

Autooxidation of alkyl mercaptans catalysed by cobalt(II) phthalocyanine tetrasodium sulphonate in reverse micelles

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Received 10 January 1995; revised 16 June 1995; accepted 27 July 1995

Abstract

The UV–Visible studies in different solvents and reverse micelles indicate that anionic water soluble cobalt(II) phthalocyanine tetrasodium sulphonate exists in monomeric form in cationic surfactant reverse micelles, whereas it exists in mixture of monomeric and dimeric forms in anionic surfactant reverse micelles at different pH as well as in homogeneous aqueous solution. Higher yields of dibenzyl disulphide are obtained by catalytic oxidation of benzyl mercaptan in water in oil microemulsions prepared from cationic surfactant than that of anionic surfactant at different pH range as well as homogeneous solution.

Keywords: Autooxidation; Mercaptans; Cobalt; Phthalocyanine; Reverse micelles

1. Introduction

The sulphur and nitrogen containing impurities are present in crude petroleum and they are responsible for environmental pollution during processing or their practical applications. The sulphur compounds especially alkyl mercaptans cause corrosion and they are responsible for poisoning of the different catalysts. Further they affect the performance of antioxidant additives blended in finished fuels. The autooxidation of alkyl mercaptans, phenol, catalysed by cobalt(II) phthalocyanine tetrasodium sulphonate 1 (CoTSPc) in aqueous solution is an important sweetening process for removal and extraction of sulphur compounds from petroleum. However, the CoTSPc 1 forms dimers and are less reactive

in homogeneous medium. The removal of catalysts from homogeneous medium is difficult, hence the Co(II) catalysts are immobilized on a variety of solid supports [1–4].

Microemulsions are thermodynamically stable colloidal dispersions of surfactant molecules either in oil or in water [5,6]. The reverse microemulsions are formed by the dissolution of surfactants in oil or hydrocarbons [7–9]. They provide unique and variable reaction media depending on the ratio of water to surfactant (W_o) to study the peptide bond formation [10], oxidation of iron salts [11], nucleophilic substitution [12] and other reactions [13–15].

The CoTSPc forms oligomers [16] in aqueous solution and they exist in monomeric form in the presence of surfactants including hexadecyl trimethyl ammonium chloride (HTAC) [17] and

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cetyl trimethyl ammonium bromide (CTAB) [18]. The incorporation of Co(II)TSPc in water droplets provide large surface area for interaction with substrates solubilized in organic phase of water-in-oil microemulsions. In this paper we report the autooxidation of alkyl mercaptans catalysed by CoTSPc in different water-in-oil microemulsions.

2. Experimental

2.1. Materials and methods

Cetyltrimethyl ammonium bromide (CTAB), sodium-bis-(2-ethyl-hexyl) sulphosuccinate (Aerosol-OT) were obtained from Fluka. CTAB was recrystallized from acetone and Aerosol-OT was purified following the literature procedure [19]. The oxidation products were identified and quantified using Waters HPLC equipped with photodiode array detector (Model 991) on a μ -Bondapak C¹⁸ column (3.9×300 mm) using methanol as the eluent at a flow rate of 0.5 ml/min.

2.2. Preparation of Co(II)phthalocyaninetetrasodium sulphonate 1

The condensation of phthalic anhydride, urea and cobalt chloride in presence of ammonium molybdate gave cobalt(II) phthalocyanine. The reaction of cobalt(II)phthalocyanine with oleum at 75°C for 5 h gave the required cobalt(II)phthalocyanine tetrasodium tetrasulphonate in 65% yield [20]. It was also prepared by cyclocondensation of 4-sulphophthalic acid, cobalt(II) sulphate and urea in presence of ammonium molybdate [21]. The structure of 1 was confirmed by UV-Visible spectroscopy. The ESR spectra ($g = 1.97$) shows that cobalt exists in the Co(II) oxidation state.

2.3. General method for the UV-Visible spectroscopic study of 1 in phosphate buffer at different pH

A stock solution of CoTSPc (5.7 mg, 6.5 mM) in phosphate buffer (pH 5.0, 0.2 M) was prepared. The aqueous solution of phthalocyanine 5.4 μ l is drawn from a stock solution and injected into a UV cell containing 3 ml of buffer. The resulting solution was shaken thoroughly and the spectrum was recorded. Similarly the reactions were performed at pH 7.0, 10.2 and 13.2.

2.4. General procedure for the incorporation of 1 in reverse micelles

The anionic surfactant Aerosol-OT (4.4 g, 0.1 M) and CTAB (3.2 g, 0.1 M) reverse micelles were prepared following the literature procedure [22]. The incorporation of Co(II)TSPc in CTAB and aerosol-OT (AOT) water in oil microemulsions have been carried out by following the literature procedure [22,23]. The entrapment of 1 was monitored by UV-Visible spectroscopy at different pH.

2.5. General method for the UV-Visible spectroscopic study of 1 in cationic and anionic reverse micelles at different pH

A solution of cobalt phthalocyanine 1 (6.5 mM, 5.4 μ l) in buffer of appropriate pH (5.0, 7.0, 10.2 and 13.2) was injected into 3 ml of 0.01 M CTAB in CHCl₃-isooctane in a UV cell. The solution was shaken and UV-Visible spectra were recorded after the solution became transparent. Additional 5.4 μ l of buffer was injected into the cell for each increment of W_o. After each addition the solution was shaken thoroughly and kept aside for 3 min to obtain a transparent solution. Then the spectra were recorded between 300–800 nm (Fig. 1 and Fig. 2).

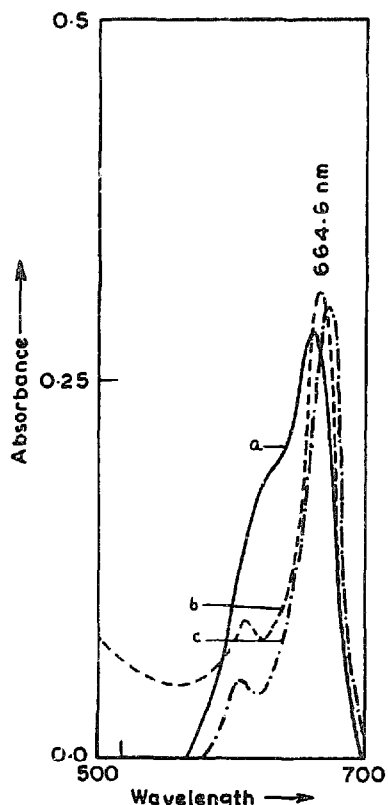


Fig. 1. Change in the UV spectrum of Co(II) TSPc at different water/CTAB ratios: (a) Co(II)TSPc in phosphate buffer pH=7.0; (b) Co(II)TSPc in CTAB ($W_o=9$); (c) Co(II)TSPc in CTAB ($W_o=19$).

2.6. General procedure for the reaction of benzyl thiol with molecular oxygen catalysed by **1** in cationic and anionic reverse micelles

To a stock solution of CTAB in CHCl_3 -isooctane or AOT in isooctane (3 ml, $W_o=19$) containing 5.4 μl of phthalocyanine from stock solution (6.5 mM), benzyl thiol (0.124 g, 1 mmol) was added. Oxygen was bubbled through the agitated reaction mixture for 1 h at room temperature. The solvent was evaporated and the residue was dissolved in methanol and was subjected to HPLC analysis. The above reaction is carried out at different W_o and pH. The results are tabulated in Table 1 and Table 2.

3. Results and discussion

Microemulsions are isotropic and optically clear dispersions of oil in water or water in oil droplets prepared from the surfactant molecules.

They form variable reaction media depending on the ratio of water to surfactant molecules (W_o) [22]. The incorporation of Co(II)TSPc in water droplets provide large surface area for the interaction with substrate solubilized in organic phase of microemulsions and thus they may increase the efficiency of the catalyst Co(II)TSPc **1** in different reaction conditions. Hence the UV-Visible spectrum of anionic water soluble Co(II)TSPc has been examined in different solvents, cationic and anionic reverse micelles.

3.1. Effect of pH and solvents

The UV-Visible absorption maxima of **1** in aqueous solution appeared at 660 and 627 nm whereas in methanol at 659 and 598 nm. The UV-Visible absorption maxima of **1** appeared at 656 nm (ϵ max 260) and at 620 nm (max 17.0) in phosphate buffer at pH 5.0 at room temperature.

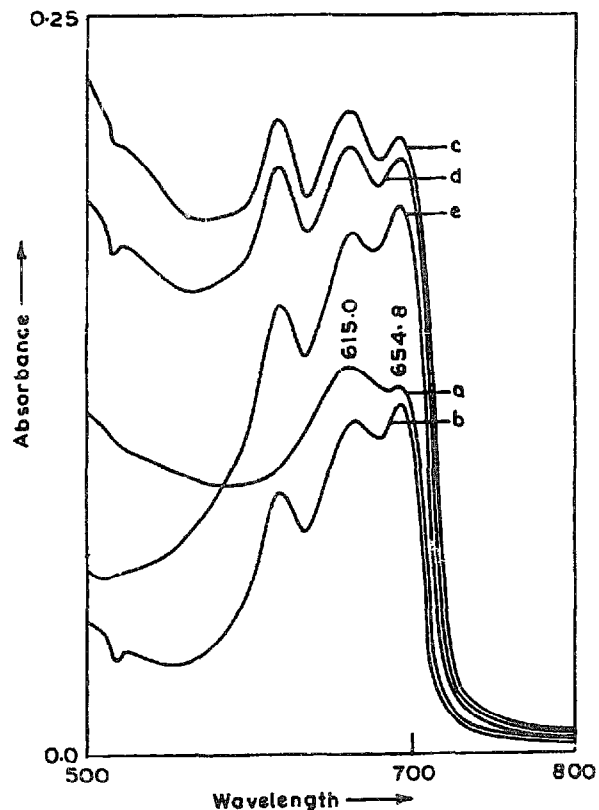


Fig. 2. Change in the UV spectrum of Co(II)TSPc at different water/AOT ratios: (a) Co(II)TSPc in AOT (isooctane); (b) Co(II)TSPc in AOT ($W_o=9$); (c) Co(II)TSPc in AOT ($W_o=14$); (d) Co(II)TSPc in AOT ($W_o=19$); (e) Co(II)TSPc in AOT ($W_o=25$).

Table 1

Oxidation of benzyl thiol with oxygen catalysed by cobalt(II) phthalocyanine tetrasodium sulphonate (Co(II)TSPc, **1**) in water in chloroform–isooctane at different H₂O/CTAB ratios (W₀)

| Exp. No. | Reaction conditions | Yield of dibenzyl disulphide (%) |
|-----------------|--|----------------------------------|
| 1 | Co(II)TSPc, H ₂ O/CTAB (W ₀ =1) (pH=7.0) | 63.0 |
| 2 | Co(II)TSPc, CTAB (1.2 × 10 ⁻⁵ M) | 80.0 |
| 3 | Co(II)TSPc, H ₂ O/CTAB (W ₀ =9) (pH=7.0) | 85.0 |
| 4 | Co(II)TSPc, H ₂ O/CTAB (W ₀ =19) (pH=5.0) | 70.0 |
| 5 | Co(II)TSPc, H ₂ O/CTAB (W ₀ =19) (pH=7.0) | 100.0 |
| 6 | Co(II)TSPc, H ₂ O/CTAB (W ₀ =25) (pH=7.0) | 100.0 |
| 7 | Co(II)TSPc, H ₂ O/CTAB (W ₀ =19) (pH=10.2) | 100.0 |
| 8 | Co(II)TSPc, H ₂ O/CTAB (W ₀ =19) (pH=13.2) | 32.0 |
| 9 | Co(II)TSPc, TBAB, phosphate buffer, CH ₂ Cl ₂ (1:1) (pH=7.0) | 50.0 |
| 10 | Co(II)TSPc, H ₂ O/CTAB (W ₀ =35) (pH=7.0) | 46.0 |
| 11 ^a | CoTSPc(II), H ₂ O/CTAB (W ₀ =19) (pH=7.0) | 34.0 |
| 12 ^a | CoTSPc(II), H ₂ O/CTAB (W ₀ =25) (pH=7.0) | 38.0 |
| 13 ^b | CoTSPc(II), H ₂ O/CTAB (W ₀ =19) (pH=7.0) | 65.0 |

All the reactions were performed at room temperature in phosphate buffer (pH = 5.0, 7.0, 10.2 and 13.2) for 1 h. HPLC analyses were carried out on a μ -Bondapak C¹⁸ column, flow rate 0.5 ml/min and a photodiode array detector is used for detection. HPLC retention time for dibenzyl mercaptan is 4.10 min and for dibenzyl disulphide is 4.45 min (Fig. 4).

^a Reaction time is 15 min.

^b Reaction time is 30 min.

The UV–Visible absorption peaks were also observed at pH 7 and 10.2. At pH 13.2 these maxima values shifts to 663.8 (max 59.6) and 598.8 (max 1.18) nm. The change in absorption maxima at pH 13.2 shows that phthalocyanine is in aggregated form, which is responsible for the low yield of disulphide formation. These results are consistent with the UV–Visible spectroscopic studies of Co(II)TSPc and its existence in monomeric and dimeric form in phosphate buffer [16,24].

3.2. Effect of microemulsions

The absorption maxima of Co(II)TSPc in cationic reverse micelle appear at 664.4 and 609.2 nm. These values indicate that CoTSPc exists more in the monomeric form than in the dimeric form (Fig. 1). In anionic reverse micellar conditions these values appeared at 654.8 and 615.0 nm, indicating that Co(II)TSPc exists more in the dimeric form when using cationic surfactants. Further these values indicate that Co(II)TSPc is in equilibrium between its monomeric and dimeric forms (Fig. 2). The UV–Visible studies indicate that **1** exists more in monomeric form in cationic

microemulsions than that of anionic microemulsions.

3.3. Oxidation of benzyl mercaptan with molecular oxygen catalysed by Co(II)TSPc in different reaction conditions

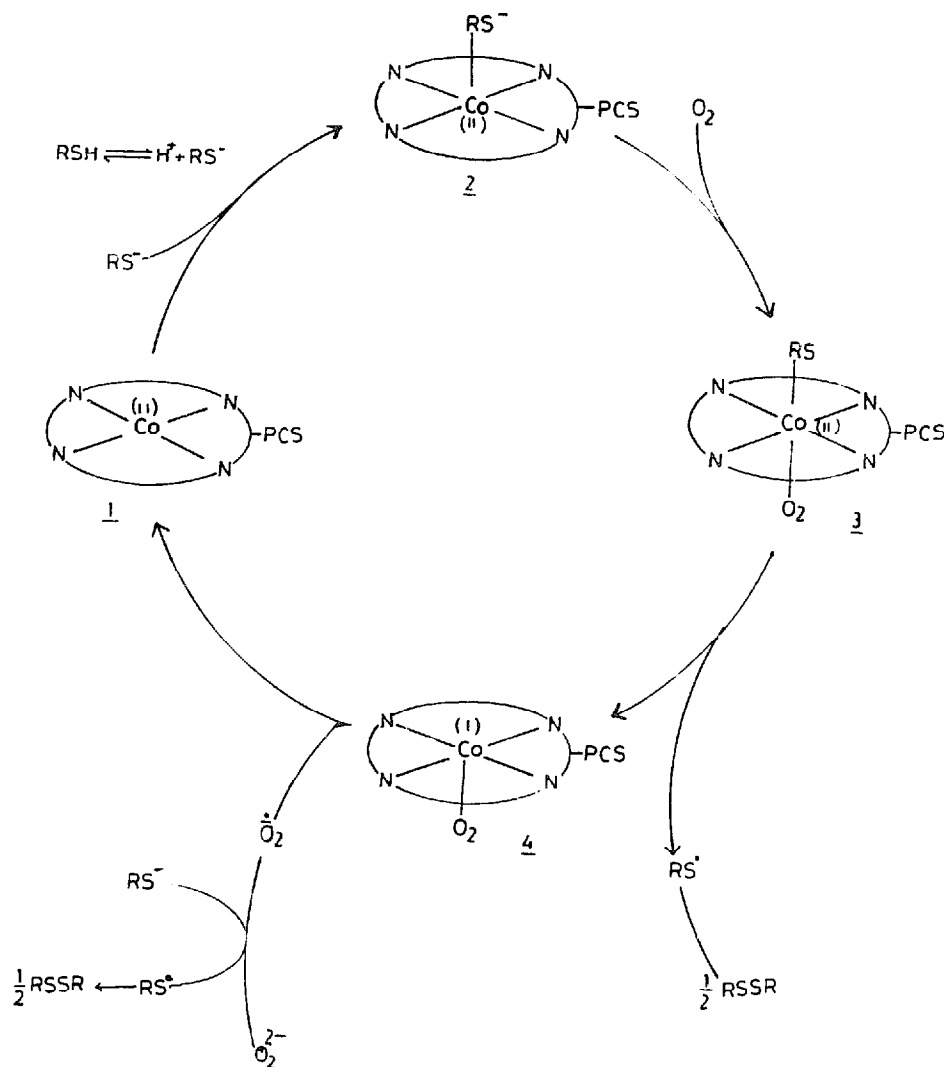
In the first step benzyl mercaptan (pK_a = 10.4) is ionized to RS⁻ which reacts with Co(II)TSPc **1** to form the intermediate **2**. The reaction of molecular oxygen form a ternary complex **3**. This step is ligand exchange process. These species

Table 2

Oxidation of benzyl thiol with oxygen catalyzed by cobalt(II) phthalocyanine tetrasodium sulphonate (Co(II)TSPc, **1**) in water in isooctane at different H₂O/AOT ratio at room temperature

| Exp. No. | Reaction conditions | Yield of dibenzyl disulphide (%) |
|----------|---|----------------------------------|
| 1 | Co(II)TSPc, AOT (1.2 × 10 ⁻⁵ M) | 27.0 |
| 2 | Co(II)TSPc, H ₂ O (W ₀ =1) | 35.0 |
| 3 | Co(II)TSPc, H ₂ O (W ₀ =9) | 68.0 |
| 4 | Co(II)TSPc, H ₂ O (W ₀ =19) | 70.0 |

Retention time for benzyl thiol is 4.10 min and for dibenzyl disulphide is 4.45 min. All the reactions were performed at pH = 7.0.



Scheme 1. Predicted mechanism of oxidation of mercaptans by Co(II)TSPc.

were detectable in the UV–Visible spectrum of mixture of Co(II)TSPc and benzyl thiol. The absorption maxima of Co(II)TSPc **1** in cationic reverse micelles at $Wo = 5$ appeared at 663.2 and 596.2 nm. On the addition of benzyl mercaptan, the absorption maxima of **1** appeared at 675.6, 620.0, 542.0 and 443.4 nm. These absorption maxima were consistent with coordination of RS^- at axial position followed by enhanced coordination of O_2 and then one electron charge transfer proceeds from RS^- to Co(II) in the coordination sphere to give RS^\bullet and O_2^\bullet via intermediate **4** which was in Co(I) oxidation state [25]. The absorption band at 443.4 nm has also been attributed to Co(I). The one electron transfer process was the rate determining step. The dibenzyl disul-

phide was formed by the dimerisation of RS^\bullet radicals. Further the reaction of O_2^\bullet with RS^- results in the formation of RS^\bullet radical leading to disulphide along with the generation of O_2^{2-} [25] (Scheme 1). After 12 h the same solution exhibits a visible spectrum which corresponds to the original Co(II)TSPc (Fig. 3). This type of mechanism was originally suggested by Theorell and Chance [26,27]

The reaction of benzyl mercaptan with molecular oxygen catalysed by Co(II)TSPc gave different yields of dibenzyl disulphide depending on the reaction conditions (Fig. 4). Higher yields of disulphide were obtained in water in oil microemulsions as compared to phase transfer conditions. The reaction of benzyl mercaptan with

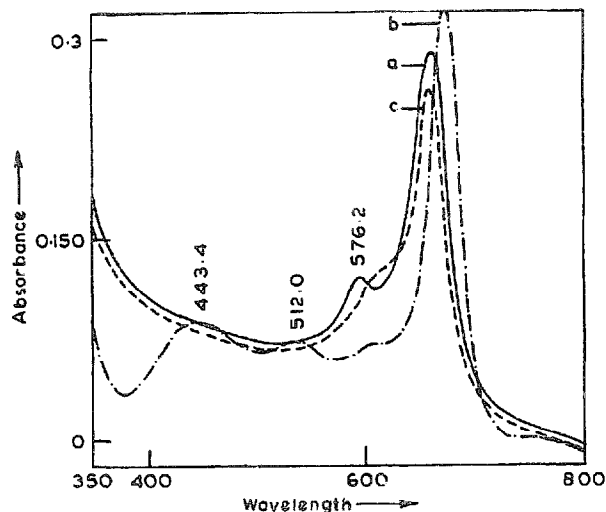


Fig. 3. Change in UV spectrum by addition of benzyl thiol (after 12 h): (a) Co(II)TSPc in CTAB $W_o = 7.0$; (b) Co(II)TSPc in CTAB/benzyl thiol (after 5 min); (c) Co(II)TSPc in CTAB/benzyl thiol.

Co(II)TSPc in cationic reverse micelles at $W_o = 19$ for 1 h gave dibenzyl disulphide in 100% yield (Table 1), whereas in anionic reverse

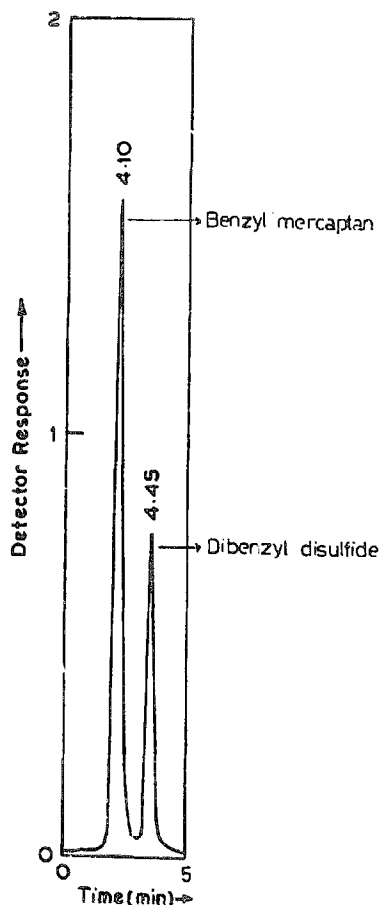


Fig. 4. HPLC profile for Co(II)TSPc + benzyl mercaptan + O_2 in CTAB/ $CHCl_3$ -isooctane $W_o = 1.0$, pH = 7.0.

micelles in 70% (Table 2). The optimum yield of dibenzyl disulphide was obtained at $W_o = 19$, due to the size of the aqueous core well adapted to entrap the maximum number of phthalocyanine molecules. Further increment of the W_o after 19 gave similar yields of dibenzyl disulphide as was obtained at $W_o = 19$. This was confirmed by performing the reaction for only 15 min. The oxidation reactions were performed up to $W_o = 29$ but after $W_o = 29$ phase separation takes place in the reverse micelles with decrease in the yield of dibenzyl disulphide (Table 1).

4. Conclusion

The results from the above studies indicate that the higher yields of oxidation products with molecular oxygen catalysed by Co(II)TSPc are obtained in cationic reverse micelles than anionic reverse micelles.

Acknowledgements

This work was supported by Council of Scientific & Industrial Research and Department of Science & Technology, New Delhi, India.

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