



# Oxidation of 2-aminophenol with molecular oxygen and hydrogen peroxide catalyzed by water soluble metalloporphyrins

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## ABSTRACT

5,10,15,20-Tetrakis-(p-sulfonatophenyl)porphinatocobalt(II) and 5,10,15,20-tetrakis-(p-sulfonatophenyl)porphinatomanganese(III) chloride have been used as catalysts for the oxidative coupling of 2-aminophenol to 2-aminophenoxazine-3-one with molecular oxygen and hydrogen peroxide. The effects of pH and concentration of catalysts, hydrogen peroxide and oxygen on the oxidation reaction and yield of 2-aminophenoxazine-3-one have been studied. The oxidation of 2-aminophenol with molecular oxygen catalyzed by cobalt(II) tetra(4-sulfophenyl)porphyrin involves a hydrogen atom abstraction from 2-aminophenol by cobalt(II) superoxo species. UV-vis analysis indicated that oxomanganese(IV) is the active species in the oxidation of 2-aminophenol with hydrogen peroxide and manganese(III)tetra(4-sulfophenyl)porphyrin.

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## 1. Introduction

The oxidation of organic substrates with molecular oxygen and hydrogen peroxide under mild conditions is of great interest for industrial and synthetic processes both from an economical and environmental point of view [1–3]. The oxidative coupling of 2-aminophenol (OAP) to 2-amino-3H-phenoxazine-3-one (APX) through catalytic activation of dioxygen by transition metal complexes (Scheme 1) has been considered as one of the important reactions [4–17]. The enzyme phenoxazinone synthase is involved in the last stages of the biosynthesis of actinomycin D, a naturally occurring antibiotic, which is used clinically for the treatment of Wilm's tumor, gestational choriocarcinoma and other tumors [18–20].

Transition metals and complexes such as copper salts [4], forroxime(II) [5], dioximatomanganese(II) [6] and manganese(II) isoindoline based complexes have been reported as phenoxazinone synthase models [7] for the oxidative coupling of OAP. Cobalt salts [8], cobalt(II) salen [9,10] bis-(dimethyl-glyoximate)cobalt(II) complexes [11] and cobalt(II) phthalocyanine derivatives [12,13] have been used as catalysts for the oxidative coupling of OAP. TEMPO (2,2,6,6-tetramethyl-1-piperidinolxyl) initiated oxidation of OAP has been reported by Speier and co-workers [14]. Transition metal complexes immobilized on polymers and mesoporous

silica [15–17] have been reported also as catalysts for the oxidative coupling of OAP.

Synthetic metalloporphyrins have been widely used as catalysts for a great variety of oxidation reactions [21–42].

We now report the oxidation of 2-aminophenol with molecular oxygen and hydrogen peroxide catalyzed by 5,10,15,20-tetrakis-(p-sulfo-natophenyl)porphinatocobalt(II) CoTPPS and 5,10,15,20-tetrakis-(p-sulfonatophenyl)porphinatomanganese(III) chloride MnTPPS. To the best of our knowledge, this is the first report on the oxidation of 2-aminophenol using metalloporphyrins as catalysts.

## 2. Experimental

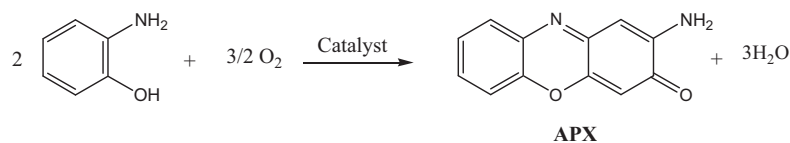
### 2.1. Materials and reagents

2-Aminophenol (Aldrich) and aqueous hydrogen peroxide solution (30.0% by weight; Merck) were used as received. 5,10,15,20-Tetrakis-(p-sulfonatophenyl)porphyrin (TPPS) was prepared based on a literature procedure [43] and its metallation with cobalt chloride and manganese chloride was carried out as described previously [44]. Doubled distilled deionized water was used in all reactions.

### 2.2. Measurements

Spectrophotometric measurements were carried out on Shimadzu 3101 UV-vis Spectrometer.

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E-mail address: [saharelkhalfy@hotmail.com](mailto:saharelkhalfy@hotmail.com) (S.H. El-Khalafy).



Scheme 1.

### 2.3. Oxidation reactions

#### 2.3.1. General procedure for the oxidation of OAP with $O_2$ catalyzed by Co(II)TPPS

Oxidation reactions were carried out by stirring 100 ml of an aqueous reaction mixture containing 5 vol% methanol in a 250-ml round bottomed flask attached to a gas buret. All reactions were carried out at 40 °C and at constant oxygen pressure. Low partial pressure of oxygen was obtained by using of oxygen/nitrogen mixture at 1 atm total pressure. The pH of the medium was adjusted to 9.0 using borate buffer. The reaction mixture was extracted with diethyl ether (50 ml) and the extract was tested by TLC (Merck) using  $CHCl_3$ -MeOH mixture (20:1 by volume) as eluent, which showed the presence of APX along with unreacted OAP. The organic layer was then washed with dilute aqueous sodium hydroxide solution (10%; 50 ml), dried with anhydrous  $Na_2SO_4$  and the ether was evaporated to give the product.

#### 2.3.2. Oxidation of 2-aminophenol with $H_2O_2$ catalyzed by Mn(III)TPPS

A mixture of OAP (0.296 g; 2.7 mmol), Mn(III)TPPS (5.40 mg;  $4.9 \times 10^{-3}$  mmol) and  $H_2O_2$  (1 ml; 10 mmol) in water (30 ml) was stirred at room temperature for 4.5 h. The pH of the mixture was adjusted to 8.0 using borate buffer. The reaction was worked up as reported in Section 2.3.1.

## 3. Results and discussion

#### 3.1. Oxidation of 2-aminophenol with dioxygen catalyzed by Co(II)TPPS

The catalytic activity of water soluble Co(II)TPPS was investigated in the oxidation of OAP with dioxygen. The rate of 2-aminophenol consumption was determined by measuring the amount of dioxygen using a gas buret. After a short induction period, the volume of dioxygen consumed was linear with time, indicating a zero-order dependence on the concentration of the substrate. Oxidation of OAP under standard conditions of pH=9.0 and slightly less than 1 atm of dioxygen gave within 2 h APX (65%) and unreacted OAP. The zero-order rate constant  $k_{obs}$  calculated from the plots of the oxygen consumption with time shows that the oxidation reaction of OAP catalyzed by Co(II)TPPS is three times faster than oxidation of OAP in the absence of catalyst.

Data in Fig. 1 illustrate the effect of pH in the range 7.0–11.0 on the rate constant  $k_{obs}$  for the auto-oxidation of OAP. The decreases in reaction rate at pH values higher than 9 indicates that the *o*-aminophenoxide anion is not the active species [13].

The data in Fig. 2 show the effect of Co(II)TPPS concentration on the rate constant  $k_{obs}$  of the oxidation reaction. The rate constant  $k_{obs}$  increased linearly with increasing catalyst concentration from  $0.75 \times 10^{-5}$  M to  $3.35 \times 10^{-5}$  M.

The temperature dependence of the rate constant  $k_{obs}$  from 30 to 60 °C gave an Arrhenius activation energy of 10.84 kJ/mol.

The dependence of the rate constant  $k_{obs}$  of oxidation reaction on the concentration of OAP was investigated in the range  $(0.5\text{--}2.5) \times 10^{-3}$  M (Fig. 3). The reaction rate constants  $k_{obs}$

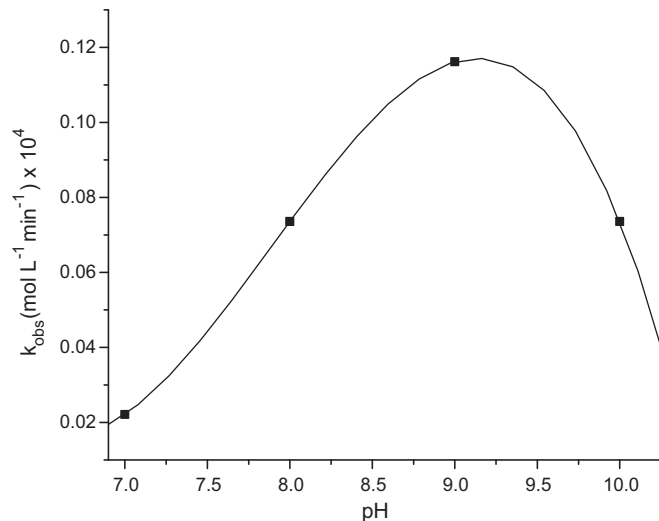


Fig. 1. Effect of pH on the rate of auto-oxidation of OAP. All reactions were carried out at 40 °C and dioxygen pressure of 730 mmHg with magnetic stirring of 2 mmol of OAP dissolved in 5.0 ml of methanol and  $1.5 \times 10^{-5}$  of Co(TPPS). The volume of reaction mixture was maintained at 100 ml. The pH 7.0 was adjusted using a mixture of  $Na_2HPO_4$  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  $NaHCO_3$  and NaOH mixture.

increased with increasing the concentration of 2-aminophenol to  $1.5 \times 10^{-3}$  M and then leveled off.

A double reciprocal Lineweaver plot (Fig. 4) showed that the rate fit Michealis–Menten kinetic model [45,46] for saturation of catalyst site with increasing concentration of 2-aminophenol.

The effect of partial pressure of molecular oxygen on the auto-oxidation of OAP was investigated by using oxygen/nitrogen mixture to obtain reduced partial pressure of 1 atm total pressure

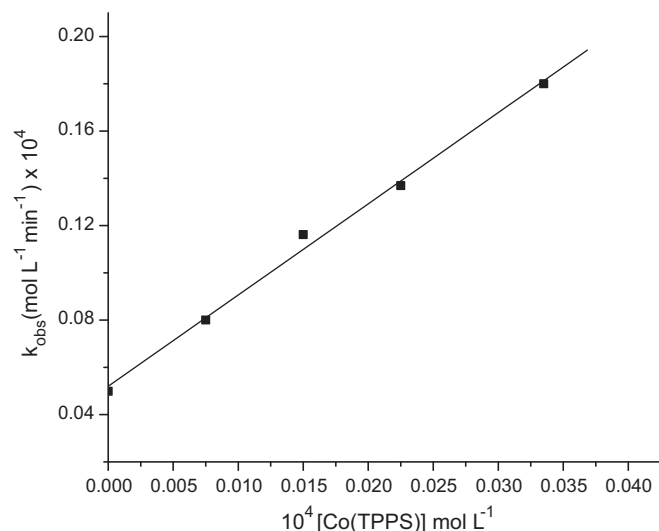


Fig. 2. The dependence of the rate constant  $k_{obs}$  on Co(TPPS) concentration. For reaction conditions, see Fig. 1.

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