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Efficient Catalyst 5, 10, 15, 20-Tetraphenylporphyrinatocobalt(II) Complex for the Oxidation of 3,5-Di-tert-butylcatechol to the Corresponding Quinone with Molecular Oxygen

Sahar H. El-Khalafy*, Mahmmoud.T. Hassanein and Samah A. Shendy

Tanta University, Faculty of Science, Department of Chemistry, Tanta 31527, Egypt

Abstract

5, 10, 15, 20-tetraphenylporphyrinatocobalt(II) complex has been found to be an efficient catalyst for the oxidationn of 3,5-di-tert-butylcatechol to 3,5-di-tert-butylbenzoquinone by molecular oxygen) in dimethylformamide. Measurement of dioxygen uptake was used to monitor the oxidation process. The oxidation reaction rate constant was reported to be linearly related to the concentration of catalyst, and saturation kinetics were shown to be dependent on both 3,5-di-tert-butylcatechol concentration and dioxygen pressure. The Michaelis-Menten method was used to obtain the kinetic parameters. A mechanism also has been proposed according to kinetic data, production of a ternary complex involving catalyst, substrate, and dioxygen and the formation of the semiquinone anion radical (3,5-DBSQ$^{.}$) which detected by ESR spectroscopy. The system investigated is a functional model of catecholase like activity, based on free-radical intermediates, a possibility recently demonstrated for certain oxidoreductases.

1. Introduction

Transition metal-catalyzed autoxidation of phenols is important in both industry and biology (Punniyamurthy and Rout 2008). Only a few published articles have been published on the metalloporphyrin-catalyzed oxidations and photo-oxidations of phenols. Catechol oxidase is a CuII-containing enzyme that oxidises catechol to quinone preferentially (Klabunde et al. 1998 ;Hakulinen et al. 2013). Catecholase activities has been shown in many of mononuclear and dinuclear copper (II) complexes as models to mimic the enzyme and illustrate its mechanism (Kumari et al. 2017; Emirik et al.2016; Anbu et al. 2015; Caglar et al. 2014; Sreenivasulu 2009; Banerjee et al. 2009; Gasque et al. 2008; Merkel et al 2005; Gottschaldt et al. 2004; Mukherjee and Mukherjee 2002; Belle et all 2002; Reim and Krebs 1997) and a number of functional model compounds of other metal ions (Dey and Mukherjee 2016; Basak et al. 2018; Ghosh et al.

2018; Posada et al. 2018 ;Suman and Arindam 2014; Majumder et al 2013; Banerjee et al 2013). Synthetic metalloporphyrins have been utilized to oxidase a variety of organic molecules as effective and selective catalysts (Meunier et al. 2004; Hassanein et al. 2005, 2007, 2013; Que and Tolman 2008; Ortiz de Montellano 2010; Che et al. 2011; Lu and Zhang 2011; El-Khalafy and Hassanein 2012; Castro et al. 2017). Metalloporphyrins are abundant in nature and serve an vital role in biological fields as cofactors in photosynthesis and respiration (Senge et al. 2015; Agam et al. 2020), where they contribute to the catalytic activity of numerous enzymes. Such compounds can be used in a broad spectrum of applications, encompassing photomedicine, sensing, and energy/electron-transfer systems as well as catalysis and photocatalysis. As a result, there are only a few studies on the catecholase activity of transition metal porphyrin complexes in the literature (Castro et al. 2016, 2019).

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Castro et al., examined the catechol oxidase mimicking the performances of certain soluble copper porphyrin complexes including copper-porphyrin based metal organic frameworks in the oxidation of 3,5-di-tert-butylcatechol and catechol to the relevant quinones. Catechol oxidase is a catecholase-active type III active site protein with a copper-containing active site. Catechol oxidase can oxidise a wide spectrum of catechols to quinones by reducing molecular oxygen to water by four electrons (Koval et al. 2006; Blaschek and Pesquet 2021). The enzyme's active site has a dinuclear copper(II) core that is strongly antiferromagnetically coupled in its natural state, with three histidine nitrogens and a bridge OH ion coordinating each copper(II). As a result, research on model compounds that imitate catecholase activity is extremely valuable and encouraging for the creation of new, highly efficiency bioinspired, environmentally conscious catalysts for oxidation processes (Costas Salgueiro 2008; Koval et al. 2008; Afewerki et al. 2020). Within the last thirty years, several mononuclear and binuclear copper (II) complexes' catecholase activity have been investigated. Owing to their capacity to bind dioxygen reversibly (Herrero Álvarez et al. 2021) and their catalytic activities for organic molecules oxidation (Muthusami et al. 2021; Tazeev et al. 2021), cobalt(II) porphyrin complexes are fascinating substances.

According the literature studies on many copper (II) model compounds and the known crystal structure of catechol oxidase, the functional models would definitely have accessible coordination sites on the metal atoms wherein the substrates can interact (Bhardwaj et al. 2010; Castro et al. 2016). As a consequence, ligands bearing fewer donor atoms are significantly more effective.

Hereby, the research work was designed to assess the catalytic activity of 5,10,15,20-tetraphenyl-porphyrinatocobalt (II) complex (Co(II)TPP) during the oxidation of 3,5-di-tert.-butylcatechol (3,5-DTBC) with molecular oxygen to the relevant quinone (catecholase like activity) .

2. Experimental
2.1. Materials and methods
According to the published methods, 5,10,15,20-tetraphenylporphyrinatocobalt(II) was synthesized and purified (Alder et al. 1967; Smith 1975). 3, 5-di-tert.-butylcatechol (3,5-DTBC) was purchased from Across Co. (Germany). Meanwhile, dimethylformamide (DMF) was obtained from Sigma-Aldrich Co. (USA). Taking into consideration that all utilized chemicals (analytical grade) were used as received without further modification.

2.2. Instruments
On a Varian Germany 200 NMR, ^{1}H-NMR spectra were collected. The FT-IR spectra were acquired utilizing KBr Pellets on a Perkin-Elmer 1420 spectrophotometer in the range 4000-400 cm^{-1}. Spin resonance of electrons A JEOL-X-band spectrophotometer (500-5500) GAUSS JES-FE 2XG (It was equipped with an E 101 microwave bridge) in order to obtain ESR spectra. The internal standard was diphenyl-1-picryl-hydrazone (DPPH) (g = 2.0023).

2.3 Oxidation reactions
The oxidation procedures of 3,5-DTBC were conducted as described earlier (Hassanein et al. 2005, 2017), using via dissolving Co(II)TPP (1.0x 10^{-5} M) in 25 mL of DMF and magnetically stirred in at 40 °C and a dioxygen pressure of 740 mmHg. To monitor response rates, a gas burette was employed. The reaction product was detected using ^{1}H NMR and IR techniques after column chromatography on silica gel (60-100 mesh) with a combination of petroleum ether and ethyl acetate as the eluent. ^{1}H NMR and IR techniques.
^{1}H-NMR (DMSO, $(CH_3)_4$Si): δ 1.19 (s, 9H, tBu), 1.22 (s, 9H, tBu), 6.138 (d, 1H, Ph-H), 6.97 (d, 1H, Ph-H) ppm; IR (KBr) $v$cm^{-1}: 1656.55(vC=O), 2960.2 (vCH alkyl protons). All kinetic experiments were repeated twice, yielding consistent findings.

3. Results and discussion
3.1. Catalytic oxidation of 3,5-DTBC with molecular oxygen .
In DMF, Co (II)TPP's catecholase-like activities was evaluated utilizing 3,5-DTBC as a substrate (Scheme 1). The amount of dioxygen consumed was measured that used a gas burette to calculate the rate of 3,5-DTBC consumption. 3,5-DTBC was oxidised under conventional circumstances of 740 mmHg dioxygen pressure at 40 °C for 3 h, yielding 75% of 3,5-DTBQ and unreacted 3,5-DTBC. Using the same conditions of reaction but without Co (II)TPP, only 5% of 3,5-DTBQ was synthesized. The oxidation reaction of 3,5-DTBC catalyzed by Co(II)TPP is roughly four times faster than the oxidation of 3,5-DTBC if the catalyst isn't present, according to the initial rate constant k_{obs} determined from plots of oxygen consumption versus time.
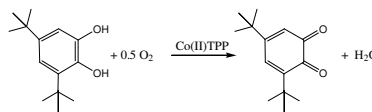
Scheme 1: Catalytic oxidation of 3,5-DTBC with molecular oxygen

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Castro et al., (Castro et al. 2016) reported previously that in a methanol/phosphate buffer, catalytic oxidation of 3,5-DTBC in the presence of soluble copper based porphyrins achieved conversions of 28 to 31.4 % of 3,5-DTBC to 3,5-DTBQ. In comparison to reported earlier, soluble copper porphyrin complexes, the current investigation found that Co (II)TPP has high catalytic activity for oxidation of 3,5-DTBC toward the relevant quinone. The dependence of the rate of 3,5-DTBC conversion to 3,5-DTBQ on the various reaction factors, including such the concentration of Co (II)TPP and the substrate as well as the temperature and oxygen pressure has been investigated.

3.2. Effect of concentrate on of Co (II)TPP on the oxidation of 3,5-DTBC.

As illustrated from **Fig. 1** Varying concentration of Co(II)TPP from 1.0×10^{-5} mol/L to 4.0×10^{-5} mol/Lwere used in the reaction while keeping other parameters constant 3,5- DTBC (1.0×10^{-3}M) in 25 ml of DMF at 40 °C, the initial rate constants k_{obs} of the oxidation process of 3,5-DTBC rose linearly with increasing the concentration of Co(II)TPP .
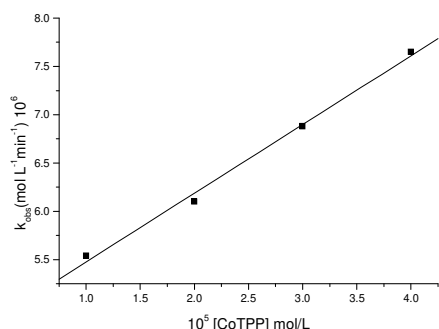

Figure 1: Effect of different concentration of Co(II) TPP on the initial rate constant k_{obs} . All experimentals were carried out at dioxygen pressure of 740 mmHg. with magnetic stirring of 3,5-DTBC (1.0×10^{-3}M) in 25 ml of DMF at 40 °C

3.3. Effect of concentrate on of 3,5-DTBC on the oxidation reaction.

Data illustrated in **Fig. 2** show the effect of different concentration of 3,5-DTBC (0.5×10^{-3} mol/L to 3.0×10^{-3} mol/L) on the initial rate constants k_{obs} of oxidation reaction. The rate constant k_{obs} of oxidation reaction increased with increasing the concentration of 3, 5-DTBC up to 1.0×10^{-3} mol/L and then leveled off. The data fit a Michaelis-Menten kinetic model for saturation of the catalyst site (Johnson and Goody 2011), as seen in **Fig. 2** and the double reciprocal Lineweaver-Burk plot (**Fig. 3**) (Lineweave and Burk 1934). It nonetheless suggests that in a pre-equilibrium phase, an intermediate metal complex-substrate adduct could develop. The obtained data was proved by Banerjee et al. who found similar results mostly on oxidation of 3,5-

DTBC mediated by Schiff-base Cobalt(II) complexes (Banerjee et al. 2013). The maximal response rate V_{max}=5.5×10^{-6} M min^{-1}, Michaelis constant K_M = 2.69×10^{-4} M, and k_{cat} = 33 h^{-1} were estimated through using Lineweaver–Burk plot.
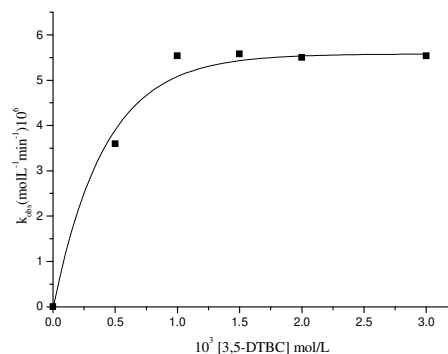

Figure 2: Dependence of initial rate constant k_{obs} on the concentration of 3,5-DTBC . Experimentals were carried out under reaction conditions reported in Fig. 1, using 1.0×10^{-5} M of Co(II)TPP
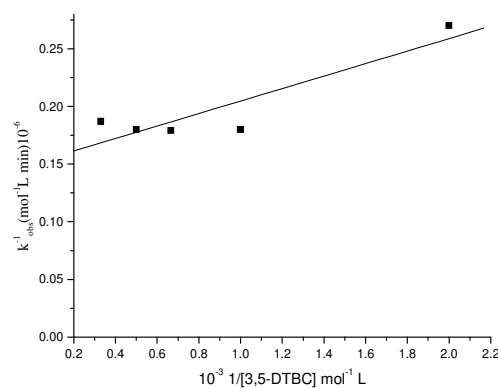

Figure 3: Lineweaver-Burk plot for the data in **Figure 2**

3.4. Effect of the partial pressure of molecular oxygen on the oxidation of 3, 5-DTBC.

The effect of dioxygen partial pressure on the oxidation of 3,5-DTBC was investigated using an oxygen/nitrogen combination to create a decreased partial pressure of 1 atm on the reaction mixture. As demonstrated from **Fig. 4** and the double reciprocal plot (**Fig. 5**), the initial rate constants k_{obs} are dependent on the partial pressure of dioxygen for catalyst site saturation.
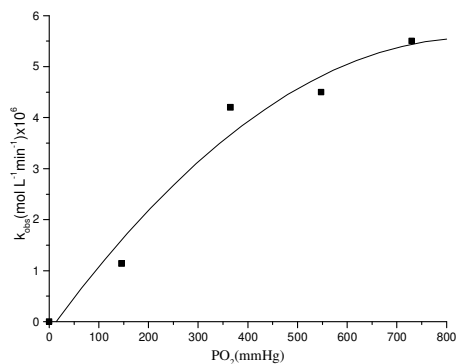
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Figure 4: The initial rate constant k_{obs} versus by the partial pressure of dioxygen. The reactions were carried out according to the reaction conditions shown in **Figure 2**
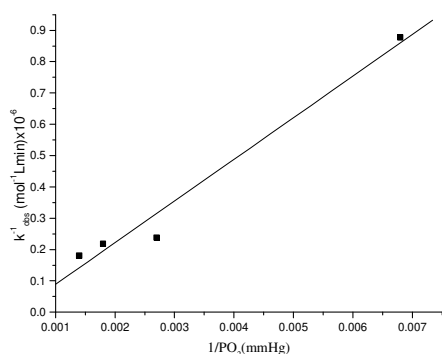

Figure 5: Lineweaver-Burk plot for the data in **Figure 4**

3.5. Effect of reaction temperature on the oxidation of 3,5-DTBC.

The Arrhenius activation energy (Ea) was 40 KJ/mol when the rate constant k_{obs} was temperature dependent from 40 to 60 °C (**Fig. 6**).
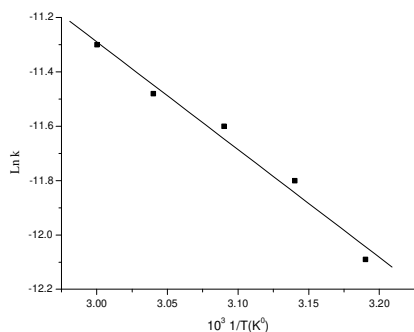

Figure 6: The Arrhenius plot of rate data at 40-60°C under the conditions in Fig. 1, using 1.0×10^{-5} M of Co(II)TPP.

3.6 Proposed mechanism

When 3,5-DTBC is catalytically oxidised, ESR spectra measurements revealed that, the ESR signal is depicted in **Fig. 7,** which corresponds to 3,5-DBSQ· (go = 2.09, a_H = 3300 Gauss).
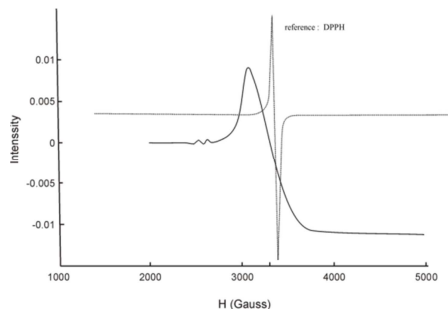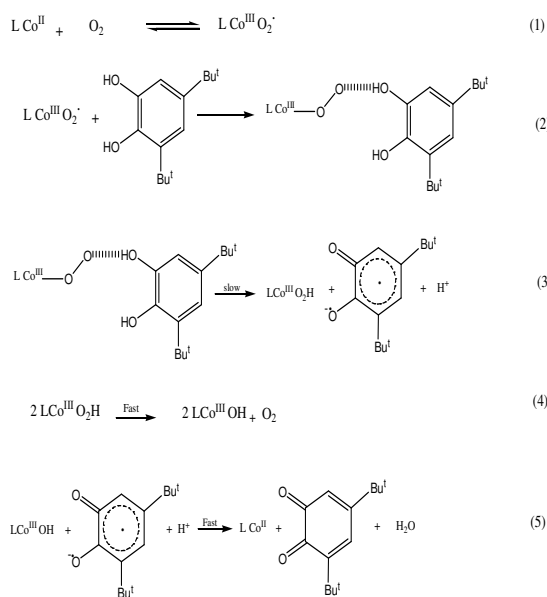

Figure 7: X-band ESR spectrum of 3,5-di-tert-butyl-1,2-semiquinone anion radical detected during the progress of reaction. Reaction was carried out under experimental conditions reported in Figure 4 at 740 mmHg.

The possible explanation for the oxidation of 3,5-DTBC catalysed by Co(II)TPP is outlined in Scheme 2. Based on the rate dependency on 3,5-DTBC concentration, dioxygen pressure, and the visible intermediate from ESR measurements, which revealed mostly by ESR signal matching to 3,5 di-tert-butyl-1,2-semiquinone anion radical (3,5-DBSQ·) (**Figure 7**). In addition, Scheme 2 depicts a suggested process for the oxidation of 3,5-DTBC catalyzed by Co(II)TPP. In a reversible process, dioxygen binds to Co^{II} porphyrin complex to create a superoxo cobalt prophyrine $LCo^{III} O_2$·, which interacts with 3,5-DTBC to generate the ternary catalyst-substrate-dioxygen complex LCo^{III} 3,5-DTBC O_2 intermediate (steps 1 and 2 in Scheme 2). Steps 1 and 2 are considered to be in a state of pre-equilibrium.

Within the ternary complex, the abstraction of intramolecular hydrogen from the substrate reveals that the hydroperoxo cobalt porphyrin complex ($LCo^{III}O_2H$) and the semiquinone anion radical (3,5-DBSQ·) (step 3) (Simándi and Simándi 1998). The hydroperoxocobalt porphyrin complex $LCo^{III}O_2H$ undergoes disproportionation, regenerating oxygen and producing the hydroxocobalt porphyrin complex $LCo^{III}(OH)$ (step 4). The hydroxocobalt porphyrin complex reacts with semiquinone anion radical to produce 3,5-DTBQ· , in which oxygen was reduced to H_2O (step 5).

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$$LCo^{II} + O_2 \rightleftharpoons LCo^{III}O_2^{\cdot} \qquad (1)$$

(2)

(3)

$$2\,LCo^{III}O_2H \xrightarrow{\text{Fast}} 2\,LCo^{III}OH + O_2 \qquad (4)$$

(5)

$$LCo^{II} = Co(II)TPP$$

Scheme 2: the steps for the oxidation of 3,5-DTBC that catalysed by Co(II)TPP

4. Conclusion

Cobalt (II)tetraphenylporphyrin complex has been found to be a selective catalyst for the oxidative dehydrogenation of 3,5-di-tert-butylcatechol to the corresponding 1,2-benzoquinone via molecular oxygen. The system investigated demonstrated catecholase-like activity, based on free-radical intermediates. The rate constant of the oxidation process was linearly related to catalyst concentration. Data fit a Michaelis-Menten kinetic model for saturation of the catalyst site with raising the concentration of both 3,5-di-tert-butylcatechol concentration and dioxygen pressure. Proposed mechanism have been investigated based on kinetic data, assuming the production of a ternary complex involving catalyst, substrate, and dioxygen followed by the abstraction of intramolecular hydrogen atom from the substrate reveals that the formation of hydroperoxo cobalt porphyrin complex ($LCo^{III}O_2H$) and the semiquinone anion radical (3,5-DBSQ$^{\cdot}$) which detected by ESR spectroscopy.

Conflicts of interest
The authors report no financial or any other conflicts of interest in this work.

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