



Study of the oxidation of 2-aminophenol by molecular oxygen catalyzed by cobalt(II) phthalocyaninetetrasodiumsulfonate in water

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ABSTRACT

The oxidation reaction of 2-aminophenol with dioxygen to 2-amino-phenoxazin-3-one has been investigated in water using cobalt(II) phthalocyaninetetrasodiumsulfonate as catalyst. The oxidation reaction was followed by measuring dioxygen uptake. Cobalt(II) phthalocyaninetetrasodiumsulfonate has been found to enhance the rate of oxidation of 2-aminophenol to 2-amino-phenoxazin-3-one. The rate constants of oxidation reaction showed linear dependence on catalyst concentration and saturation kinetics in both 2-aminophenol concentration and dioxygen pressure. A mechanism has been suggested for the oxidation reaction.

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1. Introduction

Considerable attention has been given to selective oxidations of organic compounds with dioxygen metal complexes [1] and metal-ion activation of oxygen [2,3] since these reactions could mimic some biological oxidations [4,5]. The oxidative coupling of 2-aminophenol (OAP) to 2-amino-3*H*-phenoxazine-3-one (APX) **1** through catalytic activation of dioxygen by transition metal complexes has been considered as one of the important reactions [6–17].

2-Amino-3*H*-phenoxazine-3-one also known as questionmycin A, is related to the naturally occurring antineoplastic agent actinomycin D, which acts by inhibiting DNA-directed RNA synthesis [18,19] and is used clinically for the treatment of certain types of cancer [19–23]. APX has been used as a model for the behaviour of actinomycin D. Phenoxazinone synthase 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. Actinomycin biosynthesis has generated interest in the conversion of OAP into APX catalyzed by transition-metal complexes with a view to the possible modeling of phenoxazinone synthase activity.

Soluble as well as polymer-supported cobalt(II) phthalocyanine catalysts have been used successfully for the oxidation of vari-

ous organic substrates [24–41]. Examples are the auto-oxidation of ascorbic acid [25], phenols [26–29], thiols [29–36], sulfides [37–40], hydrazine and hydroxylamine [41].

We report in this paper the ability of cobalt(II) phthalocyaninetetrasodiumsulfonate **2** to catalyze the oxidation of 2-aminophenol to 2-amino-3*H*-phenoxazine-3-one in aqueous medium.

2. Experimental

2.1. Materials and reagents

2-Aminophenol (Aldrich) was used as received. Cobalt(II) phthalocyaninetetrasodiumsulfonate (CoPcTSNa₄) was prepared and purified as reported by Weber and Busch [42]. Water used in the reaction was double distilled (deionized water).

2.2. Auto-oxidation reactions

Oxidations of 2-aminophenol were performed as previously [34] 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. Ionic strength was kept constant by using 0.1 M KCl. 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

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analyzed quantitatively with preparative layer chromatography, PLC (PSC-GF₂₅₄ Silica gel plates, Merk) plates, 2-mm thickness, 20 cm × 20 cm using chloroform–methanol (volume ratio 20:1) as eluent. The products were identified by comparison with authentic samples. All kinetic experiments were carried in duplicate and reproducible results were obtained.

3. Results and discussion

3.1. Auto-oxidation of 2-aminophenol

Auto-oxidation of 2-aminophenol in aqueous mixture at pH 9.0 and slightly less than 1 atm of dioxygen at 40 °C catalyzed by cobalt(II) complex of phthalocyaninetetrasodiumsulfonate **2** gave within 2 h APX in 70% yield and unidentified tar-like material.

Gas burette measurements of dioxygen consumption as the reaction proceeded showed that after an induction period, the volume of dioxygen consumed was linear with time, indicating a zero-order dependence on substrate concentration. Results illustrated in Fig. 1 shows the faster reaction and shorter induction time achieved with CoPcTSNa₄ compared with the reaction in the absence of the catalyst.

3.2. Effect of pH on the auto-oxidation of 2-aminophenol

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

3.3. Effect of concentration of catalyst **2** on the auto-oxidation of 2-aminophenol

Data illustrated in Fig. 3 shows the effect of concentration of CoPcTSNa₄ on the observed rate constant k_{obs} of the auto-oxidation of 2-aminophenol.

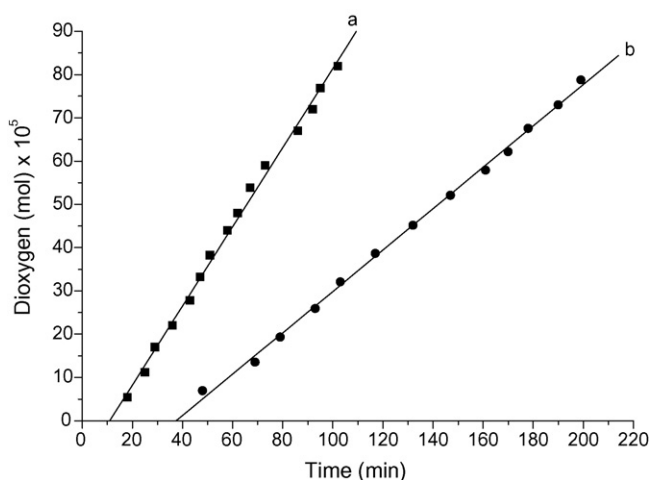


Fig. 1. Dioxygen consumption with time during auto-oxidation of 2-aminophenol (a) with CoPcTSNa₄ and (b) without CoPcTSNa₄. All reactions were carried out at 40 °C and dioxygen pressure of 740 mmHg with magnetic stirring of 2 mmol of OAP dissolved in 5.0 ml of methanol and 5×10^{-3} M of CoPcTSNa₄. The total volume of reaction mixture was maintained at 100 ml. The pH was adjusted to 9.0 using borate buffer.

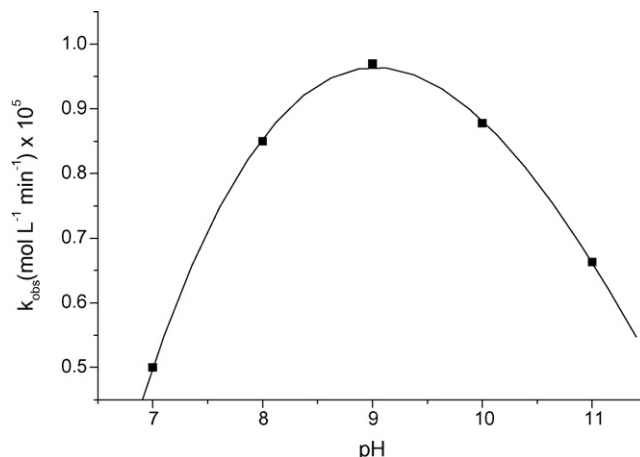


Fig. 2. Effect of pH on the rate of auto-oxidation of 2-aminophenol. All reactions were carried out under the same conditions of Fig. 1. The pH 7.0 was adjusted using a mixture of Na₂HPO₄ and HCl. The pH was adjusted to 8.0 and 9.0 by using sodium borate and HCl mixture and the pH was adjusted to 10.0 using NaHCO₃ and NaOH mixture.

The observed rate constant k_{obs} increased linearly with increasing the concentration of CoPcTS from 0.5×10^{-5} M to 5×10^{-5} M.

3.4. Effect of temperature on the auto-oxidation of 2-aminophenol

The temperature dependence of the rate constant k_{obs} from 35 °C to 60 °C gave an Arrhenius activation energy of 12.07 kJ/mol (Fig. 4).

3.5. Effect of concentration of 2-aminophenol on the rate of auto-oxidation

The dependence of the rate constant k_{obs} of oxidation reaction on the concentration of OAP was investigated in the range 1×10^{-3} M to 3×10^{-3} M (Fig. 5). The reaction 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. 6) showed that the rate fit a Michealis–Menten kinetic model for saturation of catalyst site with increasing concentration of 2-aminophenol.

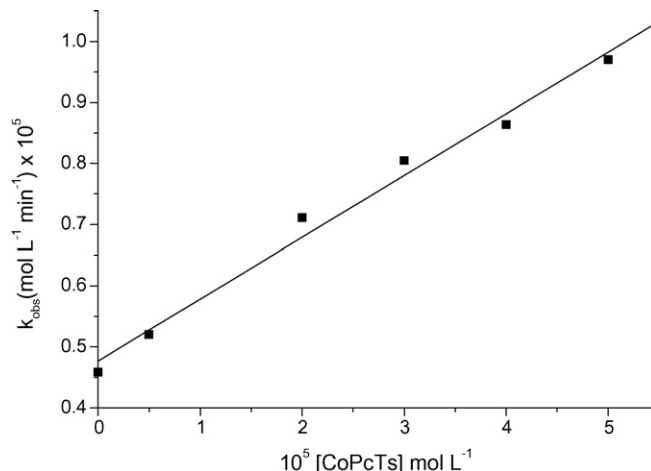


Fig. 3. The dependence of rate constant on CoPcTSNa₄ concentration. For reaction conditions, see Fig. 1.

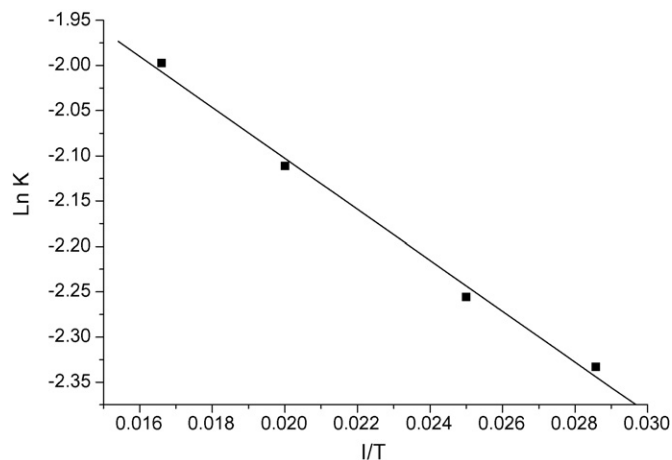


Fig. 4. The Arrhenius plot of rate data at 35–60 °C under conditions given in Fig. 1.

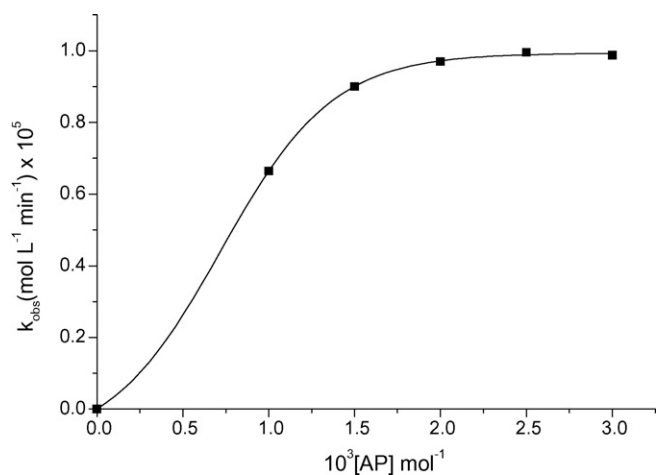


Fig. 5. The dependence of rate constant on 2-aminophenol concentration. For reaction conditions, see Fig. 1.

3.6. Effect of partial pressure of dioxygen on the auto-oxidation of 2-aminophenol

The effect of partial pressure of dioxygen on the auto-oxidation of 2-aminophenol was investigated by using oxygen/nitrogen mix-

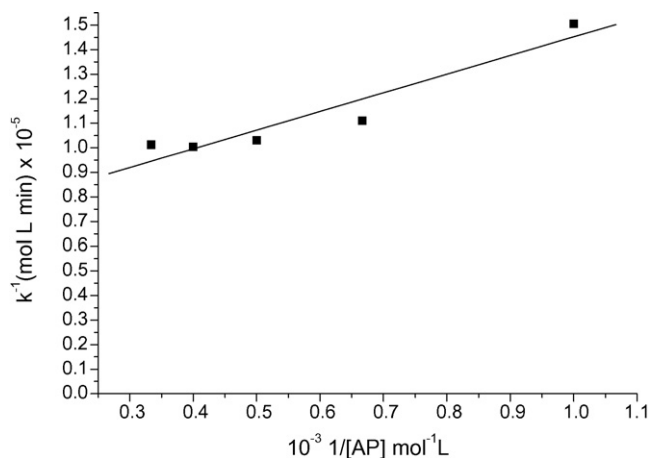


Fig. 6. Lineweaver–Burk plot of the data in Fig. 5.

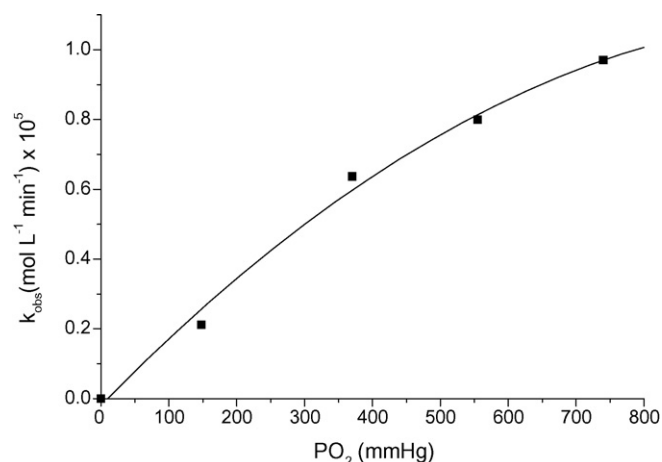


Fig. 7. The dependence of rate constant in the oxidation of 2-aminophenol on dioxygen pressure. For reaction conditions, see Fig. 1.

ture to obtain reduced partial pressure of 1 atm total pressure on the reaction mixture. The data illustrated in Figs. 7 and 8 show that the observed rate constants k_{obs} depend on the partial pressure of dioxygen for saturation of catalyst site.

It is known that metal-bound oxygen is an active species in the auto-oxidation of phenols catalyzed by cobalt(II) phthalocyanine [26].

The observed rate dependence on 2-aminophenol concentration indicates coordination of 2-aminophenol to CoPcTSNa₄ through the lone pair of electrons on the nitrogen [10].

The mechanism of auto-oxidation of 2-aminophenol catalyzed by cobalt(II) phthalocyaninetetrasodiumsulfonate (Scheme 1) probably involves a superoxo derivative containing one 2-aminophenol molecule in the axial ligand [10,11].

The cobalt superoxo adduct (3) reacts with 2-aminophenol by abstracting H-atom forming the reactive 2-aminophenoxy radical which disproportionate leading to the key intermediate *o*-benzoquinone monoimine. Its further conversion into the product APX is shown in Scheme 1. The overall reaction requires several oxidative dehydrogenation steps involving OAP, dioxygen and *o*-benzoquinone monoimine as reactants on the way to APX [8,13,14,18].

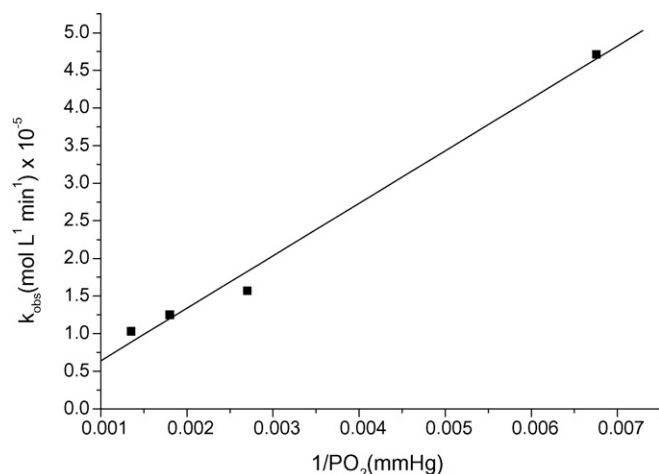
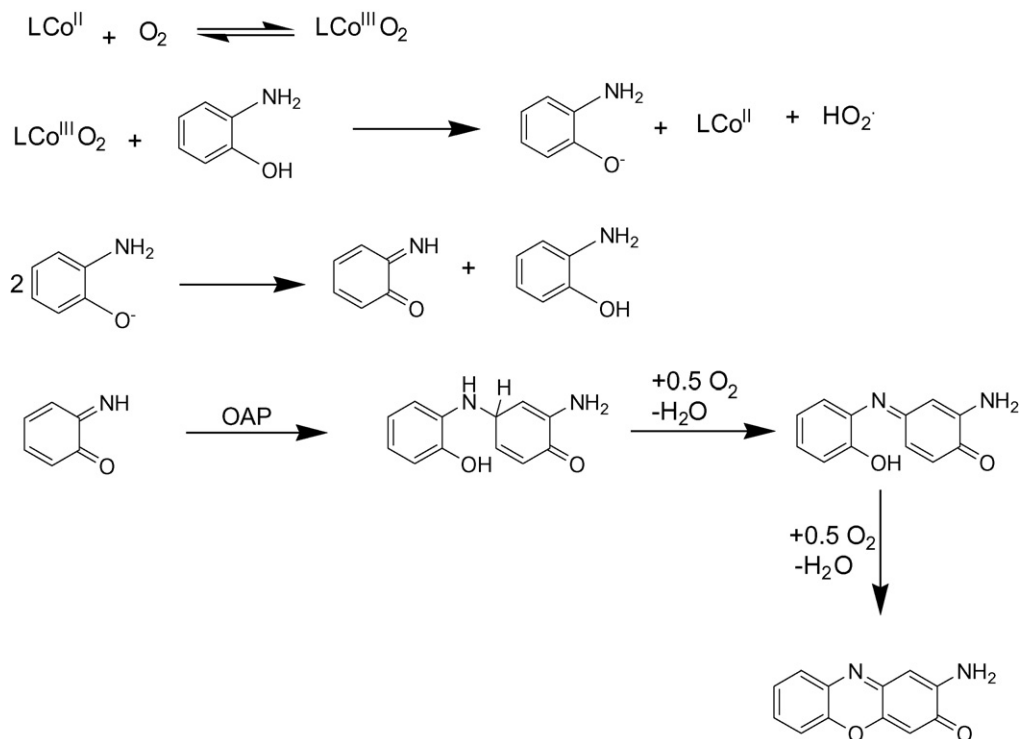


Fig. 8. Lineweaver–Burk plot of the data in Fig. 7.



Scheme 1.

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