Oxidation of diphenylmethane catalyzed by complexes of the type \([\text{Cu}_2(\eta^2-\text{O}_2\text{CR})_4(4-\text{CNpy})_2]\)

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Three dicopper(II) tetracarboxylate complexes, viz. \([\text{Cu}_2(\eta^2-\text{O}_2\text{CC}_6\text{H}_5)_4(4-\text{CNpy})_2]\), \([\text{Cu}_2(\eta^2-\text{O}_2\text{CCH}_2\text{Cl})_4(4-\text{CNpy})_2]\) and \([\text{Cu}_2(\eta^2-\text{O}_2\text{CCH}_3)_4(4-\text{CNpy})_2]\), where 4-CNpy stands for 4-cyanopyridine, have been examined as catalysts in the oxidation of diphenylmethane using 70% aqueous TBHP as the terminal oxidant under solvent-free condition. 100% conversion of diphenylmethane is achieved in 8 h to obtain benzophenone at 100% selectivity with \([\text{Cu}_2(\eta^2-\text{O}_2\text{CCH}_2\text{Cl})_4(4-\text{CNpy})_2]\) as the catalyst.

Keywords: Dicopper(II) tetracarboxylates, catalytic oxidation, diphenylmethane oxidation, TBHP, copper-catalyzed oxidation.

Introduction

The aromatic ketone benzophenone is an important intermediate for drugs, pharmaceuticals, flavoring agents, agrochemicals, etc.1 It can be obtained from the selective oxidation of diphenylmethane (DPM). However, the catalytic oxidation of the aliphatic C-H bonds in this hydrocarbon compound is quite difficult because of their inert nature making DPM a challenging target.2 Earlier, the oxidation of the methylene group attached to the aromatic rings in DPM and related compounds was performed3 using stoichiometric quantities of oxidizing agents like KMnO₄ or K₂Cr₂O₇. Since the use of these stoichiometric reagents is expensive and, at the same time, lead to the release of heavy metal ions as part of industrial wastes, attention has been given in recent times to develop more efficient and environmentally friendly catalysts for this type of oxidation processes.4,5 It was demonstrated earlier that by making use of air (i.e. O₂) as the oxidant, it is possible to oxidize ethylbenzene to acetophenone using a supported catalyst based on a cobalt(III)-oxocubane cluster.6 For such purposes, the use of environmentally benign oxidizing agents like hydrogen peroxide (H₂O₂) and tert-butyldihydroperoxide (TBHP) which produce water and t-butanol as by-products is also viewed as preferable.7 In an earlier study published8 from this laboratory, a heterogeneous catalyst prepared by supporting a tetraneuclear cubane-like Co₁⁺O₀ cluster supported on porous silica was found to catalyze the 100% conversion of DPM with TBHP as the oxidant in acetonitrile (MeCN). However, in this case the turnover number (TON) was low and a small amount of benzhydrol was found to form as a co-product.

A CuII complex was earlier shown to act as a catalyst in the oxidation of DPM by 30% aq. H₂O₂ at 353 K in MeCN to afford benzophenone in 87% yield in 5 h.9 A molybdenum(VI) oxo-diperoxo complex was reported10 to catalyze the oxidation of DPM with H₂O₂ in MeCN at 353 K to yield a 3:2 mixture of diphenylmethanol and benzophenone in 12 h. When Co-doped mesoporous titania-silica was used to catalyze the oxidation of DPM in acetic acid using 30% aq. H₂O₂, benzophenone, 2-hydroxybenzophenone (2-HOBP), 2-benzylphenol, and diphenylmethanol were obtained as products.11

It is thus clear that although many catalytic systems have been studied for the oxidation of DPM, most of them suffer from various drawbacks. Some systems exhibited low to moderate catalytic activity under severe reaction conditions such as long reaction time or relatively high temperature. Moreover, in many of them the preparation of catalysts involved tedious procedures as well as high cost. In view of this, discovery of new and effective catalysts for these reactions constitutes an important goal. Herein we shall describe the effectiveness of dimeric tetracarboxylates of copper(II) as catalysts in the homogeneous oxidation of DPM using 70% aq. TBHP as the oxidant.
fied by the dinuclear structure of ‘copper(ii) acetate monohydrate’ reported first by Niekerk and Schoening in 1953 from ‘X-ray evidence’, and then redetermined by Brown and Chidambaram in 1973 by ‘neutron-diffraction analysis’, were studied extensively because of their antiferromagnetic behaviour. Complexes of this type have been described earlier as effective catalysts in the TBHP oxidation of alcohols. A few of these complexes including [Cu₂(µ-O₂CC₆H₅)₄(4-CNpy)]₂ have also been found to catalyze the selective epoxidation of styrene. Herein we describe the catalytic activity of three complexes of the type Cu₂(µ-O₂CR)₄L₂, viz. [Cu₂(µ-O₂CC₆H₅)₄(4-CNpy)]₂, [Cu₂(µ-O₂CCH₂Cl)₄(4-CNpy)]₂ and [Cu₂(µ-O₂CCH₃)₄(4-CNpy)]₂ in the oxidation of DPM.

Experimental

Materials and methods:

Copper(ii) chloride dihydrate (E. Merck, India), 4-cyanopyridine (Aldrich, USA), diphenylmethane (Aldrich, USA), benzophenone (Aldrich, USA), 70% aq. TBHP (Aldrich, USA), cyanopyridine (Aldrich, USA), diphenylmethane (Aldrich, USA), chloroacetic acid (E. Merck, India) were all used as received. Solvents used in the study were sourced from various Indian manufacturers and used without purification. Determination of copper in [Cu₂(µ-O₂CCH₂Cl)₄(4-CNpy)]₂ was done by iodometric titration method after preparing the test solution via acid digestion. The magnetic susceptibility measurement was carried out at 298 K on a Sherwood Mark 1 Magnetic Susceptibility Balance using Hg[Co(NCS)]₂ as the reference. The susceptibilities were corrected for diamagnetism using Pascal’s constants.

Solution phase UV-Visible spectra were recorded using a Shimadzu UV-1800 spectrophotometer. Infrared spectra were recorded using a Shimadzu IR Affinity spectrophotometer for KBr pellets. In order to follow the course of the catalytic reactions, a Varian-450 GC with FID fitted with a CP-Sil 8 CB capillary column was used. Species identification and quantification were achieved by making use of authentic samples.

Preparation of catalysts:

The catalytically active complexes [Cu₂(µ-O₂CC₆H₅)₄(4-CNpy)]₂ and [Cu₂(µ-O₂CCH₃)₄(4-CNpy)]₂ were prepared as reported earlier. To prepare [Cu₂(µ-O₂CCH₂Cl)₄(4-CNpy)]₂, 1 mmol cupric chloride dihydrate (0.17 g) was taken in 20 mL methanol. To this, 2 mmol sodium chloroacetate (0.232 g) was added and the mixture was stirred at room temperature for 10 min. To the green solution, 1 mmol 4-cyanopyridine (0.014 g) was added and stirring was continued for 2 h. The resulting greenish blue precipitate was filtered off, washed with cold methanol and dried in a vacuum desiccator over fused CaCl₂ Yield: 0.25 g (71%); %Cu = 17.81 (calcld.), 16.49 (obs.); μ_eff (BM) = 1.61; IR spectral data (KBr disc, cm⁻¹): 3424 (s, br), 3103 (sh), 2352 (m), 2240 (w), 1600 (s), 1420 (m), 1350 (sh), 1212 (m), 1060 (m), 829 (m), 560 (m).

Oxidation of DPM:

In a typical procedure, a required amount of the catalyst was added to a mixture of 0.84 g diphenylmethane (5 mmol) and 3 mL of 70% aqueous TBHP in a round-bottomed flask. The resultant mixture was magnetically stirred at 383 K for 8 h. The flask was maintained at the specified temperature using an electrically heated oil bath. All the reactions were performed under solvent free condition.

Results and discussion

Complexes of the type Cu₂(µ-O₂CR)₄L₂ constitute a broad class and various methods for their preparation have been developed by researchers. We have developed a more or less general method to prepare species belonging to this series, although slight modifications thereof may be necessary to ensure high yield of a given species. To prepare the complexes, as described above for [Cu₂(µ-O₂CCH₂Cl)₄(4-CNpy)]₂, a copper(ii) salt is added to a methanolic solution of the sodium salt of the appropriate carboxylic acid. The desired product is obtained as a precipitate at room temperature from the stirred solution in about 2 h after adding of 4-cyanopyridine by ensuring an 1:2:1 molar ratio of the reactants. The product yields are to the higher side of 70%.

Crystal structures of [Cu₂(µ-O₂CC₆H₅)₄(4-CNpy)]₂ and [Cu₂(µ-O₂CCH₃)₄(4-CNpy)]₂ have been determined by single crystal X-ray diffraction method to find that both of them have the familiar dinuclear structure that is often termed as the ‘paddle-wheel geometry’. The third species, [Cu₂(µ-O₂CCH₂Cl)₄(4-CNpy)]₂, shows an infrared spectrum (Fig. 1) in which bands due to both the ligands are observed. While the presence of the 4-CNpy ligands is evident from the appearance of a weak band at 2241 cm⁻¹, the mono-chloroacetato ligands display the ν_asym(CO₂) and ν_sym(CO₂)
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![Infrared spectrum of [Cu$_2$(μ-O$_2$CCH$_2$Cl)$_4$(4-CNpy)$_2$].](image1)

vibrations at 1616 and 1417 cm$^{-1}$ respectively. The separation (Δν) of 199 cm$^{-1}$ between these two vibrations is indicative of the presence of the carboxylato ligands in the bridging mode of coordination in the complex$^{18}$. Further, the μ$_{eff}$ value of 1.61 BM/Cu$^{2+}$ observed for the complex is lower than the expected spin-only magnetic moment of 1.73 BM, putatively on account of antiferromagnetic exchange coupling effects$^{13}$. In view of this, the species under discussion is also believed to be dinuclear as shown in Scheme 1. The complex [Cu$_2$(μ-O$_2$CCH$_2$Cl)$_4$(4-CNpy)$_2$] shows absorptions at 273, 459 and a broad absorption envelope having $\lambda_{max}$ ~779 nm in its MeCN phase UV-Visible spectrum (Fig. 2). The low energy band also displays a sharp absorption feature to the left at 653 nm. This feature is usually not seen in spectra shown by other species in the series$^{15}$. In the electronic spectra shown by complexes of the type [Cu$_2$(μ-O$_2$CR)$_4$L$_2$] three bands (i) in the 250–305 nm range, (ii) at ~385 nm and (iii) in the 670–704 nm range are found to occur. These absorptions are ascribed to the $\pi\rightarrow\pi^*$ transition of the axial pyridyl ligand, transitions involving MOs related to the dimeric structure of the complexes and the d-d transition for individual Cu$^{2+}$ centers of distorted square pyramidal geometry respectively$^{15}$. In the present instance, however, the halogenated R (CH$_2$Cl) group in [Cu$_2$(μ-O$_2$CR)$_4$L$_2$] is electronically quite different from the unsubstituted alkyl or aryl groups and thus the band expected near 385 nm, with its origin in the singlet electronic state of dimeric Cu$^{II}$ carboxylates$^{19}$, undergoes a red shift to 459 nm, while the d-d transition moves to 779 nm giving the blue colour to the powder samples of [Cu$_2$(μ-O$_2$CCH$_2$Cl)$_4$(4-CNpy)$_2$] in contrast to the greenish blue, green and yellowish green colours of other members in these complexes wherein the axial ligand is bound to Cu$^{II}$ via a pyridyl-N atom.

The dimeric complexes [Cu$_2$(μ-O$_2$CC$_6$H$_5$)$_4$(4-CNpy)$_2$], [Cu$_2$(μ-O$_2$CCH$_2$Cl)$_4$(4-CNpy)$_2$] and [Cu$_2$(μ-O$_2$CCH$_3$)$_4$(4-CNpy)$_2$] have been investigated as catalysts in the homogeneous oxidation of diphenylmethane (DPM) with 70% aq. TBHP as the terminal oxidant. The reactions have been generally carried out in absence of any added solvent, because the neutral complexes are appreciably soluble in the reaction mixture consisting of aqueous TBHP and the corresponding substrate. The effect of temperature has been studied by performing the reactions at three different temperatures viz. 343 K, 363 K, and 383 K. Moreover, the effect of an added solvent on the reaction has also been studied to evaluate if
The solvent-free condition used in the present study is indeed useful. To study this effect, the reaction was carried out in acetonitrile. To study the effect of oxidants, 30% aq. H₂O₂ was used instead of TBHP. Aerobic oxidations have also been carried out both in absence and presence of TEMPO as the co-catalyst. Initial experiments were carried out to study the efficacy of the complexes [Cu₂(μ-O₂CC₆H₅)₄(4-CNpy)]₂, [Cu₂(μ-O₂CCCH₂Cl)₄(4-CNpy)]₂ and [Cu₂(μ-O₂CC₃)₄(4-CNpy)]₂ as catalysts for the oxidation of DPM. For each test reaction 0.84 g DPM (5 mmol), 0.28 mol% (0.014 mmol) of the catalysts and 3 mL TBHP were mixed and magnetically stirred at 383 K for 8 h. All the reactions were performed in absence of any added solvent. The results are presented in Table 1. Benzophenone was obtained as the sole product in all the reactions. However, at the end of 8 h, 100% conversion could be achieved only with [Cu₂(μ-O₂CCCH₂Cl)₄(4-CNpy)]₂ as the catalyst. Therefore, we extended our experiments further by making use of this complex only. In search of suitable reaction conditions to achieve the maximum conversion, the effects of varying amounts of catalyst and TBHP were studied in the next step with a view to optimizing the reaction conditions. From the above observations it is clear with 0.28 mol% catalyst the time required for complete conversion of substrate is 2 h longer than the cases where higher catalyst amounts are used. In spite of this fact, we consider entry 6 as the best possible catalyst performance because of the improved turnover frequency. For the catalyst amounts 0.48, 0.68 and 0.88 mol% the time required for complete conversion of the substrate is 6 h. Similarly, the reactions for 0.28 mol% catalyst reach completion with either 3 mL or 2 mL of TBHP in 8 h (entries 1 and 6). A blank reaction (entry 7) carried out without the catalyst shows only 3% conversion in 8 h. This proves that the presence of a catalyst is essential for the oxidation reaction under study.

In order to study the temperature dependence of the reaction, the oxidation of DPM was carried out at three different temperatures, viz. 343 K, 363 K and 383 K under the optimized condition. From the data presented in Table 3 it may be seen that at the lower temperatures the reactions proceed faster.

### Table 1. TBHP oxidation of DPM using Cu(II) tetracarboxylate catalysts

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Time (h)</th>
<th>Conversion (%)</th>
<th>Selectivity to aBP (%)</th>
<th>bTOF</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>[Cu₂(μ-O₂CC₆H₅)₄(4-CNpy)]₂</td>
<td>8</td>
<td>90</td>
<td>100</td>
<td>40.17</td>
</tr>
<tr>
<td>2</td>
<td>[Cu₂(μ-O₂CCCH₂Cl)₄(4-CNpy)]₂</td>
<td>8</td>
<td>100</td>
<td>100</td>
<td>44.64</td>
</tr>
<tr>
<td>3</td>
<td>[Cu₂(μ-O₂CC₃)₄(4-CNpy)]₂</td>
<td>8</td>
<td>85</td>
<td>100</td>
<td>37.94</td>
</tr>
</tbody>
</table>

aBP = benzophenone. bTOF (turnover frequency) = moles of substrate converted to product per mole of catalyst per hour.

Reaction conditions: 5 mmol DPM, 0.28 mol% Cu(II) catalyst, 383 K, 3 mL TBHP (22 mmol). Reported yields are GC yields in all cases.

### Table 2. DPM oxidation catalyzed by [Cu₂(μ-O₂CCCH₂Cl)₄(4-CNpy)]₂ under varied conditions

<table>
<thead>
<tr>
<th>Entry</th>
<th>Amount of catalyst (mol%)</th>
<th>Amount of TBHP (mL)</th>
<th>Temperature (K)</th>
<th>Time (h)</th>
<th>Conversion (%)</th>
<th>Selectivity to BP (%)</th>
<th>TOF</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.28</td>
<td>3</td>
<td>383</td>
<td>8</td>
<td>100</td>
<td>100</td>
<td>44.64</td>
</tr>
<tr>
<td>2</td>
<td>0.48</td>
<td>3</td>
<td>383</td>
<td>6</td>
<td>100</td>
<td>100</td>
<td>34.72</td>
</tr>
<tr>
<td>3</td>
<td>0.68</td>
<td>3</td>
<td>383</td>
<td>6</td>
<td>100</td>
<td>100</td>
<td>24.50</td>
</tr>
<tr>
<td>4</td>
<td>0.88</td>
<td>3</td>
<td>383</td>
<td>6</td>
<td>100</td>
<td>100</td>
<td>18.93</td>
</tr>
<tr>
<td>5</td>
<td>0.28</td>
<td>1</td>
<td>383</td>
<td>14</td>
<td>100</td>
<td>100</td>
<td>25.51</td>
</tr>
<tr>
<td>6</td>
<td>0.28</td>
<td>2</td>
<td>383</td>
<td>8</td>
<td>100</td>
<td>100</td>
<td>44.64</td>
</tr>
<tr>
<td>7</td>
<td>0</td>
<td>2</td>
<td>383</td>
<td>8</td>
<td>100</td>
<td>100</td>
<td>–</td>
</tr>
</tbody>
</table>

### Scheme 2

In order to study the temperature dependence of the reaction, the oxidation of DPM was carried out at three different temperatures, viz. 343 K, 363 K and 383 K under the optimized condition. From the data presented in Table 3 it may be seen that at the lower temperatures the reactions proceed faster.

### Table 3. Effect of temperature on DPM oxidation catalyzed by [Cu₂(μ-O₂CCCH₂Cl)₄(4-CNpy)]₂

<table>
<thead>
<tr>
<th>Entry</th>
<th>Temperature (K)</th>
<th>Time (h)</th>
<th>Conversion (%)</th>
<th>Selectivity to BP (%)</th>
<th>TOF</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>343</td>
<td>13</td>
<td>100</td>
<td>100</td>
<td>27.47</td>
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<tr>
<td>2</td>
<td>363</td>
<td>11</td>
<td>100</td>
<td>100</td>
<td>32.46</td>
</tr>
<tr>
<td>3</td>
<td>383</td>
<td>8</td>
<td>100</td>
<td>100</td>
<td>44.64</td>
</tr>
</tbody>
</table>
are slower, as expected. However, it is rather remarkable that even at the highest temperature of 383 K used in this study no product other than the desired one, i.e. benzophenone is formed. In view of this, the use of this temperature for the reaction under study appears to be preferable, particularly to circumvent the generally slow nature of benzylic oxidation processes. In view of the general emphasis on making oxidation processes as compatible with green chemistry requirements as possible, very often air, dioxygen and hydrogen peroxide are utilized in as oxidants in organic transformations. In order to examine if either H₂O₂ or air or both are effective oxidants for the reaction under study, the reaction was carried out with H₂O₂ (30%) as the oxidant instead of TBHP keeping all other conditions same. As given in Table 4, only 6% DPM conversion could be achieved after 8 h using H₂O₂ as the oxidant. Aerobic oxidation was also carried out both with and without TEMPO as the co-catalyst to find that no conversion of DPM occurred even after 8 h. In these two cases we had to use acetonitrile as a solvent to make the catalyst soluble. As stated above, the reactions in which TBHP and H₂O₂ were used as the oxidant, no added solvent was used for carrying out the oxidation of DPM. However, while examining if aerobic oxidation catalyzed by [Cu₂(μ-O₂CR)₄(4-CNpy)₂] is useful, acetonitrile was taken as the solvent for the reaction. In order to prove if the solvent-free condition used by us generally in the TBHP oxidized reactions is indeed essential, it was felt necessary to carry out a couple of reactions using [Cu₂(μ-O₂CCH₂Cl)₄(4-CNpy)₂] as the catalyst to examine if the presence of a solvent would enhance catalyst performance. A reaction was performed in 10 ml acetonitrile under the optimized condition of the amounts of substrate, catalyst and oxidant, and the reaction time. Although the selectivity to benzophenone was once again 100%, the conversion in this case was found to be considerably lower (63% in 8 h) in comparison with the solvent free condition used as above for the TBHP oxidation of DPM under solvent free condition.

The results described above clearly show that it is possible to make use of dinuclear tetracarboxylates of copper(II) with 4-CNpy as the axial ligand as effective catalysts in the conversion of diphenylmethane to benzophenone by carrying out the reaction at atmospheric pressure and in absence of any added solvent. Our results, when compared with works published earlier are better both in terms of conversion and selectivity. The major advantages of our method are (1) very small amount of catalyst is necessary; (2) no additives are needed for the oxidation processes to take place; (3) there is no need of an added solvent; and (4) the conversions as well as selectivity are excellent.

Conclusions

The dimeric tetracarboxylates of copper(II), [Cu₂(μ-O₂CR)₄(4-CNpy)₂], show excellent catalytic activity in the TBHP oxidation of diphenylmethane to produce benzophenone as the only product. The catalyzed reaction is more useful under solvent free condition. H₂O₂ and air are not effective as oxidants in the oxidation of diphenylmethane catalyzed by [Cu₂(μ-O₂CCH₂Cl)₄(4-CNpy)₂].

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References