

Oxidation of 2,6-Di-tert-butylphenol by Dioxygen Catalyzed by Tetrasodium Phthalocyaninatocobalt(II) Tetrasulfonate in Aqueous Micellar Media

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The oxidation of 2,6-di-tert-butylphenol by dioxygen has been investigated in aqueous micellar aggregates of cetyltrimethylammonium bromide (CTAB) using tetrasodium phthalocyaninatocobalt(II) tetrasulfonate (CoPcTsNa_4) as catalyst. The CTAB/ CoPcTsNa_4 system showed enhanced catalytic activity in the oxidation of 2,6-di-tert-butylphenol compared to that observed in the oxidation reaction in the absence of CTAB. 2,6-Di-tert-butyl-1,4-benzoquinone and 3,5,3',5'-tetra-tert-butyl-4,4-diphenoquinone were identified as reaction products. The initial rate constants of auto-oxidation reaction was found to increase with increasing the pH range from 7.0 to 13.0. The rate constants k_{obs} of auto-oxidation reaction showed linear dependence on catalyst concentration. The rate of auto-oxidation reaction was found to fit a Michealis-Menten kinetic model for the saturation of catalyst sites with increasing 2,6-di-tert-butylphenol concentration and dioxygen pressure. Tetrasodium phthalocyaninatocobalt(II) tetrasulfonate in aqueous micellar solution of CTAB was found to be mainly monomeric.

Keywords: Oxidation, Dioxygen, Cobaltphthalocyanine, 2,6-Di-tert-butyl-phenol, Surfactant, Catalysis

INTRODUCTION

The enhancement of the rate of organic reactions by colloidal assemblies such as aqueous micelles has attracted considerable interest in recent years. The unique ability of micelles to solubilize organic substrates in water and to catalyze chemical reactions, forms the basis for their use as a medium for investigating organic and bioorganic processes [1-7].

The oxidation of phenols with transition metal dioxygen carriers [8-10] is of industrial and biological importance, because it involves metal dioxygen adduct as an intermediate in the oxidation process, and serves as an appropriate model for the reaction of oxygenized enzymes [11]. Because of their cheap and facile preparation in a large scale and their relatively high chemical and thermal stability, metallophthalocyanines are attractive as potential catalysts for the oxidation of organic compounds [12-32].

Examples are oxidation of alkenes [13,14], aromatic compounds [15], ascorbic acid [16], thiols [17-24] and phenols [25-32].

The objective of the present work is to investigate the oxidation of 2,6-di-tert-butylphenol by dioxygen catalyzed by tetrasodium phthalocyaninato-cobalt(II) tetrasulfonate (**1**) in aqueous micellar media.

EXPERIMENTAL

Materials and Reagents

2,6-Di-tert-butylphenol (Aldrich) was recrystallized from n-hexane. Tetrasodium phthalocyaninatocobalt(II) tetrasulfonate (CoPcTSNa_4) was prepared and purified as reported by Weber and Busch [33]. Hexadecyltrimethylammonium bromide (Aldrich), sodium dodecylsulfate 98% (Aldrich) and triton X-100 (Merck) were used as received. Water used in the reaction was double distilled (deionized water).

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Apparatus

The UV-Vis absorption spectra of the catalyst was recorded on Shimadzu 3101 Pc UV-Vis Spectrophotometer.

Autoxidation Reactions

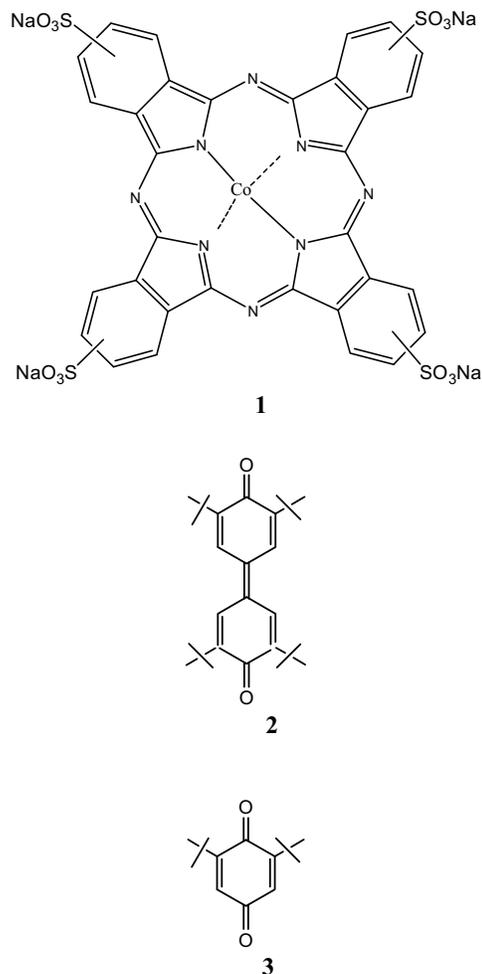
Oxidations of 2,6-di-*tert*-butylphenol were performed as previously [28] by stirring of 100 ml of an aqueous mixture containing 5 volume% methanol in a 250 ml round bottomed flask attached to a gas burette. The pH was adjusted for universal buffer mixture. All reactions were carried out at 40 °C at constant oxygen pressure. Lower partial pressures of dioxygen were obtained by use of oxygen/nitrogen mixture at 1 atm total pressure. After the completion of the reaction the mixture was extracted by diethyl ether. The extract was analyzed quantitatively with preparative layer chromatography, PLC (PSC-GF₂₅₄ Silica gel plates, Merk) plates, 2 mm thickness, 20 cm × 20 cm using petroleum ether and ethyl acetate (volume ratio 9.5:0.5) as eluent. The products were identified by comparison with authentic samples. All kinetic runs were duplicate and were reproducible within 5%.

RESULTS AND DISCUSSION

Oxidation of 2,6-Di-*tert*-butylphenol

The catalytic activity of tetrasodium phthalocyaninato-cobalt(II) tetrasulfonate (Scheme 1) was investigated in the auto-oxidation of 2,6-di-*tert*-butylphenol in aqueous micellar aggregates. The oxidation reaction was followed by measuring dioxygen uptake. 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.

The data summarized in Table 1 show the enhanced catalytic activity of CoPcTSNa₄ in the presence of surfactant aggregates in the auto-oxidation of 2,6-di-*tert*-butylphenol compared to that observed in the absence of surfactant. The rate acceleration of the oxidation reaction in the presence of surfactant aggregates could be attributed to the high local concentration of 2,6-di-*tert*-butylphenol and the catalyst CoPcTSNa₄ in the pseudo phase in the micelle compared with the bulk solution [4,7]. The higher rate of auto-oxidation reaction of 2,6-di-*tert*-butylphenol catalyzed by CoPcTSNa₄ in the presence of CTAB (Table 1), is also due to the reduction of the repulsive forces between the active species phthalocyaninatocobalt(II) tetrasulfonate and 2,6-di-



Scheme 1

tert-butylphenoxide anions by binding them at the surface of the cationic micelle.

The auto-oxidation of 2,6-di-*tert*-butylphenol in aqueous micellar solution of CTAB gave 90% conversion of 2,6-di-*tert*-butylphenol within 5 h to 3,5,3',5'-tetra-*tert*-butyl-4,4'-diphenylquinone **2** and 2,6-di-*tert*-butyl-1,4-benzoquinone **3** (Table 2). The oxidation reaction in the absence of CTAB gave only 20% conversion of 2,6-di-*tert*-butylphenol under the same reaction conditions. Data illustrated in Table 2 show that micelle could also affect the product distribution of the auto-oxidation reaction of 2,6-di-*tert*-butylphenol. The oxidative coupling product **2** was the major product in the oxidation reaction catalyzed by aqueous CoPcTSNa₄ in the absence of CTAB. The yield of 2,6-di-*tert*-butyl-1,4-benzoquinone **3** increased in the reaction catalyzed by

Table 1. Auto-oxidation of 2,6-Di-tert-butylphenol Catalyzed by Tetrasodium phthalocyanatocobalt (II) Tetrasulfonate in Aqueous Micellar Media^a

Surfactants	$10^6 k_{\text{obs}}$ (M min ⁻¹)
-	0.96
CTAB ^b	4.70
SDS ^c	1.60
Triton X-100	1.30

^aAll experiments were carried out at 40 °C and oxygen pressure of 0.9 atm. with magnetic stirring of 1.5 mmol of 2,6-di-tert-butylphenol in 100 ml distilled water containing 4×10^{-5} M of CoPcTSNa₄. The pH of the reaction was adjusted to 11.0 using universal buffer mixture. ^bhexadecyltrimethylammonium bromide. ^csodium dodecyl sulfate.

Table 2. Oxidation of 2,6-Di-tert-butylphenol Catalyzed by Tetrasodium Phthalocyanatocobalt(II) Tetrasulfonate in Presence of CTAB^a

Phenol conversion (%) ^b	Reaction time (h)	Selectivity (%) ^b	
		DPQ ^c	BQ ^d
20 ^e	5	70	30
90	5	40	60

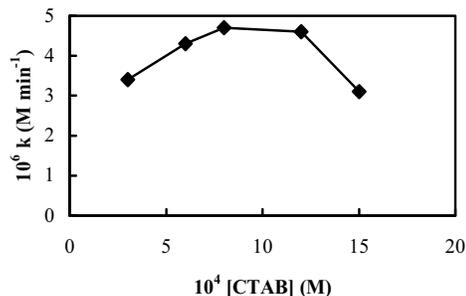
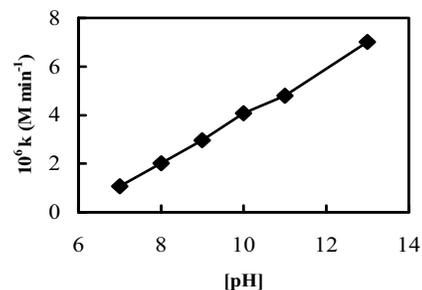
^aAll experiments were carried out under experimental conditions as reported in Table 1 in presence of 12×10^{-4} M solution of CTAB. ^b%Conversion and selectivity are based on isolated products after completion of the reaction. ^cDPQ: 3,5,3',5'-tetra-tert-butyl-4,4'-diphenoquinone. ^dBQ: 2,6-di-tert-butyl-1,4-benzoquinone. ^eReaction carried out in absence of CTAB.

CoPcTSNa₄/CTAB system.

Previous results had indicated that CoPcTSNa₄/CTAB system was the best catalyst; it was therefore further investigated at various reaction conditions.

Effect of [CTAB] on the Auto-oxidation of 2,6-Di-tert-butylphenol

Data illustrated in Fig. 1 show the effect of concentration

**Fig. 1.** Effect of concentration of CTAB on the auto-oxidation of 2,6-di-tert-butylphenol catalyzed by cobalt(II) phthalocyanine complex **1** in aqueous micellar solution of CTAB. All reactions were carried out under conditions reported in Table 1.**Fig. 2.** Effect of pH on the auto-oxidation of 2,6-di-tert-butylphenol catalyzed by cobalt(II) phthalocyanine complex **1** in aqueous micellar solution of CTAB. All reactions were carried out under conditions reported in Table 1. The pH of the reaction mixture was adjusted using universal buffer mixtures.

of hexadecyltrimethylammonium bromide on the rate constant k_{obs} of the auto-oxidation of 2,6-di-tert-butylphenol catalyzed by CoPcTSNa₄. The oxidation rate increases as the CTAB concentration increases and reaches a maximum and then decreases. Similar results were reported previously [4,34].

Effect of pH on the Auto-oxidation of 2,6-Di-tert-butylphenol

The auto-oxidation of 2,6-di-tert-butylphenol was studied in the pH range 7.0-13.0, using universal buffer mixture. The zero-order rate constant k_{obs} was found to

increase with increasing the pH value of the reaction medium (Fig. 2). This indicates that 2,6-di-tert-butylphenoxide anion is the active species.

Effect of Concentration of CoPcTSNa₄ on the Auto-oxidation of 2,6-Di-tert-butylphenol

The dependence of the rate constant k_{obs} of the auto-oxidation of 2,6-di-tert-butylphenol on the concentration of CoPcTSNa₄ in aqueous micellar solution of hexadecyltrimethylammonium bromide was investigated in the concentration range 0.5×10^{-5} to 5×10^{-5} M (Fig. 3). The rate constants k_{obs} increased linearly with increasing the concentration of CoPcTSNa₄.

Effect of Concentration of 2,6-Di-tert-butylphenol on the Rate of Auto-oxidation

The effect of concentration of 2,6-di-tert-butylphenol on the rate constants k_{obs} of the auto-oxidation reaction has been investigated in the concentration range 0.5×10^{-3} M to 4×10^{-3} M. The initial rate constants k_{obs} of 2,6-di-tert-butylphenol consumption depend on the initial concentration of 2,6-di-tert-butylphenol as shown in Fig. 4. A linear double reciprocal Lineweaver-Burk (Fig. 5) shows that the data fit a Michaelis-Menten kinetic model for the saturation of the catalyst sites with increasing 2,6-di-tert-butylphenol concentration.

Effect of Partial Pressure of Dioxygen on the Auto-oxidation of 2,6-Di-tert-butylphenol

The effect of partial pressure of dioxygen on the auto-oxidation of 2,6-di-tert-butylphenol in aqueous micelle of CTAB was investigated by using oxygen/nitrogen mixture to obtain reduced partial pressure of 1 atm total pressure on the reaction mixture. The data illustrated in Figs. 6 and 7 show that the observed rate constants k_{obs} depend on the partial pressure of dioxygen for saturation of catalyst site.

The oxidation of phenols by dioxygen catalyzed by cobalt(II) phthalocyanine complexes represents a typical example for a reaction involving the activation of dioxygen by transition metal cation [26]. Metal-bound oxygen is an active species in the auto-oxidation of phenols catalyzed by cobalt(II) phthalocyanine [26].

Metal phthalocyanine complexes are generally known to exist as dimers in equilibrium with monomers in aqueous solutions. Their UV-Vis spectra thus consists of two peaks in the Q band region. The lower energy absorption band near 670 nm is associated with the monomeric species while

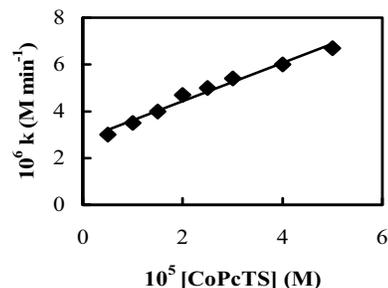


Fig. 3. Dependence of rate constant on catalyst 1 concentration. For reaction conditions see footnote (a) of Table 1.

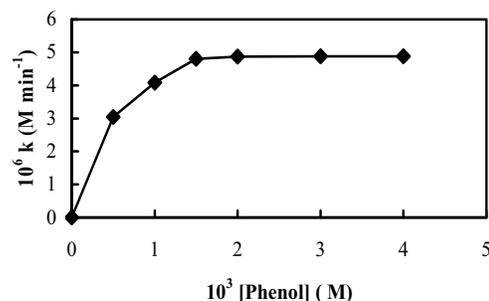


Fig. 4. Dependence of rate auto-oxidation on 2,6-di-tert-butylphenol concentration. For reaction conditions see footnote (a) of Table 1.

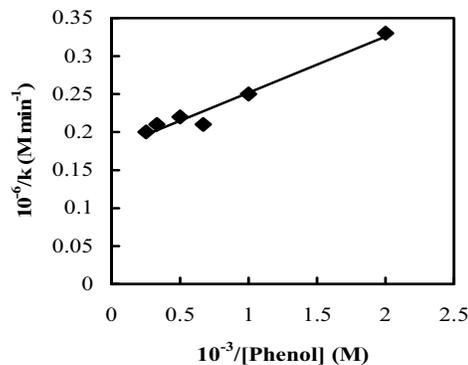


Fig. 5. Lineweaver-Burk plot for the data in Fig. 4.

the high energy absorption band near 620 nm is due to the dimeric species [30]. The spectroscopic data illustrated in Fig. 8 show that aqueous CoPcTSNa₄ in the presence of CTAB under reaction conditions is present mainly in the monomeric form. The surfactant promoted site isolation of the CoPcTSNa₄ prevents the formation of inactive μ -oxo

Oxidation of 2,6-Di-tert-butylphenol by Dioxygen

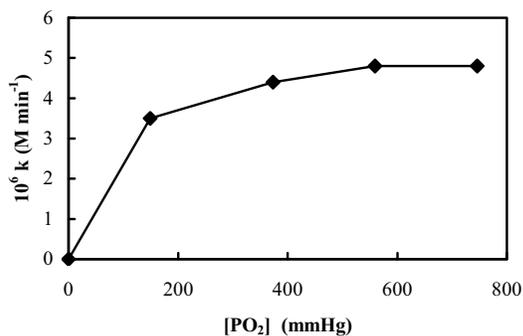


Fig. 6. Dependence of rate of auto-oxidation of 2,6-di-tert-butylphenol catalyzed by cobalt(II) phthalocyanine complex **1** in aqueous micellar aggregates of CTAB on partial pressure of dioxygen. For reaction conditions see footnote a of Table 1.

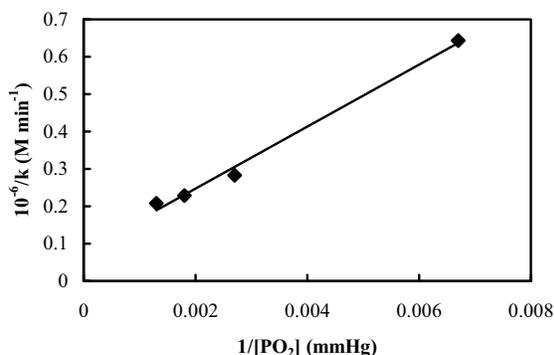
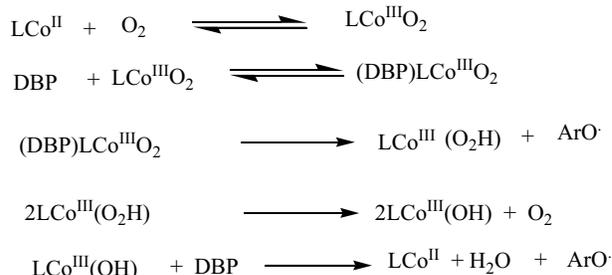


Fig. 7. Lineweaver-Burk plot for the data in Fig. 6.

dimers. The monomeric CoPcTS-dioxygen adduct (Scheme 2) is therefore the active species in the oxidation reaction of 2,6-di-tert-butylphenol in the presence of cationic surfactant CTAB.

In the literature, there is a general consensus that, the phenoxy radical is the first intermediate in the mechanism of the formation of coupled product **2** and the oxygen insertion product **3** in the oxidation of substituted phenols catalyzed by dioxygen-cobalt complexes [26-28,35]. The coupling product **2** in the oxidation reaction is formed by dimerization of the phenoxy radical (Scheme 3). The oxygen insertion product 2,6-di-tert-butyl-1,4-benzo-quinone **3** is formed through the cobalt(III) complex (Scheme 3).



DBP = 2,6-di-tert-butylphenol
ArO[·] = 2,6-di-tert-butylphenoxy radical

Scheme 2

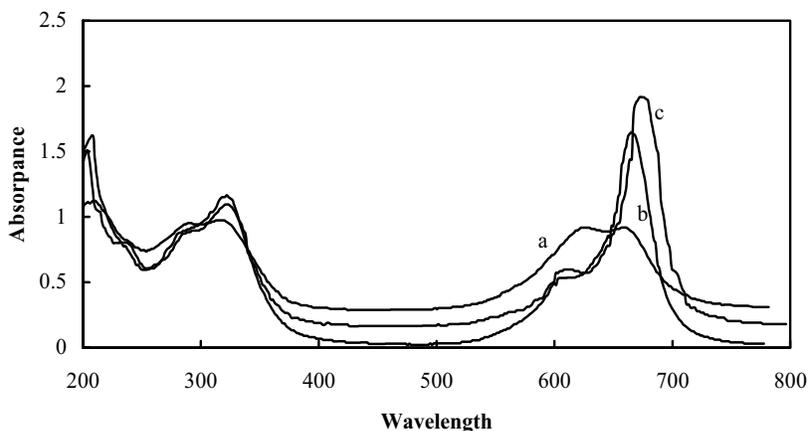
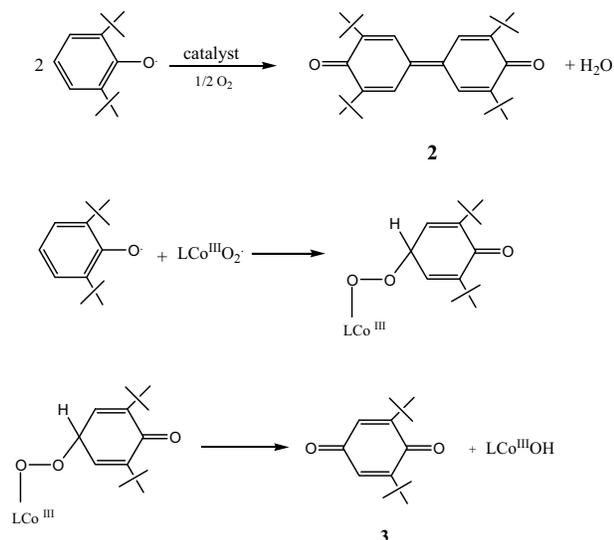


Fig. 8. Electronic absorption spectra of CoPcTSNa₄ **1**: a) electronic absorption spectra of CoPcTSNa₄ in water. b) Spectrum obtained after addition of CTAB. c) Spectrum obtained in presence of surfactant in pH 11.



Scheme 3

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