Iron(III)-Salen-Catalyzed H₂O₂ Oxidation of Dibenzyl Sulphide

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Iron(III)-salen complexes {salen = N,N'-*bis*(salicylidene)-ethylene diaminato} efficiently catalyze the H₂O₂ oxidation of organic sulphides. This reaction leads to the formation of sulphoxides as the major product. The spectrophotometric kinetic study shows that the reaction follows Michaelis-Menten kinetics. The rate of the reaction is highly sensitive to the nature of the substituents present in the phenolic moiety of salen ligand based on the spectral and kinetic studies. A mechanism involving electron transfer from the substrate to the oxidant in the rate controlling step has been proposed.

Key Words: Iron(III)-salen catalyst, H₂O₂ oxidation, Dibenzyl sulphide, Dibenzyl sulphoxide.

INTRODUCTION

The metal-salen[N,N'-*bis*(salicylidene)-ethylenediamine] complexes are simpler analogues of metal-porphyrin complexes. Salen, a tetradendate ligand, consists of two nitrogen atoms and two oxygen atoms available for coordination with a metal rather than the four nitrogen donors involved in porphyrin. However these salen ligands have been shown to form metal complexes that parallel the catalytic activity of metal-porphyrins[1-3]. For example iron(III)-salen complexes are similar to iron(III)-porphyrins in which both tetradendate ligands take up a square planar geometry, often with a fifth ligand (*e.g.*, H₂O) in an apical position and an open sixth coordination site[4,5]. Most importantly, salens are relatively easy to synthesize from readily available precursors, through the condensation derivatives of salicylaldehyde and ethylenediamine[6-8]. In recent years, Fe(III)-salen complexes have been widely used as catalysts for the oxidation of organic substrates. Traditional methods for the oxidation of organic substrates involve the use of stoichiometric amounts of high-valent metal compounds, such as CrO₃. Unfortunately these kinds of reactions generate huge amounts of toxic waste and are becoming less popular in the face of growing environmental concerns[9]. Besides being environmentally more benign, catalytic oxidation of organic compounds with oxidants such as dioxygen and hydrogen peroxide is less economically wasteful than the traditional methods and is now an important reaction in both research laboratories and industry[10,11]. Herein we report the results of kinetic studies on the oxidation of dibenzyl sulphide mediated by iron-salen complexes (**I-VI**)

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EXPERIMENTAL

Salicylaldehyde and the substituted salicylaldehyes (5-methyl, 5-bromo, 5-chloro, 3,5-di-*tert*butyl, 5-methoxy) were purchased from Aldrich and used as such. Dibenzyl sulphide purchased from Sigma-Aldrich was used as received. CH_3CN of HPLC grade was purchased and used as such. All other reagents were of analar grade or were used after purification. The kinetic study of the reaction was performed after the purities of the reactants and solvents used in the system were confirmed.

Synthesis of ligands and iron(III)-salen complexes: Various salen ligands were prepared from ethylene diamine and the corresponding salicylaldehydes (Aldrich) by standard methods[4,5,7]. Iron(III)-salen complexes **I-VI** (eqn. 1) were synthesized using established procedures[12-15]. The complexes were characterized by IR and UV-visible absorption spectral techniques and the data obtained were compared with the reported values (Table-1).
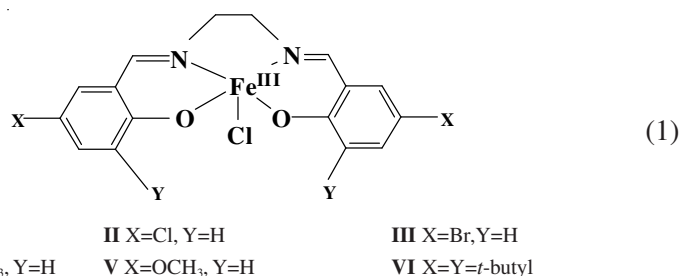

(1)

I X=Y=H   **II** X=Cl, Y=H   **III** X=Br, Y=H
IV X=CH$_3$, Y=H   **V** X=OCH$_3$, Y=H   **VI** X=Y=*t*-butyl

TABLE-1
ABSORPTION MAXIMUM FOR IRON(III)-SALEN COMPLEX

Complexes[a]	λ_{max} (nm)	IR data (cm^{-1})	
		$\bar{\nu}$ (C=N)	$\bar{\nu}$ (C-O)
I	301, 470	1628	1294
II	358, 472	1635	1288
III	342, 467	1637	1290
IV	301, 489	1621	1301
V	304, 501	1624	1300
VI	322, 503	1614	1304

a: **I-VI** as in eqn. 1.

Kinetic measurements: The absorption spectra of iron(III)-salen complexes was obtained using a ELICO SL-164 UV-vis spectrophotometer. The kinetic study of the H_2O_2 oxidation of dibenzyl sulfide catalyzed by iron(III)-salen ion in 100 % CH_3CN is conducted under pseudo first order conditions. The progress of the reaction was monitored spectrophotometrically by following the decay of the respective absorbance maximum of iron(III)-salen complexes **I-VI** at definite time intervals at 298 K. The pseudo-first-order rate constant (k_1) value for each kinetic run was

evaluated from the linear least-square plots of log (absorbance) *versus* time. The rate constant for the formation of products from the oxidant-substrate complex and the Michaelis-Menten constants were evaluated using double-reciprocal plots of k$_1$ and the concentration of the substrates.

Product analysis: A solution containing 5 mM dibenzyl sulfide, 0.2 mM iron(III)-salen complex and 5 mM H$_2$O$_2$ in 5 mL of CH$_3$CN was stirred at 298 K for 1-2 h. The reaction mixture after the completion of the reaction is extracted with chloroform to recover the products. The product is dried over sodium sulphate and after evaporating the solvent it is subjected to FT-IR analysis. The IR spectrum of the product was found to be identical with that of sulphoxide, exhibiting the S=O stretching frequency in the characteristic region 1070-1030 cm^{-1}.

RESULTS AND DISCUSSION

The structure of various iron(III)-salen complexes and the substrates used in the present study are shown in eqn. 1.

Active oxidant species: The parent iron(III)-salen complex has absorption maximum at 470 nm (Fig. 1) and it is due to the ligand to metal charge transfer, PhO$^-$ → Fe^{3+}, transition. This absorption maximum is sensitive to the nature of the substituent in the salen ligand.


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MODE          : Spectrum           REF/SAMPLE : sample1
STARTING WL : 300.0(nm)            ENDING WL    : 600.0(nm)
WL INTERVAL : 1.0(nm)
ANALYST       :
REMARKS       :
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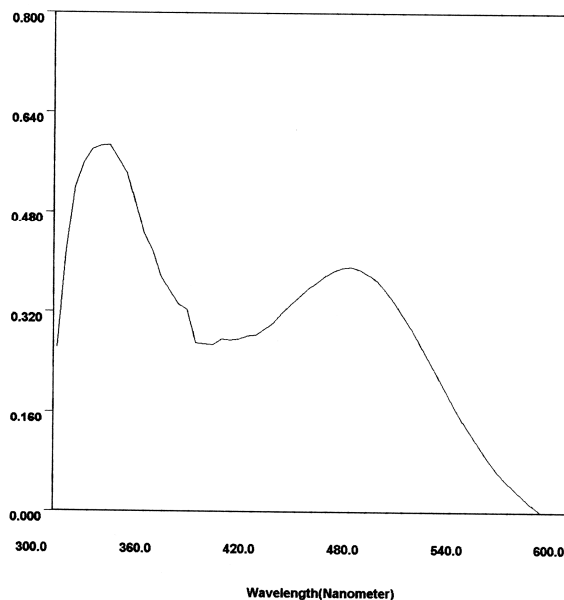
Fig. 1. UV-vis absorption spectrum for iron(III)-salen complex [I] = 2 × 10^{-4} M

Introduction of a 5-Br group shifts the value from 470-467nm whereas 5-OMe causes a large shift from 470-501 nm (Table-1). When hydrogen peroxide is added to the iron(III)-salen complex there are substantial changes in the absorption spectrum, which help to understand the nature of the active oxidant species. Spectral changes observed for the complex is shown in Fig. 2.

The possibility of self decay of the oxidant was tested by plotting OD *versus* time at the corresponding λ_{max} value in the absence of the substrate. The decay of the active oxidant species in the presence and absence of the substrate is shown in Fig. 3 for iron(III)-salen complex. It is apparent that the rate of self decay (curve A) is negligible compared to the rate in the presence of substrate (curve B). This indicates that the oxidation of dibenzyl sulphide by H_2O_2 using Fe(III)-salen ion as the catalyst is the major reaction in the presence of substrates.
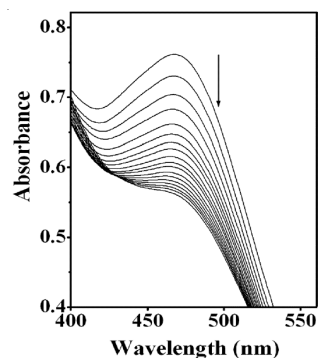
Fig. 2.   Change of absorbance of I-H_2O_2 system with time in the presence of DBS [I] = 2×10^{-4} M, [H_2O_2] = 5×10^{-3} M , [DBS] = 2×10^{-3} M
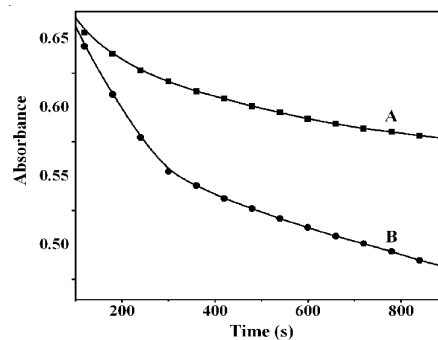
Fig. 3.   Change in absorbance with time at λ_{max} = 470 nm. (A) [I] = 2×10^{-4} M, [H_2O_2] = 5×10^{-3} M. (B) [I] = 2×10^{-4} M, [H_2O_2] = 5×10^{-3} M, [DBS] = 5×10^{-3} M

Kinetic results: The kinetics of iron(III)-salen ion catalyzed H_2O_2 oxidation of organic sulphides in acetonitrile at 298 K has been studied using spectrophoto-metric technique by measuring the change in OD with time at 470 nm for the parent complex and a sample run is shown in Fig. 2. The rate constant of the oxidation reaction is measured from the decrease in absorbance with time. The reaction is found to be first order in the oxidant, which is evident from the linear log (absorbance) *versus* time plots. The dependence of the reaction rate on substrate concentration is studied with different substrate concentrations and the kinetic results are shown in Fig. 3. From figure it is evident that the rate of the reaction increases with increase in substrate concentration but attains saturation in high substrate concentration. The inference from the saturation kinetics is that the substrate binds to the oxidant before the rate controlling step. Thus the redox reaction proceeds through Michaelis-Menten kinetics, eqns. 1 and 2. From eqns. 1 and 2, the rate law can be derived and the rate expression is given by eqn. 3. The rearrangement of eqn. 3 leads to eqn. 4.

$$\text{Oxidant + Substrate} \rightleftharpoons \text{Complex} \tag{1}$$

$$\text{Complex} \xrightarrow{\ k\ } \text{Products} \tag{2}$$

$$k_1 = k_{obs} = k\,[\text{substrate}]/k_M + [\text{substrate}] \tag{3}$$

$$1/k_1 = 1/k + k_M/k\,[\text{substrate}] \tag{4}$$

From the plot of $1/k_1$ *versus* $1/[\text{substrate}]$, the values of k and k_M have been evaluated and are given in Table-2. Here k and k_M are the rate constant for the product formation and Michaelis-Menton constant, respectively. From the linear plot of $1/k_1$ *versus* $1/[\text{substrate}]$ the values of k and k_M have been calculated. From data both k and k_M values are sensitive to the change of substituents in the salen ligand of the catalyst. The analysis of the substituent effect provides a clue on the nature of the transition state of the reaction.

TABLE-2
RATE CONSTANTS AND MICHAELIS-MENTEN CONSTANT FOR THE IRON(III)-
SALEN COMPLEXES-H_2O_2-DBS IN CH_3CN SYSTEM AT 298 K

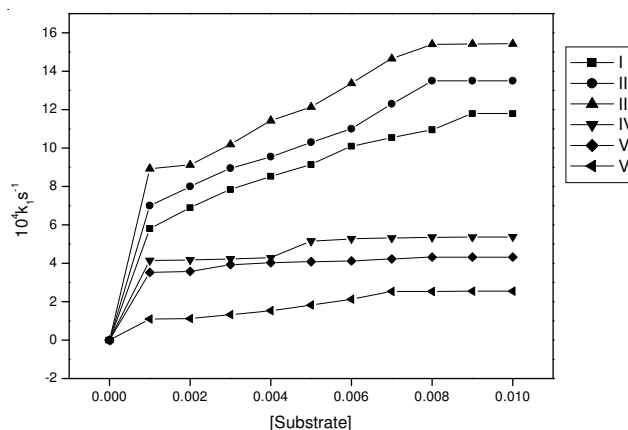| Complexes	Rate constant $10^3\ ks^{-1}$	Michaelis-Menten constant $10^3\ k_M$
I	2.10	28.0
II	5.90	30.0
III	5.10	26.0
IV	1.30	9.0
V	0.79	5.0
VI	0.43	5.1

Fig. 4. Plot of k_1 *versus* [substrate]

Substituent effect: The sulphoxidation is highly sensitive to the nature of the substituent in the salen ligand. To understand the extent of charge separation in the transition state the k values collected in Table-2 are analyzed in terms of Hammett equation. The effect of introducing substituents in the salen ligand is investigated. These kinetic data are treated using Hammett equation and the ρ value is positive +0.6 (Fig. 5). This positive ρ value points out the development of negative charge

on the oxidant in the transition state. The saturation kinetics observed and low k_M values (Table-2) indicate strong binding of substrate with the oxidant[5].

Mechanism: The kinetic and spectral results and product investigations help us to propose the most probable mechanism for this sulphoxidation reaction. The Michaelis-Menten kinetics observed here leads us to conclude that the reaction proceeds through the complex formation between the oxidant and substrate. The rate-controlling step involves an electron transfer (ET) from the substrate to the oxidant to form sulphide radical cation and iron(III)-salen complex. The conversion of sulphide radical cation to sulphoxide can be formulated in terms of steps shown in eqns. (7-9). (**Scheme-I**). Similar formulations have been proposed for the formation of sulphoxide from sulphide radical cation in [16]Fe(bpy)$_3$[3], [17]Ru(bpy)$_3$[3+] and in the polyoxometalate catalyzed *tert*-butylhydroperoxide oxidation of organic sulphide[18].
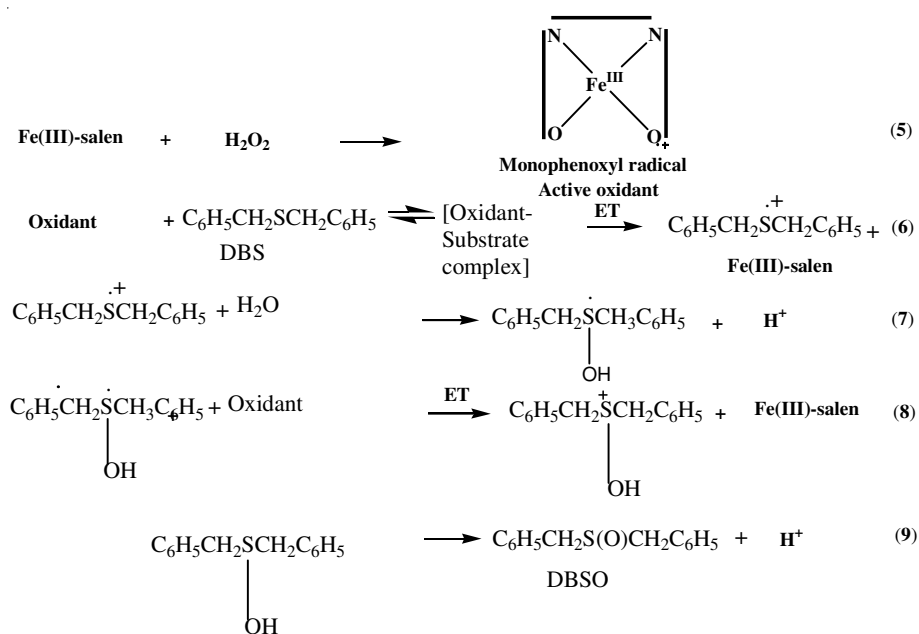
Scheme-I: Mechanism for the oxidation of dibenzyl sulfide to dibenzyl sulfoxide

Conclusion

The oxidation of aromatic sulphides with H_2O_2 catalyzed by iron(III)-salen ions in CH_3CN is an efficient and environmentally benign process. This reaction is facile to produce selectively the corresponding sulphoxides under the experimental conditions. The kinetic studies were performed spectrophotometrically and the characterizations of products were done by FTIR analysis. To account for the experimental observations, an electron transfer in the rate determining step is proposed for this oxidation reaction.
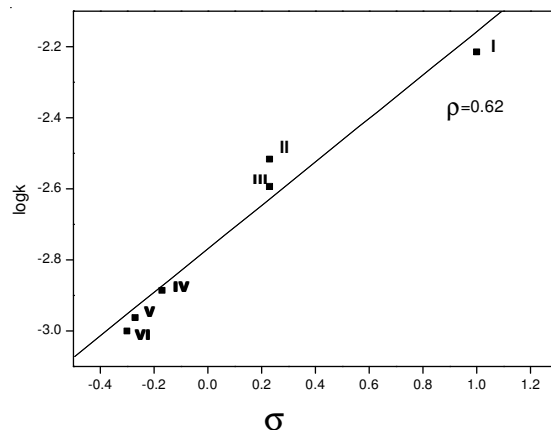
Fig. 5.   Hammett plot for the oxidation of dibenzyl sulfide with H_2O_2 catalyzed by iron(III)-salen complexes **I-IV**

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