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Short Communication

5,10,15,20-Tetrakis-(4-sulfonatophenyl)porphyrinatocobalt(II) supported on ion exchange resin as reusable and effective catalyst for the oxidative coupling of 2-aminophenol to 2-aminophenoxazine-3-one

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ABSTRACT

5,10,15,20-Tetrakis-(4-sulfonatophenyl)porphyrinatocobalt(II) supported on Amberlite ion exchange resin showed good catalytic activity as heterogeneous catalyst for the biomimetic oxidative coupling of 2-aminophenol (OAP) to 2-aminophenoxazine-3-one (APX). The reaction rate was found to fit a Michaelis–Menten kinetic model for saturation of catalyst site with increasing OAP concentration. Recycling of the Co(II)TPPS-resin system showed no loss of activity after six successive runs.

1. Introduction

Oxidation reactions catalyzed by metalloporphyrins have attracted attention in relevance to the activation of molecular oxygen and oxygen atom transfer to organic substrates, which are processes dependent on cytochrome P-450 in biological systems [1,2]. The utility of these catalysts would be increased significantly if they could be attached to solid supports, since this should stabilize the catalysts and aid their recovery and reuse. Moreover, the local environment of the support can bring higher selectivity and prevent catalyst self-oxidation [3,4]. Synthetic metalloporphyrins have been used to catalyze the transfer of an oxygen atom from a great variety of oxidizing agents into organic molecules [1,2,5–18]. Over the past few years, the oxidation of 2-aminophenol to 2-amino-3*H*-phenoxazine-3-one through catalytic activation of dioxygen by transition metal salts and complexes has been intensively studied with the aim to mimic the activity of phenoxazinone synthase which catalyzes the oxidative coupling of two molecules of substituted 2-aminophenol to the phenoxazinone chromophore in the final step at the biosynthesis of actinomycin D [19–25]. The naturally occurring antineoplastic agent actinomycin D is used clinically for the treatment of certain types of cancer [26,27]. The catalytic oxidation of OAP to APX has mostly been studied in homogenous systems [19–25]. However, several studies have been reported on the heterogeneous oxidation of AOP to APX, using transition metal complexes immobilized on polymers and mesoporous silica [28,29] as catalysts.

In the present investigation, we report 5,10,15,20-tetrakis-(4-sulfonatophenyl)porphyrinatocobalt(II) [Co(II)TPPS] immobilized on the resin Amberlite 400 bearing quaternary ammonium groups as heterogeneous catalyst for the oxidative coupling of 2-aminophenol to 2-amino-3*H*-phenoxazine-3-one in water.

2. Experimental

2.1. Materials and reagents

2-Aminophenol (Aldrich) was used as received. Meso-tetraphenylporphyrin was synthesized and purified as reported [30]. The sulfonation of meso-tetraphenylporphyrin was performed with fuming sulfuric acid according to the published method [31]. Metallation of the sulfonated tetraphenylporphyrin with cobalt chloride was carried out as previously reported [32]. Elemental microanalysis of sulphur in Co(II)TPPS found:11.5% S. Resin Amberlite CG-400 (Cl) (Prolabo, 100–200 mesh) was washed with a four-fold (v/v) excess of 5% aqueous sodium chloride followed by water, methanol and acetone. Elemental analysis of chlorine indicated 3.4 mmol of Cl/g of resin. Water used in the reactions was double distilled (deionized water).

2.2. Preparation of Co(II)TPPS supported on Amberlite resin

A solution of Co(II)TPPS (0.015 mmol) in 10 ml of water was added dropwise to a stirred suspension of resin(0.088 g, 0.3 mmol) in 10 ml of

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water. The reaction mixture was stirred under nitrogen atmosphere overnight at room temperature. The resin was then filtered off and washed with methanol. UV–vis spectra indicated no Co(II)TPPS in the filtrate.

2.3. Auto-oxidation reactions

Oxidations of 2-aminophenol were performed as previously [25] by stirring of 100 ml of an aqueous mixture containing 5% volume methanol in a 250 ml round bottomed flask attached to a gas burette. The pH was adjusted to 9.0 using borate buffer. All reactions were carried out at 40 °C and at constant oxygen pressure. Lower partial pressures of oxygen were obtained by use of oxygen/nitrogen mixture at 1 atm total pressure. After completion of the reaction the mixture was extracted by diethyl ether. The extract was analyzed by means of silica gel thin- layer chromatography using chloroform/methanol (volume ratio of 20:1). The reaction products were identified by comparison with authentic samples. All kinetic experiments were carried in duplicate and reproducible results were obtained.

To test the effect of mass transfer on the oxidation reaction a shaker water thermostat (Julabo SW 20 C) was used to shake the heterogeneous reaction mixture at 120 rpm at fixed temperature of 40 ± 0.1 °C. The reaction was carried out under conditions reported in Section 2.3.

3. Results and discussion

3.1. Auto-oxidation of 2-aminophenol

The activity of Co(II)TPPS supported on ion exchange resin CG-400 was investigated as heterogeneous catalyst for the autoxidation of OAP to APX. Auto-oxidation of OAP catalyzed by Co(II)TPPS bound to ion exchange resin CG-400 at pH 9.0 and slightly less than 1 atm of dioxygen at 40 °C gave within two hour APX in 85% yield and 15% of unreacted OAP. While the oxidation of OAP catalyzed by soluble Co(II)TPPS under the same reaction conditions gave 65% yield of APX. The higher activity of Co(II)TPPS supported on ion exchange resin compared to soluble Co(II)TPPS could be attributed to absorption of the OAP by the resin, which provides a high concentration of the reactant at the active site.

The rate of 2-aminophenol consumption was determined by measuring the amount of dioxygen consumed using a gas burette. After a short induction period, the volume of dioxygen consumed was linear with time, indicating a zero-order dependence on substrate concentration.

Table 1
Effect of pH on the rate of autoxidation of OAP[a].

pH[b]	k_{obs}[c] (mol L^{-1} min^{-1}) × 10^5
7.0	0.36
8.0	0.98
9.0	1.18
10.0	1.1
11.0	0.76

[a] All experiments were carried out at 40 °C and oxygen pressure of 740 mm Hg with magnetic stirring of 1.5 mmol of OAP dissolved in 5 ml of methanol dispersed in 100 ml of distilled water containing 0.015 mmol of Co(II)TPPS supported on 0.3 mmol of resin.

[b] The pH was adjusted to 8.0–10.0 using sodium borate buffers and the pH was adjusted to 7and 11 using phosphate buffers.

[c] Initial rate constant calculated from the plot of oxygen consumption vs. time.

Table 2
Effect of [resin] on the rate of autoxidation of OAP[a].

Amberlite resin (gm)	k_{obs}[b] (mol L^{-1} min^{-1}) × 10^5
0.022	0.645
0.044	0.949
0.088	1.187
0.176	0.989
0.264	0.791

[a] All reactions were carried out under conditions reported in (Table 1) at pH = 9.0.

[b] Initial rate constant calculated from the plot of oxygen consumption vs. time.

The auto-oxidation of 2-aminophenol was studied in the pH range of 7.0–11.0, using sodium borate and sodium phosphate buffers. The initial rate constant k_{obs} of the auto-oxidation reaction reached an optimum at pH 9.0 and then decreased at higher pH values (Table 1). The decrease of reaction rate at pH values higher than 9 indicates that the 2-aminophenoxide anion is not the active species.

The effect of concentration of ion exchange resin on the initial rate constant k_{obs} has been studied by varying the concentration of resin systematically while the concentration of Co(II)TPPS was kept constant (0.015 mmol). Data summarized in Table 2 shows that maximum activity has been attained at 0.3 mmol of the resin (resin/Co(II)TPPS ratio = 20). The decrease in the rate constant k_{obs} at higher concentration of resin could be attributed to a decreased concentration of Co(II) TPPS in the resin phase.

Fig. 1 shows the effect of varying the concentration of Co(II)TPPS supported on fixed amount of resin (0.3 mmol) on the initial rate constant k_{obs} of the oxidation reaction. The rate constants increased with increasing the concentration of Co(II)TPPS from 0.38 × 10^{-5} M to 1.5 × 10^{-5} M then decreased at higher Co(II)TPPS concentrations. Two major causes are believed to be responsible for the decrease of rate constant k_{obs} at high concentration of cobalt(II) porphyrin complex: (a) aggregation of Co(II)TPPS and (b) intraparticle diffusion

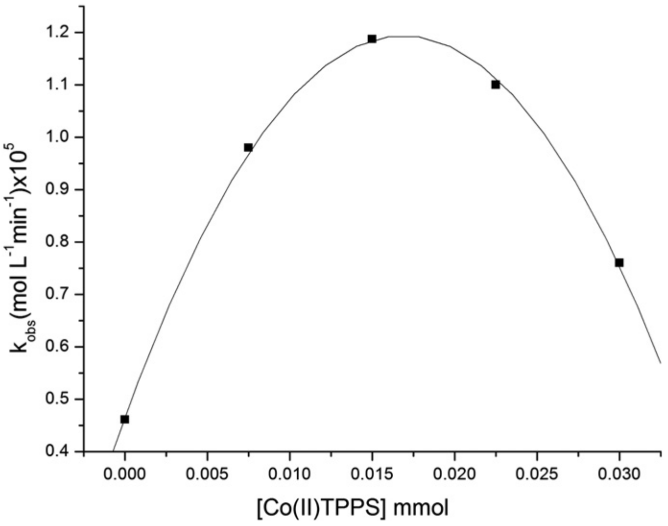


Fig. 1. Dependence of initial rate constant k_{obs} on Co(II)TPPS concentration. Reactions were carried out at pH = 9, for conditions, see footnote (a) of Table 1.

limitation. Aggregated Co(II)TPPS is known to be less reactive than the monomeric form [33].

To test for possible external mass transfer limitation of the overall reaction rate, the reaction was conducted with vigorous shaking of the reaction mixture instead of magnetic stirring under standard reaction conditions of Table 1 at pH 9.0. Magnetic stirring gave a reaction 1.2 times faster as vigorous shaking. The rate constants are considered identical within experimental error, since the variation in the rate constant was typically ±10%. This indicates that the rate of autoxidation of OAP is not limited by mass transfer of dioxygen or OAP to the active site. The temperature dependence of the rate constant k_{obs} from 28 °C to 55 °C gave an Arrhenius activation energy of 10.08 kJ/mol.

The dependence of the initial rate constant k_{obs} of the oxidation reaction of OAP on the concentration of 2-aminophenol was investigated in the range of 5×10^{-4} M to 3×10^{-3} M (Fig. 2a). The initial rate constants k_{obs} increased with increasing the concentration of 2-aminophenol to 1.5×10^{-3} M and then leveled off. A double reciprocal Lineweaver–Burk plot (Fig. 2b) showed that the rate fit a Michaelis–Menten kinetic model for saturation of catalyst site with increasing concentration of OAP [34].

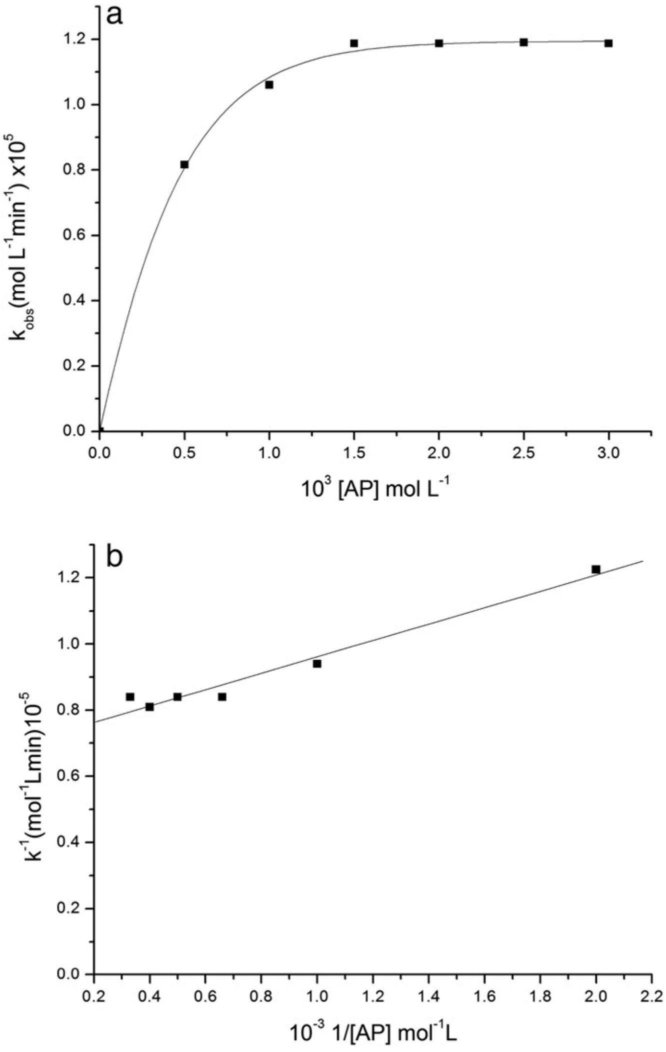


Fig. 2. a) Dependence of initial rate constant on OAP concentration. Reactions were carried out at pH = 9, for conditions, see footnote (a) of Table 1. b) Lineweaver–Burk plot of data in Fig. 2a.

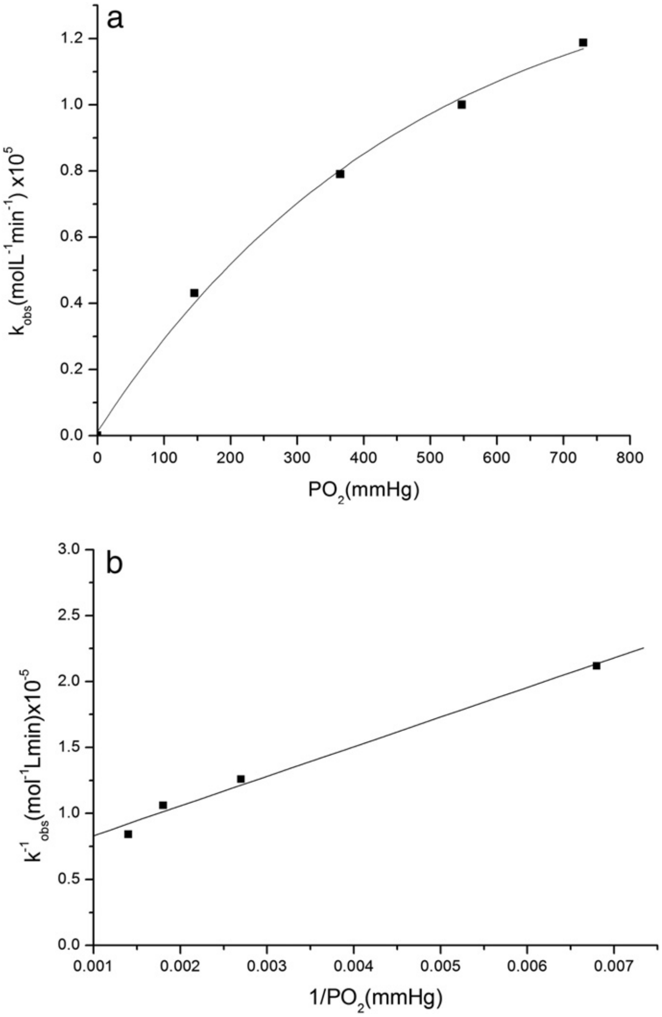
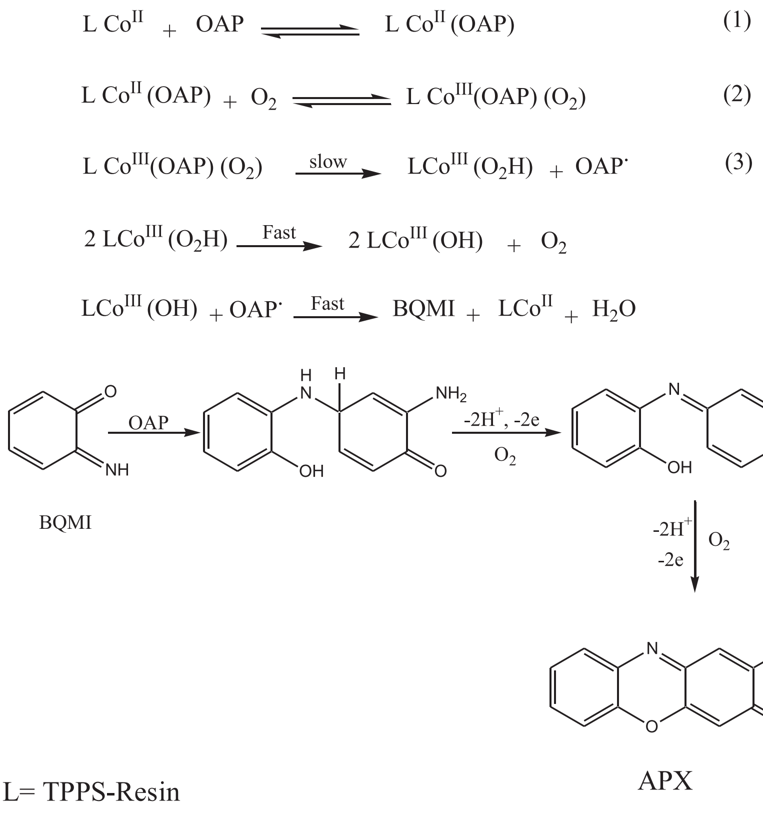


Fig. 3. a) Dependence of initial rate constant on partial pressure of dioxygen. Reactions were carried out at pH = 9, for conditions, see footnote (a) of Table 1. b) Lineweaver–Burk plot of data in Fig. 3a.

The results evaluated from the Lineweaver–Burk plot are $V_{\max} = 1.32 \times 10^{-5}$ M min^{-1}, $K_M = 3.25 \times 10^{-3}$ M. The data illustrated in Fig. 3 show that the rate constants k_{obs} of auto-oxidation of OAP catalyzed by Co(II)TPPS bound to resin depend on the partial pressure of dioxygen for saturation of catalyst site.

It is well known that o-benzoquinone monoimine (BQMI) is the key intermediate in the oxidative coupling of OAP to APX [19–25]. The overall reaction requires several oxidative dehydrogenation steps involving OAP, molecular oxygen and o-benzoquinone monoimine as reactants to produce APX [19–25].

On the basis of the results of the observed rate dependence on 2-aminophenol concentration and pressure of dioxygen, the proposed mechanism for the auto-oxidation of 2-aminophenol catalyzed by Co(II)TPPS supported on ion exchange resin involves interaction of the catalyst with a mole of OAP, which reacts with a mole of O_2 to form superoxo derivative (steps 1 and 2 in Scheme 1). Both steps 1 and 2 are assumed to be pre-equilibria involving the catalyst, substrate (OAP) and O_2. The rate determining step involves H-atom abstraction within the ternary complex forming the reactive amino-phenoxyl radical (step 3, Scheme 1) which disproportionate leading to the key intermediate o-benzoquinone monoamine (BQMI) in Scheme 1. The o-benzoquinone monoimine reacts with OAP in the presence of oxygen to produce APX [19–25].



$$\mathrm{L\,Co^{II}} + \mathrm{OAP} \rightleftharpoons \mathrm{L\,Co^{II}(OAP)} \quad (1)$$

$$\mathrm{L\,Co^{II}(OAP)} + \mathrm{O_2} \rightleftharpoons \mathrm{L\,Co^{III}(OAP)(O_2)} \quad (2)$$

$$\mathrm{L\,Co^{III}(OAP)(O_2)} \xrightarrow{\text{slow}} \mathrm{LCo^{III}(O_2H)} + \mathrm{OAP^{\cdot}} \quad (3)$$

$$2\,\mathrm{LCo^{III}(O_2H)} \xrightarrow{\text{Fast}} 2\,\mathrm{LCo^{III}(OH)} + \mathrm{O_2}$$

$$\mathrm{LCo^{III}(OH)} + \mathrm{OAP^{\cdot}} \xrightarrow{\text{Fast}} \mathrm{BQMI} + \mathrm{LCo^{II}} + \mathrm{H_2O}$$

Scheme 1. Proposed mechanism for the oxidation of OAP catalyzed by Co(II)TPPS-resin.

3.2. Re-use of catalyst

Reuse of Co(II)TPPS supported on ion exchange resin was tested for its stability in repeat experiments. The re-use of the catalyst was carried out under reaction conditions of Table 1 at pH 9.0. The reaction was followed by dioxygen uptake. After 100% conversion of OAP, the initial amount of 2-aminophenol was again fed into the reaction mixture without removal of the reaction products. The recycled Co(II)TPPS/resin catalyst showed no change in reactivity after six successive runs. The site isolation of the Co(II)TPPS by supporting it on the ion exchange resin prevented porphyrin aggregation and intermolecular self-oxidation of the cobalt porphyrin catalyst [4].

4. Conclusion

Co(II)TPPS bound to resin Amberlite-CG 400 showed good catalytic activity for the autoxidation of OAP to APX. High conversion of OAP to 2-amino-3*H*-phenoxazine-3-one has been obtained under mild reaction conditions. The rate of oxidation was found to be affected by the pH and the concentration of Co(II)TPPS and the resin. Immobilizing cobalt(II) porphyrin complex on the ion exchange resin improved its stability. Recycling of the Co(II)TPPS-resin system showed no loss of activity after six successive runs.

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