Short Communication

Microwave-assisted and solvent-free peroxidative oxidation of 1-phenylethanol to acetophenone with a Cu[II]–TEMPO catalytic system

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ABSTRACT

The water-soluble copper(II) complex [Cu(H$_2$R)(HL)]·H$_2$O (**1**) was prepared by reaction of copper(II) nitrate hydrate with (*E*)-2-(((1-hydroxynaphthalen-2-yl)methylene)amino) benzenesulfonic acid (H$_2$L) and diethanolamine (H$_3$R). It was characterized by IR and ESI-MS spectroscopies, elemental and X-ray crystal structural analyses. **1** shows a high catalytic activity for the solvent-free microwave (MW) assisted oxidation of 1-phenylethanol with *tert*-butylhydroperoxide, leading, in the presence of TEMPO, to yields up to 85% (TON = 850) in a remarkably short reaction time (15 min, with the corresponding TOF value of 3.40×10^3 h^{-1}) under low power (25 W) MW irradiation.

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1. Introduction

The oxidation of primary and secondary alcohols to carbonyl compounds is one of the most important reactions in synthetic organic chemistry [1,2]. Although traditional oxidation reactions can be efficient and selective, they often involve the use of harmful oxidants, such as CrO$_3$ or KMnO$_4$, and/or halogenated solvents, that results in the generation of large amounts of waste. To eliminate the harmful wastes, the development of catalytic oxidation procedures which involve green oxidants, e.g. dioxygen or peroxides [H$_2$O$_2$, *tert*-butylhydroperoxide (TBHP)], is a matter of current interest [2,3]. Moreover, it is known that microwave irradiation (MW) can provide a much more efficient synthetic method than conventional heating, so that similar yields can be obtained in a shorter time and/or the selectivity can be improved [3–6].

Another advantage is obtained via the promotion of the use of environmentally benign solvents and catalysts. Thus, the synthesis of water-soluble catalysts with pH-tunable sites is of interest for novel green catalytic processes and recycling systems [7]. The sulfo group is a good candidate to be introduced into the catalyst to fulfil these goals [8,9]. On the other hand, Schiff bases and amines are relatively cheap and environmentally tolerable ligands, which are available commercially or through simple synthetic procedures [10–12]. For example, Schiff base complexes with *O,N,O*-donor sites have drawn much attention due to their interesting catalytic properties [10], while many copper compounds are inexpensive but effective catalysts for a number of oxidation reactions, in particular aerobic or peroxidative (with *tert*-butylhydroperoxide) oxidation of 1-phenylethanol into acetophenone (Scheme 1) [3,6,13,14].

From another perspective, the TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl) radical is an efficient mediator for the *aerobic* oxidation of alcohols [15–17], and hence it would be interesting to check its cooperative action with a copper(II) Schiff base complex towards the *peroxidative* oxidation of 1-phenylethanol to acetophenone. The choice of those model reactions was justified by their importance in organic synthesis used by the chemical industry [18].

Hence, taking in mind all the above considerations, in this contribution we describe the synthesis of a new copper(II) complex with Schiff base and diethanolamine ligands and evaluate its activity in the

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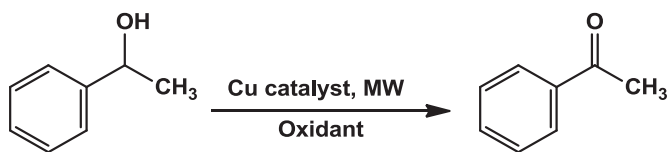
Scheme 1. MW-assisted oxidation of 1-phenylethanol to acetophenone.

production of acetophenone by MW-assisted and TEMPO-mediated solvent-free peroxidative oxidation of 1-phenylethanol.

2. Experimental

2.1. General procedure for the peroxidative oxidation of 1-phenylethanol

In a typical experiment, 1-phenylethanol (5.00 mmol), TBHP (70% aqueous solution, 10.0 mmol) and catalyst precursor **1** (5 μmol, 0.1 mol% vs. substrate) were introduced to a cylindrical Pyrex tube, which was then placed in the focused microwave reactor. The system was stirred and irradiated (25 W) for 15 min at 80 °C. After the reaction, the mixture was allowed to cool down to room temperature. 300 μL of benzaldehyde (internal standard) and 5 mL of NCMe (to extract the substrate and the organic products from the reaction mixture) were added. The obtained mixture was stirred for 10 min and then a sample (1 μL) was taken from the organic phase and analysed by GC (or GC–MS) using the internal standard method. Blank tests indicate that only traces (<0.5%) of acetophenone are generated in a Cu-free system.

3. Results and discussion

3.1. Synthesis and characterization of H_2L and **1**

The new Schiff base (E)-2-(((1-hydroxynaphthalen-2-yl)methylene) amino)benzenesulfonic acid (H_2L) was prepared by reaction of 2-aminobenzenesulfonic acid with 1-hydroxy-2-naphthaldehyde in methanol (see Electronic Supplementary Information). Greenish-black crystals of complex $[Cu(H_2R)(HL)]\cdot H_2O$ (**1**, Fig. 1) were obtained after reaction of $Cu(NO_3)_2\cdot 2.5H_2O$ with H_2L in the presence of diethanolamine (H_3R) in methanol. In the ^1H-NMR spectrum of H_2L in DMSO-d_6, CH=N and OH are observed at 9.82 and 12.00 ppm, respectively. The bands at 1627 cm^{-1} and 1285, 1202, and 1085 cm^{-1} in its IR spectrum are assigned to ν(C=N) and ν(SO$_3$), respectively. In the complex **1,** these bonds shift correspondingly to 1608 cm^{-1} and 1271, 1167, and 1071 cm^{-1}, what testifies the coordination of the N atom and the sulfonate group to the metal ion. In addition, the strong and

broad ν(OH) absorptions at 3665 and 3263 cm^{-1} are assigned to the crystallization water molecule. Elemental analysis and ESI-MS in methanol (peak at m/z 495.1 [M–H_2O + H]$^+$) support the proposed formulation of **1** as a monomer, which is shown by X-ray crystallography (see Electronic Supplementary Information).

3.2. Microwave-assisted catalytic peroxidative oxidation of 1-phenylethanol

Complex **1** was tested as a catalyst precursor for the oxidation of 1-phenylethanol to acetophenone using aqueous tert-butylhydroperoxide (Bu^{t}OOH, TBHP) as oxidizing agent, under typical conditions of 80 °C, low power (25 W) microwave irradiation (MW), 15 min reaction time and in a solvent-free medium (Scheme 1). The influence of various reaction parameters such as the amounts of catalyst precursor and oxidant, type of oxidant, time, temperature and presence of additives was investigated, and the results are summarized in Table 1 and Fig. 2.

Under typical solvent- and additive-free conditions (Table 1, entry 1), **1** exhibits a high catalytic activity, leading to the production of acetophenone in 66% yield and TON (moles of product per mol of catalyst precursor) of 6.59×10^2 in the short reaction time of 15 min, with the corresponding TOF (TON per hour) value of 2.63×10^3 h^{-1}. High selectivity towards the formation of ketone was found, and no traces of by-products were detected by GC and GC–MS analyses of the final reaction mixtures (only unreacted alcohol, apart from the ketone product).

In the present study, hydrogen peroxide (30% aqueous solution) is not such an efficient oxidant as TBHP, and 26% yield of acetophenone was achieved (entry 6, Table 1, Fig. 2). The lower yield in this case can be related to the decomposition of H_2O_2 under the used reaction conditions. On the other hand, while a 10-fold excess of the TBHP oxidant does not lead to a better conversion (entry 9, Table 1), a similar excess of hydrogen peroxide leads to a significant increase in yield as shown in Table 1 via a comparison of entries 7 and 8. Moreover, an equimolar amount of TBHP relative to substrate does not seem to be sufficient to achieve high yields (compare entries 1 and 19, Table 1) within 15 min reaction time.

The activity of **1** in the peroxidative (with tert-butylhydroperoxide) oxidation of 1-phenylethanol was also studied in the presence of 2,2,6,6-tetramethylpiperidyl-1-oxyl (TEMPO) [13–16]. The TEMPO additive provided the significant increase in yield of acetophenone (Fig. 2) from 66% to 85% under the same reaction conditions (entries 1 and 2, Table 1). A similar increase was observed when the reaction was carried out with hydrogen peroxide (instead of TBHP) in the presence of TEMPO (entries 6 and 7, Table 1 and Fig. 2).

To our knowledge, no MW-assisted TBHP (or H_2O_2)/TEMPO/Cu catalytic system has been previously reported, while several efficient aerobic TEMPO-mediated oxidations of primary and secondary alcohols
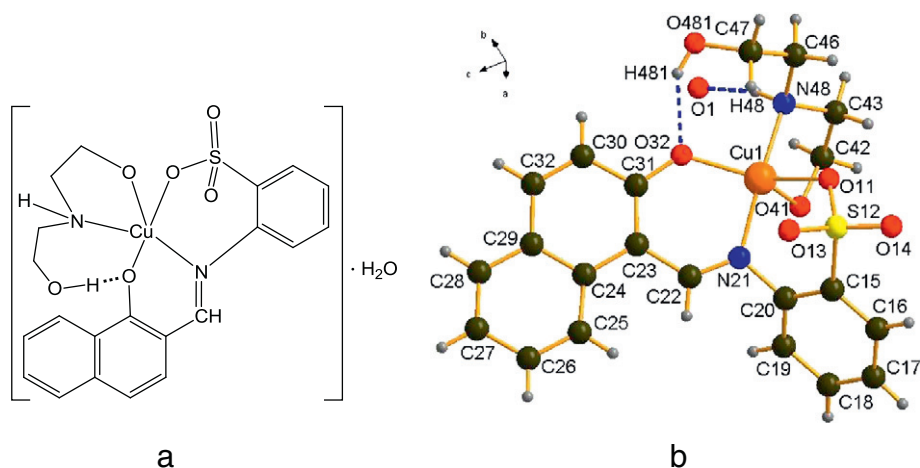

Fig 1. Schematic representation (a) and crystal structure (b) of **1**. Hydrogen bonds shown as dotted lines.

Table 1
MW-assisted solvent-free oxidation 1-phenylethanol using **1** as catalyst precursor.[a]

Entry	Catalyst amount (mol% vs. substrate)	Reaction time (h)	Additive (mol% vs. substrate)	Yield[b] (%)	TON [TOF (h^{-1})][c]
1	0.1	0.25	–	65.9	659 (2.63×10^3)
2	0.1	0.25	TEMPO (2.5)	85.0	850 (3.40×10^3)
3	–	0.25	TEMPO (2.5)	8.6	–
4	0.02	0.25	–	16.9	845 (3.38×10^3)
5	0.2	0.25	–	65.2	326 (1.30×10^3)
6[d]	0.1	0.25	–	26.2	262 (1.05×10^3)
7[d]	0.1	0.25	TEMPO (2.5)	40.6	406 (1.62×10^3)
8[e]	0.1	0.25	TEMPO (2.5)	53.8	538 (2.15×10^3)
9[f]	0.1	0.25	–	8.4	84 (336)
10	0.1	0.25	K$_2$CO$_3$ (2.5)	11.2	112 (448)
11	0.1	0.25	HNO$_3$ (2.5)	18.3	183 (732)
12	0.1	0.25	Ph$_2$NH (100)	4.8	48 (193)
13	0.1	0.25	CBrCl$_3$ (100)	5.1	51 (205)
14	0.1	0.12	TEMPO (2.5)	79.8	798 (6.65×10^3)
15	0.1	0.5	–	31.8	318 (636)
16	0.1	1	–	19.2	192 (192)
17[g]	0.1	0.25	TEMPO (2.5)	83.1	831 (3.32×10^3)
18[h]	0.1	0.25	TEMPO (2.5)	27.5	275 (1.10×10^3)
19[i]	0.1	0.25	–	21.7	217 (868)

[a] Reaction conditions unless stated otherwise: 5 mmol of 1-phenylethanol, 1–10 μmol (0.02–0.2 mol% vs. substrate) of **1**, 10 mmol of TBHP (2 eq., 70% in H$_2$O), 80 °C, MW irradiation (25 W power).

[b] Moles of ketone product per 100 mol of alcohol.

[c] Turnover number = number of moles of product per mol of catalyst precursor; TOF = TON per hour (values in brackets).

[d] 10 mmol of H$_2$O$_2$ (30% aqueous solution) instead of TBHP.

[e] 50 mmol of H$_2$O$_2$ instead of TBHP.
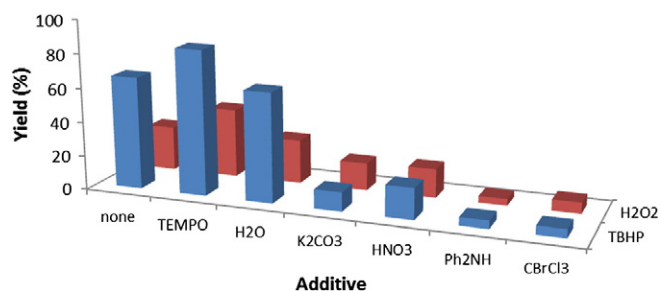
[f] 50 mmol of TBHP.

[g] T = 90 °C.

[h] T = 50 °C.

[i] 5 mmol of TBHP.

in the presence of copper(II) complexes have been reported [6,19]. Hence, this study demonstrates the viability of using the TEMPO additive for the MW-assisted peroxidative oxidations of alcohols.

The previously recognised promoting effect of basic additives [15,16,20–26] is not observed for the present catalytic system; in contrast, addition of 1 M solution of K$_2$CO$_3$ hampers the reaction (Table 1, entries 1 and 10). The presence of HNO$_3$ also exhibited an inhibitory effect on the acetophenone yield (Table 1, entries 1 and 11, Fig. 2), as found e.g., for the MW-assisted oxidation of 1-phenylethtanol with TBHP catalysed by Cu(II) complexes bearing the 1,6-bis(2′-pyriyl)-2,5-dithiahexane ligand [26,27]. In fact, the mechanism of alcohol oxidation with TBHP does not seem to require the presence of protons as verified [13,14] in the oxidation of 1-phenylethanol with TBHP catalysed by bi- or tetra-nuclear cage-like copper(II) silsesquioxanes.

Moreover, carrying out the reaction in water (2 mL) does not change markedly the yield of acetophenone (Fig. 2), either using H$_2$O$_2$ or TBHP as oxidant.

The effect of the amount of catalyst precursor **1** was also studied (entries 1, 4 and 5, Table 1). It was observed that its increase from 1 μmol (0.02 mol% vs. substrate) to 5 μmol (0.1 mol%) results in an

yield growth from 17% to 66%. However, if more than 10 μmol of the catalyst precursor is added, the yield remains almost unchanged, leading to the corresponding TON decrease (compare e.g. entries 4 and 5, Table 1). Blank tests in the absence of the catalyst precursor, performed under the typical reaction conditions, reveal no significant conversions (< 0.5%). It should be noted that TEMPO, by itself (i.e., in the absence of **1**), leads to a low but noticeable yield (entry 3, Table 1).

The relevance of the ligands on the catalytic activity of **1** is shown by testing also the catalytic performance of Cu(NO$_3$)$_2$ in the same oxidation experiment and comparing the result, under the same reaction conditions, with that obtained from **1**. The oxidation of 1-phenylethanol (5 mmol) at 80 °C and after 15 min, in the presence of the same molar amount of Cu(NO$_3$)$_2$, led to a much lower yield of acetophenone (14%) than that obtained with **1** (66%, entry 1, Table 1).

The reaction strongly depends on the temperature. Attempts to perform the oxidation of 1-phenylethanol in the presence of **1** at room temperature failed, whereas when the reaction was conducted at 50 °C, this resulted in a marked drop in the yield of acetophenone relative to that obtained at 80 °C (from 85% at 80 °C to 28% at 50 °C, entries 2 and 18, respectively, Table 1). A temperature above 80 °C does not lead to a higher ketone yield (entry 17, Table 1).

A noteworthy feature of the studied oxidations is that the MW-assisted reaction proceeds very fast even under low irradiation power (25 W). In fact, after 7 min the maximum yield has nearly reached (80%, Table 1, entry 14) with a remarkable TOF (6.65×10^3 h^{-1}) value. This contrasts with most of the known MW-assisted organic reactions [4,5,29,30], which require a much higher power (typically above 200 or even 500 W).

The peroxidative oxidation of 1-phenylethanol is believed to proceed mainly via a radical mechanism which involves both carbon- and oxygen-centred radicals [31–34]. In the example studied here a strong inhibition effect (Fig. 2) is observed when the reaction is carried out in the presence of either a carbon-radical trap CBrCl$_3$ (Table 1, entry 13) or an oxygen-radical trap Ph$_2$NH (Table 1, entry 12). Thus, we can suppose that the MW-assisted oxidation of 1-phenylethanol involves free-

Fig. 2. Influence of different additives (TEMPO, H$_2$O solvent, K$_2$CO$_3$, HNO$_3$, radical traps) on the yield of acetophenone from MW-assisted proxidative oxidation of 1-phenylethanol.

Table 2
MW-assisted solvent-free oxidation of selected secondary alcohols using **1** as catalyst precursor.[a]

Entry	Substrate	Product	Reaction time (h)	Yield[b] (%)	TON [TOF (h^{-1})][c]	Selectivity[d] (%)
1	Cyclohexanol	Cyclohexanone	0.25	28.1	281 (1.12×10^3)	77.2
2			3	65.6	656 (219)	89.0
3	2-Hexanol	2-Hexanone	0.25	21.3	213 (852)	53.3
4			3	59.9	599 (200)	66.4
5	3-Hexanol	3-Hexanone	0.25	18.4	184 (736)	61.7
6			3	41.8	418 (139)	49.5

[a] Reaction conditions unless stated otherwise: 5 mmol of substrate, 5 μmol (0.1 mol% vs. substrate) of **1**, 10 mmol of TBHP (2 eq., 70% in H$_2$O), 125 μmol of TEMPO, 80 °C, 15 min reaction time, MW irradiation (25 W power).
[b] Moles of ketone product per 100 mol of alcohol.
[c] Turnover number = number of moles of product per mol of catalyst precursor; TOF = TON per hour (values in brackets).
[d] Moles of ketone per mole of converted substrate.

radicals, e.g. *t*BuO• [9,13,21] produced in the Cu promoted decomposition of TBHP. It may proceed via the coordination of 1-phenylethanol to an active site of the catalyst, and its deprotonation to form the ethoxide ligand, followed by a metal-centred (and TEMPO assisted) dehydrogenation [15,24]. As a result, the formation of TEMPOH and of a subsequent alkoxy-Cu(II) complex is postulated. The latter reacts with another molecule of TEMPO, leading to the aldehyde and TEMPOH, with regeneration of the copper catalyst.

Other secondary alcohols (C$_6$, linear and cyclic) were also tested (Table 2) as substrates. The ketones are the only oxidation products obtained. As expected, aliphatic alcohols are less reactive than the benzylic 1-phenylethanol, leading, under the same reaction conditions, to moderate yields (Table 2), as reported in other cases [6,28]. To achieve considerably better conversions, an extended reaction time (3 h) is required.

Another important benefit of **1** concerns the fact that only low loadings (typically 0.1 mol% vs. substrate) are necessary to reach high yields of ketone (e.g. up to 85% for acetophenone) with substantial TON and TOF values (850 and 3.40×10^3 h^{-1}, respectively, Table 1, entry 2). Furthermore, **1**/TBHP (or H$_2$O$_2$)/MW is a solvent-free oxidation system, which is an obvious advantage over the many state-of-the-art oxidations of alcohols which involve organic solvents or costly ionic liquids [29,35].

4. Conclusions

In summary, a new copper(II) complex [Cu(H$_2$R)(HL)]·H$_2$O (**1**) was prepared by an easy and convenient synthesis and fully characterized. **1** acts as an effective catalyst precursor for the mild and selective peroxidative oxidation of 1-phenylethanol to acetophenone in a solvent-free MW-assisted process, thus widening the scope of peroxidative catalytic systems suitable for MW assisted oxidative transformations of alcohols. Moreover, the use of low power MW irradiation in a solvent-free process is a significant step towards the development of green and energy saving catalytic systems in that field.

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.catcom.2014.01.024.

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