



[Iron(III)–salen] ion catalyzed H₂O₂ oxidation of organic sulfides and sulfoxides

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ABSTRACT

[Iron(III)–salen] complexes (salen = N,N′bis(salicylidene)ethylenediaminato) efficiently catalyze the H₂O₂ oxidation of organic sulfides and sulfoxides. The spectrophotometric kinetic studies show that these reactions follow Michaelis–Menten kinetics. The rate of the reaction is highly sensitive to the nature of the substituent present in the aryl moiety of ArSMe or ArS(O)Me and phenolic moiety of salen ligand. The plot of log *k* values of *p*-XC₆H₄SMe and *p*-XC₆H₄S(O)Me with Hammett σ constant give the reaction constant (ρ) values in the range of –0.7 to –1.5 and –0.7 to –1.0, respectively, for different iron(III)–salen complexes. But the plot of log *k* values with σ gives positive ρ value when we introduce substituents in the phenolic moiety of iron(III)–salen complexes. The binding of the substrates with iron(III)–salen complexes is more pronounced with the sulfoxides. The product analyses show the selective oxidation of sulfides to sulfoxides and sulfoxides to sulfones. Based on the spectral and kinetic studies the possible mechanisms have been proposed.

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1. Introduction

Iron is the most prominent transition metal in biological perspective, as many enzymes containing ferrous or ferric ion catalyze various bio-transformations [1–17]. In general, the biological relevance of iron–porphyrin systems makes the investigations of their role as catalysts attractive [18–20]. The chemistry of heme and non-heme iron in its high valent states is currently of intense interest [1,21,4,22–25]. Recently Fujji and co-workers [26] have examined the non-heme center in protocatechuate 3,4-dioxygenase (3,4-PCD) with sterically hindered iron–salen complexes as models and pointed out that the distorted trigonal–bipyramidal iron site might not be preorganised by 3,4-PCD proteins but could be electronically induced upon the binding of an external hydroxide ligand to the iron(III)–center.

Horseradish peroxidases (HRP) are protoheme-containing monomer enzymes which catalyze the oxidation of organic molecules by H₂O₂ as the specific oxidant [27]. It is well established that this redox reaction proceeds through two intermediates

called compound I and compound II [16,27,28]. The active species of heme peroxidases, such as HRP or cytochrome *c* peroxidases (CcP), contain an oxo iron group embedded in a heme [29]. Recently Nam [21] reviewed the paths followed by the intermediate iron(III)–hydroperoxo, Fe^{III}–OOH species.

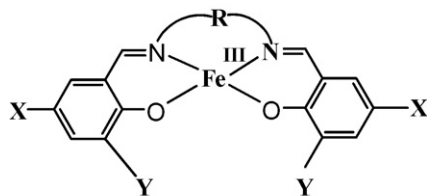
Model compounds play significant role in establishing the structure of enzymic intermediates and contribute to our understanding of their spectroscopic properties and reaction mechanism. Therefore, over the past three decades biomimetic approaches towards mimicking the catalytic role of these enzymes on the oxygenation reactions have been focused on synthetic iron(III)–porphyrin complexes and their interaction with oxygen donors such as iodosylbenzene, peroxy acids, and hydroperoxides. Spectroscopic techniques such as electronic absorption, NMR, EPR, resonance Raman and Mossbauer have been extensively used in the elucidation of the structure of active oxidant [30]. Recently Sivasubramanian et al. [30] reported a mechanistic study to establish the role of iron(III)–salen complexes as model compounds for non-heme enzymes by using them as catalysts for the oxygenation of organic sulfides and sulfoxides utilizing PhIO as the oxygen source.

Though organic sulfides and sulfoxides are similar substrates, under certain conditions sulfoxides behave differently because of the presence of the polar S–O bond. The sulfoxide moiety is involved in important biological activities [31–35], serves as a ligand for asymmetric synthesis [36,37] and the chiral sulfoxides are valuable synthetic intermediates [38–40]. The interesting feature of the organic sulfoxides is that they may act both as electrophiles and nucleophiles depending on the nature of the oxidant

Abbreviations: Salen, N,N′bis(salicylidene)ethylenediaminato; MPS, methyl phenyl sulfide; MPSP, methyl phenyl sulfoxide; ArSMe, aryl methyl sulfide; FT-IR, Fourier transform infra red spectroscopy; ¹H NMR, proton nuclear magnetic resonance spectroscopy; GC–MS, gas chromatography–mass spectrometry; GC, gas chromatography; OD, optical density; 3,4-PCD, protocatechuate 3,4-dioxygenase.

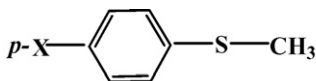
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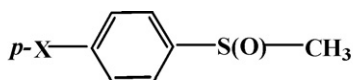
- I** X = Y = H;
II X = Cl, Y = H;
III X = Br, Y = H;
IV X = CH₃, Y = H;
V X = OCH₃, Y = H;
VI X = Y = Cl;
VII X = Y = *t*-Butyl;

Chart 1. Structure of iron(III) salen complexes.



X = H (1), OCH₃ (2), CH₃ (3), F (4), Cl (5), Br (6), NO₂ (7)

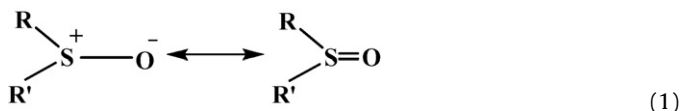
Chart 2. Phenyl methyl sulfides (1–7).



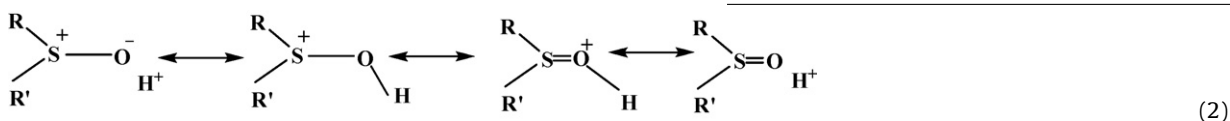
X = H (8), OCH₃ (9), CH₃ (10), F (11), Cl (12), Br (13)

Chart 3. Phenyl methyl sulfoxides (8–13).

[31,41–44,33,34,37,38]. The two resonating forms of sulfoxides may be represented as in Eq. (1).



The protonation of sulfoxides makes polarization of S–O bond and thereby becoming weaker nucleophile and less reactive compared to sulfides [45] (Eq. (2)).



In this present study, it is decided to use hydrogen peroxide as oxygen source. It is advantageous to use H₂O₂ as the oxidant instead of PhIO. Its inherent chemistry as an oxidant continues to give it a role beyond that of oxygen, especially in selective oxidations [46–48]. It is a safe, readily available and cheap reagent. Further this eco-friendly redox system may serve as peroxidase model and leaves water as the only byproduct. With this aim of using eco-friendly reagents, we have synthesized seven iron(III)–salen complexes **I–VII** (Chart 1) and used them as catalysts for the H₂O₂ oxidation of sulfides **1–7** (Chart 2) and sulfoxides **8–13** (Chart 3).

2. Experimental

2.1. Materials

Salicylaldehyde and the substituted salicylaldehydes (5-methyl, 5-bromo, 5-chloro, 3,5-dichloro, 3,5-di-*tert*-butyl, 5-methoxy)

Table 1

λ_{max} values of iron(III)–salen complexes used to follow the kinetics of the reaction.

Iron(III)–salen complex	λ_{max} , nm
I	470
II	472
III	467
IV	489
V	501
VI	477
VII	503

were purchased from Aldrich and used as such. Methyl phenyl sulfide (MPS) and the *para*-substituted phenyl methyl sulfides (*p*-methoxy, *p*-methyl, *p*-fluoro, *p*-chloro, *p*-bromo, and *p*-nitro) were also purchased from Aldrich and used as such. HPLC grade acetonitrile and 30% H₂O₂ were used as received.

2.2. Preparation of catalysts and substrates

2.2.1. Synthesis of ligands and iron(III)–salen complexes (**I–VII**)

The general procedure [49–53] for the preparation of salen ligands involves the condensation of salicylaldehyde with ethylene diamine in the ratio of 2:1 in an alcoholic medium. 5,5'-(CH₃)₂-salen, 5,5'-(OCH₃)₂-salen, 5,5'-(Cl)₂-salen, 5,5'-(Br)₂-salen, 3,3',5,5'-(Cl)₄-salen and 3,3',5,5'-(*tert*-Bu)₄-salen are prepared by condensing the corresponding substituted salicylaldehyde with ethylene diamine in ethanol and recrystallized from cold methanol. The ¹H NMR spectral data are given in Supporting information (Table S1) and the data are in close agreement with the previous reports [54].

Iron(III)–salen complexes (**I–VII**) are prepared by the literature procedures by the reaction of stoichiometric amounts of the respective ligand with ferric chloride in alcohol solution. All the seven iron(III)–salen complexes are characterized [55–61] by UV–vis, ESI-MS, FT-IR spectral studies and cyclic voltammetric measurements.

2.2.2. Preparation of aryl methyl sulfoxides (**8–13**)

The following general method is used for the preparation of most of the sulfoxides used in the present study. A solution of methyl phenyl sulfide 15 g (121 mmol) in acetic acid (80%, 250 ml) is treated with chromic anhydride 9.0 g (90 mmol) dissolved in the minimum

amount of water. While adding chromic anhydride, the sulfide solution is cooled in ice. The mixture is then heated on a water bath at 60–70 °C for 30 min and poured into ice water. The solution is neutralized with a saturated solution of sodium carbonate and extracted with chloroform. The extract is washed with water and dried over anhydrous sodium sulfate. The solvent is removed under reduced pressure and the residue is fractionated.

2.3. Kinetic studies

The kinetic studies are carried out using Analytic Jena Specord S100 diode array spectrophotometer. An inbuilt program Win Aspect has been used to collect data at the desired wavelength. The concentrations of iron(III)–salen complex and H₂O₂ taken are 2×10^{-4} M and 5×10^{-3} M, respectively, unless otherwise stated. The strength of H₂O₂ is carefully monitored in all the measurements. The kinetic study on the H₂O₂ oxidation of organic sulfides

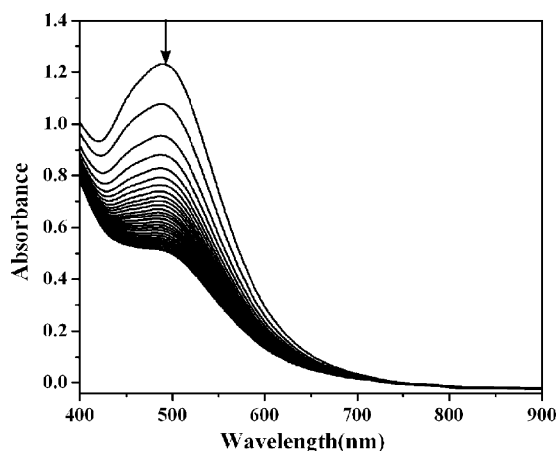


Fig. 1. Decay of absorbance of IV–H₂O₂ system with time in the presence of I, [IV] = 2 × 10^{−4} M, [H₂O₂] = 5 × 10^{−3} M, [I] = 2 × 10^{−3} M.

and sulfoxides catalyzed by iron(III)–salen ion in 100% CH₃CN is conducted under pseudo first order conditions. The progress of the reaction is followed by maintaining the concentration of the substrate (sulfides or sulfoxides) at least 10 times greater over the iron(III)–salen complex. The rate of the reaction is measured following the decay of absorbance of iron(III)–salen complex with time at appropriate wavelength (λ_{\max}) collected in Table 1. Fig. 1 shows the decay of absorbance during H₂O₂ oxidation of organic sulfides catalyzed by iron(III)–salen ion in 100% CH₃CN (the corresponding decay curve for sulfoxide oxidation is given in Supporting information SI 1).

2.4. Product analysis

A solution containing 5 mM substrate, 0.2 mM iron(III)–salen complex and 5 mM H₂O₂ in 5 ml of CH₃CN was stirred at 298 K for 1–2 h depending upon the nature of the substrate and complex. The reaction mixture after completion of the reaction was extracted with chloroform to recover the organic products. It was dried over sodium sulfate. The solvent was evaporated and the product was analyzed using ¹H NMR, IR, GC and GC–MS techniques. The product investigations through the spectral studies reveal the formation of aryl methyl sulfoxides when the substrate is sulfides and sulfones when the substrate is sulfoxides as the major product of the reaction. The details of the product analyses are elaborated in the discussion section.

3. Results and discussion

3.1. Spectral studies

When H₂O₂ is added to the iron(III)–salen complex, there are substantial changes in the absorption spectrum which help us to understand the nature of the active oxidant species. The absorbance at 350 and 470 nm decreases and at 390 and 550–700 nm increases with time for complex I (Supporting information SI 2). The decrease in absorbance with time at 470 nm upon addition of substrate to the iron(III)–salen–H₂O₂ system is followed spectrophotometrically. The reaction is found to be first order in the oxidant which is evident from the linear log OD vs. time plot (Supporting information SI 3).

3.1.1. Michaelis–Menten behaviour

The dependence of the rate of the reaction on substrate concentration is studied by measuring the rate of the reaction at

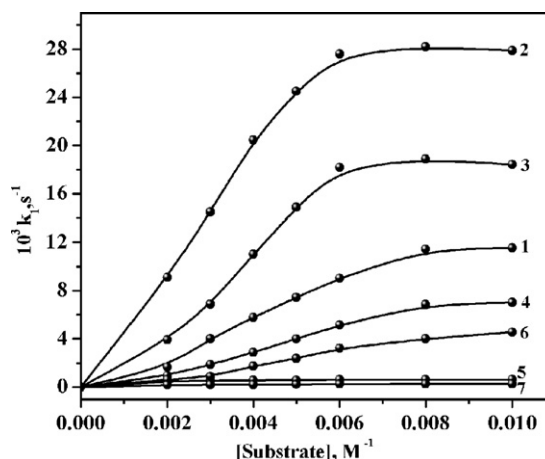


Fig. 2. Plot of k_1 vs. [substrate] for complex I catalyzed H₂O₂ oxidation of 1–7.

different substrate concentration. The kinetic results are shown in Supporting information (Table S2) and in Fig. 2.

It is obvious from Fig. 2 and the data collected in Table S2 that the rate of the reaction increases with increase in substrate concentration but attains saturation at high substrate concentration. The inference from the saturation kinetics is that the substrate binds to the oxidant before the turnover limiting step. Thus the redox reaction proceeds through Michaelis–Menten kinetics and the kinetics of the reaction can be analyzed in terms of Eqs. (3) and (4).



From Eqs. (3) and (4), the rate law can be derived and the rate expression is given by Eq. (5).

$$k_1 = k_{\text{obs}} = \frac{k[\text{substrate}]}{K_M + [\text{substrate}]} \quad (5)$$

The rearrangement of Eq. (5) leads to Eq. (6).

$$\frac{1}{k_1} = \left(\frac{1}{k}\right) + \left(\frac{K_M}{k[\text{substrate}]}\right) \quad (6)$$

Here k and K_M are the rate constant for the product formation and Michaelis–Menten constant, respectively. From the linear plot of $1/k_1$ vs. $1/[\text{substrate}]$ (Eq. (6)), the values of k and K_M have been evaluated and the values are given in Tables 2 and 3, respectively. These data indicate that both k and K_M values are sensitive to the change of substituents in the substrate XC₆H₄SMe and in the salen ligand of the catalyst. The analysis of the data on the substituent effect provides a clue on the nature of the transition state of the reaction.

The oxidation of sulfoxides also proceeds through Michaelis–Menten kinetics, i.e. saturation kinetics is observed with respect

Table 2

Rate constants $k \times 10^3 \text{ s}^{-1}$ for the iron(III)–salen catalyzed H₂O₂ oxidation of *p*-XC₆H₄SCH₃ in CH₃CN at 298 K^a.

X	I	II	III	IV	V	ρ	r	VI	VII
H	2.5	6.0	5.5	1.7	0.89	0.80	0.98	15	0.53
OMe	10	34	23	2.5	1.8	1.2	0.98	66	1.1
Me	5.9	23	19	1.9	0.96	1.3	0.98	43	0.76
F	1.6	5.4	6.2	0.90	0.62	1.0	0.99	11	0.42
Cl	1.1	2.8	2.5	0.84	0.51	0.80	0.97	8.0	0.40
Br	0.90	2.9	2.6	0.72	0.40	0.80	0.99	6.5	0.30
NO ₂	0.27	0.90	0.80	0.23	0.17	0.70	0.97	2.1	0.19
ρ	−1.5	−1.4	−1.4	−0.9	−1.0			−1.4	−0.7
r	0.98	0.95	0.96	0.99	0.99			0.97	0.96

^a Data provided are reproducible in duplicate runs within $\pm 5\%$.

Table 3

Michaelis–Menten constant, $K_M \times 10^3$ values obtained for the iron(III)–salen complexes catalyzed H_2O_2 oxidation of p -XC₆H₄SCH₃ in CH₃CN at 298 K.

X	I	II	III	IV	V	VI	VII
H	29	31	28	11	6.0	5.4	6.1
OMe	21	35	17	28	10	23	9.3
Me	14	17	20	18	6.8	11	8.2
F	2.7	17	19	6.5	5.1	54	3.6
Cl	4.2	3.0	2.6	3.2	2.8	3.3	3.0
Br	5.6	2.9	2.0	4.6	4.5	11	1.8
NO ₂	0.86	0.29	0.22	0.73	4.1	1.3	0.53

Table 4

Rate constants $k \times 10^4 s^{-1}$ for the iron(III)–salen catalyzed H_2O_2 oxidation of organic sulfoxides p -XC₆H₄S(O)CH₃ in CH₃CN^a.

X	I	II	III	IV	V	ρ	r	VI	VII
H	1.7	3.4	3.0	0.85	0.67	0.7	0.98	4.0	0.23
OMe	2.8	4.4	4.2	1.9	1.8	0.4	0.97	5.2	0.82
Me	2.2	4.2	4.0	1.6	1.7	0.4	0.96	5.0	0.70
F	1.3	1.7	1.5	0.67	0.55	0.5	0.99	2.0	0.17
Cl	1.2	1.6	1.7	0.64	0.6	0.4	0.99	2.4	0.18
Br	1.1	1.8	1.6	0.65	0.57	0.5	0.97	1.6	0.14
ρ	-0.7	-0.9	-0.9	-0.9	-1.0	-	-	-	-
r	0.99	0.96	0.97	0.96	0.94	-	-	-	-

^a Data provided are reproducible in duplicate runs within $\pm 5\%$.

to the substrate (Supporting information SI 4). This is also evident from the kinetic data collected in Supporting information (Table S3). The saturation kinetics observed here is similar to the results obtained with organic sulfides and thus explained in terms of treatment applied to the oxidation of sulfides (Eqs. (3)–(6)). The rate constants, k obtained from the $1/k_1$ vs. $1/[\text{substrate}]$ plots are tabulated in Table 4 and the Michaelis–Menten constant, K_M , values are given in Table 5. Michaelis–Menten constant values collected in Table 5 ensures the more strong binding of sulfoxides to the oxidant compared to sulfides because of low K_M value observed with sulfoxide. From the data provided from Tables 3 and 5, it is apparent that under the similar experimental conditions, the binding is more pronounced in the case of sulfoxides compared to sulfides.

3.2. Active oxidant species

The parent iron(III)–salen complex has absorption maximum at 470 nm and it is due to the ligand to metal charge transfer (LMCT), $PhO^- \rightarrow \text{iron(III)}$, transition. Addition of H_2O_2 to iron(III)–salen complex results in substantial change in the absorption spectrum and the spectral changes are shown in Fig. 3. The interesting observation is that in the presence of H_2O_2 the absorbance of parent $[\text{Fe(III)–salen}]^+$ ion at 470 nm decreases and a new peak emerges at 370 nm and in the wavelength region 550–700 nm. Fujji and co-workers [22,26] reported that when sterically hindered iron(III)–salen complex was oxidized electrochemically in CH_2Cl_2 –ethanol mixture at 203 K and oxidized with m -CPBA at 193 K, iron(III)–monophenoxyl radical as the active oxidizing species. The formation of monophenoxyl radical in this present

Table 5

Michaelis–Menten constant, $K_M \times 10^3$ values obtained for I–VII catalyzed H_2O_2 oxidation of p -XC₆H₄S(O)CH₃ in CH₃CN^a.

X	I	II	III	IV	V	VI	VII
H	1.3	2.2	0.88	2.2	5.5	0.44	7.2
OMe	0.34	0.45	0.27	4.7	3.1	0.21	4.5
Me	0.88	0.66	0.64	3.8	4.0	0.25	2.8
F	0.67	0.25	0.55	1.9	5.1	0.74	1.5
Cl	0.71	0.86	0.36	4.7	4.1	0.45	5.5
Br	0.72	0.55	1.0	2.2	3.6	0.77	7.9

^a Data provided are reproducible in duplicate runs within $\pm 5\%$.

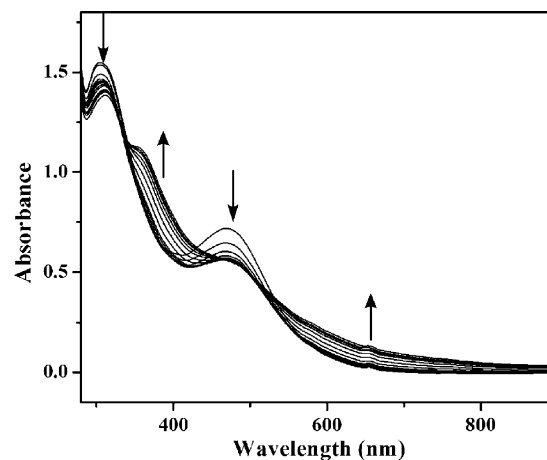


Fig. 3. Change in absorbance of I with time in the presence of H_2O_2 [I] = 2×10^{-4} M, [H_2O_2] = 5×10^{-3} M.

experimental set up may be ruled out since the reaction is carried out at 298 K. Further van Edlic and co-workers [19] very recently presented the details of absorbance change in the region 550–750 nm during the formation of active species from the reaction between Fe(III)–porphyrin complex and m -CPBA. From the spectral and kinetic data obtained, the authors are able to follow the rate constant for decay of compound 0 and the rate constant for the formation of $P^{*+}Fe^{IV}=O$, compound I. The similar spectral changes are observed in the present system and the details of decrease in absorbance at 470 nm (spectrum A) and the increase in absorbance at 550–750 nm (spectrum B) are given in Supporting information SI 5. The spectral changes observed in the present work help us to conclude that the possible active oxidant under the present experimental conditions is iron oxo species similar to the proposal of van Edlic and co-workers [19].

3.3. Binding of substrate with the catalyst in sulfoxide oxidation

In the case of sulfoxides, the binding of the substrate to the catalyst is more prominent. As the sulfoxide concentration increases, there is a substantial increase in the absorbance of the iron(III)–salen complex (Supporting information SI 6). The increase of absorbance of iron(III)–salen complex with the addition of sulfoxide indicates the binding of substrate with the catalyst. From the change of absorbance with the change of [substrate], the binding constant values have been estimated using Benesi–Hildebrand method (Supporting information SI 7). The estimated values range from 20 to $122 M^{-1}$ and the values are collected in Supporting information (Table S4).

It is interesting to note that iron(III)–salen complex with electron withdrawing substituents in the phenolic moiety of the salen ligand has higher binding constant values than the parent iron(III)–salen complex and the complex with electron donating groups in the 5,5'-positions of the salen has lesser value than the parent complex.

3.4. Substituent effects

The rate of iron(III)–salen ion catalyzed H_2O_2 oxidation of aryl methyl sulfides is highly sensitive to the nature of the substituents present in the aryl moiety of ArSMe and the phenolic part of the salen ligand (Table 2). The introduction of electron donating substituents in the phenyl ring of ArSMe accelerates the rate whereas the electron withdrawing substituents retard the rate. In order to understand the extent of charge separation in the transition state of the reaction, the rate constant values are analyzed in terms of Hammett's σ values and Brown–Okamoto's σ^+ values.

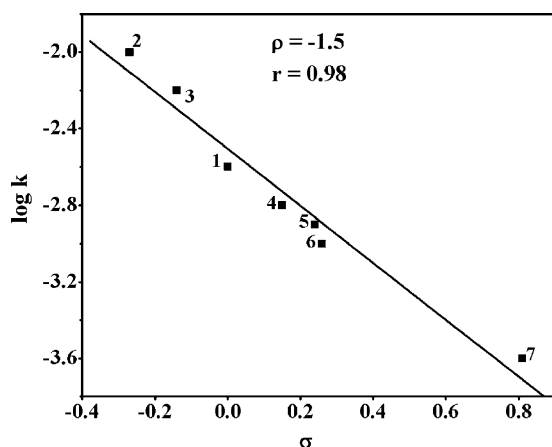


Fig. 4. Hammett plot for the oxidation of the substrates 1–7 with H_2O_2 catalyzed by I.

It is found that the correlation of $\log k$ values of aryl methyl sulfides with Hammett's sigma constant is better ($r=0.98$, $n=7$). The Hammett plot for the reaction of complex I catalyzed H_2O_2 oxidation of seven *para*-substituted phenyl methyl sulfides is presented in Fig. 4.

Similar Hammett plots have been drawn for other catalysts also and the reaction constant (ρ) value ranges between -0.7 and -1.5 for different iron(III)–salen complexes and the ρ values are collected in Table 2. The negative ρ value indicates that a positive charge is developed on the sulfur center of the substrate in the transition state. The correlation is not improved if σ^+/σ^- values are used instead of sigma ($r=0.97$, $n=7$, $\rho^+ = -1.1$ for complex I).

The effect of introducing substituents in the salen ligand of iron(III)–salen complex on the rate of oxidation is also investigated. These kinetic data are also treated using Hammett's σ values and the ρ value is positive ranging from $+0.7$ to $+1.3$. Sample plot of $\log k$ vs. 2σ values is presented in Supporting information SI 8. This positive ρ value points out the development of negative charge on the oxidant in the transition state. In order to understand the steric effect of the substituents, H_2O_2 oxidation of phenyl methyl sulfides has been carried out using VII as the catalyst with bulky *tert*-butyl groups in 3,3',5,5'-positions of the phenyl ring of salen ligand. The rate constant data observed for the catalyst VII are very small compared to the values obtained when we use complex IV as the catalyst. This observation gives information about the role of steric effect in addition to the polar effect.

The saturation kinetics observed and low K_M values (Table 3) indicate strong binding of substrate with the oxidant [30] and the inference from the observation is the high catalytic efficiency of iron(III)–salen complexes. The rate of iron(III)–salen ion catalyzed H_2O_2 oxidation of aryl methyl sulfoxides is also highly sensitive to the nature of the substituents present in the aryl moiety of ArS(O)Me and the phenolic part of the salen ligand. When electron donating substituents are present in the phenyl ring of ArS(O)Me , the rate of the title reaction is enhanced whereas the electron withdrawing substituents have opposite effect. It is found that the correlation of $\log k$ values of aryl methyl sulfoxides with Hammett's sigma constant is good ($r=0.99$, $n=6$). The Hammett plot for complex I with six *para*-substituted phenyl methyl sulfoxides is presented in Supporting information SI 9. The ρ value is negative and ranges from -0.7 to -1.0 . The negative ρ value points out that the sulfoxides are nucleophilic in nature and the positive charge is developed on the substrate in the transition state. The effect of introducing substituents in the

salen ligand of the iron(III)–salen on the rate of the reaction is also analyzed in terms of Hammett equation (Supporting information SI 10) and the ρ value is positive and it ranges from $+0.4$ to $+0.7$.

It is interesting to compare the values obtained for the oxidation of organic sulfides with sulfoxides. The lower ρ value (-0.7) observed with sulfoxides compared to sulfides (-1.5) points out that sulfoxides are less powerful nucleophiles than sulfides. This less nucleophilicity explains the less reactivity of sulfoxides compared to sulfides. It is interesting to point out that similar results were observed when PhIO was used as the oxidant instead of H_2O_2 .

3.5. Product analysis

3.5.1. Oxidation of sulfides

We have used FT-IR, ^1H NMR, GC and GC–MS techniques for the analysis of the products obtained during the course of the reaction.

The FT-IR spectral analysis of the product obtained from methyl phenyl sulfide shows S=O stretching frequency at 1049 cm^{-1} and no stretching frequency at 1150 cm^{-1} corresponding to the formation of sulfone. This product analysis study demonstrates that sulfoxide is the only product formed under the present reaction conditions.

The ^1H NMR spectrum for the products obtained during the course of the reaction is shown in Fig. 5. CDCl_3 is used as the solvent. There are distinct peaks at δ 2.4 and 2.7 ppm. It is known from the literature that the methyl groups of $\text{C}_6\text{H}_5\text{SCH}_3$ and $\text{C}_6\text{H}_5\text{S(O)CH}_3$ in deuterated solvents show distinctive peaks at δ 2.4 and 2.72 ppm, respectively [62]. Hence in the present study, the peak at δ 2.7 ppm is identified as S(O) stretching frequency which confirms sulfoxide as the only 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 7.6 and 7.7 ppm, respectively [63,64].

In the absence of peaks corresponding to sulfones, ^1H NMR study confirms the selective oxidation of sulfides to sulfoxides under the present experimental condition.

Based on GC analysis, the percentage yield of sulfoxides was found to depend on the nature of substituents present in the aryl moiety of ArSMe . The yield is more for electron donating substituents and less for electron withdrawing substituents. The percentage yield of sulfoxides obtained in the oxidation of seven *para*-substituted phenyl methyl sulfides by H_2O_2 catalyzed by I is given in Table 6. Further evidence for the selective sulfoxidation of sulfides under the present experimental condition is obtained from the GC–MS analysis of the product. A sample GC–MS of the product obtained for complex I catalyzed H_2O_2 oxidation of methyl phenyl sulfide is shown in Supporting information SI 11. The peaks at m/z values 124 and 140 correspond to MPS and MPSO, respectively.

3.5.2. Oxidation of sulfoxides

When the product obtained by the H_2O_2 oxidation of methyl phenyl sulfoxides catalyzed by I is subjected to FT-IR spectral analysis, the distinct peaks obtained at 1049 and 1150 cm^{-1} are due to the stretching frequency of S(O) and S(O)_2 groups. Thus under the experimental condition sulfoxides are converted into sulfones.

Sulfoxide oxidation catalyzed by iron(III)–salen complexes are also monitored via ^1H NMR to determine the identity of the products formed during the course of the reaction. In the present study we are able to identify the peaks at δ 2.74 and 3.10 ppm which correspond to the methyl groups of sulfoxides and sulfones, respectively. The ^1H NMR spectrum is shown in Supporting information SI 12. Thus the product analysis study reveals that sulfone is the only product formed under the present reaction conditions.

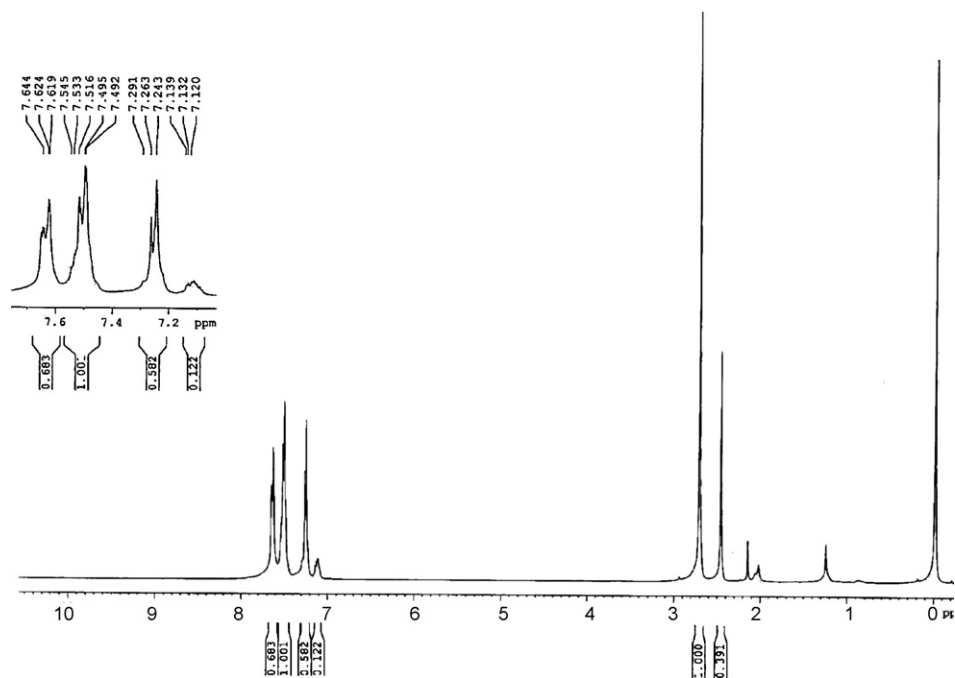


Fig. 5. ^1H NMR spectrum of products observed from the H_2O_2 oxidation of **1** catalyzed by **I**.

3.6. Mechanism

3.6.1. Mechanism for sulfides oxidation

The spectral changes obtained in the present work and comparison of these results with the recent literature on similar systems help us to conclude the possible active species as iron oxo species. The Michaelis–Menten kinetics observed here lead us to conclude that the reaction proceeds through the complex formation between the oxidant and the substrate. The observed saturation kinetics and low K_M values indicate the strong binding of substrate with the oxidant. Similar type of saturation kinetics is observed in some reactions involving Fe(III) complexes [30,65,66]. The oxygen atom transfer from the oxo iron species to the substrate has been proposed as the mechanism of these reactions which is facilitated by the strong binding of methyl phenyl sulfide with the oxidant. Interestingly when the $\log k$ values obtained in the present study are plotted against oxidation potentials of substituted phenyl methyl sulfides, E_{ox} linear plots are obtained. A sample plot is depicted in Supporting information SI 13 (slope = -3.0 for **I**).

The slopes obtained from the linear plots are also comparable with the values obtained by Goto et al. [67]. Since the active oxidant species is generated *in situ*, the attempt to find the redox potentials of $[\text{O}=\text{Fe}^{\text{IV}}-(\text{salen})]^{+\bullet}$ species under the present experimental condition is beyond the scope of the study. With the kinetic and spectral data presented above, it is possible to propose two alternate mechanisms (Schemes 1 and 2).

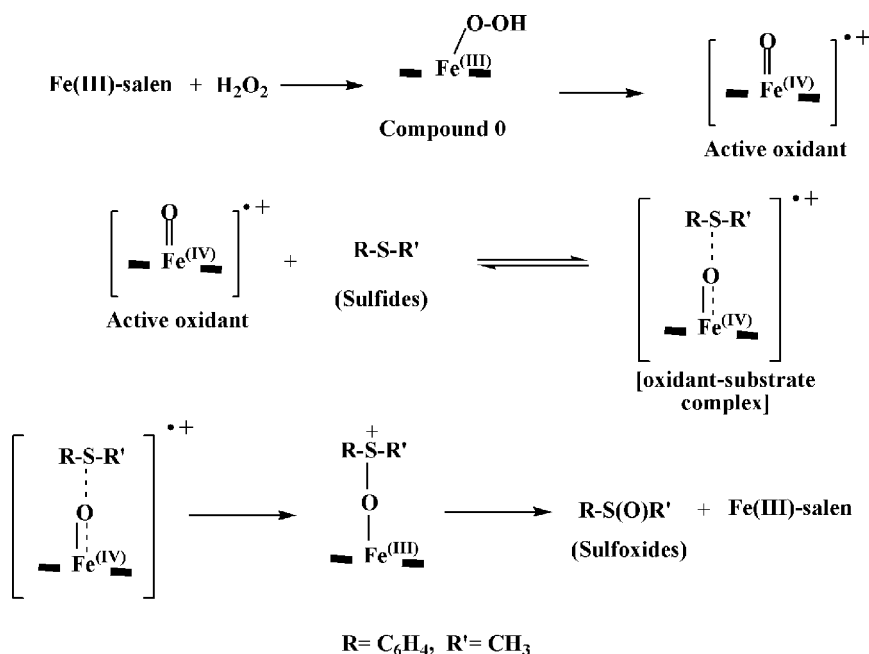
Table 6
Percentage yields of sulfoxides from the oxidation of $p\text{-XC}_6\text{H}_4\text{SCH}_3$ by H_2O_2 catalyzed by **I**.

X	Sulfoxide (yield %)
H	94
OCH_3	93
CH_3	89
F	62
Cl	60
Br	64
NO_2	58

When iron(III)–salen and H_2O_2 are considered as the catalyst and oxidant, the formation of the active oxidant species $[\text{Fe}^{\text{IV}}=\text{O}]^{+\bullet}$ may be formulated via compound **0** formation. The following observations support the above formulation: (i) on adding H_2O_2 to the iron(III)–salen complex, the substantial changes observed in the absorption spectrum and the comparison of these changes with the published data help us to formulate the nature of the active oxidant species as $[\text{Fe}^{\text{IV}}=\text{O}(\text{salen})]^{+\bullet}$. The absorbance at 350 and 470 nm decreases and at 390 and 550–700 nm increases with time (Fig. 3). (ii) The active oxidant generated forms oxidant–substrate complex that facilitates oxygen atom transfer to the substrate. (iii) The oxidation is selective and sulfoxide is the only product of the reaction.

The formation of oxo iron species $[\text{Fe}^{\text{IV}}=\text{O}(\text{salen})]^{+\bullet}$ as the active oxidant from the reaction of iron(III)–salen and PhIO [30] has been reported from this laboratory and it was characterized by UV–vis, resonance Raman, EPR, ESI-MS and Mossbauer spectral techniques. Mossbauer spectral study reveals that iron is in the 4+ oxidation state in the active species [oxo(salen)iron]. The oxygen atom transfer from the oxidant to substrate has been proposed as the mechanism of the reaction. Bryliakov and Talsi [68,69] have proposed the reactive species as iron(III)–salen–PhIO adduct at low temperature based on NMR studies. The interesting spectral observations in this redox system are highlighted in the preceding section. The UV–vis spectral study clearly shows the formation of $\text{Fe}^{\text{III}}-\text{OOH}$ which undergoes heterolytic cleavage resulting in the formation of reactive species $[\text{Fe}^{\text{IV}}=\text{O}(\text{salen})]^{+\bullet}$. This active oxidant generated forms oxidant–substrate complex that facilitates oxygen atom transfer to the substrate for the selective oxidation of sulfides to sulfoxides.

The alternative mechanism may be described by the details shown in Scheme 2. After the formation of reactive species $[\text{Fe}^{\text{IV}}=\text{O}(\text{salen})]^{+\bullet}$, there is an electron transfer (ET) from sulfide to compound **I** in the rate controlling step leading to the formation of compound **II**. Compound **II** and sulfide radical cation produce iron(III)–salen complex and sulfoxide as products through rebound mechanism.



Scheme 1. Oxygen atom transfer mechanism for the selective oxidation of sulfides to sulfoxides in CH_3CN .

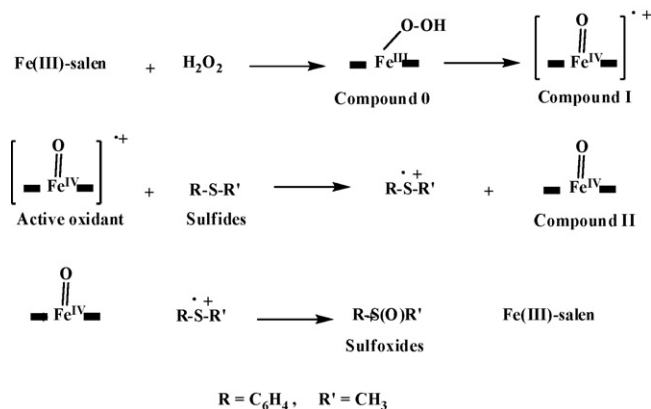
3.6.2. Mechanisms for sulfoxides oxidation

Based on the UV–vis absorption spectral studies, we understand that the active species is arrived as iron oxo species. The significant rise in the absorption intensity of the iron(III)–salen ion in the presence of sulfoxides indicates the strong binding of substrate with the catalyst. The Michaelis–Menten kinetics observed here lead us to conclude that the reaction proceeds through the complex formation between the oxidant and the substrate. The low K_M values (Table 5) obtained from the saturation kinetics also point out the stronger binding of sulfoxide with oxidant compared to sulfides.

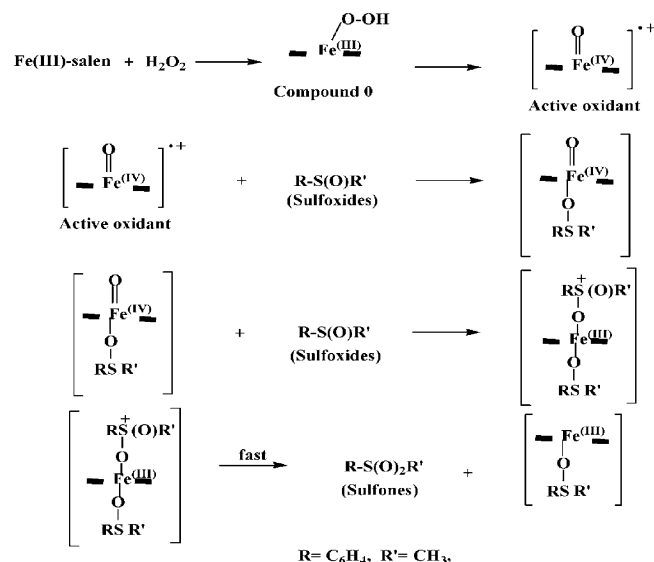
The interesting feature of organic sulfoxides is that it can transfer oxygen atom to the metal ion to produce oxo metal species, which in turn can transfer oxygen atom to other substrate [70,71]. There are evidences for the different behaviour of sulfides and sulfoxides towards the same oxidant permanganate ion. For example, towards MnO_4^- ion sulfides and sulfoxides act as nucleophiles and electrophiles, respectively [72–74]. The significant increase in absorbance (OD) of iron(III)–salen– H_2O_2 system with increase in sulfoxide concentration, points out that sulfoxides bind efficiently to iron(III) complexes through oxygen atom of sulfoxides. Since the

binding of sulfoxides to the metal center is more pronounced, it tempts us to propose the iron(IV)–sulfoxides adduct as the oxidant rather than unbound oxo iron(IV) ion (Scheme 3). There are at least three different possibilities for explaining the oxygenation of sulfoxides to sulfones: (i) oxygen atom transfer from active oxidant to sulfoxides through a bimolecular electrophilic mechanism, (ii) ligand coupling (nucleophilic oxygen transfer) and (iii) a bimolecular electrophilic oxidation by oxidant–sulfoxide adduct.

Based on kinetic and spectral evidences, it is better to explain the mechanism through oxidant–sulfoxide adduct formation followed by oxygen atom transfer. The strong binding of sulfoxides to the metal center weakens the $Fe=O$ bond and thereby facilitates the oxygen atom transfer from the adduct to the excess sulfoxide present in the moiety. Similar mechanism has been proposed by Venkataraman et al. [75] for the [oxo(salen)chromium(V)] ion oxidation of organic sulfoxides where sulfoxides bind strongly with the oxidant.



Scheme 2. Electron transfer mechanism for the selective H_2O_2 oxidation of sulfides to sulfoxides in CH_3CN .



Scheme 3. Mechanism for selective oxidation of sulfoxides to sulfones in CH_3CN .

4. Conclusion

The oxidation of aromatic sulfides and sulfoxides with H₂O₂ catalyzed by iron(III)–salen ions in CH₃CN is an efficient and environmentally benign process. This reaction is facile to produce selectively the corresponding sulfoxides and sulfones, respectively, under the experimental conditions. The kinetic studies were performed spectrophotometrically and the characterization of products was done by ¹H NMR, FT-IR, GC and GC–MS analysis. To account for the experimental observations, the possible mechanisms were proposed.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2009.05.004.

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