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REGULAR ARTICLE

Homogeneous oxidation of alcohol and alkene with copper (II) complex in water

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Abstract. A new water-soluble copper(II) complex bearing 4-bromobenzoate/2,2'-dipyridylamine ligands was successfully synthesized and characterized by using single crystal X-ray diffraction and spectroscopic techniques. The catalytic activity of the compound was investigated as a homogeneous catalyst in the oxidation of several alcohols (benzyl alcohol, cinnamyl alcohol, 1-phenylethanol, cyclohexanol, 1-heptanol) and alkenes (styrene, ethylbenzene, cyclohexene) in aqueous medium. The copper(II) catalyst was found to be active for the studied alcohols and alkenes. H_2O_2 was used as an active oxidant for alcohol oxidation, while *t*-BuOOH (TBHP) was used for alkenes. The compound exhibited high selectivity toward benzaldehyde (88%) in cinnamyl alcohol oxidation under mild conditions (70 °C) after 4 h. Particularly, remarkable results were obtained for the oxidation of styrene and cyclohexene; transformation *via* allylic oxidation to 2-cyclohexene-1-one as one product in 2 h ($\text{TOF} = 50\,\text{h}^{-1}$) and benzaldehyde in 1 h (100% conversion, TOF = 86 h^{-1}, 100% selectivity). The Cu(II)/TBHP (or H_2O_2)/H_2O system proved to be an alternative for catalytic oxidations in the green chemistry concept.

Keywords. Copper (II) complex; oxidation; alcohol; alkene.

1. Introduction

Chemical reaction in green solvent systems is one of the major investigation areas of green synthesis. The number of published environmentally friendly catalytic systems in the literature is increasing over time. There are many examples of catalytic reactions performed in supercritical fluids,[1] ionic liquids,[2] fluorous solvents,[3] or solvent-free systems.[4,5] Reactions especially applied in water solvent systems are extremely important because they have many advantages, such as non-toxicity, absence of hazards, low wastage in production, economical method, and so on. Water has been used as a solvent in many types of transition metal-catalyzed reactions, *i.e.*, carbonylation,[6] arylation,[7] hydroformylation,[8] and hydrogenation.[9] In synthetic chemical production processes, such as those in the dye, pigment, medicine, and perfume industries, selective alcohol and alkene oxidations are important reactions for obtaining numerous starting or intermediate chemicals, aldehydes, ketones, diols, and carboxylic acids. Expensive transition metal catalysts, *i.e.*, as palladium,[10] platinum,[11] and ruthenium[12] have been reported to be efficient catalysts for alcohol and alkene oxidations in water. Compared to the aforementioned high-cost metal compounds, relatively low-cost metal catalysts, such as copper,[13] iron,[14] and manganese[15] compounds are a lot scarce for homogeneous catalytic oxidations in water. In this respect, the catalytic oxidation of alcohol and alkenes in water to the corresponding products has always attracted interest in the past decade.[13,16–22]

Many copper complexes have been found to catalyze for peroxidative oxidation in homogeneous and heterogeneous catalytic systems.[23–27] Some Cu–Schiff base complexes in a heterogeneous system can lead to a higher yield (∼90%, TOF = 18.2 h^{-1}) of products in cyclohexene oxidation.[28] Mizar *et al.*, published a study of an effective catalyst for benzyl alcohol for benzaldehyde transformation with copper(II)-2-N-arylpyrrolecarbaldimine catalysts under atmospheric oxygen pressure at 80 °C within 2 h in water (yield : 68–99%).[29] Hu *et al.*, synthesized and used some copper complexes with tetradentate pyridyl-imine terminated

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Schiff base ligands to investigate their aerobic alcohol oxidation activities in aqueous media.[30]

To the best of our knowledge, water-soluble carboxylate-Cu(II)-catalyzed reactions of alkenes to ketones and also the oxidation of alcohols in water are very scarce. Recently, we published a successful application of a new copper(II)/triphenylacetic acid/bipyridyl complex for oxidation of primary and secondary alcohols with H_2O_2 under mild conditions in pure water.[31] Water-soluble copper(II) complexes with sulfonic-functionalized arylhydrazone of β-diketone are used as catalyst precursors for the selective peroxidative (with TBHP) allylic oxidation of cyclohexene to cyclohex-2-enol (Cy-ol) and cyclohex-2-enone (Cy-one) with a total yield of ∼70% and TONs of up to 350,[29] but that is lower than those (>90%) we observed in our Cu(II)-complex. Copper(II) catalytic systems with mixed-ligand aminoalcohol-dicarboxylate coordination polymers act as homogeneous catalysts in aqueous acetonitrile under mild conditions (50–60 °C): the oxidation of cyclohexene through H_2O_2 and in the presence of a trifluoroacetic acid promoter results in total product yields (∼15–18% based on the substrate).[32–36] Cu-MOF, $[Cu(bpy)(H_2O)_2(BF_4)_2(bpy)]$ (bpy: 4,4'-bipyridine), exhibited catalytic activity and high selectivity in the allylic oxidation of cyclohexene with molecular oxygen under solvent-free conditions (TON = 13–37).[25] However, these catalysts show lower selectivity than our systems. Therefore, the title Cu(II)-complex is the best catalyst precursor for selective allylic cyclohexene oxidation, which results in the formation of ketone as a single product.

Herein, we present a new water-soluble copper(II)/4-bromobenzoate/2,2'-dipyridylamine complex ($[Cu(OOC(C_6H_5)Br)(C_{10}H_9N_3)](ClO_4)$) and its successful application for selective oxidation of alcohols and alkenes under mild reaction medium (70 °C) with H_2O_2 or *t*-BuOOH in green solvent water.

2. Experimental

2.1 *Materials and Physical measurements*

All chemicals were obtained from commercial companies (≥ 98%, Sigma-Aldrich and Merck, Germany) and used without further purification. IR spectra were recorded with Jasco FT/IR-300 E Spectrophotometer using KBr pellets between 4000 and 400 cm^{-1}. UV spectra were recorded using a Shimadzu UV-2450 spectrophotometer. Crystallographic data were collected with Bruker APEX II CCD using Mo-Ka radiation at room temperature and corrected for absorption with SADABS. A complex structure solution was performed using direct methods. Non-hydrogen atoms were refined anisotropically using full-matrix least squares on F2.

2.2 *Synthesis of complex,* ($[Cu(OOC(C_6H_5)Br)(C_{10}H_9N_3)](ClO_4)$),*([aqua(4-bromobenzoato)(2,2'dipyridylamine)copper(II)](perchlorate))*

Neutralized solution of 4-bromobenzoic acid (100 mg, 0.49 mmol, 10 mL methanol) with sodium hydroxide (19.5 mg, 0.49 mmol) was added dropwise to the methanolic solution of copper(II) perchlorate hexahydrate (10 mL, 181 mg, 0.49 mmol) at 50 °C for 2 h. Then, 2,2'-dipyridylamine solution in methanol (84 mg, 0.49 mmol, 5 mL) was reacted overnight with a metal salt-bromobenzoate solution to obtain a copper(II) complex. Dark-blue crystals were obtained from the evaporation of the solvent after 7 days (180 mg, yield 69%, M.p.: 250 °C) FT-IR (KBr; ν, cm^{-1}) (s. strong; m. medium; w. weak): 3416w ν_{N-H}; 1590m $\nu_{C=N}$; 1644m $\nu_{COOasym}$; 1484m ν_{COOsym}; 1530m $\nu_{C=N-C=C}$; 1114m ν_{O-H}; 1088s ν_{C-O}; 769m ν_{C-N}; 625m $\nu_{Cu-O-Cu}$ UV–Vis λ_{max} nm (CH_3CN): 244. 295. 312. Magnetic moment (μ) = 1.4 B.M. at room temperature.

2.3 *X-ray crystallography*

Diffraction data for the complex collected with Bruker AXS APEX CCD diffractometer equipped with a rotation anode at 296 (2) K, respectively using graphite monochromated Mo Kα radiation at $\lambda = 0.71073$ Å. The data reduction was performed with the Bruker SMART program package.[37] The structures were solved by direct methods and the non-hydrogen atoms were located through subsequent difference Fourier syntheses.[38] Structure solution was found with the SHELXS-97 package using the direct methods and were refined SHELXL-97[39] against F^2 using first isotropic and later anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were added to the structure model at calculated positions. The molecular drawing was obtained using MERCURY.[40] Geometric calculations were performed with PLATON.[41]

2.4 *General procedure for alcohol/alkene oxidation*

Alcohol or alkene (9.3×10^{-4} mol) (substrate/catalyst ratio = 100) copper catalyst (9.3×10^{-6} mol) and oxidant H_2O_2 (2 mL, 1.92×10^{-4} mol) or *t*-BuOOH (2 mL, 1.4×10^{-2} mol) were mixed in 10 mL water in a 50 mL reaction flask with a condenser at 70 °C for 24 h. Internal samples were taken from reaction media after certain time intervals for monitoring the substrate/product(s) percentage on a GC with an HP-5 quartz capillary column (30 m × 0.32 mm × 0.25 μm) and a flame ionization detector (FID). An unknown peak definition was made by analyzing real GC standards.

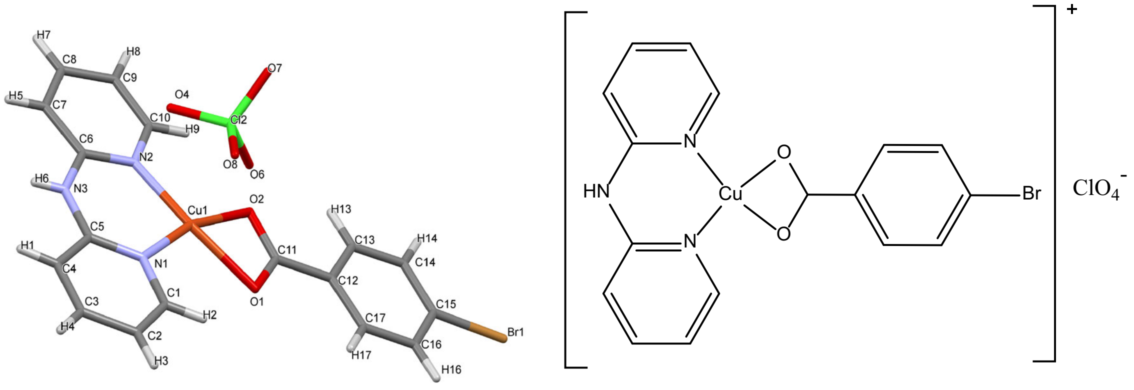


Figure 1. Molecular and ChemDraw structures of the complex **1**.

Table 1. Crystal data and structure refinement for complex **1**.

Empirical formula	$C_{17}H_{13}BrClCuN_3O_6$
Formula weight	534.20
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system, space group	monoclinic, P21/c
Unit cell dimensions	a = 7.018(3) Å alpha = 90 °
	b = 20.472(8) Å beta = 99.25(3)*degr*
	c = 13.619(6) Å gamma = 90 ^{o}
Volume	1931.3(13) A^3
Z, Calculated density	4, 1.837 Mg/m^3
Absorption coefficient	3.379 mm^{-1}
F(000)	1060
Crystal size	0.22 × 0.18 × 0.09 mm
Theta range for data collection	1.81 to 28.97 *degr*
Limiting indices	−9 <=h<=9, -27<=k<=24, -14<=l<=18
Reflections collected/unique	16900/4864 [R(int) = 0.0670]
Completeness to theta = 28.97	94.7%
Absorption correction	Integration
Max. and min. transmission	0.7507 and 0.5235
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4864/0/274
Goodness-of-fit on F^2	0.951
Final R indices [I>2sigma(I)]	R1 = 0.0570, wR2 = 0.1491
R indices (all data)	R1 = 0.1076, wR2 = 0.1777
Largest diff. peak and hole	0.580 and −1.052e.A^{-3}

3. Results and Discussion

3.1 *Structural analysis of the complex 1*

The copper(II)-complex, ([Cu(OOC(C_6H_5)Br)($C_{10}H_9N_3$)](ClO_4)), with 4-bromobenzoate (bba) and 2,2'-dipyridylamine (dpya) ligands, was successfully synthesized *via* the stoichiometric reaction of reactants in ethanolic solution. Dark-blue crystals were obtained through solvent evaporation within one week. The crystals of the compound exhibited monoclinic, P21/c and symmetry. The molecular structure of the compound **1** is presented in Figure 1. Crystallographic data, bond distances, and angles relevant to the metal coordination sphere of the compound **1** are listed in Tables 1–2.

Copper(II) has a disordered square planar geometry and is coordinated with two nitrogen atoms (Cu–N = 1.928 (4) and 1.938 (4) Å) from a chelating dpya ligand and two oxygen atoms (Cu–O = 1.976 (3) and 2.017 (3) Å) from the carboxylate group of the dpya ligand in μ^2 mode. The +2 charge on the copper ion is balanced with a coordinated deprotonated dpya and perchlorate anion as counter ion. The geometry is far removed from the ideal square plane, principally because of the "bite" of dpya (N1-Cu1-N2 = 95.34 (16)*degr*) and bba (O1-Cu1-O2 = 65.19(14)*degr*). Large deviations were

Table 2. Selected bond lengths (Å) and angles (*degr*).

Bond Lengths		Bond Angles	
Br(1)-C(15)	1.895(5)	N(1)-Cu(1)-O(2)	165.29(15)
Cu(1)-N(1)	1.928(4)	N(2)-Cu(1)-O(2)	98.38(14)
Cu(1)-N(2)	1.938(4)	N(1)-Cu(1)-O(1)	100.41(15)
Cu(1)-O(2)	1.976(3)	N(2)-Cu(1)-O(1)	161.48(15)
Cu(1)-O(1)	2.017(3)	O(2)-Cu(1)-O(1)	65.19(14)
C(10)-N(2)	1.346(6)	C(11)-O(1)-Cu(1)	87.3(3)
N(3)-C(6)	1.355(6)	N(2)-C(10)-C(9)	123.4(5)
N(1)-Cu(1)-N(2)	5.34(16)	O(1)-C(11)-O(2)	118.4(4)
		C(11)-O(2)-Cu(1)	89.1(3)
		C(6)-N(2)-Cu(1)	124.2(3)
		C(10)-N(2)-Cu(1)	117.3(3)
		C(5)-N(1)-Cu(1)	124.7(3)

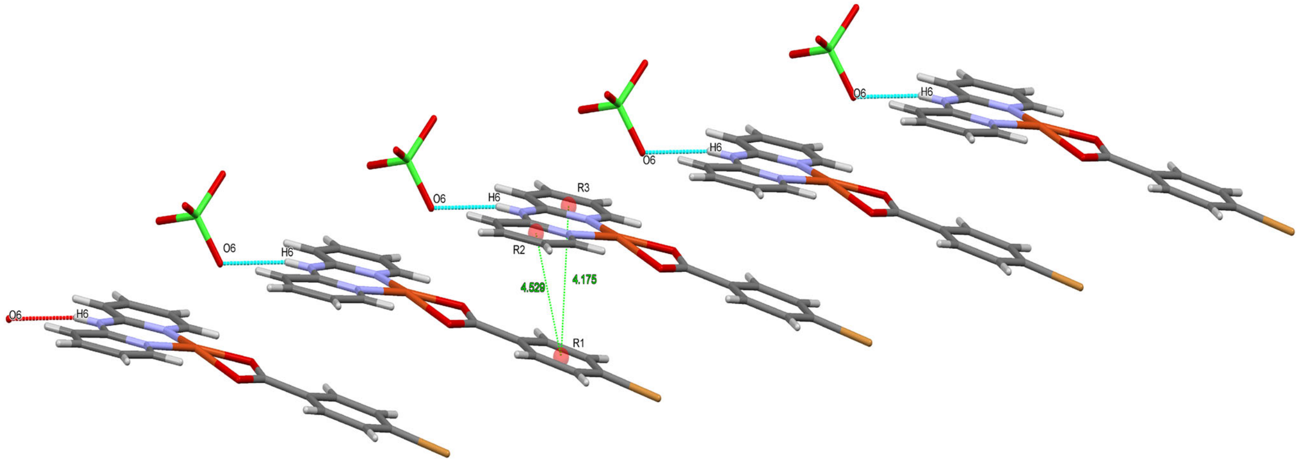


Figure 2. Chain formation of complex *via* hydrogen bonding and π ⋯ π interactions along *a* direction.

observed from 180*degr* for the N1-Cu1-O2 (165.29 (15)*degr*) and N2-Cu1-O1 angle (161.48 (15)*degr*). The chelate ring adopts an approximate plane conformation, which the observed torsion angles; C5N3N1C6 and Cu1O2C11O1 are –1.0(8)*degr* and 1.2(4)*degr*, respectively.

Weak intermolecular hydrogen bonding interactions are observed between the perchlorate ion and dpya. Two mononuclear units are linked by two N-H ⋯ O hydrogen bonds between the nitrogen atom of the coordinated dpya and the oxygen atoms of the lattice perchlorate ion, with an N3 ⋯ O6 distance of 2.898 (6) Å (N3 – H6 ⋯ O6). In addition, the $\pi \cdots \pi$ interactions between the two parallel rings of the dpya and bba ligands (R1=C12C13C14C15C16C17, R2=N1C1C2C3C4, and R3=N2C6C7C8C9C10), R1 ⋯ R2 = 4.529 Å and R1 ⋯ R3 = 4.175 Å, form a chain along *a* direction (Figure 2).

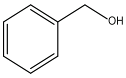
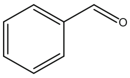
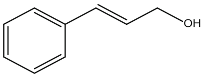
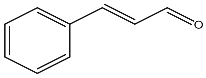
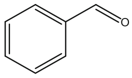
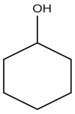
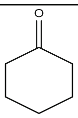
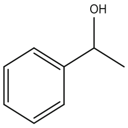
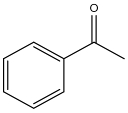
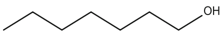
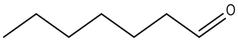
3.2 *Spectroscopic study*

The X-ray structure of the complex is consistent with the infrared spectra. The band observed between 3042 and 3094 cm^{-1} is attributed to the aromatic ν(C-H) vibration of two coordinated ligands. Carboxylate group asymmetric and symmetric vibration peaks were observed at 1644 and 1484 cm^{-1}, respectively. The neutral ligand azomethine ν(C=N) vibration peak difference between the coordinated and the uncoordinated form is found to be about 60 cm^{-1}, indicating that metal center and nitrogen atom coordination occurs. Two bands encountered at 625 and 769 cm^{-1} are related to the nitrogen atoms of dipyridylamine and metal center coordination.

The UV-Vis spectrum of the complex shows three absorption bands at 244, 295 and 312 nm in acetonitrile solution. The lower wavelength band is dedicated to anionic carboxylate group π → π* transitions. The other two absorption bands are related to the n → π* transitions of dpya ligand. Additionally, d → d transitions were not observed.

Based on the magnetic measurements of the solid Cu(II) complex at room temperature, the magnetic moment value is 1.4 B.M., and it is consistent with one unpaired electron system.

Table 3. Copper complex catalyzed oxidation of primary and secondary alcohols.

Entry	Substrate	Products, Conv. (%)	Total Conv.[b] (%)	TON/TOF (h^{-1})
1		 14 (1 min) 36 (2 h) 71 (6 h)	71 (6h)	71/12
2		  22 (1 min) 13 (1 min) 17 (2 h) 59 (2 h) 10 (4 h) 74 (4 h)	35 (1 min) 76 (2 h) 90 (6 h)	90/15 (6h)
3		 29 (6 h) 100 (24 h)	100 (24 h)	100/4 (24h)
4		 20 (1 min) 86 (6 h) 100 (24 h)	100 (24 h)	100/4
5		 13 (6h)	13 (6 h)	13/2

[a] Reaction conditions: alcohol (9.3×10^{-4} mol), catalyst (0.1 mol%), H_2O_2 (0.192 mmol), water (10 mL), T = 70 °C

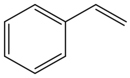
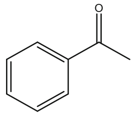
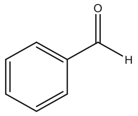
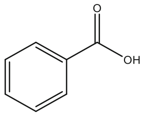
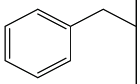
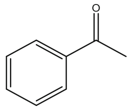
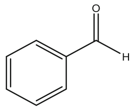
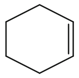
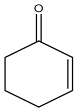
[b] Determined with GC analysis

3.3 *Catalytic experiments*

The catalytic oxidation reactions of primary/secondary alcohol and alkene were performed in a 50 mL round-bottom flask with a temperature-controlled magnetic stirrer at 70 °C. The experiments were carried out in water and H_2O_2 or TBHP as the oxygen source. Comparison of catalytic results was presented in Tables 3–4 and Figures 3–4. A blank experiment showed that the uncatalyzed oxidation of the studied alcohols and alkenes were negligible under the applied conditions.

The results indicated that a synthesized compound **1** has a catalytic effect on both the studied alcohol and alkene oxidations in water. The activity of the Cu(II)/H_2O_2/H_2O catalytic system is found to be higher in aromatic alcohols than in aliphatic ones. In a 6 h reaction time, the total % conversions of 90,

Table 4. Copper complex catalyzed oxidation of alkenes.

Entry	Substrate	Products, Conv. (%)	Total Conv.[b] (%)	TON/TOF (h^{-1})
1		 2 (1 h)  85 (1 h) 100 (4 h) 23 (24 h)  77 (24 h)	100 (4h)	86/86 (1 h) 100/25 (4h)
2		 62 (1 h) 97 (6 h)  2 (1 h) 2 (6 h)	100 (6 h)	64/64 (1 h) 100/17 (6h)
3		 71 (15 min.) 100 (2 h)	100 (2 h)	70/278 (15 min.) 100/50 (2h)

[a] Reaction conditions: alkene (9.3 × $^{-4}$ mol), catalyst (0.1 mol%), TBHP (14.5 mmol), water (10 mL), T = 70 °C
[b] Determined with GC analysis

86, 71, 29, and 13 were obtained for cinnamyl alcohol, 1-phenylethanol, benzyl alcohol, cyclohexanol, and 1-heptanol, respectively. Benzaldehyde was detected as a major product of both benzyl alcohol and cinnamyl alcohol oxidations (Table 3, Entries-2, 4, 1, 3, 5).

In benzyl alcohol oxidation, the substrate selectively converted to one product, benzaldehyde, with 71% formation in 6 h reaction time (Entry 1). Additionally, formation of the over oxidation product, benzoic acid, was not observed even when the reaction was prolonged to 24 h. In the oxidation of secondary alcohol phenyl ethanol, a TOF value of 1200 was reached at the first minute of the catalytic oxidation with 20% acetophenone formation. After a 6 h reaction time, acetophenone was the only product observed at 86% (Entry 4). The highest TOF value was obtained in allylic-type alcohol, cinnamyl alcohol oxidation (2100 h^{-1} at the first minute of the reaction with 35% total conversion). After a 4 h reaction time, conversion increased to 84%, and the aldehyde selectivity was found to be 88% as benzaldehyde (Entry 2). Cinnamaldehyde is a minor product with a selectivity value of 12% after 4 h. The result that needs to be emphasized is cinnamaldehyde carboxylation, which is converted to benzaldehyde through the carboxylation process as the reaction proceeds. As a cyclic alcohol, cyclohexanol was poorly oxidized to the corresponding ketone, and 29% cyclohexanone formation was obtained at 6 h reaction time (Entry 3). The lowest conversion rate was observed in 1-heptanol oxidation as the primary aliphatic alcohol (13% total conversion, Table 3, Entry 5). Generally, aliphatic alcohols are less reactive than aromatic alcohols, and these findings are in agreement with published results.[42,43]

In alkene oxidation reactions, hydrogen peroxide has been found to be an ineffective oxygen source. That is why TBHP was used as oxidant. The Cu(II)/TBHP/H_2O

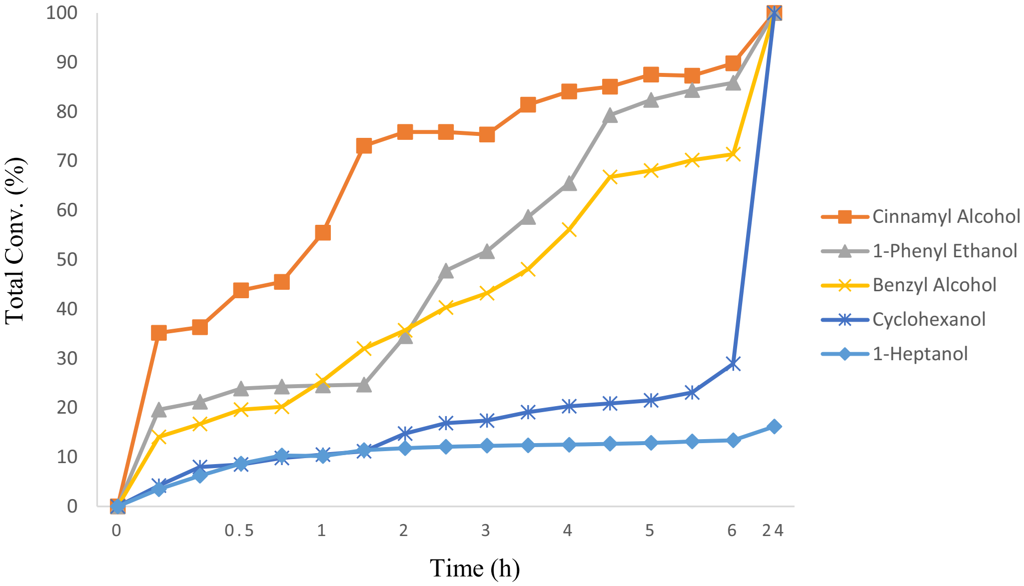


Figure 3. Comparison of alcohol oxidation with compound in water.

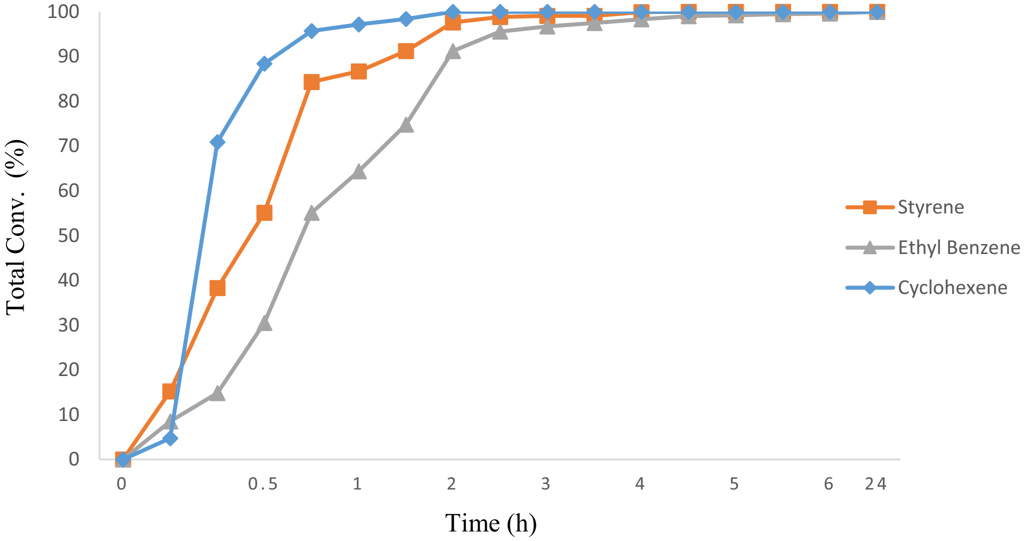


Figure 4. Comparison of alkene oxidation with compound in water.

catalytic system shows good activities of styrene, ethylbenzene, and cyclohexene oxidation with reasonably good selectivity (Table 4) at 70 °C. In styrene oxidation, acetophenone (2%) and benzaldehyde (85%, selectivity 98%) were observed in the initial period of reaction with a TON value of 87. After 4 h of reaction time, complete conversion of styrene to benzaldehyde was observed as the sole product. When the reaction continued, the over-oxidation product, benzoic acid, was obtained (77% after 24 h) (Entry 1). In ethylbenzene oxidation, acetophenone was obtained as a major product and changed from 62% (TOF = 64.4) to 97% (TOF = 17 h^{-1}.) within a 1–6 h reaction time (overall selectivity ~97%) (Entry 2). Among the studied alkenes, cyclohexene oxidation is the fastest catalytic reaction (in the first 15 min of the reaction time, 71% yield and TOF = 280 h^{-1}). In cyclohexene, the oxidation of the carbon-carbon double bond does not convert to cyclohexene oxide (epoxide) with TBHP, whereas the oxidation of the allylic C-H bond results in 2-cyclohexene-1-ol, which is further oxidized to 2-cyclohexene-1-one as one product within a reaction time of 2 h (TOF = 50 h^{-1}) (Table 2, Entry 3).

The adopted Cu(II)/TBHP(or H_2O_2)/H_2O system was simpler, greener, and more efficient for alcohol and especially alkene oxidation under mild reaction conditions. A clean oxidant H_2O_2 was used since it produces water, and more importantly, using water as a solvent is an important feature of a green chemical reaction.

It should be emphasized that such level of yields is extremely good in the field of alkene (particularly cyclohexene) oxidation, especially for the inertness of the saturated hydrocarbon and mild reaction conditions.[44,45] The obtained products and yields are also comparable with or even superior to those achieved using other related copper catalysts bearing carboxylate and N-based ligands.[32–36]

4. Conclusions

We have developed a new water-soluble copper(II)-complex (**1**) as a catalyst precursor bearing 4-bromobenzoate and neutral 2,2'-dipyridylamine ligands. The compound has been fully characterized using X-ray and other spectroscopic techniques. It is found that compound is an active catalyst for the peroxidative oxidation of alkenes and alcohols with H_2O_2 and/or TBHP under mild conditions without any promoter in water, a green solvent system. In particular, high conversions for alkene oxidation, and an excellent selectivity for 2-cyclohexe-1-one for cyclohexene oxidation in water were obtained. Using a low-cost catalyst, TBHP/H_2O_2, and water as solvent made our catalytic system attractive and environmentally sustainable.

Supplementary Information (SI)

All spectroscopic measurement data (FT-IR, UV-Vis and Single crystal x-ray structure) are given in supplementary file. CCDC 1578707 contains the supplementary crystallographic data for the compound **1**. These data can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary Information is available at www.ias.ac.in/chemsci

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