

Catalytic activity and stability of anionic and cationic water soluble cobalt(II) tetraarylporphyrin complexes in the oxidation of 2-mercaptoethanol by molecular oxygen

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Abstract

The catalytic activity and stability of anionic cobalt(II) porphyrin complexes: 5,10,15,20-tetrakis(2,6-dichloro-3-sulfonatophenyl)porphyrinatocobalt(II), 5,10,15,20-tetrakis(2,4,6-trimethyl-3,5-disulfonatophenyl)porphyrinatocobalt(II) and the cationic cobalt(II) porphyrin: 5,10,15,20-tetrakis[4-(diethylmethylammonio)phenyl]porphyrinatocobalt(II) tetraiodide have been investigated in the oxidation of 2-mercaptoethanol by dioxygen. All complexes were efficient catalysts for the auto-oxidation of 2-mercaptoethanol. The cationic cobalt(II) porphyrin has been found to be the most reactive catalyst. The rate of auto-oxidation of 2-mercaptoethanol catalysed by 5,10,15,20-tetrakis(2,4,6-trimethyl-3,5-disulfonatophenyl)porphyrinatocobalt(II) has been found to increase with increasing the pH from 7 to 9 then decreased at higher pH. The rate constants of auto-oxidation reaction showed linear dependence on catalyst concentration and saturation kinetics in both 2-mercaptoethanol concentrations and dioxygen pressure. Anionic cobalt(II) porphyrin complexes showed higher stability than the cationic catalyst in repeat oxidation reactions. Immobilizing the anionic catalysts on ion exchange resin and supporting the cationic catalyst on clay mineral montmorillonite improved their stabilities towards oxidation.

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Keywords: Catalytic oxidation; 2-Mercaptoethanol; Metalloporphyrins

1. Introduction

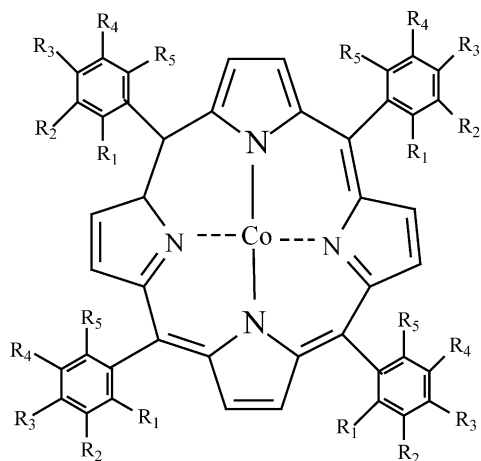
The oxidation of thiol to disulfide is an important biological [1,2] and industrial process [3,4]. In industry, it is used for eliminating offensive odours (sweetening) of petroleum products and is necessary for the treatment of some industrial and domestic waste waters. Several investigations are reported on the transition-metal catalysed oxidations of thiols to disulfide [5–15]. Cobalt(II) sulfophthalocyanine and its polymeric systems have been widely used as catalysts in the oxidation of thiols [5–11]. There are only a few reports in the literature dealing with the metalloporphyrins catalysed oxidations of thiols [12–15]. Cobalt(II) tetraarylporphyrin complexes

showed good catalytic activity for the oxidation of thiols by molecular oxygen. However, most of these complexes were slowly consumed or decomposed during oxidation of thiols [12]. It is well known that oxidative stability of metallo-tetraarylporphyrins can be dramatically enhanced by bulky substituents on the *ortho*-positions of the aryl groups [16] and by immobilizing them on the surface of solid supports [17,18].

The objective of the present paper is to study the catalytic activity of sterically hindered anionic cobalt(II) porphyrin complexes: 5,10,15,20-tetrakis(2,6-dichloro-3-sulfonatophenyl)porphyrinatocobalt(II) **1**, 5,10,15,20-tetrakis(2,4,6-trimethyl-3,5-disulfonatophenyl)porphyrinatocobalt(II) **2** and the cationic cobalt(II) porphyrin complex: 5,10,15,20-tetrakis[4-(diethylmethylammonio)phenyl]porphyrinatocobalt(II) tetraiodide **3** (Scheme 1) in the auto-oxidation of 2-mercaptoethanol and to investigate their stabilities in

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	R ₁	R ₂	R ₃	R ₄	R ₅
1	Cl	SO ₃ Na	H	H	Cl
2	CH ₃	SO ₃ Na	CH ₃	SO ₃ Na	CH ₃
3	H	H	N ⁺ (Et) ₂ Me I ⁻	H	H

Scheme 1.

homogenous oxidation reactions as well as immobilized on solid supports. The polymeric resin amberlite-CG 400 bearing quaternary ammonium groups have been used as support for the anionic cobalt porphyrin complexes **1** and **2**. Clay mineral sodium montmorillonite was used as support for cationic cobalt porphyrin complex **3** in the present study.

2. Experimental

2.1. Materials and reagents

2-Mercaptoethanol (98%, Aldrich) was distilled before use. meso-Tetra(2,6-dichlorophenyl)porphyrin and meso-tetramesitylporphyrin were prepared as described by Lindsey et al. [19]. The sulfonation of these porphyrins was performed with fuming sulfuric acid according to the published method [20]. The cobalt complexes of these tetra-arylporphyrins were prepared and purified as reported [21]. 5,10,15,20-tetrakis[4-(diethylmethylammonio)phenyl]porphyrinatocobalt(II) tetraiodide **3** was prepared in three steps: fusion of 4-(*N,N*-diethylamino)benzaldehyde with pyrrole according to the published method [22] gave 5,10,15,20-tetrakis(4-*N,N*-diethylaminophenyl)porphyrin. Cobalt(II) complex of meso-tetra(4-*N,N*-diethylaminophenyl)porphyrin was prepared as described previously [23]. 5,10,15,20-tetrakis[4-(diethylmethylammonio)phenyl]porphyrinatocobalt(II) tetraiodide **3** was obtained by methylation of the cobalt complex with methyl iodide [24]. Resin Amberlite CG-400 (Cl) (Pro-labo, 100–200 mesh) was washed with a four-fold (v/v)

excess of 5% (w/v) aqueous sodium chloride followed by water, methanol and acetone. Montmorillonite mineral clay (Mineral Colloid-BP, ECC America Inc.) with cation exchange capacity CEC of 114.8 meq/100 g was used as received.

2.2. Measurements

Microanalysis was performed by Microanalysis Unit at Tanta University, Egypt.

X-ray diffraction data were measured on Philips 1729 instrument with Cu K α ($\lambda = 1.54180$ nm) as the X-ray source. The porphyrin-clay intercalate was scanned at $2\theta = 2^\circ - 18^\circ$.

2.3. Preparation of montmorillonite clay supported cationic cobalt(II) porphyrin catalyst **3**

A solution of 5,10,15,20-tetrakis[4-(diethylmethylammonio)phenyl]porphyrinatocobalt(II) tetraiodide **3** (0.075 mmol) in 30 ml water was added to a suspension of sodium montmorillonite clay (1.50 gm) in 30 ml water with stirring for 48 h under nitrogen atmosphere. The product was filtered off, washed several times with water, and dried in vacuum at room temperature. Visible spectrophotometric analysis of the filtrate indicated complete binding of porphyrin complex on clay. Nitrogen analysis of the vacuum-dried cationic cobalt(II) porphyrin complex–montmorillonite clay intercalate indicated 0.543 mmol N/g (analysis: found N: 0.76%). The X-ray diffraction patterns of clay-catalyst **3** intercalate showed basal expansion to 14.243 Å from 9.6 of the dehydrated sodium montmorillonite.

2.4. Oxidation of 2-mercaptoethanol

The oxidation reactions of 2-mercaptoethanol were carried out as reported previously [6] at 35.0 °C and dioxygen pressure of 740 mmHg. Lower pressures of dioxygen were achieved by use of nitrogen–oxygen mixtures at 740 mmHg total pressure. Rate of reactions was monitored using gas burette. The reaction product was extracted from reaction mixture using chloroform. The disulfide was identified by comparison with authentic sample.

Oxidation of 2-mercaptoethanol using catalysts **1** and **2** supported on ion-exchange resin was carried out by stirring aqueous solution of the cobalt complexes with the polymeric resin (0.029 gm) for half an hour then the reaction was followed under reaction conditions of Table 1.

Oxidation reactions using intercalated cationic cobalt(II) porphyrin **3** as catalyst were carried out using 0.127 gm of the intercalated complex.

2.5. Catalysts reuse

Reuse of the catalysts **1–3** was carried out as follows: auto-oxidation of 2-mercaptoethanol was carried out under standard reaction conditions of Table 1. The reaction was

Table 1
Activities of cobalt(II) porphyrin complexes **1–3** in the auto-oxidation of 2-mercaptoethanol^a

Catalyst	k_{obs} (mol/(L min)) $\times 10^5$
–	2.599
1	4.946
2	8.276
3	10.778

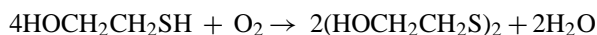
^a All experiments were carried out at 38 °C and oxygen pressure of 740 mmHg with magnetic stirring of 5.7×10^{-3} M of 2-mercaptoethanol in 100 ml of distilled water containing 5.7×10^{-6} M of catalyst. The pH of the reaction was adjusted to 9.0 by using borax and HCl.

followed by dioxygen uptake. After the completion of the first run, the initial amount of 2-mercaptoethanol was again fed into reaction mixture without removal of the reaction products.

3. Results and discussion

3.1. Auto-oxidation of 2-mercaptoethanol

The catalytic activities of water soluble cobalt(II) porphyrin complexes **1–3** were investigated in the auto-oxidation of 2-mercaptoethanol to disulfide. The rate of thiol consumption was determined by measuring the amount of dioxygen consumed using a gas burette. The dioxygen consumption was in agreement with the stoichiometry of the equation:



After a short induction period, the volume dioxygen consumed was linear with time, indicating a zero-order dependence on the concentration of the substrate.

The data summarized in Table 1 demonstrate the catalytic activity of water soluble cobalt(II) tetraarylporphyrin catalysts **1–3** in the auto-oxidation of 2-mercaptoethanol to disulfide in water. All cobalt(II) porphyrin complexes showed high activity for auto-oxidation of 2-mercaptoethanol. The zero-order rate constants k_{obs} in Table 1 show that the cationic cobalt(II) porphyrin complex **3** is the most reactive catalyst. The high catalytic activity of cationic cobalt(II) porphyrin complex **3** could be due to the following reasons: the positive charge around the complex may accelerate the dissociation of the weakly acidic thiol into thiolate anions which is the reactive species [25]. The quaternary ammonium groups also help binding of the thiolate anions RS^- to the active site.

Detailed study of the auto-oxidation of 2-mercaptoethanol was carried out using cobalt(II) porphyrin complex **2** as catalyst.

Data in Fig. 1 illustrate the effect of pH in the range 7–10 on the rate constant k_{obs} for the thiol consumption. The zero-order rate constant k_{obs} reached an optimum at pH about 8.7 indicating that the thiolate anion is the active species [26]. The decrease of the reactivity at higher pH could be due to the competing ion effect of the hydroxide ion with the thiolate anion [6]. At high pH, a large amount of hydroxyl

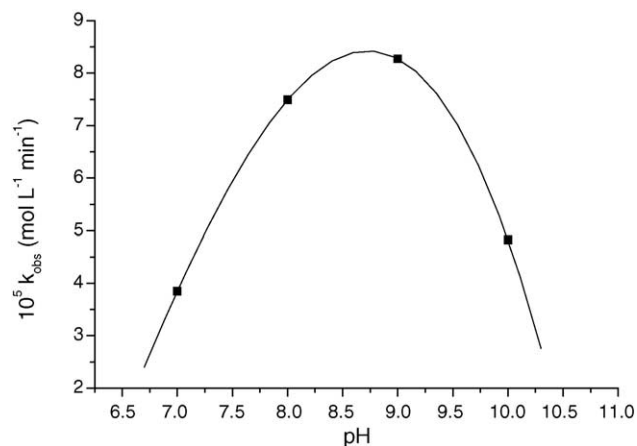


Fig. 1. Dependence of the initial zero-order rate constant k_{obs} of the auto-oxidation of 2-mercaptoethanol catalysed by cobalt(II) complex **2** on the pH of the reaction. For reaction conditions see footnote of Table 1.

ions also induce the formation the inactive μ -oxo dimers and thus lower the efficiency of the cobalt complex [15].

The data in Fig. 2 show a linear dependence of the rate constant k_{obs} on the concentration of the catalyst **2**.

The temperature dependence of the rate constant from 40 to 60 °C gave an Arrhenius activation energy of 18.28 kJ/mol (Fig. 3).

The rate constants k_{obs} of thiol consumption depend on initial concentration of thiol as shown in Fig. 4. A double reciprocal Lineweaver–Burk plot (Fig. 5) shows that the data fit a Michaelis–Menten kinetic model for saturation of catalyst sites with increasing thiol concentration.

Similarly the observed rate constants k_{obs} depend on the partial pressure of dioxygen for saturation of catalyst site as shown in Figs. 6 and 7.

These data suggest that Michaelis–Menten mechanism can be described for the auto-oxidation of 2-mercaptoethanol catalysed by cobalt(II) porphyrin complex **2** [8,26].

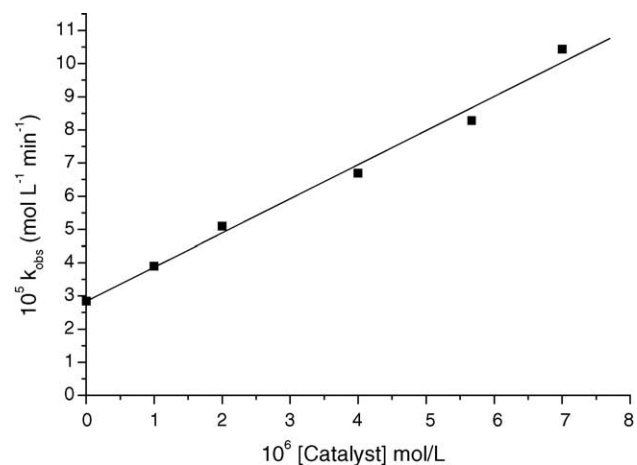


Fig. 2. Dependence of the initial zero-order rate constant k_{obs} of the auto-oxidation of 2-mercaptoethanol on the concentration of catalyst **2**. All reactions were carried out under experimental conditions as reported in Table 1.

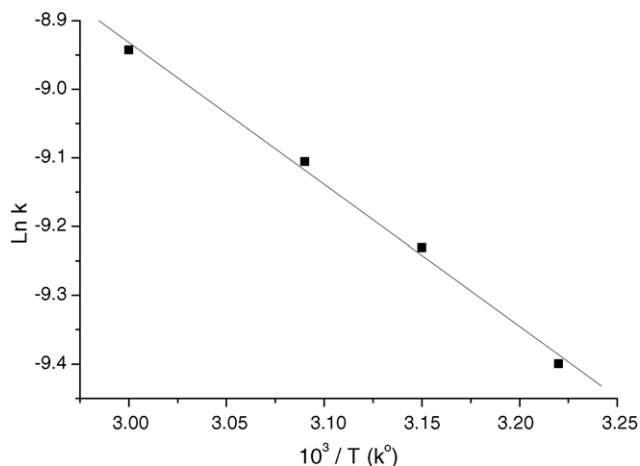


Fig. 3. Arrhenius plot of the zero-order rate data at 40–60 °C. Experimental conditions see Table 1.

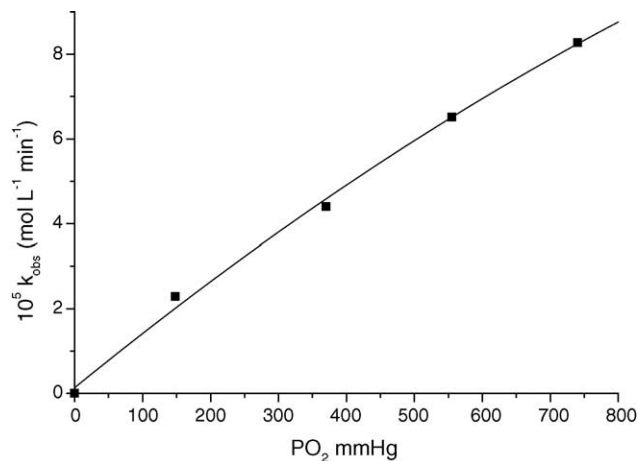


Fig. 6. Dependence of the initial zero-order rate constant k_{obs} of the auto-oxidation of 2-mercaptoethanol catalysed by cobalt(II) complex **2** on the pressure of dioxygen. Experimental conditions see Table 1.

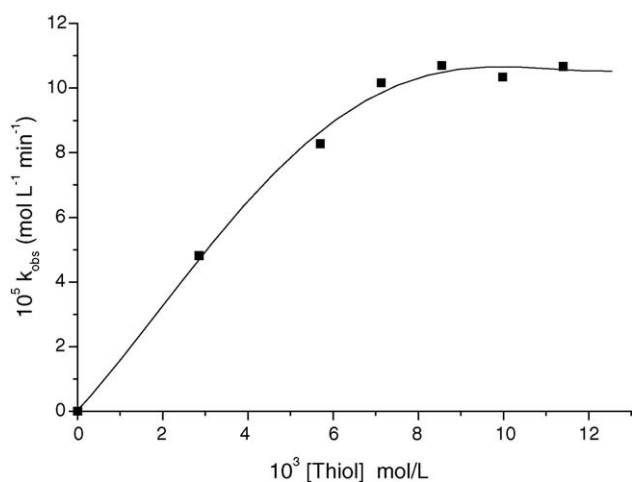


Fig. 4. Dependence of the initial zero-order rate constant k_{obs} of the auto-oxidation of 2-mercaptoethanol catalysed by cobalt(II) complex **2** on the concentration of thiol. All reactions were carried out under experimental conditions as reported in Table 1.

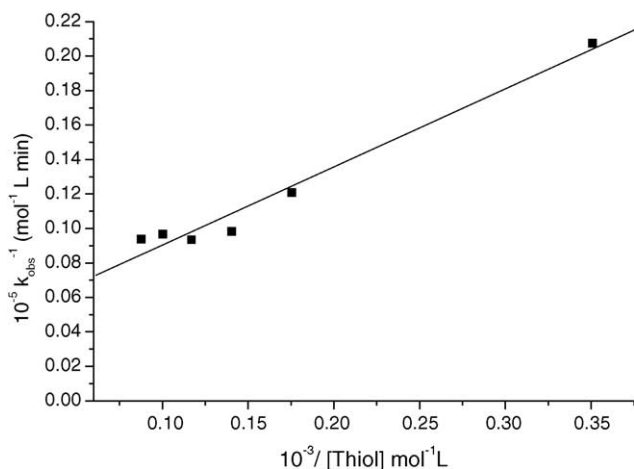


Fig. 5. Lineweaver–Burk plot of the data in Fig. 4.

3.2. Catalytic activity of anionic cobalt(II) porphyrin complexes **1** and **2** supported on ion exchange resin

The activity of catalysts **1** and **2** adsorbed on ion exchange resin Amberlite CG-400 was examined for enhancing the rate of auto-oxidation of 2-mercaptoethanol. The resin supported catalysts **1** and **2** showed almost the same reactivities as their homogenous analogues.

3.3. Catalytic activity of clay-supported cationic cobalt(II) porphyrin complex **3**

Cationic cobalt(II) porphyrin complex **3** supported on clay montmorillonite was prepared by addition of aqueous solution of cationic catalyst **3** to suspension of clay sodium montmorillonite in water. The X-ray diffraction patterns of clay-supported catalyst **3** showed basal expansion to 14.243 Å from 9.6 of dehydrated sodium montmorillonite. The basal spacing d_{001} of 14.243 Å corresponds to interlamellar spac-

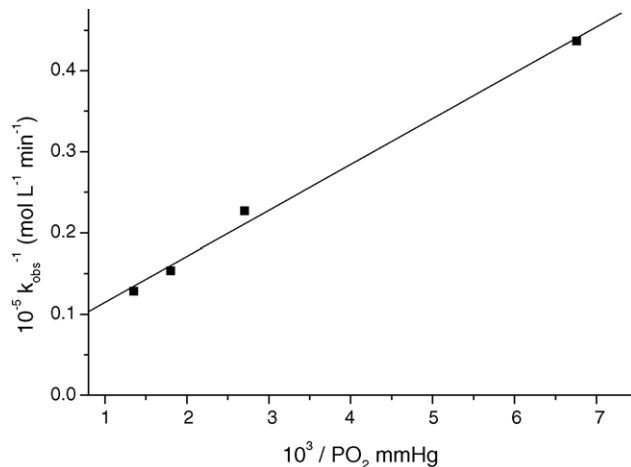


Fig. 7. Lineweaver–Burk plot of the data in Fig. 6.

ing of 4.943 Å this indicates that the catalyst **3** has accessed the interlamellar spacing of the mineral clay. In comparison to homogenous auto-oxidation of 2-mercaptoethanol catalysed by soluble complex **3**, the catalyst **3** intercalated in clay montmorillonite showed lower reactivity and was found to be 0.55 times as active as the soluble catalyst **3**.

3.4. Stability of the anionic and cationic cobalt(II) porphyrin catalysts **1–3** in repeats oxidations

Cobalt(II) porphyrin complexes **1–3** were tested for their stability in successive experiments. The reuse of these catalysts was carried out under the experimental conditions of Table 1. After 100% conversion of 2-mercaptoethanol, the initial amount of the thiol was injected into the reaction mixture without separation of reaction products. Water soluble catalysts **1–3** showed no change in reactivity after three successive runs. All catalysts showed some deactivation after the fourth run. The recycled anionic catalysts **1** and **2** were about 0.75 times as active as the fresh catalysts. The recycled cationic porphyrin complex **3** showed reduced to 0.6 that of the fresh catalyst.

Cobalt(II) anionic porphyrin complexes **1** and **2** adsorbed on ion exchange resin CG-400 were monitored for six repeat oxidations of 2-mercaptoethanol. The supported catalyst showed no deactivation after six reaction cycles. The clay intercalated cationic cobalt(II) porphyrin complex **3** has been found to be stable after six repeat oxidation reactions of 2-mercaptoethanol.

In general, metalloporphyrins are readily oxidized in systems containing free radicals [12]. The thiol reaction system would fall into this group. In recent publications [17,18,27], it has been reported that degradation of metalloporphyrins arises also through the aggregation of metalloporphyrins in solution favouring intermolecular self-oxidation of the catalyst.

The site isolation of anionic cobalt porphyrin complexes **1** and **2** by supporting them on the surface of the ion exchange resin prevented porphyrin aggregation and intermolecular self-oxidation of the cobalt porphyrin catalysts.

The enhanced stability of the intercalated cationic cobalt(II) porphyrin **3** into the layered structure of clay montmorillonite may be attributed to the better distribution of the intercalated cobalt porphyrin than the aggregated form of porphyrin in solution, which prevented the formation of inactive μ -oxo dimers and the degradation of cationic cobalt porphyrin in the oxidation reaction.

Comparing the results of the present work with that reported previously on the oxidation of thiol catalysed by soluble and latex-supported cobalt(II) sulfophthalocyanine [6,9]. Indeed the cobalt(II) sulfophthalocyanine and latex cat-

alysts exhibited higher reactivities for the oxidation of thiols, however these catalysts showed deactivation after only one catalytic cycle.

Acknowledgement

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