in ionic liquid [1]. The active species in this catalysis was firstly isolated and structurally characterized. A mechanism was also proposed according to the active species. As we know, TMQ is one of the important intermediates in the production of Vitamin E. So far TMQ is generally produced from multi-step oxidation of 2,3,6-trimethyl-phenol [2,3]. Traditional procedure is sulfonation, oxidation and reduction. The sulfonation of TMP with sulfuric acid produces 4-hydroxyltrimethylbenzenesulfonic acid, which is oxidized by inorganic metal oxidants, such as manganese dioxide to afford us TMQ. In general this traditional method brings a great deal of solid and liquid wastes because of the use of sulfuric acid and stoichiometric solid oxidants. Several catalytic

systems using hydrogen peroxide as clean oxidant have been developed, such as heteropoly acids [4,5] and ruthenium salts [6].

New catalysts for aerobic oxidation of TMP have always been sought because the procedure with dioxygen as oxidant is environmentally friendly. Dioxygen can be catalytically activated by metal complexes [7]. We have known that the oxidation of TMP to TMQ can be catalysed by copper(II) chloride with applying co-catalyst, such as lithium chloride, magnesium chloride, hydroxyamine hydrochloride [8–13]. But all of the studies have one or two disadvantages. In some of the reports almost or even over stoichiometric amount of catalyst is used for a complete and selective transformation from TMP to TMQ. In other cases the co-catalysts, such as hydroxyamine hydrochloride, are partly consumed during the oxidation. Therefore, improvement of the copper(II) catalyst system has been long expected.

We herein describe a novel and greatly improved synthesis of TMQ attained by oxidation of TMP with copper salt catalyst. The oxidation of TMP was carried out with a catalytic amount of copper(II) salt as catalyst under relatively low pressure of oxygen in ionic liquid with alcoholic solvents.

* Corresponding author. Tel.: +86 531 88361350; fax: +86 531 88564464.
E-mail address: hjsun@sdu.edu.cn (H. Sun).

In this paper we shall report more and complete experimental results about the oxidation of TMP to TMQ under different conditions.

2. Experimental

2.1. Materials

2,3,6-Trimethyl-phenol was donated by BASF AG. 2-Methyl-1-naphthol, *n*-butanol, copper salts were reagent grade from Aldrich or Fluka. 1-*n*-Butyl-3-methyl-imidazolium chloride and other ionic liquids were prepared according to literature method [14].

2.2. General procedure

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 pressurised with oxygen (10 bar) and heated to 60 °C. After 5 h the autoclave was cooled to the ambient temperature and depressurised. The conversions and yields were determined by GC using an AHRGC-5300 Capillary GC with column DB-5 without isolation. 1-Brom-2-nitro-benzene was applied as an inner standard for quantitative analysis. Temperature programs were used.

3. Results and discussion

The first results (Table 1) show that with stoichiometric amount of ionic liquid, [BMIm]CuCl$_3$, a selectivity of 98% (also yield 98%) could be reached. With the decrease of the amount of [BMIm]CuCl$_3$ the selectivity gradually declines. When 2.5 mol% [BMIm]CuCl$_3$ copper(II) chloride was used in the experiment, a yield of 86% could still be reached. Instead of 1-*n*-butyl-3-methyl-imidazolium chloride, 1,3-didecyl-imidazolium chloride was used in the oxidation of TMP to TMQ. Under the same conditions the catalytic activity of system CuCl$_2$/1,3-didecyl-imidazolium

Table 1
Influence of the amount of catalyst on the selectivity of TMQ

Entry[a]	Catalyst (mol%)	Selectivity[b] (%)
1[c]	2.5	86
2[c]	5.0	89
3[c]	10	94
4[c]	20	96
5[c]	100	98
6[d]	2.5	87
7[d]	5.0	90
8[d]	10	93

[a] 2 mmol TMP, 2 ml *n*-BuOH, 10 bar O$_2$, 60 °C, 5 h.
[b] Conversion is 100% in all of the experiments.
[c] [BMIm]CuCl$_3$.
[d] [1,3-Didecyl-Im]CuCl$_3$.

Table 2
Influence of cations on the selectivity of TMQ

Entry[a]	Cation	Selectivity[b] (%)
1	[1-H-3-Me-Im]$^+$	82
2	[1-^{n}Bu-3-Me-Im]$^+$	94
3	[1,3-didecyl-Im]$^+$	93
4	[1-H-3-Me-Py]$^+$	84
5	[1-^{n}Bu-3-Me-Py]$^+$	84
6	[1-H-4-^{i}Nonyl-Py]$^+$	92
7	[1-^{n}Bu-4-^{i}Nonyl-Py]$^+$	84

[a] 2 mmol TMP, 2 ml *n*-BuOH, 10 bar O$_2$, 60 °C, 5 h, CuCl$_2$ 10 mol%, CuCl$_2$:[cation]Cl = 1:1.
[b] Conversion is 100% in all of the experiments.

chloride is very close to that of system CuCl$_2$/1-*n*-butyl-3-methyl-imidazolium chloride. In all of the experiments the conversion is 100%.

Table 2 shows the results obtained with copper(II) chloride as catalyst and with different cations in ionic liquids. We found that better selectivity of TMQ could be reached with 1-*n*-butyl-3-methyl-imidazolium chloride or with 1,3-didecyl-imidazolium chloride than with 3-methyl-imidazolium chloride (entries 1–3). The types of substituted alkyl group on the imidazole ring do not play an important role for the catalytic activity (entries 2 and 3). With 4-*i*-nonyl-pyridinium chloride the selectivity (92%) of TMQ is much better than that (84%) with 1-*n*-butyl-4-*i*-nonyl-pyridinium chloride (entries 6 and 7). There is no difference of the selectivity of TMQ for 3-methyl-pyridinium chloride and 1-*n*-butyl-3-methyl-pyridinium chloride (entries 4 and 5). Therefore, 1,3-dialkyl imidazolium chloride is more active than 3-alkyl-imidazolium chloride. It seems that there is no obvious difference of the selectivity of TMQ with 3-alkyl-pyridinium chloride and with 1,3-dialkyl-pyridinium chloride. But with 4-alkyl-pyridinium chloride higher selectivity (92%) can be obtained than that (84%) with 1,4-dialkyl-pyridinium chloride. The explanation to these results needs to be further explored.

In Table 3 the results of oxidation of TMP to TMQ using different copper salts as catalysts are listed. Copper(II) chloride dihydrate (entry 1) is the best catalyst among the seven copper salts. No great difference of the activities was observed between copper(II) chloride dihydrate and anhydrous copper(II) chloride (entries 1 and 2). The activities of

Table 3
Different copper salts as catalysts for oxidation of TMP

Entry[a]	Copper salt	Selectivity[b] (%)
1	CuCl$_2$·2H$_2$O	94
2	CuCl$_2$	92
3	CuBr$_2$	84
4	Cu(NO$_3$)$_2$·3H$_2$O	69
5	CuCl	51
6	Cu(SO$_4$)$_2$·5H$_2$O	47
7	Cu(OAc)$_2$·H$_2$O	26

[a] 2 mmol TMP, 2 ml *n*-BuOH, 10 bar O$_2$, 60 °C, 5 h, copper salt 10 mol%, [1-H-3-Me-Im]Cl 10 mol%.
[b] Conversion is 100% in all of the experiments.

Table 4
TMP oxidation with copper chloride and *N*-heteroaromatic compound

Entry[a]	*N*-heteroaromatic compound	Selectivity[b] (%)
1[c]	1-Me-Im (1:1)	86
2[c]	1-Me-Im (1:3)	6
3[d]	1-Me-Im (1:1)	84
4[d]	1-Me-Im (1:3)	6
5[e]	4-(diMe)N-Py (1:1)	71
6[e]	4-(diMe)N-Py (1:3)	0

[a] 2 mmol TMP, 2 ml *n*-BuOH, 10 bar O_2, 60 °C, 5 h, $CuCl_2$ 10 mol%.
[b] Conversion is 100% in all of the experiments.
[c] Entry 1 with 10 mol% 1-methyl-imidazole; entry 2 with 30 mol% 1-methyl-imidazole.
[d] Entry 3 with 10 mol% 1-methyl-imidazole and 10 mol% 2,4,6-triphenylphenoxy-dimer; entry 4 with 30 mol% 1-methyl-imidazole and 10 mol% 2,4,6-triphenylphenoxy-dimer.
[e] Entry 5 with 10 mol% 4-(dimethylamino)pyridine; entry 6 with 30 mol% 4-(dimethylamino)pyridine.

both copper(II) chlorides are much better than that of copper(II) bromide and also copper(I) chloride (entries 1–3 and 5). The worst catalyst among them is copper(II) acetate monohydrate. We consider that Cl^- ion is better bridging ligand and plays an important role in the catalytic oxidation. In the proposed mechanism the formation of Cl^- ion bridged intermediate is a decisive step for release of TMQ [1].

Instead of ionic liquids, imidazolium chloride and pyridinium chloride, *N*-heteroaromatic compounds were directly used in the catalytic system (Table 4). With utilization of 1-methyl-imidazole or 4-(dimethylamino)-pyridine in the proportion to copper chloride 1:1, the moderate selectivity can be reached (entries 1 and 5). With the proportion 1:3 very poor results were obtained (entries 2 and 6). In the case of the proportion of 1:3 (copper chloride to 4-(dimethylamino)pyridine) no transformation from TMP to TMQ could be detected (entry 6, selectivity is 0%). These results show that the catalytic activity of copper(II) chloride can be completely inhibited in the case of full coordination of copper atom with strong donor N-heteroaromatic compound as ligand. Because of the radical mechanism [1] 2,4,6-triphenylphenoxyl-dimer was added as radical source to support the catalytic reaction, but it was not effective (entry 3 and 4).

It was found that the best catalytic results could be obtained when the reaction was carried out for 5 h (Table 5). If the reaction time is less or more than 5 h, the selectivity will decrease. When the catalytic reaction was carried out at 22 °C without changing of the other reaction conditions, the

Table 5
Influence of the reaction time on the selectivity of TMQ

Entry[a]	Reaction time (h)	Selectivity[b] (%)
1	1	81
2	3	84
3	5	94
4	7	68

[a] 2 mmol TMP, 2 ml *n*-BuOH, 10 bar O_2, 60 °C, 5 h, $CuCl_2$ 10 mol%.
[b] Conversion is 100% in all of the experiments.

Table 6
Influence of temperature and O_2 pressure on the selectivity of TMQ

Entry[a]	Temperature (°C)	O_2 pressure (bar)	Selectivity[b] (%)
1	60	1	88
2	60	10	94
3	22	10	90

[a] 2 mmol TMP, 2 ml *n*-BuOH, 10 bar O_2, 60 °C, 5 h, [1-*n*Bu-3-Me-Im]$CuCl_3$ 10 mol%.
[b] Conversion is 100% in all of the experiments.

Table 7
Influence of the Amount of *n*-BuOH on the Selectivity of TMQ

Entry[a]	*n*-BuOH (mol%)	Selectivity[b] (%)
1	0	88
2	5	94
3	50	97
4	100	98

[a] 2 mmol TMP, 10 bar O_2, 60 °C, 5 h, [1-*n*Bu-3-Me-Im]$CuCl_3$ 100 mol%.
[b] Conversion is 100% in all of the experiments.

selectivity is lower than that at 60 °C (Table 6). When the catalytic reaction was carried out under 1 bar at 60 °C, the selectivity is lower than that under 10 bar. It was proposed that dimers of TMP and TMQ are intermediates during the oxidation of TMP to TMQ [4,12]. We consider that the higher temperature (60 °C) is favourable to decomposition of these dimers and formation of TMQ as viewed from thermodynamics.

The best result could be obtained if the catalytic reaction was carried out with 100 mol% *n*-butanol (Table 7, entry 4). This implies that *n*-butanol takes part in the mechanism. It seems that the OC_4H_9 group performs as a bridging functional group [1]. This conjecture should be further studied with experimental method. The selectivity was moderate without usage of *n*-butanol in the reaction (entry 1).

The catalytic activity of this system for oxidation of 2-methyl-1-naphthol, which is the precursor of 2-methyl-1,4-naphthoquinone (menadione, Vitamin K_3), was also tested. Menadione is also starting material for production of other Vitamin K compounds. Though the conversion in all of the experiments is 100%, the selectivity is remarkably much lower than that in the oxidation of TMP (Table 8). With 10 mol% catalyst the selectivity of 2-methyl-1,4-naphthoquinone was 35% at 22 °C (entry 2) and 45% at 60 °C (entry 3), respectively. Under the same conditions as in the oxidation of TMP only 47% selectivity of the naphtho-

Table 8
Oxidation of 2-methyl-1-naphthol to 2-methyl-1,4-naphthoquinone

Entry[a]	[BMIm]$CuCl_3$ (mol%)	Selectivity (%)	Conversion (%)
1	0	19	100
2[b]	10	35	99
3	10	45	93
4	100	47	100

[a] 1 mmol 2-Methyl-1-naphthol, 1 ml $CHCl_3$, 10 bar O_2, 60 °C, 5 h.
[b] 22 °C.

quinone could be reached even with 100 mol% catalyst. This result indicates that with the increment of catalyst amount from 10 to 100 mol% there is no marked raise in selectivity (from 45 to 47 mol%). Oxidation of 2-methyl-1-naphthol into 2-methyl-1,4-naphthoquinone is accompanied by oxidative oligomerization. In these processes dimmer and/or trimer of 2-methyl-1-naphthol were formed [15].

4. Conclusion

The oxidation of TMP to TMQ with 2.5 mol% copper(II) chloride catalyst in ionic liquid [BMIm]Cl with *n*-butanol as co-solvent affording 86% yield provides a new alternative to the copper(II) chloride catalysed aerobic oxidation. The advantage in this catalytic system is that only a catalytic amount of copper(II) chloride is necessary. The scope of this catalytic system and the influence of some other reaction conditions on the selectivity and yield are reported. It is also applicable for oxidation of 2-methyl-1-naphthol to 2-methyl-1,4-naphthoquinone.

Acknowledgment

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