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Dimeric copper(II) tetracarboxylates as catalysts in the selective epoxidation of styrene

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ABSTRACT

Dicopper(II) tetracarboxylate complexes of the type $[Cu_2(\mu-O_2CR)_4L_2]$ have received a great deal of attention from inorganic chemists in the past. However, these well-known species have been rarely studied as catalysts. Herein we describe the synthesis, UV-visible spectral behavior and catalytic properties of six species of this type, viz. $[Cu_2(\mu-O_2CC_6H_5)_4(py)_2]$ (I), $[Cu_2(\mu-O_2CC_6H_5)_4(4-CNpy)_2]$ (II), $[Cu_2(\mu-O_2CC_6H_5)_4(3-CNpy)_2]$ (III), $[Cu_2(\mu-O_2CC_7H_{15})_4(4-CNpy)_2]$ (V) and $[Cu_2(\mu-O_2CC_7H_{15})_4(3-CNpy)_2]$ (V). As evidenced by their solid state and solution UV-visible spectra, these complexes retain their dinuclear integrity in solution and therefore they have been investigated as homogenous catalysts for styrene epoxidation. They exhibit very good to excellent catalytic activities towards the oxidation of styrene with aqueous *tert*-butylhydroperoxide (TBHP) as the terminal oxidant. The reactions give styrene oxide (SO) and benzaldehyde (Bzal) as products in varying proportions, but with good selectivity for SO. Under optimized conditions, a maximum of 82% selectivity towards SO is obtained at 78% styrene conversion catalyzed by I at room temperature.

Keywords: Dicopper(II) tetracarboxylates; Solid and solution UV-visible spectra; Cu-catalyzed oxidation; *tert*-butylhydroperoxide; Styrene epoxidation

1. Introduction

Aside from the applications angle as well as biological relevance, complexes of copper(II) occupy a position of prime importance in coordination chemistry, sometimes due to their structural significance and mostly due to their exceptional electronic properties. Among copper(II) complexes of various types, the dinuclear compounds of the type $[Cu_2(\mu-O_2CR)_4L_2]$ have received a good deal of attention due to their prototypical molecular structure resulting in

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superexchange-driven antiferromagnetism in the dimeric complexes [1]. Species of this kind have been used as secondary building units (SBUs) to form metal-organic framework compounds having potentially useful attributes [2], and their bonding and magnetic behavior have been studied in detail. In spite of this, these well-known dinuclear compounds have been rarely studied as catalysts for organic reactions. An earlier publication [3] from this laboratory demonstrated that these complexes display very good catalytic behavior in the oxidation of alcohols with *tert*-butylhydroperoxide (TBHP) as the oxidant. Presently, their catalytic behavior has been examined in the oxidation of styrene.

Transition-metal-catalyzed epoxidation is an important reaction [4] because epoxides find use as raw materials in the production of a variety of chemicals [5]. Further, the epoxidation of styrene is interesting because it is often found to be a challenging task to achieve high epoxide selectivity in view of a competing reaction leading to the formation of benzaldehyde as a co-product. In this context, it has been found worthwhile to explore options to replace processes practiced in the fine chemicals industry utilizing stoichiometric amounts of peroxy acids as oxidants for alkenes to obtain epoxides with environmentally acceptable catalytic ones. In such studies involving transition-metal-based catalysts, TBHP is often the oxidant of choice because of its lower sensitivity to metal contamination leading to safer handling compared with H_2O_2 or percarboxylic acids [6].

In view of the commercial importance of styrene oxide (SO) as an intermediate [7], and also due to the fact that the established routes for styrene to SO conversion often rely on environmentally undesirable steps [8], it is highly useful to explore the development of catalytic routes of styrene epoxidation which are environmentally friendly, and relatively easy and cheaper to implement. It has been demonstrated that cobalt [9] and manganese [10] complexes can catalyze olefin epoxidation; however, benzaldehyde (Bzal), phenylacetaldehyde (PA) and benzoic acid (Bzac) form as undesirable byproducts in most cases. To cite an important example [11], epoxidation of styrene at -78 °C with MCPBA as the oxidant and (salen)Mn as the catalyst affords SO in 99% yield. However, the requirement of using N-methylmorpholine-N-oxide (NMO) as an additive and the need to maintain the low temperature during the course of the reaction make the process cost-ineffective. Vanadium silicalite with ferrierite type topology has also been examined as a catalyst in styrene oxidation with molecular oxygen as the oxidant and TBHP as the initiator. A maximum selectivity of 59.18% for SO was observed by these authors at 373 K under 200 psi of pressure [12]. In a number of other reports [13,14,15] the selectivity towards SO has been stated to be low because of the formation of Bzal as the major product. On the other hand, in the oxidation of styrene over TS-1 catalyst, phenylacetaldehyde and Bzal are found to be the main products [16]. In case of a reported TBHP oxidation of alkenes catalyzed by ruthenium(II) a maximum of 27.9% selectivity for SO at 17.9% styrene conversion could only be achieved [17]. Copper(II) catalyzed styrene oxidation with TBHP was earlier shown [13] to yield as many as five products viz. SO, Bzal, Bzac, PA, and 1-phenylethane-1,2-diol.

Keeping in mind the above literature examples, and in continuation of earlier work published [3] from this laboratory demonstrating the suitability of the well-known compounds of the type $[Cu_2(\mu-O_2CR)_4L_2]$ as catalysts in alcohol oxidation with TBHP, we presently describe results on our investigation of several dicopper(II) tetracarboxylate complexes of the above type as catalysts for the oxidation of styrene under homogeneous condition in the liquid phase using aqueous TBHP as the oxidant.

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2. Material and methods

All materials utilized in the present study were obtained from commercial sources and used without further purification. Pyridine (E. Merck, India), 4-cyanopyridine (Aldrich, U.S.A.), 3-cyanopyridine (Aldrich, U.S.A.), styrene (Aldrich, U.S.A.), styrene oxide (Aldrich, U.S.A.), benzaldehyde (E. Merck, India), 70% aq. TBHP (Aldrich, U.S.A.), TBHP in decane (Aldrich, U.S.A.), 2,2,6,6-tetramethylpiperidine-N-oxyl radical, i.e. TEMPO (Aldrich, U.S.A.), sodium caprylate (E. Merck, India), copper(II) acetate monohydrate (E. Merck, India), copper(II) acetate monohydrate (E. Merck, India), copper(II) chloride dihydrate (E. Merck, India), 30% H₂O₂ (E. Merck, India) were all used as received. The sodium salt of benzoic acid was prepared by neutralizing the acid. While methanol used for synthesis was of reagent grade, acetonitrile used for recording UV-visible spectra of dicopper(II) tetracarboxylates was of HPLC grade (E. Merck, India). The magnetic Susceptibility measurements were carried out at 298 K on a Sherwood Mark 1 Magnetic Susceptibility Balance by Evans Method using Hg[Co(NCS)₄] 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. UV-visible spectra of solids were recorded in the diffuse reflectance mode using a Hitachi U-4100 spectrophotometer. BaSO₄ powder was used as reference (100% reflectance). FTIR spectra were recorded in the 500-4000 cm⁻¹ range 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. Procedures followed for single crystal X-ray crystallographic studies are given below in a separate section.

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2.1. Preparation of complexes

The complexes $[Cu_2(\mu-O_2CC_6H_5)_4(py)_2]$ (**I**), $[Cu_2(\mu-O_2CC_6H_5)_4(4-CNpy)_2]$ (**II**) and $[Cu_2(\mu-O_2CC_6H_5)_4(3-CNpy)_2]$ (**III**) have been prepared by following a general procedure in which 1 mmol of CuCl_2.2H_2O is stirred with 2 mmol of sodium benzoate in 20 mL methanol at room temperature for 10 min. To the resulting green solution, 1 mmol of the relevant pyridyl ligand is added and stirring is continued for 2 h. The resultant green precipitate is filtered off, washed with cold methanol and dried in a vacuum dessicator over fused CaCl_2 to obtain **I**, **II** and **III** in 66, 70 and 72 % respectively. $[Cu_2(\mu-O_2CC_7H_{15})_4(4-CNpy)_2]$ (**V**) and $[Cu_2(\mu-O_2CC_7H_{15})_4(3-CNpy)_2]$ (**VI**) have been obtained at 82 and 83 % respectively by following a procedure used earlier [18] for preparing an analogous species. The complex $[Cu_2(\mu-O_2CCH_3)_4(py)_2]$ (**IV**) has been prepared via a literature procedure [19]. The infrared spectral data on the complexes are listed in Table 1.

Table 1 Infrared spectral data on dicopper(II) tetracarboxylates (I-VI).

Compdound	IR Spectral Bands (cm ⁻¹)
$Cu_2(\mu - O_2CC_6H_5)_4(py)_2$ (I)	3422(s,br), 1628(s), 1593(s), 1400(s), 1354(sh), 1068(m), 1030(m),
	714(s), 690(s)
$Cu_2(\mu - O_2CC_6H_5)_4(4-CNpy)_2$ (II)	3445(s,br), 2237(w), 1624(s), 1592(sh), 1485(w), 1408(s), 1354(sh),
	1215(m), 721(s), 682(m), 559(m)
$Cu_2(\mu - O_2CC_6H_5)_4(3-CNpy)_2$ (III)	3414(s,br), 2249(w), 1620(s), 1608(s), 1589(s), 1404(s), 1350(sh),
	717(m), 687(m)
$Cu_2(\mu - O_2CCH_3)_4(py)_2$ (IV)	3445(s,br), 1620(s), 1593(s), 1508(w), 1435(m), 1384(m), 1350(m),
	1219(m), 1068(m), 1037(m), 814(s), 579(s)
$Cu_2(\mu - O_2CC_7H_{15})_4(4-CNpy)_2(V)$	342b(s,br), 3047(w), 2951(sh), 2924(s), 2843(s), 2241(w), 1612(s),
	1589(sh), 1554(sh), 1458(sh), 1431(s), 1416(s), 1315(m), 1223(m),
	1196(m), 1111(m), 1068(m). 1014(m), 826(s), 783(m), 721(m), 660(m),
	617(w), 559(m)
$Cu_2(\mu - O_2CC_7H_{15})_4(3-CNpy)_2$ (VI)	3445(s,br), 3105(sh), 3074(w), 2955(sh), 2924(s), 2855(s), 2237(m),
	1612(s), 1593(s), 1508(w), 1470(sh), 1423(sh), 1319(m), 1211(sh),

1188(m),	1126(m),	1115(m),	1064(w),	1041(m),	1030(m),	818(m),
791(sh), 7	/21(m), 698	8(m), 644(n	n), 559(w)			

2.2. X-ray crystallographic studies

A suitable crystal of compound **II** obtained via slow evaporation of its solution in methanol has been characterized by single crystal X-ray diffraction. The intensity data were collected on a Bruker AXS Smart Apex II CCD diffractometer. The structure was solved by direct methods (SHELXS-2013) and standard Fourier techniques, refined on F^2 using full matrix least squares procedures using the SHELXL-2013 [20] incorporated in WinGX [21] by following standard procedures. All hydrogen atoms could be easily found via difference Fourier synthesis and their positional and (isotropic) thermal parameters were freely refined along with all other parameters. Crystal and structure refinement data for the complex are presented in Table 2. The structural illustration was drawn using ORTEP-3 for Windows [22].

•	
Empirical formula	$C_{20}H_{14}CuN_2O_4$
Formula weight	409.9
Wavelength	0.71073 Å
Crystal system, space group	Tetragonal, $I4_1/a$ (#88)
Unit cell dimensions	a = b = 12.5697(4) Å, $c = 24.1212(12)$ Å
	$\alpha = \beta = \gamma = 90^{\circ}$
Volume	3811.1(3) Å ³
Z, Calculated density	8, 1.429 g/cm ³
θ range for data collection	1.83° to 28.44°
Limiting indices	-16<= <i>h</i> <=16, -15<= <i>k</i> <=16, -28<= <i>l</i> <=29
Absorption coefficient (mm ⁻¹)	1.17
F(000)	1672.0
Reflections collected / unique	18979 / 2335 [R(int) = 0.0274]
Completeness to $\theta = 25.442^{\circ}$	99.9%
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2335 / 0 / 153
R indices [†] [$I > 2\sigma(I)$]	R1 = 0.0289, wR2 = 0.0753
R indices [†] (all data)	R1 = 0.0636, w $R2 = 0.0910$

Table 2 Crystal and structure refinement data for $[Cu_2(\mu-O_2CC_6H_5)_4(4-CNpy)_2]$ (**II**)

Goodness-of-fit [*] on F^2	0.984
Largest diff. peak and hole	0.175 and -0.143 e.Å ⁻³
$^{\dagger}RI = \Sigma F_o - F_c / \Sigma F_o ; ^{\dagger}wR2 = \{ \Sigma$	$[w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2] \}^{\frac{1}{2}}$ where
$w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ with $P = [2]$	$F_c^2 + Max (F_o^2, 0)]/3.$
[*] GooF = $S = \{\Sigma[w(F_o^2 - F_c^2)^2] / (n-p)\}^{\frac{1}{2}}$.	

2.3. Oxidation of styrene

In a typical reaction, a required amount of the catalyst was added to a mixture of 0.52 g styrene (5 mmol) and 3 mL of 70% aqueous TBHP in a round-bottomed flask and the resultant mixture was magnetically stirred for 25 h at room temperature (~303 K). The reactions were generally performed in absence of any added solvent. To study the effect of temperature on the reaction, the flask was maintained at the specified temperature using an electrically heated oil bath. Progress of the reactions was monitored by gas chromatography (GC).

3. Results and discussion

3.1. Preparation and characterization of catalysts

In order to evaluate the catalytic activities of dicopper(II) tetracarboxylates in the oxidation of styrene, six analogous compounds of general formula $Cu_2(\mu-O_2CR)_4L_2$ have been synthesized (**Scheme 1**). To prepare complexes **I-III**, 1 mmol of a copper(II) salt was added to a neutralized solution of the appropriate carboxylic acid (2 mmol) in methanol. The solution was stirred for 10 minutes. Then 1 mmol of the pyridyl ligand (L) was added to it and the mixture was magnetically stirred for 2 more hours at room temperature. For the preparation of complexes **V** and **VI** commercially procured sodium caprylate was used instead of a neutralized solution of caprylic acid. As stated in the experimental section, the complex [$Cu_2(\mu-$

O₂CCH₃)₄(py)₂] (**IV**) was prepared using a literature procedure **Error! Reference source not** found.



Scheme 1

All six complexes are soluble in common organic solvents like methanol, acetonitrile, and acetone. This solubility behavior is indicative of the charge-neutral nature of the species. The dinuclear formulation of the compounds is supported by the observed magnetic moments of the compounds. The μ_{eff} values obtained for **I**, **II**, **III**, **V** and **VI** are 1.67, 1.68, 1.69, 1.65 and 1.63 BM respectively and all these values are lower than the expected spin-only magnetic moment of 1.73 BM / Cu for d⁹-Cu(II) complexes. Such lower-than-expected μ_{eff} values are known to be an outcome of antiferromagnetic exchange coupling effects in complexes that are analogous to Cu₂(μ -O₂CCH₃)₄(H₂O)₂ [1]. The dimeric molecular structure and also the antiferromagnetism of compound **IV** are already reported in the literature [23].

In these putatively dimeric complexes having the so-called 'paddle-wheel geometry', one would expect to see infrared absorptions attributable to $v_{asym}(COO)$ and $v_{asym}(COO)$ vibrations occurring with a Δv value of ~180 cm⁻¹ for the four equivalent, bridging carboxylato ligands [24]. In the present complexes of the type $Cu_2(\mu - O_2CR)_4L_2$, I-VI, where L is a N-donor ligand - pyridine, 4-cyanopyridine, or 3-cyanopyridine the pyridyl ring vibrations interfere with the asymmetric and symmetric carboxyl vibrations. A strong absorption occurring near 1590 cm^{-1} for all the complexes may be attributed to the $v_{asym}(COO)$ vibration, while the medium to strong absorptions around 1400 cm⁻¹ observed for all the complexes are likely to correspond to the $v_{sym}(COO)$ vibration of the carboxylate ligands present in the symmetrically bridging coordination mode. Weak bands near 2240 cm⁻¹ for **II**, **III**, **V** and **VI** are assigned to the nitrile group present at the 3- and 4-positions of the pyridyl rings of 3-CNpy and 4-CNpy. As mentioned earlier, the crystal structure of species IV was reported earlier in the literature [23]. The crystal structures of species V and VI also have been determined to find that these two compounds also have the commonly encountered dinuclear structure of paddle-wheel geometry [25]. The brief description of the molecular structure of II, as determined by single crystal Xray crystallography, is presented below as a representative case.

As shown in the ORTEP diagram of the molecular structure of **II** (Fig. 1), it is a binuclear complex having the familiar *paddle-wheel* or lantern geometry. In this structure, the two Cu centers are bridged by four benzoato ligands with the four O atoms on each Cu forming a square basal plane on which the pyridyl-N atom of the 4-cyanopyridine ligand takes up the apical position to give rise to two square pyramidal Cu(II) centers per molecule. The Cu···Cu distance is 2.6461(6) Å. This distance is shorter than those found in $[Cu_2(\mu-O_2CC_6H_5)_4(py)_2]$ (2.658 Å) [26] and $[Cu_2(\mu-O_2CC_6H_5)_4(4-Etpy)_2]$ (2.671 Å) [18]. The Cu–N bond length of 2.196(2) Å) is longer than the corresponding distances found in these two complexes (2.170 Å and 2.173 Å respectively). These differences in the bond lengths may be due to the electron withdrawing nature of the nitrile group present at the 4-position of the 4-CNpy ligand. In the analogous species $[Cu_2(\mu-O_2CCH_3)_4(4-CNpy)_2]$ reported [27] earlier from this laboratory, all metal-ligand bonds are of comparable length; however, the Cu...Cu distance of 2.600(1) Å in this compound is considerably shorter than that observed in **II**. This finding is ascribed to the difference in inductive effect between the methyl and phenyl groups in the bridging carboxylato ligands.



Fig. 1. A labeled ORTEP (30% probability) representation of complex $[Cu_2(\mu-O_2CC_6H_5)_4(4-CNpy)_2]$ (II).

Fig. 2 displays the UV-visible spectra of complexes **I-VI** recorded for their solutions in acetonitrile. The spectral data on the complexes in solution and solid phases are presented in Table 3.



Fig. 2. Solution phase UV-visible spectra of complexes I-VI.

Table 3	
UV-visible spectral data on complexes I-VI in solid and solution phases	

Species	λ, nn	Se Way	olid phase velength, n	m		
Ι	280 (3968)	385 (117)	704 (590)	290	382	725
Π	290 (3985)	384 (101)	692 (332)	295	392	711
III	305 (3985)	385 (112)	690 (582)	273	390	690
IV	250 (3439)	376 (109)	670 (100)	273	396	685
V	255 (3928)	382 (115)	670 (397)	294	384	686
VI	255 (3921)	381 (125)	672 (393)	286	384	682

Three absorptions occur in the solid as well as solution phase spectra shown by the species under study. The band at the higher energy region (250-305 nm) is believed to be of ligand origin, most probably the $\pi \rightarrow \pi^*$ transition of the pyridine ring – but, visibly influenced by the presence of phenyl ring of benzoato ligands in complexes **I**, **II**, and **III**. A more notable

feature appearing as a shoulder, approaching the shape of a broadened peak in a few cases, is observed around 385 nm for all the complexes. On the basis of the dependence of its intensity on temperature, it was earlier suggested that this absorption had origin in the spin singlet ground state of dicopper(II) tetracarboxylates [28]. This finding, in combination with the spectral traces presented in Fig. 2, clearly suggests that the absorption near 380 nm is indicative of the dimeric nature of the complexes [29]. The broad band occurring in the 670-704 nm range may be considered to be due to d-d transition for individual Cu²⁺ centers of distorted square pyramidal geometry, particularly because the present spectral results have been obtained at room temperature whereat both triplet and singlet spin states for the dinuclear complexes coexist. However, a more recent work supported by TD-DFT calculations on 'cupric acetate monohydrate' has revealed that the visible band may have its origin in configuration interactions between the ' σ - σ * transitions of the Cu–O bonds' [30].

The rather notable facet of the solution and solid state spectra presented in Fig. 3 is the close similarity of the spectra to suggest that the dimeric integrity of the species under investigation is maintained in the solution phase. This result is in consonance with an earlier finding which is based on magnetic measurements on solutions of copper(II) acetate monohydrate in non-aqueous media [31]. It is to be noted, however, that there is a systematic blue shift of the λ_{max} value of the visible band in the solution spectra of the compounds relative to the solid spectra. This is an indication of weakening of the Cu–N bonds in solution. As the Cu–N bond becomes weaker, the Cu–O bonds in the CuO₄ basal plane will become relatively stronger to maintain the electron neutrality over the whole complex molecule. This leads to a larger split of the d-d energy levels resulting in a blue shift of the band [29].



Fig. 3. UV-visible spectra of I in (a) acetonitrile and (b) solid state (recorded in the diffuse reflectance mode).

3.2. Catalytic studies

Encouraged by the catalytic activity shown by Cu(II) dimers of the type Cu₂(μ -O₂CR)₄L₂ in the TBHP oxidation of alcohols [3], and guided by UV-visible spectral evidence that the Cu(II) species under study retain their dimeric identity in the solution phase, we chose to examine dicopper(II) tetracarboxylate complexes **I-VI** as homogeneous catalysts in the TBHP oxidation of styrene in the liquid phase. Although as many as five products viz. styrene oxide (SO), benzaldehyde (Bzal), phenylacetaldehyde (PA), 1-phenylethane-1,2-diol (PED) and benzoic acid (Bzac) may form as a result of styrene oxidation [13], the present work involving styrene oxidation with TBHP has led to the formation of only two products viz. SO and Bzal (**Scheme 2**). The reactions have been generally carried out in absence of any added solvent, because the charge neutral complexes are soluble in the reaction mixture consisting of aqueous TBHP and styrene. Effect of temperature has been studied by performing the reactions at three different temperatures viz. room temperature (303-306 K), 323 K and 353 K. Additionally, the possible effect of an added solvent on the reaction has also been studied to evaluate if the

solvent-free condition is indeed preferable. To study this effect, reactions were carried out in acetonitrile and acetone. To find out the usefulness of TBHP as the oxidant, it was also examined if H_2O_2 could be used instead of TBHP. Aerobic oxidation of styrene was also investigated with and without TEMPO (2,2,6,6-tetramethylpiperidine-N-oxyl) as co-catalyst. The identity and yield of products in all cases are based on GC results.



Initial experiments were carried out to study the efficacy of all six Cu(II) complexes as catalysts for the oxidation process under study. For each test reaction a mixture of 0.52 g styrene (5 mmol), 0.13 mol% (0.0065 mmol) of the catalysts and 3 mL TBHP was stirred at room temperature for 25 hours. The results are presented in Table 4. It was observed that styrene conversion as well as SO yield was the highest with $[Cu_2(\mu-O_2CC_6H_5)_4(py)_2]$ (I) as the catalyst. A conversion of 78% was obtained where SO yield was 64% at a selectivity of 82%. For all the reactions Bzal was also obtained as a co-product along with SO. The formation of Bzal is likely to be an outcome of direct oxidative cleavage of the styrene side chain double bond via a radical mechanism [16].

TBHP oxidation of styrene catalyzed by various Cu(II) species Catalyst Selectivity^a Entry Time % Conversion SO (h)

25

Table 4

Ι

1

78

TON^b

600

Bzal

18

82

2	II	25	73	77	23	561
3	III	25	74	77	23	569
4	IV	25	52	81	19	400
5	V	25	67	79	21	515
6	VI	25	62	77	23	477
7	Cu(CH ₃ COO) ₂ .H ₂ O	25	61	76	24	469
8	CuCl ₂ .2H ₂ O	25	59	31	69	227

^a SO = styrene oxide; Bzal = benzaldehyde.

^b TON (turnover number) = moles of substrate converted to product per mole of catalyst.

Since selectivity towards SO is the highest in the reaction catalyzed by **I**, and also because SO happens to be the most desirable product in the reaction, we extended our experiments further by making use of only this complex as catalyst.

The effects of the amount of catalyst and the quantity of TBHP were studied and thus the reaction conditions were optimized for maximum selectivity toward SO. It is observed from data presented in Table 5 that the maximum selectivity toward SO may be obtained with 0.26 mol% (0.013 mmol) of the catalyst and 3mL of TBHP. In spite of this, entry 1 in the table may perhaps be considered as the best result under conditions used by us because of the hugely improved turnover number (TON) at only marginally lower selectivity for SO. Thus, the use of 0.13 mol% (0.0065 mmol) of compound **I** as the catalyst may be considered optimal for styrene epoxidation with 3 mL aq. TBHP at room temperature.

	•							
Entry	Amount of	Amount of	Temp	Time	%	Selectivity	TON	
	catalyst	TBHP (mL)	(°C)	(h)	Conversion	towards		
	(mol%)					SO (%)		
1	0.13	3	R.T.	25	78	82	600	
2	0.26	3	R.T.	25	78	86	300	
3	0.39	3	R.T.	25	61	52	156	

 Table 5

 Oxidation of styrene in presence of varying amounts of catalyst I and TBHP

4	0.13	2	R.T.	25	47	51	361
5	0.13	4	R.T.	25	65	65	500
6	0.13	5	R.T.	25	61	62	469

To study the effect of temperature, the reactions were performed at three different temperatures under optimized conditions (Table 6). As expected, a considerable increase in the conversion was observed with increase in temperature. When the reaction was carried out at 50°C, 100% conversion could be achieved in 9h, as compared to the 78% conversion obtainable at room temperature. No conversion was observed when the reaction was carried out at 5°C. The reaction became much faster on raising the temperature to 80°C, where 100% conversion was achieved only in 3h. However, the selectivity toward SO decreased linearly with increase in temperature, but Bzal selectivity became higher at higher temperatures. For the reaction carried out at 80°C the product distribution after 3h was: Bzal = 72%, SO = 28%. Although the substrate conversion was complete in 3h, the reaction was allowed to proceed for an additional hour to observe that Bzal yield increased up to 78% with 22% of SO. Therefore, it may be concluded that with time SO decomposes to Bzal during the course of the reaction. Thus, for achieving highest SO yield, the reaction needs to be carried out at room temperature.

Entry	Temperature	Time	Conversion	Selec	tivity (%)	
	(°C)	(h)	(%)	SO	Bzal	
1	5	255	0	-	-	
2	R.T. (~30°C)	25	78	82	18	
3	50	9	100	30	60	
4	80	3	100	28	72	
5	80	4	100	22	78	

 Table 6

 Effect of temperature on TBHP oxidation of styrene catalyzed by I

The progress of the reaction with time under optimized condition has been studied. As expected, there is an increase in conversion of the substrate with increasing reaction time. As shown in Table 7, the substrate conversion in the reaction increases only marginally beyond 25 h with the conversion reaching 79% in 30 h from 78% in 25 h. The reaction was not studied beyond 30 h.

Table 7
Effect of time on styrene oxidation catalyzed by complex I

Entry	Time(h)	%	Selectivity (%)		TON
		Conversion	SO	Bzal	_
1	5	21	86	14	162
2	10	41	85	15	315
3	15	49	84	16	377
4	20	70	80	20	538
5	25	78	82	18	600
6	30	79	81	19	608

The same reaction was also studied under scaled up conditions. The amounts of substrate, catalyst and oxidant were increased 3.5 times to observe whether there was any change in substrate conversion and / or selectivity toward products. It can be seen from data presented in Table 8 that the selectivity towards SO improves from 82% to 93% in spite of the drop in the conversion rate from 82% to 76%. When 5.0-6.0 M solution of TBHP in decane was used instead of aqueous TBHP keeping the other conditions the same, the catalytic oxidation was still effective; however, the relative selectivity towards Bzal rises significantly. Apparently, aqueous TBHP is a better oxidant than non-aqueous TBHP for the conversion of styrene to selectively form the epoxide using the presently developed Cu^{2+} -catalyzed method.

Entry	Catalyst	Time	% Conversion	Selectivity		TON
		(h)		SO	Bzal	_
1	Ι	25	76	93	7	585
2*	Ι	25	73	67	33	561

 Table 8

 TBHP oxidation of styrene catalyzed by I under scaled up condition

Reaction condition: 17.5 mmol styrene (1.82g), 10.5 mL TBHP, 0.13 mol% catalyst, R.T. *TBHP, 5.0-6.0M solution in decane used instead of aqueous TBHP.

It has been stated above that in carrying out styrene oxidation with TBHP the reaction mixture consists only of the catalyst, substrate and the oxidant. The reaction has also been studied under optimized conditions using acetonitrile and acetone as solvents, where the catalytically active dinuclear complex is soluble to allow the reaction to take place homogeneously. It may be noticed from data presented in Table 9 that for both solvents the conversion as well as the product selectivities are almost the same, but in both cases the selectivity toward SO is poorer compared to the corresponding value obtained under solventfree condition. Our results clearly show that there is no particular advantage of using an additional solvent in the TBHP oxidation of styrene catalyzed by $Cu_2(\mu-O_2CR)_4L_2$. This redundancy of a reaction solvent may be viewed as a green chemistry advantage.

 Table 9

 TBHP oxidation of styrene catalyzed by I in presence of added solvents

Entry	Solvent	Time	%	% Selectivity		TON
		(h)	Conversion	SO	Bzal	_
1	Acetonitrile	25	69	79	21	531
2	Acetone	25	70	75	25	538

In order to examine if other oxidants also may be useful in styrene oxidation catalyzed by **I**, aq. H_2O_2 (30%) and air were also examined as oxidants in place of TBHP while keeping

all other conditions the same. By making use of an amount (30%) H₂O₂ which is equivalent to 3 mL of aqueous (70%) TBHP, i.e. 22 mmol, it was found that at the end of 25 h, there was only 28% styrene conversion, and the products consisted of 22% SO and 78% Bzal. Clearly, H₂O₂ is not an ideal oxidant for styrene oxidation catalyzed by dicopper(II) tetracarboxylate complexes. Aerobic oxidation of styrene was also found to be ineffective for the catalytic oxidation reaction under study. Whether or not TEMPO was used as the co-catalyst, there was no substrate conversion. In reactions aimed at aerobic oxidation of styrene with complex I as the catalyst, acetonitrile was used as a solvent to maintain homogeneity of the reaction mixture.

In order to obtain mechanistic information on the reaction under study, electronic spectral studies have been carried out. The spectra of the reaction mixture, recorded at the starting point and at the end of the reaction show significant differences between the two (Fig. 4). The d-d band for the dimeric Cu(II) complex in the reaction mixture at the beginning of the reaction occurs at 718 nm, while the same is observed at ~660 nm for the reaction mixture at the end of 25 h. As discussed earlier in Section 3.1, the visible spectral band due to d-d transition for I in acetonitrile occurs at 704 nm, while the same spectral transition occurs at 710 nm and 692 nm in MeOH and t-butanol respectively. The visible spectrum of compound I has also been studied in *t*-butanol because upon consumption of TBHP in the oxidation of styrene this tertiary alcohol forms as the product that remains as a component of the reaction mixture at the end of 25 h. Our studies also showed that while complex \mathbf{I} is not soluble in 70% aqueous TBHP, it is soluble in styrene wherein compound I shows a visible spectrum with $\lambda_{max} = 723$ nm. Since the highest styrene conversion observed by us at 30°C is ~80%, the final reaction mixture will consist of H_2O , TBHP, styrene, *t*-butanol, styrene oxide and benzaldehyde as liquid species. Since the λ_{max} value for the final reaction mixture (660 nm) is significantly different from the

value of \sim 718 nm for the reaction mixture at the beginning, the present result may be indicative of the presence other Cu(II) complex species along with complex **I** in the final reaction mixture.



Fig. 4. UV-visible spectra of the reaction mixture (a) at the beginning and (b) after 25 h.

Till now, at least three copper-oxygen species having side-on Cu^{III}-(μ - η^2 -peroxo)-Cu^{III}, bis(μ -oxo-Cu^{III}) and Cu^{III}-O-O-H (copper-hydroperoxide) have been proposed as intermediates in Cu(II)-catalyzed oxidation processes [13,32]. Therefore, although it is very difficult to propose an accurate reaction mechanism, it can be argued that as a result of interaction of the dinuclear catalyst with TBHP, there is a possibility of formation of the LCu³⁺–O· radical which could interact with styrene. Thus, a probable mechanism may be as shown in **Scheme 3**.



Scheme 3

A similar mechanism was proposed for Fe-catalyzed H_2O_2 oxidation of styrene. The formation of metal-oxy radical (Fe⁴⁺–O·) on the catalyst surface was thought to be involved in the initiation step of the reaction. It was concluded that the formation of Bzal was a result of further oxidation of SO formed in the first step by a nucleophilic attack of Fe⁴⁺–O· on styrene followed by cleavage of the intermediate carbon-carbon double bond [33]. Benzaldehyde may thus form by further oxidation of SO.

4. Conclusions

Through the present studies it has been demonstrated that the complexes of the type $Cu_2(\mu-O_2CR)_4L_2$ retain their dimeric identity in the solution phase. These complexes act as homogeneous catalysts in the oxidation of styrene using TBHP as the source of oxygen. No additives are necessary for the oxidation process. H_2O_2 and air (O_2) are not effective as oxidants

under these conditions. Use of an added solvent is unnecessary for the catalyzed reaction. The oxidation of styrene with TBHP can take place at room temperature with $Cu_2(\mu-O_2C_6H_5)_4(py)_2$ (I) as the catalyst favoring epoxidation with styrene conversion and epoxide selectivity comparable or better than examples available in published literature.

Appendix A. Supplementary data

CCDC <1837977> contains the supplementary crystallographic data for <**II**>. These data can be obtained free of charge via <u>http://www.ccdc.cam.ac.uk/conts/retrieving.html</u>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: <u>deposit@ccdc.cam.ac.uk</u>. The KBr phase infrared spectra of complexes **I-VI** and the UV-visible spectra of complex **I** in various solvent media are also deposited as supplementary information.

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