



Cobalt(III)-salen ion catalyzed H₂O₂ oxidation of dibenzyl sulfide

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Abstract: Cobalt(III)-salen complexes {salen = N,N'bis(salicylidene)ethylenediaminato} efficiently catalyze the H₂O₂ oxidation of sulfides. This reaction leads to the formation of sulfoxides as the major product. The spectrophotometric kinetic study shows that the reaction follows Michaelis-Menten kinetics. Based on the spectral and kinetic studies a suitable electron transfer mechanism has been proposed.

Keywords: Cobalt(III)-salen catalyst – H₂O₂ oxidation –DBS.

Introduction

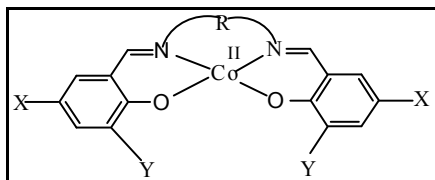
Cobalt is one of the most studied oxygen activating metals. Many of its chelate compounds are known to reversibly bind oxygen to form superoxo- or peroxo-type complexes [1]. There are no enzymes in nature which have cobalt as the central metal, but there are several enzymes which are dependent on a coenzyme B₁₂, which has cobalt as the active metal [2]. Cobalt being a biologically relevant metal, it is desirable to study the role of cobalt ion as catalyst. The oxygen binding abilities of cobalt-salen complexes stimulated the research towards reversible O₂ binding properties of cobalt(II)-salen ions and their utility as catalysts[3-6]. Cobalt-salen complexes have been used as catalysts for epoxidation reactions[7-9], ring opening[10-12], cyclopropanation[13], carbondioxide fixation[14], copolymerization of CO₂[15], asymmetric catalysis[16-18], oxidation of phenols and anilines[20,21] and catalysts for other reactions [22-26]. Metal-salen complexes are a valuable alternative to biomimetic heme-protein models [27]. The selective oxidation of sulfides to sulfoxides is a promising and important transformation in organic chemistry, since sulfoxides are useful building blocks in organic synthesis [28]. Therefore a great number of methods and procedures have been reported for this type of transformation [29,30]. The use of catalytic systems based on readily available, inexpensive and environmentally benign transition metals and green oxidants like hydrogen peroxide is very attractive [31]. The study of oxidation of organic sulfides is of wide interest because sulfur plays a major role in biology and is found in numerous peptides, proteins and low molecular weight compounds. Fukuda and Katsuki [32] reported asymmetric cyclopropanation of styrene using optically active cobalt(III)-salen complexes. With this background Co(III)-salen complexes are used as catalysts for the H₂O₂ oxidation of dibenzyl sulfide.

Experimental

Salicylaldehyde, substituted salicylaldehydes (5-methyl, 5-bromo, 5-chloro, 3, 5-di-tert butyl, 5-methoxy) and dibenzyl sulfide were purchased from Aldrich and used as such.

Synthesis of ligands and cobalt(III)-salen complexes

Various salen ligands are prepared from ethylenediamine and the corresponding salicylaldehyde by standard methods [33]. Cobalt(III)-salen complexes(Chart 1) are synthesized by established procedure[34].The cobalt(III)-salen complexes are characterized by UV-vis, FT-IR and CV studies.



I X=H, Y=H, R= CH₂CH₂;

III X=Cl, Y=H, R= CH₂CH₂;

V X =OCH₃, Y=H, R= CH₂CH₂;

II X=Br, Y=H, R= CH₂CH₂;

IV X =CH₃, Y=H, R= CH₂CH₂;

VI X =Y= *tert*-Butyl,R= cyclohexane;

Chart 1. Structure of cobalt(III)-salen complexes

Kinetic studies

The kinetic study has been carried out using Elico SL-164 spectrophotometer. The oxidation of DBS with six cobalt(III)-salen- H₂O₂ system have been carried out in 90%CH₃CN -10%DCM at 298K under pseudo first order conditions by taking DBS in 10 fold excess over the oxidant. The rate of the reaction is measured following the decay of absorbance of cobalt(III)-salen complexes with time at appropriate (λ_{max}) wavelength (Table 1).The pseudo-first-order rate constant(k_1)value for each kinetic run was evaluated from the linear least-square plots of log(absorbance) vs time .

Table 1. λ_{max} values of cobalt-salen complexes for the kinetic study

Cobalt-salen complex	λ_{max} , nm
I	384
II	396
III	383
IV	395
V	392
VI	391

Product analysis

A solution containing 5mM dibenzyl sulfide, 0.2mM cobalt(III) – salen complex and 5mM H₂O₂ in 5ml of 90%CH₃CN-10%DCM was stirred at 298K for 1-2 hours. The reaction mixture after the completion of the reaction is extracted with chloroform to recover the products. The product is dried over sodium sulfate and after evaporating the solvent it is subjected to ¹H-NMR analysis.

Results and discussion

The kinetics of cobalt(III)- salen ion catalyzed H₂O₂ oxidation of DBS in 90%CH₃CN -10%DCM at 298K has been studied using spectrophotometric technique by measuring the change in OD with time and a sample run is shown in Figure-1. The reaction is found to be first order in the oxidant, which is evident from the linear log (absorbance) Vs time plot (Figure 2). The dependence of the reaction rate on substrate concentration is studied with different substrate concentrations and the kinetic results are shown in Table-2&Figure-3. At high concentration of substrate saturation behavior is observed and the reaction proceeds through Michaelis-Menten kinetics and the rate constants are evaluated from the 1/ k_1 vs 1/ [substrate] plot and are collected in Table 3. The saturation kinetics observed and low K_M values indicate strong binding of substrate with the active oxidant.

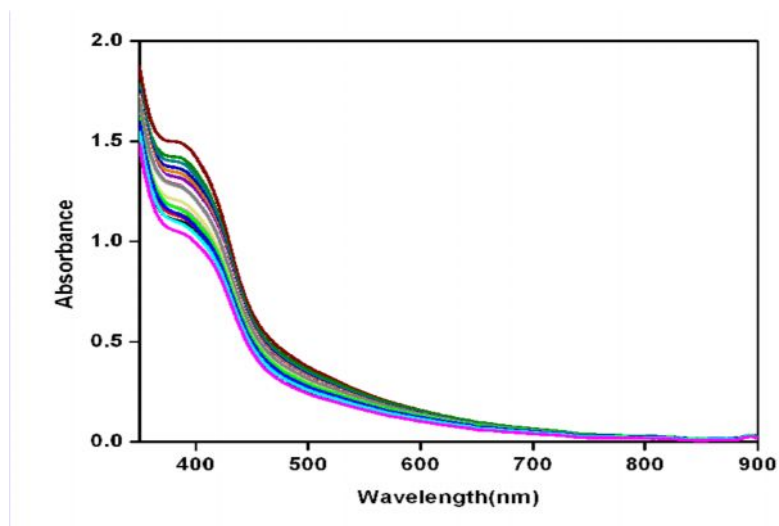


Figure 1 Change of absorbance of VII-H₂O₂ system with time for DBS [I] = 2×10^{-4} M, [H₂O₂] = 5×10^{-3} M, [BPS] = 1×10^{-3} M.

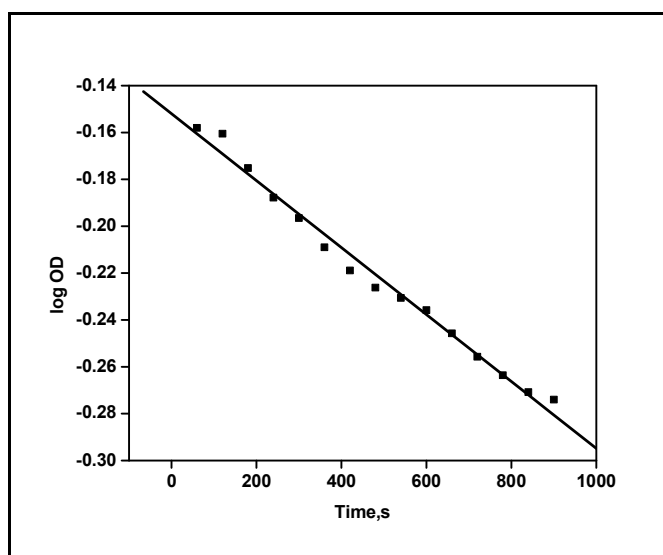


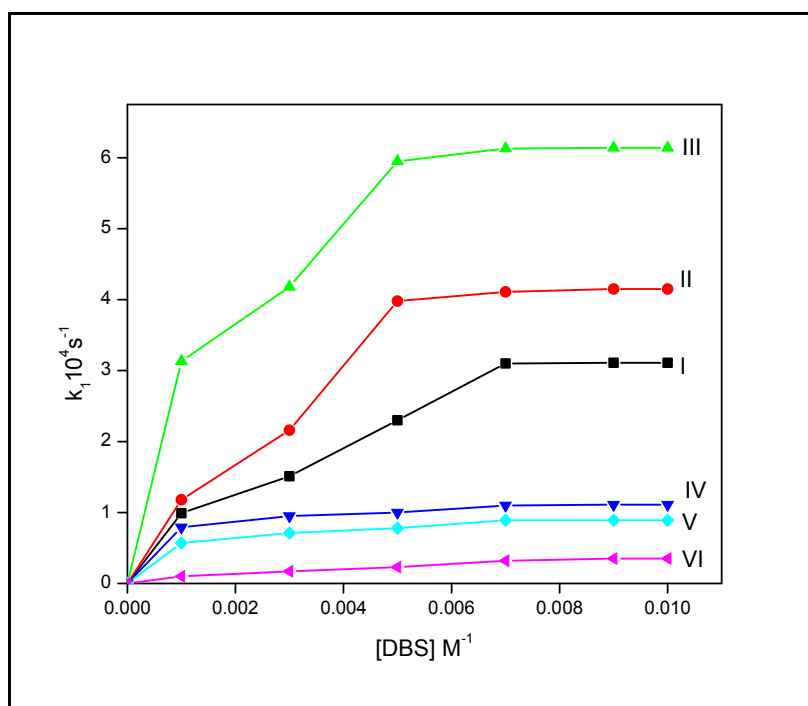
Figure 2 log OD vs time plot. [I] = 2×10^{-4} M, [H₂O₂] = 5×10^{-3} M, [DBS] = 5×10^{-3} M.

Table 2. Pseudo first order rate constants $10^4 k_1, s^{-1}$ for cobalt(III)-salen complexes catalyzed H₂O₂ oxidation of DBS in 90%CH₃CN-10%DCM at 298K.

[DBS],M	I	II	III	IV	V	VI
0.001	0.99±0.01	1.18±0.02	3.13±0.02	0.79±0.07	0.57±0.06	0.10±0.02
0.003	1.51±0.05	2.16±0.05	4.18±0.05	0.95±0.02	0.71±0.02	0.17±0.03
0.005	2.30±0.02	3.98±0.09	5.95±0.07	1.00±0.03	0.78±0.05	0.23±0.04
0.007	3.10±0.01	4.11±0.07	6.13±0.04	1.10±0.04	0.89±0.01	0.32±0.05
0.009	3.11±0.02	4.15±0.04	6.14±0.02	1.11±0.02	0.89±0.05	0.35±0.08
0.01	3.11±0.07	4.15±0.02	6.15±0.02	1.11±0.04	0.89±0.05	0.36±0.08

Table 3. Rate Constants and Michaelis-Menten constant for the cobalt(III)-salen catalyzed H₂O₂ oxidation of DBS in CH₃CN at 298K

Complexes	Rate Constant 10 ⁴ s ⁻¹	Michaelis-Menten constant 10 ³ K _M
I	5.64	1.44
II	6.22	2.08
III	6.54	3.01
IV	2.22	1.89
V	0.93	1.91
VI	0.67	1.66

**Figure 3 Plot of k₁ vs [DBS] for the Co(III)-salen complexes catalyzed H₂O₂ Oxidation of DBS.**

Product analysis

The ¹H NMR spectrum (Figure-4) for the products shows distinct peaks at δ 2.4 and 2.7 ppm. It is known from the literature [35] the peak at δ 2.7 ppm is identified as S (O) stretching frequency which confirms sulfoxide as the product of the reaction. The aromatic region is also informative as the aromatic protons of sulfides and sulfoxides appear as multiplets centered at δ values 7.2 and 7.3 ppm and at 7.6 and 7.7 ppm respectively [36,37]. In the absence of peaks corresponding to sulfones, ¹H NMR study confirms the selective oxidation of sulfides to sulfoxides under the present experimental condition.

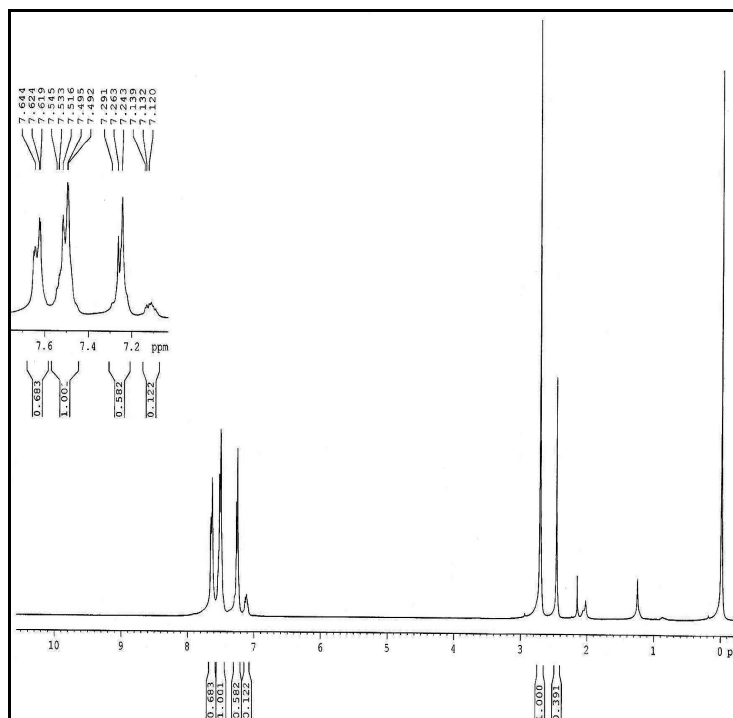
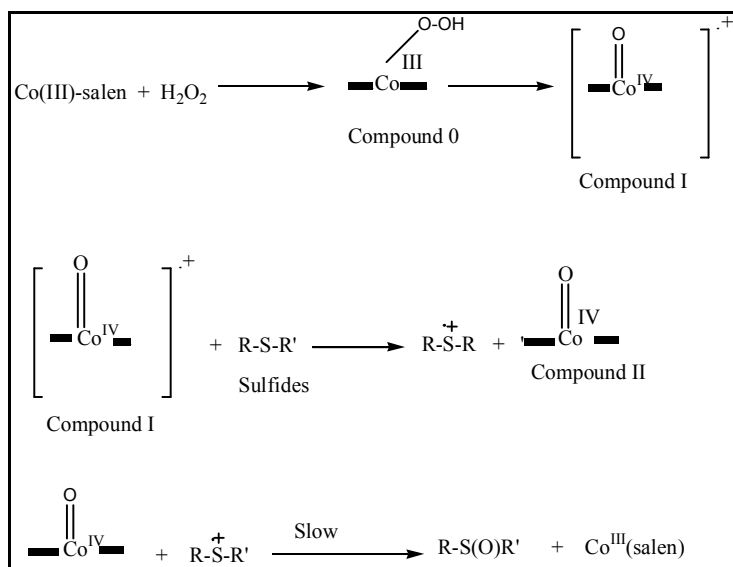


Figure8. ^1H NMR spectrum of products observed from the H_2O_2 oxidation of DBS.

Mechanism

In the present spectral and kinetic study, it is inferred that Co(III) ion reacts with H_2O_2 to produce cobalt(III)-hydro peroxide adduct $[\text{Co}^{\text{III}}\text{-OOH}]$ and it is converted into the active species called compound I. The active species (compound I) oxidizes dibenzyl sulfides to sulfoxides by electron transfer mechanism as illustrated in Scheme 1. There is one electron transfer from the sulfur to $[\text{Co}^{\text{IV}}=\text{O}(\text{salen})]^{\cdot+}$ to form a sulfur radical cation and $[\text{Co}^{\text{IV}}=\text{O}(\text{salen})]$ (compound II). An oxygen atom is transferred from $[\text{Co}^{\text{IV}}=\text{O}(\text{salen})]$ to the sulfur radical cation and sulfoxide is formed. This is called as oxygen rebound step. The mechanism was supported by Oae and coworkers [38].



$\text{R} - \text{C}_6\text{H}_5\text{CH}_2$ $\text{R}' - \text{C}_6\text{H}_5\text{CH}_2$

Scheme1. Electron transfer mechanism for the $[\text{Co(III)-salen}]^+$ catalyzed H_2O_2 oxidation of DBS.

Abbreviation: DBS-Dibenzyl sulfide, DCM-Dichloro methane.

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