Short Communication

Microwave-assisted and solvent-free peroxidative oxidation of 1-phenylethanol with a CuII–TEMPO catalytic system

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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 CrO3 or KMnO4 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 [H2O2, 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 sulfon group is a good candidate to be introduced into the catalyst to fulfill 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...
3.1 Synthesis and characterization of H2La and H2L

3. Results and discussion

3.1. Synthesis and characterization of H2L and 1

The new Schiff base (E)-2-(((1-hydroxynaphthalen-2-yl)methylene) amino)benzenesulfonic acid (H2L) 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(H2R)(HL)]H2O (1, Fig. 1) were obtained after reaction of Cu(NO3)2·2.5H2O with H2L in the presence of diethanolamine (H2R) in methanol. In the 1H-NMR spectrum of H2L, in DMSO-d6, 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(SO3), 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-H2O + 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’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 × 10² in the short reaction time of 15 min, with the corresponding TOF (TON per hour) value of 2.63 × 10³ 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 H2O2 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 increase was observed when the reaction mixture (only unreacted alcohol, apart from the ketone product).

To our knowledge, no MW-assisted TBHP (or H2O2)/TEMPO/Cu catalytic system has been previously reported, while several efficient aerobic TEMPO-mediated oxidations of primary and secondary alcohols...
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 K2CO3 hampers the reaction (Table 1, entries 10). The presence of HNO3 also exhibited an inhibitory effect on the acetophenone yield (Fig. 2), either using H2O2 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(NO3)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(NO3)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 its value (80%, Table 1, entry 14) with a remarkable TOF (6.65 × 103 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 CBrCl3 (Table 1, entry 13) or an oxygen-radical trap Ph2NH (Table 1, entry 12). Thus, we can suppose that the MW-assisted oxidation of 1-phenylethanol involves free-

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**Table 1**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst amount (mol% vs. substrate)</th>
<th>Reaction time (h)</th>
<th>Additive (mol% vs. substrate)</th>
<th>Yield (%)</th>
<th>TON (TOF) [h⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.1</td>
<td>0.25</td>
<td>–</td>
<td>65.9</td>
<td>659 (2.63 × 10⁴)</td>
</tr>
<tr>
<td>2</td>
<td>0.1</td>
<td>0.25</td>
<td>TEMPO (2.5)</td>
<td>85.0</td>
<td>850 (3.40 × 10⁴)</td>
</tr>
<tr>
<td>3</td>
<td>0.02</td>
<td>0.25</td>
<td>–</td>
<td>8.6</td>
<td>–</td>
</tr>
<tr>
<td>4</td>
<td>0.2</td>
<td>0.25</td>
<td>–</td>
<td>16.9</td>
<td>845 (3.38 × 10⁴)</td>
</tr>
<tr>
<td>5</td>
<td>0.1</td>
<td>0.25</td>
<td>TEMPO (2.5)</td>
<td>65.2</td>
<td>326 (1.30 × 10⁴)</td>
</tr>
<tr>
<td>6</td>
<td>0.1</td>
<td>0.25</td>
<td>–</td>
<td>26.2</td>
<td>262 (1.05 × 10⁴)</td>
</tr>
<tr>
<td>7</td>
<td>0.1</td>
<td>0.25</td>
<td>TEMPO (2.5)</td>
<td>40.6</td>
<td>406 (1.62 × 10⁴)</td>
</tr>
<tr>
<td>8</td>
<td>0.1</td>
<td>0.25</td>
<td>TEMPO (2.5)</td>
<td>53.8</td>
<td>538 (2.15 × 10⁴)</td>
</tr>
<tr>
<td>9</td>
<td>0.1</td>
<td>0.25</td>
<td>–</td>
<td>8.4</td>
<td>84 (836)</td>
</tr>
<tr>
<td>10</td>
<td>0.1</td>
<td>0.25</td>
<td>K2CO3 (2.5)</td>
<td>11.2</td>
<td>112 (448)</td>
</tr>
<tr>
<td>11</td>
<td>0.1</td>
<td>0.25</td>
<td>HNO3 (2.5)</td>
<td>18.3</td>
<td>183 (732)</td>
</tr>
<tr>
<td>12</td>
<td>0.1</td>
<td>0.25</td>
<td>Ph2NH (100)</td>
<td>4.8</td>
<td>48 (193)</td>
</tr>
<tr>
<td>13</td>
<td>0.1</td>
<td>0.12</td>
<td>CBrCl3 (100)</td>
<td>5.1</td>
<td>51 (205)</td>
</tr>
<tr>
<td>14</td>
<td>0.1</td>
<td>0.5</td>
<td>TEMPO (2.5)</td>
<td>79.8</td>
<td>798 (6.65 × 10³)</td>
</tr>
<tr>
<td>15</td>
<td>0.1</td>
<td>1</td>
<td>–</td>
<td>19.2</td>
<td>192 (192)</td>
</tr>
<tr>
<td>16</td>
<td>0.1</td>
<td>0.25</td>
<td>TEMPO (2.5)</td>
<td>83.1</td>
<td>831 (332 × 10³)</td>
</tr>
<tr>
<td>17</td>
<td>0.1</td>
<td>0.25</td>
<td>TEMPO (2.5)</td>
<td>27.5</td>
<td>275 (110 × 10³)</td>
</tr>
<tr>
<td>18</td>
<td>0.1</td>
<td>0.25</td>
<td>TEMPO (2.5)</td>
<td>21.7</td>
<td>217 (888)</td>
</tr>
</tbody>
</table>

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* 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 H2O), 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 H2O2 (30% aqueous solution) instead of TBHP.

e 50 mmol of H2O2 instead of TBHP.

f 50 mmol of TBHP.

g T = 90 °C.

h T = 50 °C.

i 5 mmol of TBHP.

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**Fig. 2.** Influence of different additives (TEMPO, H2O solvent, K2CO3, HNO3, radical traps) on the yield of acetophenone from MW-assisted peroxidative oxidation of 1-phenylethanol.
4. Conclusions

In summary, a new copper(II) complex [Cu(H2R)(HL)]H2O (1) was prepared by an easy and convenient synthesis and fully characterized. It acts as an effective catalyst precursor for the mild and selective peroxidative oxidation of 1-phenylethanol to acetoephone 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.

Acknowledgments

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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.

Table 2

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Product</th>
<th>Reaction time (h)</th>
<th>Yielda (%)</th>
<th>TON (TOF h−1)b</th>
<th>Selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cyclohexanol</td>
<td>Cyclohexanone</td>
<td>0.25</td>
<td>28.1</td>
<td>281 (1.12 × 104)</td>
<td>77.2</td>
</tr>
<tr>
<td>2</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>65.6</td>
<td>656 (219)</td>
<td>80.9</td>
</tr>
<tr>
<td>3</td>
<td>2-Hexanol</td>
<td>2-Hexanone</td>
<td>0.25</td>
<td>21.3</td>
<td>213 (852)</td>
<td>53.3</td>
</tr>
<tr>
<td>4</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>59.9</td>
<td>599 (200)</td>
<td>66.4</td>
</tr>
<tr>
<td>5</td>
<td>3-Hexanol</td>
<td>3-Hexanone</td>
<td>0.25</td>
<td>18.4</td>
<td>184 (736)</td>
<td>61.7</td>
</tr>
<tr>
<td>6</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>41.8</td>
<td>418 (139)</td>
<td>49.5</td>
</tr>
</tbody>
</table>

a Reaction conditions unless stated otherwise: 5 mmol of substrate, 5 μmol (0.1 mol% vs. substrate) of 1, 10 μmol of TBHP (2 eq., 70% in H2O2), 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 mol of converted substrate.

References