

Bis(2-[α -hydroxyethyl]benzimidazolato)copper(II) anchored onto chloromethylated polystyrene for the biomimetic oxidative coupling of 2-aminophenol to 2-aminophenoxazine-3-one

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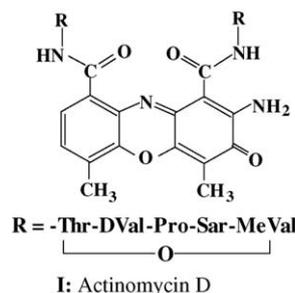
Abstract

2-(α -Hydroxyethyl)benzimidazole (Hhebmz) has been covalently anchored to chloromethylated polystyrene cross-linked with 5% divinylbenzene. This polymer-anchored chelating resin reacts with cupric acetate in presence of Hhebmz to give polymer-anchored copper(II) complex PS-[Cu(hebmz)₂]. Elemental analyses, FT-IR, electronic, scanning electron micrographs (SEM) and TGA-DTA pattern have been used to characterize the complex. Oxidative coupling of 2-aminophenol (OAP) to 2-aminophenoxazine-3-one (APX) catalyzed by PS-[Cu(hebmz)₂] in presence of air at 70 °C in DMF gave 62% substrate conversion over a period of 8 h. Kinetics of the above reaction indicated that the rate of oxidative coupling of OAP has a first order dependence with respect to substrate, catalyst and air pressure (dissolved O₂) concentrations in the range of conditions evaluated. Based on these observations, a plausible mechanism for the above reaction has been proposed. From, the study on the effect of temperature on the rates of oxidative coupling, an activation energy 34.2 kcal/degree mole was evaluated from Arrhenius plot of $-\ln$ rate versus $1/T$. Enthalpy, entropy and free energy were calculated using standard thermodynamic equations for the above reaction. © 2005 Elsevier B.V. All rights reserved.

Keywords: Bis(2-[α -hydroxyethyl]benzimidazolato)copper(II); Chloromethylated polystyrene; 2-Aminophenol; 2-Aminophenoxazine-3-one; Oxidative coupling

1. Introduction

The oxidative coupling of 2-aminophenol (OAP) to 2-aminophenoxazine-3-one (APX) through catalytic activation of dioxygen by transition metal complexes has been considered as one of the important reactions [1–10] because of the presence of 2-aminophenoxazine chromophore in Actinomycin D (see **I** for structure), a naturally occurring antibiotic. Actinomycin D is among the most potent antineoplastic agents known. It inhibits DNA directed RNA synthesis [11,12] and is used in the treatment of some kind of cancer of the bones and soft tissues like Choriocarcinoma, testis, Wilms' tumor, rhabdomyosarcoma, Kaposi's sarcoma and Ewing's sarcoma due to their high toxicity [13,14].



Copper and cobalt compounds (simple salts and complexes) [1–3], [Co(salen)] (H₂salen = *N,N'*-bis(salicylidene) ethane-1,2-diamine) [4,5], oxime and phthalocyanine based metal complexes [6–9,15] have been used as catalyst for the oxidative coupling of 2-aminophenol. TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy) initiated oxidation of OAP has been reported by Kaizer et al. [10]. An ex-

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ample dealing with copper(II)-aquo complex immobilised through the coordination with amino-functionalised HISiO_2 (hexagonal mesoporous silica) also appears in literature [16].

In the present investigation, we present our results on the preparation of a new polymer-anchored copper(II) complex of 2-(α -hydroxyethyl)benzimidazole (Hhebmz) and its catalytic activity towards the oxidative coupling of OAP to APX. To the best of our knowledge, this is the first report on the oxidation of OAP using homogeneous catalyst immobilized on polymer support. Immobilization of homogeneous catalysts onto polymer supports through covalent attachment has received attention because of the advantageous features of these heterogeneous catalysts to homogeneous systems. The polymer-supported catalysts enhance their thermal stability, selectivity, recyclability and easy separation from reaction products leading to the operational flexibility [17,18]. Chloromethylated polystyrene cross-linked with divinylbenzene is one of the most widely employed macromolecular supports for heterogenization of homogeneous catalysts [19–24].

2. Experimental

2.1. Material

Analytical reagent grade cupric acetate monohydrate, OAP and DMF were purchased from E. Merck, India and used as supplied. Chloromethylated polystyrene [18.9% Cl (5.3 mmol Cl/g of resin) and 5% cross-linked with divinylbenzene] was gifted by Thermax Limited, Pune, India. 2-(α -Hydroxyethyl)benzimidazole was prepared following the literature procedure [25]. High purity compressed air was obtained from INOX air products limited, Pune.

2.2. Characterization of catalysts

The C, H, N analyses of the polymer-anchored ligand/complex were obtained from Carlo ERBA (Italy) Model EA 1108 analyzer. Diffuse reflectance spectrum of catalyst was recorded on a Shimadzu UV–vis scanning spectrophotometer (UV-2500 PC) using barium sulphate as standard. Other spectra were recorded in DMF. FT-IR spectra of the solid samples were recorded on a Perkin-Elmer model 1600 FT-IR after grinding the sample with KBr. The copper content in the complex was measured by atomic absorption spectrometer (AAS-Hitachi Model Z-8000) after decomposing the complex with conc. HCl and diluting the filtrate with water to specific volume. A thermo gravimetric analysis of the complex was carried out using TG Stanton Redcroft STA 780. Scanning electron micrographs (SEM) of the polymer beads were obtained on a Leo instrument model 435 VP after coating the resin beads with thin film of gold to prevent surface changing and to protect the surface material from thermal damage by the electron beam.

2.3. Syntheses

2.3.1. Polymer-anchored

2-(α -hydroxyethyl)benzimidazole (PS-Hhebmz)

Chloromethylated polystyrene (3.0 g) was allowed to swell in DMF (30 ml) for 2 h. A DMF solution (40 ml) of 2-(α -hydroxyethyl)benzimidazole (1.458 g, 9 mmol) was added to the above suspension followed by the addition of triethylamine (4.50 g) in ethylacetate (100 ml). The reaction mixture was heated under reflux for 8 h with mechanical stirring in an oil bath. After cooling to room temperature, the creamish yellow resins were filtered off, washed thoroughly with hot DMF followed by ethanol and dried in air oven at 120 °C. Obs. for (PS-Hhebmz): C, 61.98; H, 8.25; N, 4.53%.

2.3.2. Synthesis of PS-[Cu(hebmz)₂]

Polymer-anchored ligand PS-Hhebmz (3.0 g) was allowed to swell in DMF (40 ml) for 2 h. A DMF solution of cupric acetate monohydrate (1.592 g, 8 mmol) was added to the above suspension and reaction mixture was heated at 90 °C in an oil bath with stirring for 8 h. After cooling to room temperature it was suction filtered, washed with hot DMF (10 ml) to remove excess of metal salt. A DMF solution (30 ml) of Hhebmz (1.296 g, 8 mmol) was further added to the resin and heated at 90 °C for 4 h in an oil bath while stirring. The polymer-anchored green copper complex thus obtained was filtered, washed with hot DMF (10 ml) followed by ethanol (5 × 5 ml) and dried in air oven at 120 °C. Obs. for [PS-Cu(Hhebmz)₂]: C, 59.34; H, 6.51; N, 4.91; Cu, 3.0%.

2.3.3. Synthesis of [Cu(hebmz)₂]

To a filtered methanolic solution of cupric acetate (0.40 g, 2 mmol in 10 ml) was added a methanolic solution (10 ml) of Hhebmz (0.648 g, 4 mmol) and the reaction mixture was refluxed on a water bath for 6 h. After cooling to room temperature, the colored product was filtered off, washed with methanol and dried at 120 °C in an oven. Yield: 55%. Obs.: C, 55.76; H, 4.88; N, 14.32%. Calc. for $\text{C}_{18}\text{H}_{18}\text{N}_4\text{O}_2\text{Cu}$: C, 56.02; H, 4.67; N, 14.52%.

2.3.4. Catalytic activity: oxidative coupling of OAP to APX

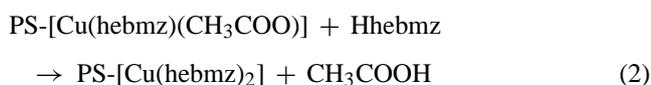
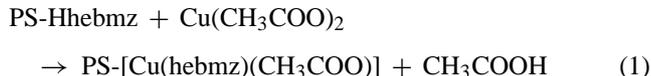
Oxidative coupling of OAP was carried out in a 300 ml Parr autoclave under purified air (O_2) pressure. The catalyst was allowed to swell in DMF (10 ml) for 2–3 h. Reaction mixture containing OAP (0.545 g, 5 mmol), catalyst (50 mg) and DMF (30 ml) was placed into autoclave. After pressuring the autoclave with air to 500 psig, the reaction mixture was heated to 70 °C under constant stirring. The reaction mixture was withdrawn at fixed time intervals and analyzed by UV–vis spectrophotometer (2101 PC). The percent conversion of OAP to APX was calculated through calibration plot method. Various parameters, such as temperature, pressure, amount of catalyst and substrate were varied in order to optimize the reaction for maximum conversion. After completion of the reaction for maximum conversion. After completion of the reaction for ca. 8 h, the reaction mixture was cooled to room tem-

perature and pressure was released. The reaction mixture was layered with diethyl ether (30 ml) and allowed to stand at ca. -20°C . After few hours (preferably over night) a red–violet material slowly crystallized out, which was suction filtered and recrystallised from benzene to give red–violet crystals of APX. Yield: 0.51 g, (47.8%). M.p: $254\text{--}256^{\circ}\text{C}$ (Lit. $254\text{--}256^{\circ}\text{C}$ [10]). Obs.: C, 67.61; H, 3.73; N, 13.0%. Calc. for $\text{C}_{12}\text{H}_8\text{N}_2\text{O}_2$: C, 67.92; H, 3.80; N, 13.20%; IR, electronic and ^1H NMR spectra match well with the authentic APX.

3. Results and discussion

3.1. Synthesis and characterization

The reaction of chloromethylated polystyrene (cross linked with 5% divinylbenzene) with 2-(α -hydroxyethyl) benzimidazole in DMF in presence of triethylamine leads to the formation of polymer-anchored ligand PS-Hhebmz. During this process, the NH group of benzimidazole reacts with $-\text{CH}_2\text{Cl}$ group as shown by Fig. 1. The elemental analysis of the polymer ligand suggests ligand loading of 1.617 mmol g^{-1} of resin. This anchored ligand on reaction with cupric acetate possibly gives an acetate coordinated complex in the first step [26], which in the presence of 2-(α -hydroxyethyl)benzimidazole gives the complex PS-[Cu(hebmz) $_2$] as shown by Eqs. (1) and (2).



The analytical data of the anchored-complex shows the formation of complex while metal (0.4720 mmol/g of resin) and ligand (0.8767 mmol/g of resin) loading suggests metal to ligand stoichiometry to be 1:2 (Obs. 1:1.8). Thermogravimetric analysis under oxygen atmosphere shows the stability of anchored-complex up to ca. 160°C and thereafter decomposes exothermically in several steps. The weight loss at various steps is not possible to calculate. However, the final residue of 3.8% at 750°C corresponding to CuO, which is nearly same to that observed by atomic absorption spectrometry. Thus, calculated efficiency of complex formation is about 29.

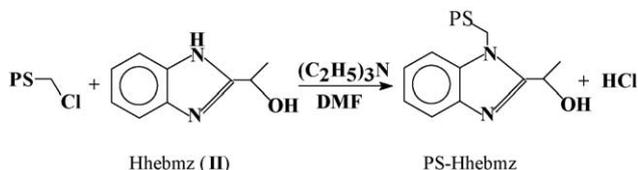


Fig. 1. Scheme to prepare PS-Hhebmz; PS represents the backbone of chloromethylated polystyrene.

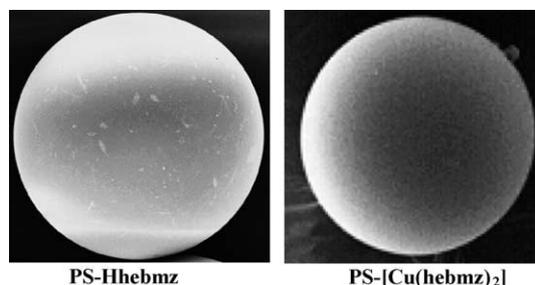


Fig. 2. Scanning electron micrographs (SEM) of PS-Hhebmz and PS-[Cu(hebmz) $_2$].

3.2. Scanning electron micrograph

Scanning electron micrographs for single bead of pure chloromethylated polystyrene, anchored-ligand and complexes were recorded to understand the morphological changes occurring at various stages. As expected pure polystyrene bead has smooth and flat surface while anchored ligand and complexes show very slight roughening of the top layer. This roughening is relatively more in the complex possibly due to interaction of copper ion with additional ligand along with the anchored one and to arrange in the fixed geometry of the complex. Accurate information on the morphological changes in terms of exact orientation of ligands coordinated to the metal ion has not been possible due to poor loading of the metal complex. Images of PS-Hhebmz and PS-[Cu(hebmz) $_2$] are presented in Fig. 2.

3.3. IR spectral studies

A weak broad band appearing at ca. 3400 cm^{-1} due to $\nu(\text{OH})$ and a broad features covering the region $2600\text{--}2850\text{ cm}^{-1}$ in the pure ligand Hhebmz indicate the presence of strong hydrogen bonding between hydrogen of the NH and oxygen of the alcohol groups [27,28]. On anchoring with polystyrene, the broad-featured band disappears suggesting the covalent bond formation after reaction between $-\text{NH}$ of ligand and $-\text{CH}_2\text{Cl}$ of polystyrene. In addition, all characteristic bands due to free ligand including a relatively stronger band at 3400 cm^{-1} due to $\nu(\text{OH})$ also appear. In neat as well as polymer-anchored copper complexes, all these characteristic bands also appear but coordination of ligand to metal can not be inferred unequivocally due to complexity in the spectral features. However, presence of several medium intensity bands in the $400\text{--}500\text{ cm}^{-1}$ region should suggest the coordination of oxygen and nitrogen of the ligand to the metal.

3.4. Electronic spectral studies

The UV–vis spectrum of ligand exhibits two intense bands in methanol at 276 ($\epsilon = 3454\text{ l mol}^{-1}\text{ cm}^{-1}$) and 283 nm ($\epsilon = 3252\text{ l mol}^{-1}\text{ cm}^{-1}$) due to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions, respectively [28]. In the reflectance spectrum of PS-[Cu(hebmz) $_2$] at least one band could be located at ca. 245 nm

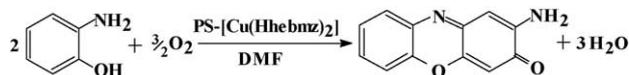


Fig. 3. Scheme representing catalytic reaction.

which is assigned to the $\pi \rightarrow \pi^*$ transition. In addition, a weak shoulder band in the visible region was also noticed at ca. 520 nm and this may be considered due to d–d transition as copper(II) has one unpaired electron in d-orbital. In nujol mull the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ appear at 225 and 281 nm while d–d transition appears as a broad band at ca. 580 nm. These data suggest the coordination of metal ion to polymer-anchored ligand.

3.5. Catalytic activity

Polymer-anchored complex PS-[Cu(hebmz)₂] catalyses the oxidative coupling of OAP to APX by dioxygen in DMF as shown by Fig. 3. The formation of APX was monitored by electronic absorption spectrophotometer as a function of time. A small aliquot was withdrawn from the reaction mixture at different time interval and absorption was recorded in the 300–600 nm ranges. Only APX absorbs at $\lambda_{\max} = 433$ nm in this region. The increments of absorption maxima due to the formation of APX for one of the reactions over a period of 8 h are shown in Fig. 4. From the absorption at $\lambda_{\max} = 433$ nm, the percent conversion of OAP to APX was calculated through absorption plot method. A series of standard solutions of varied dilutions were prepared from a standard solution of APX and the absorption maxima were noted at a fixed λ_{\max} value of 433 nm. Fig. 5 presents the calibration plot. From the concentration of APX obtained from the calibration plot the percent conversion of OAP to APX was calculated at different time.

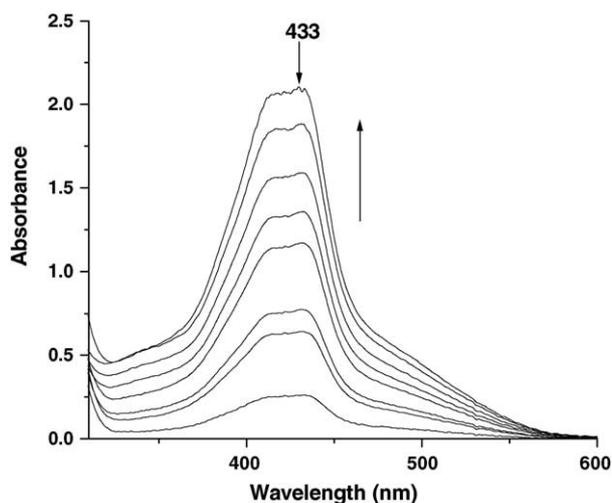


Fig. 4. Increment in the absorption band for the PS-[Cu(hebmz)₂] catalysed oxidative coupling of OAP to APX in DMF. Spectra were recorded during 8 h of reaction time.

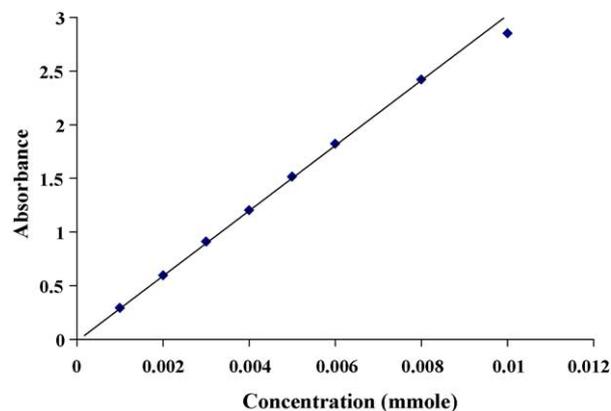


Fig. 5. Calibration plot.

The oxidative coupling of OAP was also carried out with neat [Cu(hebmz)₂] (50 mg) in DMF under identical conditions to that of immobilized complex. The results showed that polymer-anchored catalyst is at least four times more active than the neat one (Table 1). A big difference in turn over number (TON) has also been noted between neat and polymer-anchored complex. Literature mostly do not report catalytic conversion data but within the limited data available on other homogeneous catalysts, the catalytic activity of PS-[Cu(hebmz)₂] compares well with these except [Co(Hdmg)₂L₂] (H₂dmg: dimethylglyoxime, L: PPh₃, AsPh₃, SbPh₃) [6] and [Co(salen)] [5] where quantitative conversions have been reported. The dispersed active metal centres in the polymer matrix prevent the loss in the catalyst activity, generally not observed in homogeneously catalyzed reactions, and its high turn over number and recyclable property make it a better catalyst over homogeneous ones. Catalyst recycling studies were carried out by running a reaction with fresh reaction mixture and reaction was stopped after 8 h and conversion of OAP was estimated. Reaction mixture was filtered and the catalyst was separated, dried and recharged with the fresh reaction mixture and the reaction was carried out for another 8 h. Analysis of the reaction mixture in second cycle did not indicate the loss in its activity and conversion of OAP was nearly the same. This test ensured no appreciable metal or its complex leaching.

Table 1
Catalytic conversion of OAP^a

Compounds	% Conversion	TON ^b
[Cu(hebmz) ₂]	14	29.7
PS-[Cu(hebmz) ₂]	62	131.5
PS-[Cu(hebmz) ₂] first recycle	60	127.1

^a Reaction conditions: catalyst = 0.0236 mol, OAP = 0.546 g (5 mmol), temperature = 70 °C, pressure 800 psig, DMF = 30 ml.

^b TON: turn over numbers—number of moles of substrate converted per mole of catalyst.

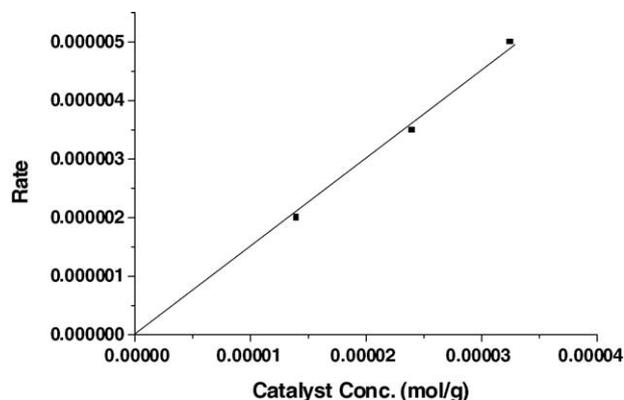


Fig. 6. Effect of catalyst concentration; conditions: OAP = 5 mmol, air = 500 psig, temperature = 70 °C, DMF = 30 ml.

3.5.1. Kinetic experiments

Kinetic experiments were conducted in a batch autoclave, and the effects of concentrations of catalyst, substrate, air pressure and temperature on the rate of reaction were evaluated by initial rate approach model. The details of the kinetic experiments conducted and kinetic parameters evaluated are described in the following text.

3.5.2. Effect of catalyst concentration

Rate of oxidative coupling of OAP dependence on catalyst concentration was studied by varying the catalyst concentration in the range (30–50 mg, 14.1×10^{-6} to 33.0×10^{-6} mol/g), keeping others parameters, such as OAP (5 mmol), air (500 psig), temperature (70 °C) and DMF (30 ml) constant. The graph of rate versus catalyst concentration shown in Fig. 6 indicated that it has a first order dependence with respect to catalyst concentration studied in the range.

3.5.3. Effect of substrate concentration

Substrate concentration was varied between 5 and 20 mmol while keeping other parameters constant, such as catalyst (50 mg, 23.6×10^{-6} mol/g), air (500 psig), temperature (70 °C) and DMF (30 ml) to study its effect on the rate of oxidative coupling of OAP. The graph of initial rate versus substrate concentration is shown in Fig. 7, which indicated a linear-first order dependence on the substrate concentration.

3.5.4. Effect of air pressure (dissolved O_2)

The dissolved concentration of O_2 was estimated from the air pressure maintained in solvent DMF taking the values of solubility of O_2 in the reaction medium [29]. The effect of air pressure (dissolved O_2) was varied in the range 200–1000 psig by keeping other parameters constant, such as OAP (5 mmol), temperature (70 °C), DMF (30 ml) and catalyst (50 mg, 23.6×10^{-6} mol/g). The rate of oxidative coupling of OAP measured as a function of dissolved O_2 is shown in Fig. 8, which showed that it also has a first order dependence on O_2 concentration. It means that both oxygen

transfer to substrate to give the product and follows a two-electron transfer mechanism.

3.5.5. Effect of temperature

To estimate the activation of the oxidative coupling of OAP, the temperature of the reaction was varied between 333 and 353 K, keeping other parameters OAP (5 mmol), catalyst (50 mg, 23.6×10^{-6} mol/g) and air pressure (500 psig) in DMF solvent as constant. From the Arrhenius plot of $-\ln$ rate versus $1/T$, activation energy of 34.2 cal/(degree mol) has been obtained from the slope of the straight-line graph shown in Fig. 9.

3.5.6. Proposed mechanism for the oxidative coupling of OAP

In the proposed mechanism, the catalyst interacts with a mole of OAP in a pre-equilibrium step (Eq. (3)) to form a mixed ligand complex inside the polymer matrix probably by expanding the coordination, which reacts with a mole of O_2 in a rate controlling step (Eq. (4)), to give hydroxyl species by exchanging with proton of OAP giving 2-aminophenoxy OAP \bullet free radical intermediate. OAP \bullet be-

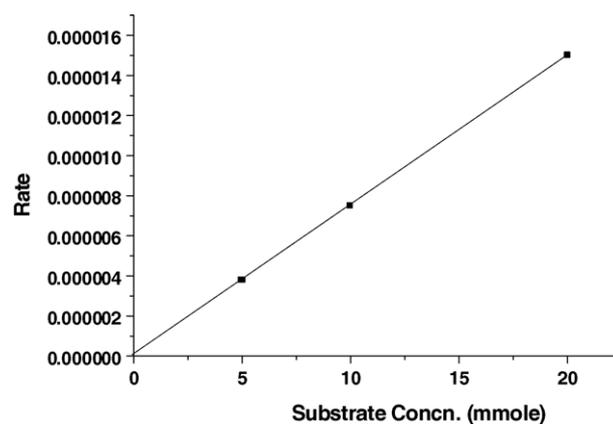


Fig. 7. Effect of substrate concentration; conditions: catalyst = 50 mg, air = 500 psig, temperature = 70 °C, DMF = 30 ml.

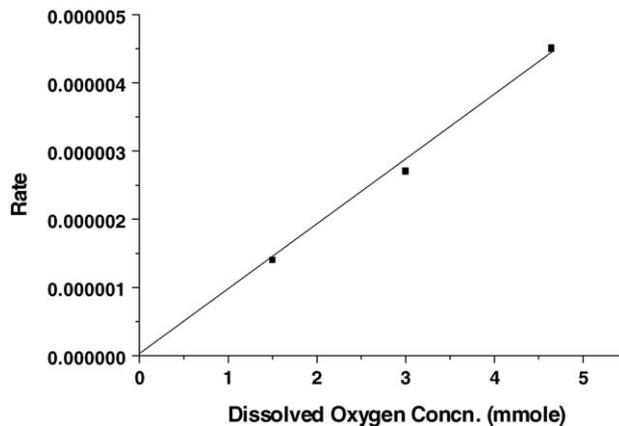
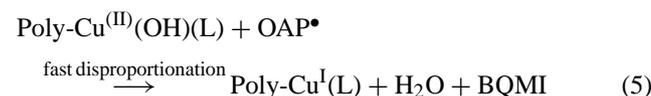
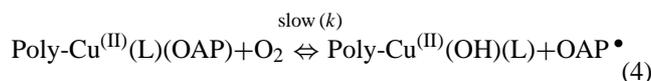


Fig. 8. Effect air pressure (dissolved O_2); conditions: OAP = 5 mmol, temperature = 70 °C, DMF = 30 ml, catalyst = 50 mg.

ing unstable will undergo fast disproportionation in a reduction step (Eq. (5)) forming Cu^{I} mixed ligand complex and 2-benzoquinone monoimine (BQMI), which is the key intermediate in oxidative coupling and this in a fast step (Eq. (6)) interacts with another mole of OAP to give final product APX, while regenerating the active catalyst in a catalytic cycle (Eq. (7)). The mechanism proposed below is the one similar to that proposed by Horváth et al. [1].



where L: (Hhebmz), 2-aminophenol (OAP), 2-benzoquinone monoimine (BQMI), 2-aminophenoxazine (APX).

Under steady conditions and based on kinetics study and the proposed mechanism, the rate law for the oxidative coupling of OAP with molecular oxygen could be written as (Eq. (8)):

$$\text{Rate} = k K_1 [\text{OAP}][\text{Poly-Cu}^{\text{(II)}}(\text{L})][\text{O}_2] \quad (8)$$

where k is the rate constant of the slowest step and K_1 , the pre-equilibrium constant and $[]$ are the concentrations of respective reacting species in the reactions.

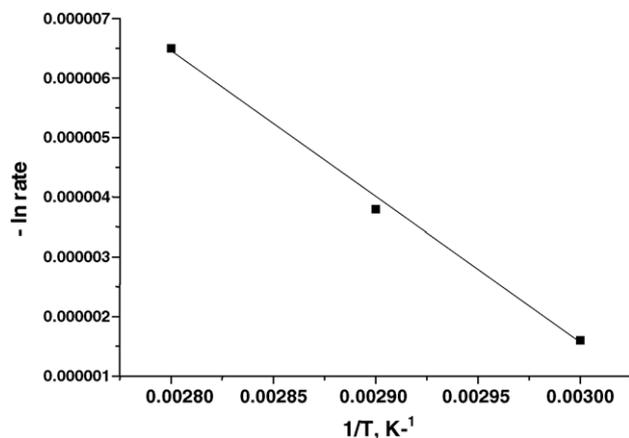


Fig. 9. Arrhenius plot; conditions: OAP = 5 mmol, catalyst = 50 mg, air = 500 psig, DMF = 30 ml.

By expressing the concentration of $[\text{Poly-Cu}^{\text{(II)}}(\text{L})]_{\text{T}}$ in terms of its total concentration present in different forms of the catalytic species in the reaction in Eq. (8) and rearranging the terms, we get final rate law as (Eq. (9)):

$$\frac{[\text{Poly-Cu}^{\text{(II)}}(\text{L})]_{\text{T}}}{\text{rate}} = \frac{1}{k K_1 [\text{OAP}][\text{O}_2]} + \frac{1}{k [\text{O}_2]} \quad (9)$$

By plotting the graph of $[\text{Poly-Cu}^{\text{(II)}}(\text{L})]_{\text{T}}/\text{rate}$ versus $1/[\text{O}_2]$, we get a straight line from which we could calculate k and K_1 from the slope and intercepts of the straight-line as:

$$\text{Slope of the straight line} = \frac{1}{k} \text{ and intercept} = \frac{1}{k K_1 [\text{OAP}][\text{O}_2]}$$

The calculated values are $k = 0.031944 \text{ mol h}^{-1}$ and $K_1 = 4.86 \times 10^5 \text{ mol}^{-1}$. The thermodynamic parameters calculated for the above reaction is:

$$E_a = 34.2 \text{ kcal mol}^{-1}, \Delta H^\ddagger = 33.52 \text{ kcal mol}^{-1},$$

$$\Delta S^\ddagger = \Delta S = 97.7 \text{ cal degree}^{-1} \text{ mol}^{-1} \text{ and}$$

$$\Delta G^\ddagger = -0.04 \text{ kcal mol}^{-1}.$$

From the thermodynamic values evaluated, it could be concluded that small positive entropy and negative free energy indicate that the reaction is associated with new bond formation during oxidative coupling.

4. Conclusions

Bis(2-[α -hydroxyethyl] benzimidazolato)copper(II) anchored onto chloromethylated polystyrene for the biomimetic oxidative coupling of OAP to give phenoxazine-2-one has been effectively carried out. Anchored catalyst is highly stable than its homogeneous analogue in this oxidative coupling reaction. There was no leaching of metal complex in the solution resulting into loss in its activity. The homogenous analogue was found to be less active. The catalyst recycle studies demonstrates that the anchored catalyst does not disintegrate (metal complex leaching) during the reaction and thus its catalytic activity is reproducible.

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