CHAPTER 5

Homogeneous and Heterogeneous Catalytic Oxidation of Substituted Benzyl alcohol, Hydrocarbons, 1,10-Phenanthroline and substituted alkynes
5.1. Introduction

This chapter deals with the use of the Schiff base copper (II) complexes as catalysts for various oxidation reactions. Catalytic activity of copper (II) complexes of the Schiff bases is divided into four sections. Section 5.3 deals with studies on the oxidation of p-chlorobenzyl alcohol. Section 5.4 presents the studies on the oxidation of hydrocarbons, section 5.5 deals with the study of oxidation of 1,10-phenanthroline and section 5.6 deals with the oxidation of substituted alkynes.

Catalytic oxidation of alcohols to carbonyl compounds is a major reaction in organic transformation, for both fundamental research and industrial manufacturing [1]. Conventionally, stoichiometric oxidants (e.g., chromate, permanganate, ruthenium(VIII) oxide and chromium(VI) reagents) have been used for oxidation of alcohols that produce environmentally undesirable heavy toxic wastes [2]. Selective catalytic oxidation of alcohols by inexpensive reagents such as oxygen, hydrogen peroxide or tert-butyl hydroperoxide is a relatively useful way of generating products like aldehydes, ketones and acids [3]. Similarly, the oxidation of primary and secondary alcohols to carbonyl compounds is a simple and useful transformation in organic chemistry [4]. The oxidation of benzyl alcohol to benzaldehyde is an important organic transformation, since benzaldehyde has applications in the perfume, pharmaceutical, dyestuff, and agrochemical industries [5]. Many transition metal complexes are used as homogeneous and heterogeneous catalyst for the oxidations of different alkenes, alkanes, alcohols, thioethers, etc. [6,7]. Some of the copper (II) complexes of Schiff base with NNO donor sites have been found to catalyze the benzyl alcohol oxidation [8]. Section 5.3 reports the oxidation of p-chlorobenzyl alcohol using copper (II) Schiff base complexes of \( \text{L1} \) series, heterogeneously.

Multinuclear copper (II) complexes and monomeric compounds, show excellent catalytic activity towards oxidation of toluene, alkenes, benzene, catechol...
etc.[9-11]. Substituted aromatic hydrocarbons and their oxidation products are industrially and commercially important[12]. Velusamy et al [13] reports the oxidation of alkylbenzenes into the corresponding ketones using H₂O₂. The controlled oxidation of toluene using copper complexes leads to benzyl alcohol, benzaldehyde and benzoic acid which are very important for industrial purpose [14]. Copper schiff base complexes have been used for oxidation of hydrocarbons and result in the formation of carbonyl compounds [15,16]. Roy et al [17] reported the oxidation of cyclohexane and toluene using tetranuclear copper (II) complexes resulting in the formation of corresponding alcohol and aldehyde. Biswas et al [18] found the schiff base with N₂O₂ donor atom as an efficient catalyst for the oxidation of aromatic hydrocarbons to the corresponding aldehyde and alcohol. In section 5.4 we report the catalytic oxidation of toluene, ethylbenzene and 2-methylnaphthalene using copper (II) complexes of L₂ schiff base series under mild condition, Homogeneously.

1,10-Phenanthroline 5,6-dione (Phen-dione) and its derivatives play important role as building blocks for the synthesis of metallo-dendrimers and supramolecular assemblies [19]. Phen-dione possesses two types of basic centers, nitrogen and an oxygen atom, both in the sp²-hybridized state [20]. Due to this Bi-functionality, it is used as quinone equivalent ligand with metals in a low oxidation state and bipyridine equivalent ligand in reactions with Lewis acids resulting in the formation of complexes of higher nuclearity [21]. Due to its varied ligating ability it is able to generate complexes with transition metal ions including Zn, Cd and Hg, inner transition as well as group 4 and 5 metals in high and low oxidation state [22,23]. This ligand is of biological interest owing to its redox activity [24] and ability to covalently bind proteins and interact with DNA [25]. Phen-dione was found to be cytotoxic against human kidney and hepatocellular adenocarcinomas and has an estimated IC50 value lower than that of cisplatin [26,27]. Oxidation of 1,10-Phenanthroline has been reported earlier with variety of oxidizing agents. Fedprova et al [28] oxidized 1,10-Phenanthroline by H₂O₂ and obtained 2,2-bipyridyl 3,3′-dicarboxaldehyde, while 2,2-bipyridyl 3,3′-dicarboxylic acid was obtained by Wimmer et al [29] using alkaline permanganate. Panari et al [30] obtained the 2,2-bipyridyl 3,3′-dicarboxaldehyde as the major oxidation product from 1,10-Phenanthroline oxidation using alkaline permanganate. The formation of Phen 5,6-dione is reported by oxidation of 1,10-
Phenanthroline using KMnO₄ [31], K₂MnO₄, oleum and conc. nitric acid [31]. Calderazzo et al [32] obtained the Phen 5,6-dione by using a oxidizing mixture of HNO₃/H₂SO₄/KBr modifying the procedure adopted by Yamada et al [33] and obtained the product with relatively high yield. In section 5.5 we report the aerobic oxidation of 1,10-phenanthroline in the presence of copper (II) complexes of L₃ schiff base series to form the phen-dione.

The oxidation of olefins in the presence of catalytic amounts of transition metal complexes has led to a large number of reports [34]. Allylic oxidation, epoxidation, and the formation of ketone and aldehyde have wide applications in organic synthesis [35]. Ren et al [36] reported the Wacker type oxidation of alkenes and alkynes catalyzed by PdBr₂ and CuBr₂ resulting in the formation of diketones using molecular oxygen [37]. Alvarez et al [38] reports the copper-catalyzed oxidation of alkenes and alkynes using TBHP as the oxidant with the formation of ester. Gao et al [39] reports the formation of 1,2-diketones as major oxidation products using Pd/Cu as catalyst. Dicarbonyl derivatives are very useful building blocks in the construction of a variety of organic intermediates, especially in the synthesis of biologically active heterocyclic compounds [40]. Although these copper-catalyzed oxidation of terminal alkynes are highly efficient, the difficulty in separating the catalyst from the reaction mixture and the impossibility of reusing it in subsequent reactions are disadvantages of homogeneous catalysis. In addition, homogeneous catalysis might result in unacceptable copper contamination of the desired isolated product. In comparison the heterogeneous catalysts can be easily separated from the reaction mixture by a simple filtration and reused in successive reactions, provided that the active sites have not become deactivated. Heterogeneous catalysis also helps to minimize waste derived from reaction work-up, so contributing to the development of green chemical processes. In section 5.6 we report the oxidation of 1-phenylpropyne and 1-phenyl pentyne using copper (II) complexes of L₄ Schiiff base series, heterogeneously.

5.2. Physical measurements

All the reagents and solvents were purchased from commercial sources. 4-Chloro benzyl alcohol, Toluene, ethyl benzene, 2-methyl naphthalene, 1,10-
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phenthroline, 1-Phenyl Propyne, 1-Phenyl Pentyne tert-butyl hydroperoxide (TBHP) and hydrogen peroxide (H₂O₂) were purchased from Sigma Aldrich. HPLC grade solvents were used for spectral work. ¹H (400 MHz) NMR spectra were recorded on a JEOL ECX-400P NMR spectrometer using tetramethylsilane (TMS) as an internal reference. Electronic spectra were obtained on a Shimadzu UV-Vis-1601 Spectrometer at University of Delhi, Delhi, India. The SEM micrographs were recorded on an Environmental Scanning Electron Microscope model FEI Quanta 200F with gold coating in SMITA research lab IIT Delhi, India. GC-MS spectra were recorded on a Shimadzu GCMS-QP2010 plus gas chromatograph mass spectrometer with AOC-20i auto injector and TD-20 thermal desorption system at AIRF, JNU Delhi, India. The powder X-ray diffraction patterns were recorded using High resolution D8 Discover Bruker diffractometer, equipped with point detector (scintillation counter), employing monochromatized Cu Kα₁ radiation with a scan rate of 1.0 second/step and step size 0.02° at 298 K over the range of 2θ = 5°–35°. Solution state EPR spectra were recorded on an X-Band JEOL JES–FA200 ESR Spectrometer with a variable temperature liquid Nitrogen cryostat at 120 K at IIT-Bombay, Mumbai, India.

Results and discussions

5.3. Catalytic oxidation of p-chlorobenzyl alcohol using copper (II) complexes (1), (2), (3) and (4), heterogeneously

Heterogeneous catalysts are widely used in industry, can be easily separated from the reaction mixture, and are often reused. Thus the use of heterogeneous catalyst has attracted a lot of interest [41]. Catalysis has been found to be dependent on the crystal face [42], as well as on the shape of the catalyst [43, 44]. Several studies of catalysis processes have been reported with distinct shapes, truncated octahedral [45], tetrahedral, cubic or spherical compounds [46]. However, there are few studies that report the changes in size distribution after recycling along with catalytic activity [47]. It has been earlier reported that both size and shape changes occur during the catalysis process [48]. In this section we report the morphology dependent catalytic activity of mononuclear and binuclear copper (II) complexes of
schiff base L1, changes are observed by SEM and PXRD study. EPR and UV-visible spectroscopy are used for identification of any intermediate species.

Copper (II) complexes [Cu(L1)Cl].MeOH(1), [Cu(L1)Br].MeOH (2), [Cu(L1)(NO3)]2(3) and [Cu(L1)NCS] (4) were used heterogeneously for the oxidation of p-chlorobenzylalcohol to its respective aldehyde, using tert-butyl-hydroperoxide as an alternate source of oxygen in CH2Cl2. In a typical reaction, catalyst (0.011 mmol), benzyl alcohol (0.11 mmol), and oxidant (0.056 mmol, 70%) [1:10:5] were mixed in 15 mL dichloromethane and warmed at 35–40 °C for 3 h (Scheme 1). The progress of reaction was monitored by TLC (5% ethyl acetate in petroleum ether). The formation of DNP derivative confirms the formation of p-chlorobenzaldehyde which was the product in all the cases. The reaction mixture was centrifuged and the isolated copper (II) catalyst was washed. The clear filtrate of the reaction mixture was checked for any dissolution of the catalyst during reaction, no band in the visible range of 500-900 nm was observed ruling out the possibility of any dissolution of the copper (II) catalyst. The clear filtrate was subjected to GC-MS analysis and the formation of p-chlorobenzaldehyde was confirmed. The isolated catalyst was reused for the oxidation of p-chlorobenzyl alcohol keeping the ratio of catalyst: substrate: oxidant fixed as 1: 10: 5 in each cycle. A decrease in the yield of benzaldehyde was observed for repeat cycles, as analyzed through GC-MS using naphthalene as an internal standard. All the complexes [(1) to (4)] were reused three times and their percentage conversions for each cycle are summarized in Table 1.

![Scheme 5.1. Oxidation of p-chloro Benzyl Alcohol](image)

**Kinetic study**

To study the kinetics of the oxidation of p-chlorobenzyl alcohol, the reaction was monitored spectrophotometrically by measuring the increase in the characteristic
p-chlorobezaldehyde absorption band at 256 nm as a function of time[49]. Complexes (1), (2), (3) and (4) were used as catalyst and tert butylhydroperoxide as an alternate

**Figure 5.1.** Time dependent uv-visible absorbance spectra for the formation of p-Cl-Benzaldehyde for every 10 min time interval. Complex (1): (A) 1st run (B) 3rd run, Complex (2): (C) 1st run (D) 3rd run
source of oxygen. The reaction was setup in the proportion of 1: 10: 5 (catalyst: substrate: oxidant). After every 10 minutes, 0.04 ml was taken out of the reaction mixture and diluted to 2 ml. This solution was taken in a sealed quartz cuvette and the development of new band at 256 nm was recorded (Figure 5.1, 5.2 (A-D). The concentration of product formed was calculated using the extinction coefficient of p-
chlorobenzaldehyde ($\varepsilon = 15920 \text{ M}^{-1}\text{cm}^{-1}$)[50]. The average rate was obtained from the plot of concentration of aldehyde formed vs time {Fig. 5.3(A-D)} and is given in

Table 1. The dimeric complex (3) has the highest rate of reaction in the series. In general the data suggest that each catalyst is reusable, however the rate of reaction drops upon each reuse. This drop in rate of reaction is substantial for the monomeric complexes (1, 2 & 4) when compared to the dimeric complex (3). The maximum percentage change in the rate of reaction upon reuse is only 7% for the dimer in comparison to the change in the rate of reaction upon reuse for monomeric complexes

Figure 5.3. Plots of Conc. vs time for the complexes. (A) complex(1): 1st, 2nd & 3rd use(B) complex (2): 1st & 3rd use(C) complex(3): 1st, 2nd & 3rd use(D) complex (4): 1st, 2nd & 3rd use
(1), (2) and (4) are 12%, 30% and 27% respectively. This may explain the higher rate of reaction and yields obtained for the dimeric complex.

**Table 5.1.** Rate of oxidation reaction of p-chlorobenzyl alcohol and its % conversion to the aldehyde of complexes (1) to (4).

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Reusability</th>
<th>Rate of reaction*10^{-6}</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Cu(L1)Cl] (1)</td>
<td>1st use</td>
<td>15.2</td>
<td>68</td>
</tr>
<tr>
<td></td>
<td>2nd use</td>
<td>14.6</td>
<td>-----</td>
</tr>
<tr>
<td></td>
<td>3rd use</td>
<td>12.1</td>
<td>52</td>
</tr>
<tr>
<td>[Cu(L1)Br] (2)</td>
<td>1st use</td>
<td>14.6</td>
<td>65</td>
</tr>
<tr>
<td></td>
<td>2nd use</td>
<td>-----</td>
<td>-----</td>
</tr>
<tr>
<td></td>
<td>3rd use</td>
<td>10.5</td>
<td>50</td>
</tr>
<tr>
<td>[Cu(L1)NO3]_2(3)</td>
<td>1st use</td>
<td>18.0</td>
<td>84</td>
</tr>
<tr>
<td></td>
<td>2nd use</td>
<td>17.3</td>
<td>74</td>
</tr>
<tr>
<td></td>
<td>3rd use</td>
<td>16.8</td>
<td>66</td>
</tr>
<tr>
<td>[Cu(L)NCS] (4)</td>
<td>1st use</td>
<td>12.6</td>
<td>74</td>
</tr>
<tr>
<td></td>
<td>2nd use</td>
<td>11.9</td>
<td>-----</td>
</tr>
<tr>
<td></td>
<td>3rd use</td>
<td>9.03</td>
<td>48</td>
</tr>
</tbody>
</table>

*Based on GC-MS with naphthalene as Internal Standard

**Scanning electron microscopy**

In order to observe the impact of surface morphology on catalysis during recycling, the catalyst was recovered after the oxidation reaction was complete. A gold coated sample of the recovered catalyst was prepared for SEM measurement. The SEM micrograph shows that the mononuclear complexes (1) & (2) before use as catalyst have a cuboid (rectangular box) like morphology whose average length lies between 75-140 μm for complex (1) and 90-170μm for complex (2) (Figure 5.4A, 5.5A) [51]. Its subsequent reuse in the catalytic oxidation of p-chlorobenzyl alcohol causes changes and the morphology changes to more or less flat 2-dimensional boxes (wafer type) with length varying from 25-40 μm for complex (1) and 10-30 μm for complex (2) (Figure 5.4B, 5.5 B). Magnified image of complex (1) before and after use are shown in Figure 5.4 C, D.
Figure 5.4. Variation in the Morphology of complex (1) during catalysis. (A) Unused Complex (B) After 3\textsuperscript{rd} use in catalysis. (C) Magnified image before use (D) Magnified image after use.

Figure 5.5. Variation in the Morphology of complex (2) during catalysis. (A) Unused Complex (B) After 3\textsuperscript{rd} use in catalysis.

The mononuclear complex (4) is found to possess a flower like morphology [52] and contains petals. The micro-petals are flat and the length of each petal ranges
from 1.3 to 1.01 µm (Fig. 5.6A). After 3rd use the petals shows a shortening in length upto 0.86 µm, while some petals are found to conjoin together, giving rise to cluster formation (Fig. 5.6B), this could have led to the inactivation of the catalyst.

![Figure 5.6](image)

**Figure 5.6.** Variation in the Morphology of complex (4) during catalysis. (A) Unused complex (B) After 3rd use in catalysis.

![Figure 5.7](image)

**Figure 5.7.** Variation in the Morphology of complex (3) During catalysis. (A) Unused Complex (B) After 1st use (C) After 2nd use (D) After 3rd use in catalysis.

The phenoxo bridged dimeric copper(II) complex (3) is found to have a hexagonal rod type morphology and the width of the rod lies in the range of 5.6–9.9 µm (Fig. 5.7A). After 1st use, some of the rods are found to degrade to rods of dimension 1.5–1.6 µm (Fig. 5.7B). After 2nd and 3rd use they are in the range of 1.2–
Minimal morphology changes take place when the complex is reacted with only tert-butyl-hydroperoxide in the absence of substrate under similar experimental conditions.

From SEM studies it is observed that morphology changes are taking place upon reuse of the catalyst and this change may have a bearing on the loss in catalytic efficiency to carry out the oxidation reaction. The morphology changes for the monomeric complexes are more drastic in comparison to the dimeric counterpart.

**Powder X-Ray Diffraction**

It is interesting to compare the Powder XRD pattern of all the complexes and the changes which occur after successive use of the catalyst for the oxidation of p-chlorobenzyl alcohol to p-chlorobenzaldehyde. The monomeric copper (II) complex (1) show that the parent complex has sharp intense peaks at 2θ (hkl) 7.6(001), 8.8(010), 11.5(100), 12.7(110), 14.3(101) 17.8(002), 21.8(020) and 26.8(202). After reuse there is significant loss in intensity at peaks 7.6, 8.8, 11.5, 12.7, 21.8 and 26.8 for the complex (1) and two new peaks are also formed after reuse at 9.7 and 24.7 (Fig. 5.8 A, B). The PXRD of complex (2) show that the parent complex has sharp intense peaks at 2θ (hkl) 7.5(001), 8.7(010), 11.3(100), 12.7(110), 14.0(101) 17.6(002), 21.6(020) and 26.6(202). After reuse there is significant change in intensity at peaks 7.5, 8.8, 11.3, 17.6 and 26.6 for the complex (2) (Fig. 5.9 A, B). The above results indicate that changes occur in the unit cell of the copper catalysts upon reaction; some planes diminish in intensity and could be responsible for the inactivation of the catalyst. This is also reflected in their SEM measurements where a change in parent cuboid like morphology to wafer type morphology is indicated.

The monomeric copper (II) thiocyanate bound complex (4) shows sharp peak at 2θ 10.1(011), 11.3(021), 16.2, 24.4, 25.8(080), 29.2 and 30.6. After reuse of the catalyst the peak at 10.1, 11.3 and 25.8 are destroyed while the peaks at 16.2, 24.4, 29.2 and 30.6 remain intact with small change in intensity of other peaks. This suggests that the diffraction planes associated with at 10.1, 11.3 and 25.8 could be involved in the promotion of catalysis, while the other planes remain inert to catalytic activity (Fig. 5.10 A, B, C). SEM studies have shown that surface morphology changes occur and agglomeration take place upon reuse.
Figure 5.8. PXRD pattern of complex (1):(A) Unused complex (B) After 3rd use

Figure 5.9. PXRD pattern of complex (2):(A) Unused complex (B) After 3rd use
Figure 5.10. PXRD pattern of complex (4): (A) Unused complex (B) After 1\textsuperscript{st} use (C) After 2\textsuperscript{nd} use (D) Represent After 3\textsuperscript{rd} use

Figure 5.11. PXRD pattern of complex (3): (A) Unused complex (B) After 1\textsuperscript{st} use (C) After 2\textsuperscript{nd} use
The Dimeric copper (II) complex (3) shows sharp peaks at 20, 7.8, 10.3, 11.1 and 13.0 in the parent form (Fig. 5.11 A). After the 1st use the relative intensity of peaks at 20, 10.3, 11.1 and 13.0 diminish to about 10–11% with respect to unused complex (Fig. 5.11 B). These changes remain nearly constant in the next cycle (Fig. 5.11 C). It is suggested that the diffraction planes associated with peaks at 20 10.3 and 11.1(011 and 002) could be involved in the promotion of catalysis, while the plane associated with 20, 7.8(100) is seemingly inert to catalytic activity. Never the less the changes in the PXRD of complex (3) are minimal in comparison to the monomeric (1), (2) and (4) compounds; while there are substantial changes in the morphology of complex (3) upon reuse. Thus one may conclude that the surface morphology plays a major role in the catalytic activity of the complexes as oxidizing catalysts.

EPR Studies

To further investigate the changes occurring during the catalytic cycle, electron paramagnetic resonance (EPR) spectroscopy was used for monomeric

![Figure 5.12.X-Band EPR spectrum of [Cu(L1)Cl] (1) complex in DMF solution at liquid nitrogen temperature for Unused complex and after 3rd use in catalysis](image-url)
Figure 5.13. X-Band EPR spectrum of [Cu(L1)Br] (2) complex in DMF solution at liquid nitrogen temperature for Unused complex and after 3rd use in catalysis.

Figure 5.14. X-Band EPR spectrum of [Cu(L1)NCS] (4) complex in DMF solution at liquid nitrogen temperature for unused complex and after 3rd use catalysis.
complexes. X-band EPR spectra of the complexes (1), (2) and (4) give four sharp peaks with $g_\| = 2.24 - 2.35$, and $g_\perp = 2.03 - 2.07$, ($A_\| = 146-170$) at liquid nitrogen temperature in MeOH. With the reuse of the catalyst the peaks in EPR spectra diminish with changes in $g_\|$ and $g_\perp$ as shown in Fig.5.12 to 5.14. The drop in EPR signal intensity during catalytic cycle could be rationalized in terms of conversion of Cu(II) to Cu(I) during catalysis, thus an intermediate copper (I) species is likely to be taking part during the catalytic cycle.

![Graph showing variation in d-d band intensity for monomeric copper(II) complexes.](image)

**Figure 5.15.** Variation in the d-d band intensity for monomeric copper(II) complexes. Unused shows: parent complex, 2: After 2\textsuperscript{nd} use, 3: After 3\textsuperscript{rd} use in catalysis.
d-d band changes

The d-d band spectral changes were measured by making a 3.8 mmolar solution of the used complex (1), (2) and (4) and measuring their visible spectra (Fig. 5.15). It is also interesting to note that after repeat cycles there is drop in the d-d band intensity in visible region. Themonomeric complexes shows drop in d-d band intensity by 22% for complex (1), 32% for complex (2) and 28% for complex (4) after third use. The loss in d-d band intensity is indication of the formation of copper (I) during catalytic cycle and has been observed earlier also [53].

X-Ray Photoelectron Spectroscopy Study

X-ray photoelectron spectroscopy shows primary ionization process in about $10^{-7}$s, this fast technique is well suited for the assignment of mixed oxidation state [54]. Earlier it has been used for the analysis of Cu(I), Cu(II) and mixed Cu(I)/Cu(II) species [55]. It has been shown earlier that the binding energies of the core electrons increase with higher oxidation state. In Cu(I), metal → Ligand back bonding may

![Figure 5.16.XPS spectra of complex [Cu(L1)NCS] (4) for unused complex and after 3rd use in catalysis](image-url)
cause a shift of electron density from filled d-orbitals of copper to empty antibonding \(\pi\)-orbital of the ligand causing a lowering of binding energy. The \([\text{Cu(L1)NCS}]\) complex shows two main peak at 935 eV and 955 eV with a satellite peak at 945 eV. These peak positions have been reported to be associated with copper in +2 oxidation state [56] (Fig. 5.16). The XPS of the reused complex shows the presence of a new shoulder, observed at 933 eV (Fig. 5.16 inset) along with peak at 935 eV and 953 eV with a satellite peak at 942 [57]. The appearance of a prominent shoulder at 933 eV has been reported to be due to copper in +1 oxidation state [57b]. This shows that the reused complex has some proportion of copper (I) besides copper (II). This is an added support for EPR and uv-visible data which indicates the formation of copper (I) species from copper(II) during catalysis. Thus it is found that the all the Cu(II) complexes carry out a selective oxidation of p-chloro benzyl alcohol to the corresponding aldehyde, and the catalysis is dependent on the morphological changes taking place during recycling, with copper (I) species being generated during catalysis.

5.4. Catalytic oxidation of Aromatic Hydrocarbons using copper(II) complexes (5), (6), (7) and (8)

Copper (II) complexes \([\text{Cu(L2)Cl}]\) (5), \([\text{Cu(L2)Br}]\) (6), \([\text{Cu(L2)(NO3)}]_2\) (7) and \([\text{Cu(L2)NCS}]\) (8) were used homogeneously for the oxidation of toluene, ethylbenzene and 2-methylnaphthalene using hydrogen peroxide as an alternate source of oxygen in acetonitrile (Scheme 5.2). In a typical reaction, the complex (0.0124 mmol) was mixed with hydrogen peroxide (0.124 mmol) in 10 ml, to this was added 40 \(\mu\)l of HNO\(_3\) followed by the addition of substrate (0.124 mmol). The final ratio of catalyst, substrate and oxidant was 1:10:10 for a 10 ml solution. It has been evident from previous studies that the presence of nitric acid has a positive role in such catalytic reactions [58-60]. Nitric acid has been used, mainly, for two reasons: (a) protonates the ligand bound to the copper (II) there by increasing the oxidative property of the catalyst; (b) in the presence of nitric acid, decomposition of peroxide is slow increasing the stability of peroxy intermediate [61].
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The reaction mixture was stirred for 8-10 h at 40°C temperature. The progress of reaction was monitored by TLC (10% ethyl acetate in pet. ether). The formation of DNP derivative confirms the formation of carbonyl product. The product was extracted from the reaction mixture using diethyl ether and the sample from the organic phase was analyzed by GC-MS using naphthalene as an internal standard (Table 5.2). Blank experiments for the oxidation of toluene, ethylbenzene and 2-methylnaphthalene were carried out without any catalyst keeping other experimental conditions unaltered; these did not produce any significant amount of oxidized samples.

Table 5.2. Rate of oxidation Reaction and % conversion of different hydrocarbon with retention time

<table>
<thead>
<tr>
<th>Complex</th>
<th>Substrate</th>
<th>Products</th>
<th>Rx. Time</th>
<th>% Conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Toluene</td>
<td>Ph-CHO</td>
<td>16.5</td>
<td>68%</td>
</tr>
<tr>
<td>Cu(L2)Cl (5)</td>
<td>Ethyl Benzene</td>
<td>Ph-CO-CH₃</td>
<td>7.0</td>
<td>60%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ph-CH(OH)-CH₃</td>
<td>8.7</td>
<td>11%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ph-CHO</td>
<td>16.4</td>
<td>15%</td>
</tr>
<tr>
<td></td>
<td>2-Methyl Naphthalene</td>
<td>Phthalic acid</td>
<td>15.2</td>
<td>57%</td>
</tr>
<tr>
<td>Cu(L2)Br (6)</td>
<td>Toluene</td>
<td>Ph-CHO</td>
<td>16.5</td>
<td>64%</td>
</tr>
<tr>
<td></td>
<td>Ethyl Benzene</td>
<td>Ph-CO-CH₃</td>
<td>7.0</td>
<td>54%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ph-CH(OH)-CH₃</td>
<td>8.7</td>
<td>9%</td>
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<tr>
<td></td>
<td></td>
<td>Ph-CHO</td>
<td>16.4</td>
<td>12%</td>
</tr>
<tr>
<td></td>
<td>2-Methyl Naphthalene</td>
<td>Phthalic acid</td>
<td>15.2</td>
<td>47%</td>
</tr>
<tr>
<td>Cu(L2)NO₃ (7)</td>
<td>Toluene</td>
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<tr>
<td></td>
<td>Ethyl Benzene</td>
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<td>15.2</td>
<td>60%</td>
</tr>
<tr>
<td>Cu(L2)SCN (8)</td>
<td>Toluene</td>
<td>Ph-CHO</td>
<td>16.5</td>
<td>57%</td>
</tr>
<tr>
<td></td>
<td>Ethyl Benzene</td>
<td>Ph-CO-CH₃</td>
<td>7.0</td>
<td>51%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ph-CH(OH)-CH₃</td>
<td>8.7</td>
<td>7%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ph-CHO</td>
<td>16.4</td>
<td>11%</td>
</tr>
<tr>
<td></td>
<td>2-Methyl Naphthalene</td>
<td>Phthalic acid</td>
<td>15.2</td>
<td>46%</td>
</tr>
</tbody>
</table>
Scheme 5.2. Reaction for the oxidation of Hydrocarbon

All the complexes of L2 catalyze the oxidation of toluene, ethylbenzene and 2-methylnaphthalene under mild condition. There could be a role of $E_{1/2}$ for the respective copper (II) complex in this oxidation reaction studied as above. It is found that $[\text{Cu}(\text{L2})\text{NO}_3]$ has the most anodic $E_{1/2}$ and also show the largest yields of oxidized products. It is likely that copper complexes having anodic $E_{1/2}$ may catalyze $\text{H}_2\text{O}_2$ to a greater extent. This is followed by $[\text{Cu}(\text{L2})\text{Cl}]$, $[\text{Cu}(\text{L2})\text{Br}]$ and $[\text{Cu}(\text{L2})\text{NCS}]$ which have relatively cathodic $E_{1/2}$.

5.5. Aerobic Oxidation of 1,10-Phenthroline using copper(II) complexes (9), (10), (11) and (12)

Four Copper(II) complexes $[\text{Cu}(\text{L3})\text{Cl}]$ (9), $[\text{Cu}(\text{L3})\text{Br}]$ (10), $[\text{Cu}(\text{L3})(\text{NO}_3)]$ (11) and $[\text{Cu}(\text{L3})\text{NCS}]$ (12) were used homogeneously for the aerobic oxidation of 1,10-phenanthroline in methanol (Scheme 5.3). The reaction between 1,10-Phenantroline and dioxygen in presence of catalytic amount of complex as catalyst was studied using UV-Visible spectroscopy. For this a known amount of complex (0.0030mmol) saturated with $\text{O}_2$ in 2 ml is mixed with 1,10-phenanthroline solution (0.030mmol) in 1 ml and the mixture is scanned spectrophotometrically. The final concentrations of complex and phenanthroline are 1 mM and 10 mM for 3 ml solution. A new band starts to increase in intensity at $\lambda_{max} = 480$ nm with the passage of time {Fig. 5.17, 5.18(A-D)}, confirming the formation of 1,10-phenanthroline 5,6-dione [62]. This band increases in intensity with time over a period of 100 min of serial scanning, after which it becomes nearly constant.
**Scheme 5.3.** Oxidation of 1,10-phenanthroline using molecular oxygen

For kinetic studies, the amount of 1,10-phenanthroline (0.056, 0.039, 0.028, 0.016, 0.0056 mmol) was varied while keeping the amount of catalyst fixed (0.0056 mmol) in 3 ml. The ratio of complex: substrate was: 1:10, 1:7, 1:5, 1:3 and 1:1. The plot of absorbance vs time for ratio 1:10, 1:7, 1:5, 1:3 and 1:1 (Catalyst: substrate) are given in Fig. 5.19(A-D). The average rates of reaction were obtained from the slope of the best fit line using the plots shown in Fig. 5.19(A-D). The optimum rate of reaction is found when the ratio between catalyst to substrate is 1:10. The oxidation by the Cu(II) catalyst appears to be quite selective. The product was quantified by forming its 2,4-DNP derivative. The final product was isolated by preparative thin layer chromatography (10% ethyl acetate in pet. Ether) and confirmed by $^1$H-NMR. NMR spectra of the phen-dione shows two peaks at 8.4 ppm and 9.0 ppm each corresponds to two proton assign a and c, while the a peak observed at 7.7 ppm correspond to two proton assign b is shown in Figure 5.20 [31(a), 62]. The yield of the phen-dione was determined by weighing the isolated products. Yield 25%.

**Monitoring the d-d band of the complex (11) during the catalytic cycle**

The [Cu(L3)NO₃] complex shows a d-d band at 640 nm. During the oxidation reaction it is found that this band drops in intensity and starts to shift its position, finally after 100 min of the reaction, it changes into a shoulder at ~ 600 nm (Fig.5.21). The drop in intensity of the d-d band is understood in terms of conversion of Cu(II) to Cu(I) as the catalysis proceeds. In this case the drop in band intensity is not very large, possibly due to rapid conversion of Cu(I) back to Cu(II) under a solution saturated with molecular oxygen.
Figure 5.17. Time dependent UV-Visible spectra of the reaction mixture of Complexes (9) and (10) Curve 1: Two min. of mixing, Curve 2: After 50 mins, Curve 3: After 100 mins of serial scanning, showing the generation of a new band at 480nm.
Figure 5.18: Time dependent UV-Visible spectra of the reaction mixture of Complexes (11) and (12). Curve 1: Two min. of mixing, Curve 2: After 50 mins, Curve 3: After 100 mins of serial scanning, showing the generation of a new band at 480 nm.
Figure 5.19. Plots of absorbance vs time for the different sets of reaction for the four complexes. (A) complex (9), (B) Complex (10), (C) Complex (11) and (D) complex (12)
Figure 5.20. $^1$H-NMR spectra of phen-dione

Figure 5.21. Changes in the d-d band of the complex [Cu(L3)NO$_3$] (11) during catalysis in MeOH
Study of EPR of the complex during catalytic cycle

To further investigate this catalytic system, electron paramagnetic resonance (EPR) spectroscopy was used. X-band EPR spectra of the unused complex gives four sharp peaks with $g_{||}=2.23$, and $g_{\perp}=2.05$, ($A_{||}=180$) at liquid nitrogen temperature in MeOH (Fig. 5.22 A). The substrate was then added in the ratio of 1:10 (catalyst: substrate), without saturating the solution with molecular oxygen. Initially minor changes are observed in EPR parameters: $g_{||}=2.25$, $g_{\perp}=2.05$ ($A_{||}=174$) (Fig. 5.22 B). After 40 mins as the oxidation proceeds, the signal intensity drops (Fig. 5.22 C), and after 75 mins only a broad weak peak is observed, as shown in fig.5.22 D. The drop in EPR signal intensity during catalytic cycle confirms that Cu(II) is being reduced to Cu(I) during catalysis.

![Figure 5.22.X-Band EPR spectrum of [Cu(L3)NO3](11) complex and substrate (1:10), in MeOH solution at liquid nitrogen temperature showing drop in EPR signal intensity during catalysis.](image-url)
Role of Molecular oxygen

The oxidation reaction was also carried out by an *in-situ* generated complex. Cu(NO$_3$)$_2$ salt (0.0033 mmol) in 3 ml MeOH gives a absorbance band at 792 nm (Fig.5.23 A). As the schiff base ligand (0.0033 mmol) was added to it, the band shifted to 646 nm (Fig.5.23 B), forming the schiff base complex, subsequently 1,10-phenanthline (0.033 mmol) was added in solid form. The ratio was [Cu: L: phen]; 1: 1: 10, the visible band shifted to 678 nm and the shoulder formed at ~500 nm at B vanishes (Fig. 5.23 C). Upon repeat scanning for 1 hr this solution did not show any oxidative catalysis under nitrogen atmosphere (Fig. 5.23(D-E)). After 1hr molecular oxygen was passed in the reaction mixture, it was found that a new band generated at 480 nm (Fig. 5.23 F) and continued to increases in intensity with time (Fig. 5.23 Q),

![UV-visible spectra](image)

**Figure 5.23.** UV-visible spectra of In-situ generated complex (A-E) and oxidation of 1,10-phenanthroleine under aerobic condition (F-Q)

while the band 678 nm in C drops in intensity and shifts back to ~ 642 nm. This suggests that there is a loss of intermediate C upon oxidative catalysis (Fig.5.23 F-Q).
Figure 5.24. Formation of Phen-dione under strict anaerobic condition

Figure 5.25. (a) Rates for the different sets of oxidation reaction using [Cu(L3)NO3] (11) complex as a catalyst under: (i) Molecular O2 (1-5) (ii) Molecular O2 with in-situ generated complex (6) (iii) Strictly anaerobic condition (7)
This confirms that the in situ generated complex also shows catalytic oxidation of 1,10-phenanthroline but only in presence of molecular oxygen. The rate of reaction for the in-situ generated complex is 3.6 times lower than that of parent complex in the presence of oxygen.

In order to further determine the role of O₂, the oxidation reaction was carried out under strict anaerobic condition. Any oxygen present in solvent (HPLC-MeOH) was first removed by a freeze–thaw cycle. This was repeated at least 2–3 times to remove the dissolved oxygen. Subsequently the catalyst and substrate were mixed in the same ratio [1:10] in this deoxygenated MeOH under nitrogen atmosphere in a septum sealed two neck flask. This mixture was then immediately syringed into a nitrogen flushed septum sealed UV-quartz cell and the reaction was monitored spectrophotometrically. A plot of phen-dione formed versus time under anaerobic condition is shown in Fig. 5.24. The concentration of phen-dione was calculated by using the extinction coefficient of 18.2 mol\(^{-1}\) L cm\(^{-1}\). The average rate in anaerobic condition is found to be 6.4 times lower (rate = 1.34*10\(^{-4}\) mol min\(^{-1}\)) when compared
to the original rate in presence of oxygen. This suggests that the absence of oxygen retards the reaction but does not inhibit it completely. The comparative rates for various sets using [Cu(L3)NO3] (11) complex are given in Fig. 5.25.

In summary, The copper (II) complexes show homogeneous catalysis for the selective oxidation of 1,10-phenanthroline using molecular oxygen. The rate of reaction shows that the catalyst is 6.4 times highly efficient under aerobic condition. *In-situ* generated catalyst is also capable of oxidizing 1,10-phenenthroline under aerobic condition, however the rate is 3.6 times lower than the original catalyst.

A blank experiment was also carried out, 1,10-phenanthroline was mixed up with Cu(NO3)2 salt under molecular O2, No oxidation occurs upon repeat scanning. The band around 732 nm corresponds to the Cu-phenanthroline complex (Fig.5.26).

### 5.6. Catalytic oxidation of substituted Alkynes using copper (II) complexes (13), (14), (15) and (16), under Acidic, Basic and Neutral condition, Heterogeneously

Copper (II) complexes [Cu(L4)Cl] (13), [Cu(L4)Br] (14), [Cu(L4)(NO3)] (15) and [Cu(L4)NCS] (16) were used heterogeneously for the oxidation of alkynes like 1-Phenyl propyne and 1-phenyl pentyne under variable condition like changes in pH, Oxidant and in presence of a surfactant. In a typical reaction, catalyst (0.0218 mmol), substrate (0.1092 mmol) and Oxidant (0.1092 mmol, 70%) in ratio of [1:5:5] were mixed in 15 mL acetonitrile and stirred at 35-40°C for 10 hrs. The progress of the reaction was monitored by TLC and formation of DNP derivative confirms the formation of carbonyl compound. The reaction mixture was centrifuged after a 10 hr reaction to isolate the copper (II) catalyst. The clear filtrate of the reaction mixture was checked for any dissolution of the catalyst during reaction, no band in the visible range of 500-900 nm was observed ruling out the possibility of any dissolution of the copper (II) catalyst. The clear filtrate was subjected to GC-MS analysis. The complexes were used for the oxidation of 1-phenyl-propyne, 1-phenyl-pentyne and their percentage conversions were analyzed through GC-MS using naphthalene as an internal standard (Table 5.3). In other reactions the pH of the solution was maintained at ~4.0 by using a sodium acetate + acetic acid buffer, while pH ~9.0 was maintained by adding 0.6 ml of 10 mM sodium acetate to the reaction solution.
Scanning electron microscopy

A SEM study was undertaken for each copper (II) complex of L4 series. The SEM micrograph shows that the all the mononuclear complexes of this series are found to possess a rod type morphology. The rods are flat and the length of the rods lies in the ranges of 5-16 μm (Fig. 5.27).

![SEM images of complexes L4](image)

**Figure 5.27.** Morphology of the complexes of L4. (A): [Cu(L4)Cl] (9), (B): [Cu(L4)Br] (10), (C): [Cu(L4)Cl] (11), (D): [Cu(L4)NCS] (12)

In order to observe the impact of surface morphology on catalytic activity, the catalyst [Cu(L4)NO3](15) and [Cu(L4)NCS] (16) was recovered and a gold coated sample was prepared for SEM measurement. The catalyst (15) and (16) after participation in the oxidation of alkynes show changes in their morphology as observed in Figure (5.28 B,C, 5.29 B). Minimal morphology changes take place when the complex [Cu(L4)NO3](15) is reacted only with oxidant in the absence of substrate under similar experimental conditions. When the complex [Cu(L4)NO3] (15) is used
at pH–9.0, all the rods collapse and cluster formation take place (Fig. 5.28 C). When the complex is used with surfactant the rods remain intact during catalysis, but the catalytic activity is greatly diminished. The larger rods breaks into smaller rod or some cluster formation taking palce after using the catalyst [Cu(L4)NCS] (16) in the catalytic cycle as shown in Fig.5.29 B.

Figure 5.28. Variation in the Morphology of the Cu(L4)NO₃ complex during Catalysis: (A) Pure Complex (B) After Reaction with substrate (C) Changes at pH 9.0

Figure 5.29. Variation in the Morphology of the [Cu(L4)NCS] complex during Catalysis: (A) Pure Complex (B) After Reaction with substrate
Powder XRD Study

The complexes (15) and (16) show the changes in the powder XRD study, which occur during use of the catalyst for the oxidation of 1-phenylpropyne.

The copper (II) nitrate bound complex (15) shows sharp peak at 20 11.1, 12.2, 16.6, 18.3, 22.4, 26.1, 27.1, 29.6 and 33.5. After reuse of the catalyst there is significant loss in intensity at peaks 11.1, 22.4, 26.1 and 33.5 while the other peaks remain intact with small change in intensity. This indicates a considerable distortion in the catalyst during recycle [63]. This suggests that the diffraction planes associated with these peaks could be involved in the promotion of catalysis, while the other planes remain inert to catalytic activity (Fig. 5.30 A,B,C).

![Figure 5.30 PXRD Pattern of complex (15) (A) Unused complex (B) After 1st use (C) After 2nd use](image)

The copper (II) thiocyanate bound complex (16) shows sharp peak at 20 7.9, 10.1, 16.4, 19.8, 25.0, 26.7 and 38.6. After reuse of the catalyst there is significant loss in intensity at peaks 7.9, 10.1 and 25.0 while the peak at 19.8 increases in intensity. This indicates a some distortion in the catalyst during recycle [63].
suggests that the diffraction planes associated with peaks that shows changes could be involved in the promotion of catalysis, while the other planes remain inert to catalytic activity [55] (Fig. 5.31 A, B).

![Figure 5.31. PXRD Pattern of complex (16) (A) Unused complex (B) After 1st use](image)

**Table 5.3 :** The percentage conversion of the alkynes products using copper complexes of L4(13) to (16)

**Table 5.3a: **Percentage conversion of products using complex (13) and (14) at pH 7.0 with TBHP

<table>
<thead>
<tr>
<th>Complex</th>
<th>Substrate</th>
<th>Products</th>
<th>% Conversion</th>
<th>Total Conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(L)Cl (13) Propyne</td>
<td>1-Phenyl</td>
<td>Ph-CO-CO-CH₃</td>
<td>19%</td>
<td>49%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ph-C=C-CHO</td>
<td>17%</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ph-COOH</td>
<td>13%</td>
<td></td>
</tr>
<tr>
<td>Cu(L)Br (14) Propyne</td>
<td>1-Phenyl</td>
<td>Ph-CO-CO-CH₃</td>
<td>11%</td>
<td>47%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ph-C=C-CHO</td>
<td>23%</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ph-COOH</td>
<td>13%</td>
<td></td>
</tr>
</tbody>
</table>
### Table 5.3b: Percentage conversion of products using complex (15) and (16) at pH 7.0 with TBHP

<table>
<thead>
<tr>
<th>Cu(L)NO₃ (15)</th>
<th>Substrate</th>
<th>Conversion (%)</th>
<th>Total Conversion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-Phenyl Propyne</td>
<td>Ph-C-O-CO-CH₃</td>
<td>23</td>
<td>60</td>
</tr>
<tr>
<td></td>
<td>Ph-C=C-CHO</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ph-COOH</td>
<td>17</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ph-CO-CH₂-CH₂-COOH</td>
<td>11</td>
<td></td>
</tr>
<tr>
<td>1-Phenyl Pentyne</td>
<td>Ph-C=C-C-CO-CH₃</td>
<td>17</td>
<td>38</td>
</tr>
<tr>
<td></td>
<td>Ph=COOH</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>Cu(L)SCN (16)</td>
<td>Ph-CO-CO-CH₃</td>
<td>13</td>
<td></td>
</tr>
<tr>
<td>1-Phenyl Propyne</td>
<td>Ph-C=C-CHO</td>
<td>10</td>
<td>33</td>
</tr>
<tr>
<td></td>
<td>Ph-COOH</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ph-CO-CH₂-CH₂-COOH</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>1-Phenyl Pentyne</td>
<td>Ph-C=C-C-CO-CH₃</td>
<td>11</td>
<td>24</td>
</tr>
<tr>
<td></td>
<td>Ph=COOH</td>
<td>6</td>
<td></td>
</tr>
</tbody>
</table>

### Table 5.3c: Percentage conversion of products using complex (15) at pH 9.0 with TBHP

<table>
<thead>
<tr>
<th>Complex</th>
<th>Substrate</th>
<th>At pH 9.0 %Conversion</th>
<th>Total Conversion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(L₄)NO₃</td>
<td>Ph-C-O-CO-CH₃</td>
<td>25%</td>
<td></td>
</tr>
<tr>
<td>1-Phenyl Propyne</td>
<td>Ph-C=C-CHO</td>
<td>42%</td>
<td>81%</td>
</tr>
<tr>
<td></td>
<td>Ph-COOH</td>
<td>14%</td>
<td></td>
</tr>
</tbody>
</table>

### Table 5.3d: Percentage conversion of products using complex (15) at pH 4.0 with TBHP

<table>
<thead>
<tr>
<th>Complex</th>
<th>Substrate</th>
<th>At pH 4.0 %Conversion</th>
<th>Total Conversion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(L₄)NO₃</td>
<td>Ph-C-O-CO-CH₃</td>
<td>47%</td>
<td></td>
</tr>
<tr>
<td>1-Phenyl Propyne</td>
<td>Ph-C=C-CHO</td>
<td>17%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ph-COOH</td>
<td>5%</td>
<td></td>
</tr>
</tbody>
</table>
Table 5.3e: Percentage conversion of products using complex (15) at pH 9.0 with H₂O₂

<table>
<thead>
<tr>
<th>Complex</th>
<th>Substrate</th>
<th>With H₂O₂</th>
<th>%Conversion</th>
<th>Total Conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(L4)NO₃</td>
<td>1-Phenyl Propyne</td>
<td></td>
<td></td>
<td>Ph-C=CO-CH₃ 6%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Ph-C=CHO        8%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Ph-COOH         4%</td>
</tr>
</tbody>
</table>

Table 5.3f: Percentage conversion of products using complex (15) at pH 9.0 with TBHP in presence of surfactant

<table>
<thead>
<tr>
<th>Complex</th>
<th>Substrate</th>
<th>At pH 9.0</th>
<th>%Conversion</th>
<th>Total Conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(L)NO₃</td>
<td>1-Phenyl Propyne</td>
<td></td>
<td></td>
<td>Ph-C=CO-CH₃ 14%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Ph-C=CHO        5%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Ph-COOH         3%</td>
</tr>
</tbody>
</table>

Effect of pH, Oxidant and Surfactant on the oxidation of Alkynes

All the complexes show efficient heterogeneous catalysis for the oxidation of 1-phenylpropyne and 1-phenyl pentyne. In case of 1-phenyl propyne the products are the diketone, aldehyde and acid. For all the catalyst, the conversion to the diketones is highest followed by the aldehyde and acid. No specific selectivity could be observed for the four catalyst employed. The overall conversion (60%) to the three products is highest for the complex [Cu(L4)NO₃] in this series. With 1-phenyl pentyne the overall conversion are found to be lower, 38% and 33% for the two catalyst employed. However in this case no diketone are generated rather a mono ketone with the triple bond intact is found to be the major product (Table 5.3).

When the oxidation reaction of 1-phenylpropyne is carried out at pH 9.0 by adding to the reaction mixture sodium acetate (0.6 ml, 10 mM.). The yield of the aldehyde is found to be much higher than the diketone and the total yield is enhanced to 81%; while the same reaction at pH~4.0 results in a higher yields for the diketone. The data
reveals that the catalyst [Cu(L4)NO$_3$] is relatively more selective for the aldehyde (42%) in basic medium, while it has greater selectivity for the diketone (47%) in acidic medium (Table 5.3 c,d).

Utilization of another oxidant like H$_2$O$_2$ at pH~9.0 results in much poorer yields. Thus the oxidizing reaction is catalyzed to a greater extent by the copper (II) complexes in the presence of tert butyl hydroperoxide rather than H$_2$O$_2$. Addition of a surfactant CTAB (Cetyl trimethyl ammonium bromide) causes inactivation of the catalyst even in the presence of tert butyl hydroperoxide (Table 5.3).

Upon comparing the morphology changes of [Cu(L4)NO$_3$] after the oxidizing reaction is complete, it is found that the initial rod like morphology changes to cluster type for reaction at pH ~7.0 and pH ~9.0. Figure 5.28, yet the percentage yield is much higher for reaction at pH~ 9.0 rather than pH~ 7.0. This suggests that the morphology is not found to have any profound effect on the oxidation of phenyl alkynes.
References


32. Calderazzo, F.; Marchetti, F.; Pampaloni, G.; Passarelli. V. J. Chem. Soc., 


