Selective H$_2$O$_2$ oxidation of organic sulfides to sulfoxides catalyzed by cobalt(III)–salen ion

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ABSTRACT

The catalytic activity of cobalt(III)–salen ion catalyzed selective H$_2$O$_2$ oxidation of organic sulfides to sulfoxides is examined using spectrophotometric technique. The catalytic reaction proceeds through Michaelis–Menten kinetics and the rate of the reaction is highly sensitive to the nature of the substituent present in the substrate as well as in the salen ligand. The product analyses show that the aryl methyl sulfides are selectively oxidized to the corresponding sulfoxides. Based on the spectral and kinetic studies two possible mechanisms have been proposed.

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1. Introduction

Salen complexes [salen = N,N′bis(salicylidene)ethylene-diaminato] of transition metals (metal – Fe, Ru, Mn, Cr, Co, V, Ti, Mo, Zr, U, Y, Pt) attract considerable interest because of their catalytic activity and easy methods of syntheses [1–11]. In the past decades, metal–salen complexes have been extensively used as catalysts for epoxidation [4,12], sulfoxidation [2,13], ring opening reaction [14], fixation of CO$_2$ in the form of carbonates [15] and as models for enzymes [16]. In our laboratory, detailed kinetic studies using spectrophotometric technique were carried out to propose the mechanism for the oxidation of aryl methyl sulfides to sulfoxides and amines to N-oxides using metal–salen complexes (Metal = Fe, Mn, Cr, V) as enzyme models and PhIO and H$_2$O$_2$ as the oxidants [2]. By introducing various substituents in the two aromatic rings of the salen ligands, the electronic and steric factors affecting the stability of active oxidants generated from metal–salen complexes and oxygen sources H$_2$O$_2$, PhIO, tert-BuOOH and their reactivity have been studied [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 O$_2$ binding properties of cobalt(II)–salen ions and their utility

as catalysts [17,18]. Punniyamurthy et al. [19] have used cobalt(II)–salen complexes as efficient catalysts for the oxidation of wide range of organic substrates (e.g., alkenes, alcohols, benzylic compounds and aliphatic hydrocarbons) with dioxygen in the presence of aliphatic aldehydes or ketones or ketoesters. Cobalt–salen complexes have been endowed as catalysts for epoxidation reactions [20,21], ring opening [22], oxidation of phenols and anilines [23–25], cyclopropanation [26], carbon dioxide fixation [27], asymmetric catalysis [28–30] and catalysts for other reactions [31–33].

As far as we know, there is no literature available on the catalytic role of cobalt–salen complexes for the oxidation of biologically important organic sulfides. The study of oxidation of organic sulfides is of wide interest because of the important role of sulfur compounds and in particular, sulfur centered radicals in biological systems [34]. As sulfoxidation reactions play vital role in biological systems because of their antioxidant nature [6,35–39], it is desirable to study the catalytic role of cobalt(II)–salen complexes for the oxidation of sulfides. As far as the nature of the active oxidant species generated from the catalyst cobalt(II)–salen complex and H$_2$O$_2$ is concerned much effort has been attempted in recent years [32,40]. From a detailed investigation Thomas and coworkers [3c] have reported that Co(III)-tris(phenolate) species as the active catalyst of the reaction. The authors examined the pathways possible for one electron oxidation of phenolate complex (Co^{II}–L) either via metal ligand radical (Co^{II}–L·) or (Co^{III}–L) and concluded the active catalyst is cobalt(III)–bis(phenolate) salen. To accomplish the

catalytic role of Co(II) ion on sulfoxidation reaction we have synthesized five Co(II)–salen complexes (I–V, Chart 1) and used them as catalyst. Seven *para*-substituted phenyl methyl sulfides (1–7, Chart 2) are used as the substrates and H_2O_2, the eco-friendly reagent, has been used as the oxidant. On addition of H_2O_2 to cobalt(II)–salen complexes, the obvious spectral changes explain the formation of active oxidant species whose spectral changes are followed to study the kinetics of sulfide oxidation.
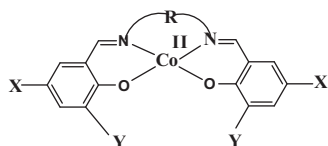
2. Experimental

2.1. Materials

Salicylaldehyde and the substituted salicylaldehydes (5-chloro, 5-methyl, 5-methoxy, 3,5-di-tert-butyl) were purchased from Aldrich and used as such. The *para*-substituted phenyl methyl sulfides (*p*-methoxy, *p*-methyl, *p*-flouro, *p*-chloro, *p*-bromo and *p*-nitro) were also purchased from Aldrich and used as such. HPLC grade acetonitrile, dichloromethane and 30% H_2O_2 were used as received.

2.2. Instrumentation

The UV–Vis absorption spectral measurements have been carried out using Analytik Jena Specord S 100 diode array spectrophotometer with a constant accumulation of 10 and a constant integration time of 40 ms over a range of 200–1000 nm. The infra red spectra of the Co(II)–salen complexes and the products have been recorded in a JASCO FT-IR–410 spectrophotometer. ^1H NMR for the salen ligands have been acquired on a Bruker 300 MHz NMR spectrometer with $CDCl_3$ as the solvent. The redox potentials of the complexes are measured in CH_3CN medium using BAS CV-50 W Voltammetric Analyzer at a platinum electrode containing 0.1 M tetrabutylammonium perchlorate as the supporting electrolyte.
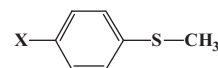
2.3. Synthesis of ligands and cobalt(II)–salen complexes (I–V)

The general procedure [41,42] for the preparation of salen ligands involves the condensation of salicylaldehyde and ethylenediamine in the ratio of 2:1 in an alcoholic medium. A mixture of salicylaldehyde (2.44 g, 19.9 mmol) and ethylenediamine (0.60 g, 9.99 mmol) in 100 ml of ethanol is refluxed for one hour. The reaction mixture is cooled to room temperature. The yellow solid is collected at the pump, and washed with cold methanol and dried in air. Yield: 97%; m.p. 128 °C, reported 128–129 °C [42]. 5,5′-(CH$_3$)$_2$-salen, 5,5′-(OCH$_3$)$_2$-salen and 5,5′-(Cl)$_2$-salen are prepared by condensing the corresponding substituted salicylaldehyde with ethylenediamine in ethanol and recrystallized from cold methanol. The ligand 3,3′5,5′-tetra-*tert*-butylcyclosalenH$_2$ is

X = H (1), OCH$_3$ (2), CH$_3$ (3), F (4), Cl (5), Br (6), NO$_2$ (7)

Chart 2. Aryl methyl sulfides (1–7).

prepared by a published procedure [43]. The ^1H NMR spectra of all substituted salen ligands are shown in our previous report [2e].

Cobalt(II)–salen complexes are synthesized by established procedures [44]. Parent salen ligand 1.8 mM (0.5 g in ethanol) is degassed under N_2. Co(OAc)$_2$.4H$_2$O (0.46 g, 1.8 mmol) in warm water is added to salen solution in small quantities at a time under N_2 atmosphere. Immediately the yellow color was changed into the dark brown. The reaction mixture is refluxed under N_2 for one hour, cooled and dried in vacuum. The product is extracted with $CHCl_3$ and dried in vacuum. Dark brown colored cobalt(II)–salen complex I is obtained. The similar procedure is followed to the synthesis of complexes II–V using appropriate salen ligand.

2.4. General procedure for sulfide oxidation

The concentrations of cobalt(II)–salen complexes and H_2O_2, have been maintained as 2×10^{-4} M and 5×10^{-3} M respectively. The strength of H_2O_2 is carefully monitored in all the experiments. The kinetics of H_2O_2 oxidation of organic sulfides catalyzed by cobalt(II)–salen ion in 90% CH_3CN and 10% DCM are followed under pseudo first order conditions. The progress of the reaction is monitored by maintaining the concentration of sulfide 10 times greater over the cobalt(III)–salen complex.

2.5. Product analysis

In a typical experiment involving oxidation of organic sulfides, 0.2 mM cobalt(II)–salen is treated with 5 mM MPS and 5 mM H_2O_2 in CH_3CN/CH_2Cl_2 (90/10 v/v) medium. The solution is stirred for 1–2 h at 298 K, depending on the nature of the reactants. The solvent is removed under reduced pressure and the organic product is extracted with chloroform. It is dried over sodium sulfate and evaporated. The residual mass is subjected to IR and NMR studies. The details of the product analyses are elaborated in the discussion section.

3. Results and discussion

The structures of metal–salen complexes and the substrates used in the present study are depicted in Charts 1 and 2 respectively. The synthesized cobalt(II)–salen complexes are characterized by UV–Vis, FT-IR and CV studies and data are collected in Supporting information (Table S1). The spectra and CV of some complexes are shown in the Supporting information (Figs. S1–S6). The spectral data obtained in this study are similar to the previous reports [45].

### 3.1. Cobalt(II)–salen complexes not suitable catalysts for sulfide oxidation

When we attempted to use cobalt(II)–salen complexes as catalysts for the oxidation of organic sulfides, there was no reaction even if we follow the course of the reaction for several hours. From this experimental observation we concluded that cobalt(II)–salen complexes were not serving as the catalysts for the oxidation of organic sulfides. According to Jacobsen and co-workers [46] and Thomas and co-workers [3c] cobalt(II)–salen complexes were catalytically inactive for hydrolytic kinetic

I	X=H,	Y=H,	R=CH$_2$CH$_2$;
II	X=Cl,	Y=H,	R=CH$_2$CH$_2$;
III	X=CH$_3$,	Y=H,	R=CH$_2$CH$_2$;
IV	X=OCH$_3$,	Y=H,	R=CH$_2$CH$_2$;
V	X=Y=*t*-Butyl,		R=cyclohexane

Chart 1. Structure of Cobalt(II)–salen complexes.

resolution but they became suitable catalysts if [Co(II)–salen] ions were subjected to one electron oxidation to produce Co(III)–salen-X (X = anionic ligand). Fukuda and Katsuki [47] achieved asymmetric cyclopropanation of styrene using optically active cobalt(III)–salen complexes by *in situ* generation from the reaction of cobalt(II)–salen with Br_2. With this background we wanted to try Co(III)–salen complexes as catalysts for the H_2O_2 oxidation of organic sulfides.

3.2. Generation of cobalt(III)–salen ion

In the present study, cobalt(III)–salen complex is generated *in situ* using H_2O_2 as the oxidant. At this juncture, it is worth mentioning that H_2O_2 is the green oxidant that converts the cobalt(II)–salen complex into cobalt(II)–salen complex [48]. The attractive spectral changes observed by the addition of H_2O_2 to the parent cobalt(II)–salen complex (**I**) is shown in Fig. 1. It is interesting to note that the intensity of the three peaks at λ_{max} = 346 nm (n–π^*), λ_{max} = 403 nm (d–π^*) and λ_{max} = 489 nm (d–d) decreases with clear isosbestic points at λ_{max} = 327 and 515 nm for the 2×10^{-4} M (**I**) on adding 5×10^{-3} M H_2O_2. The changes in the absorption spectrum are measured for every second using the diode array spectrophotometer. The conversion of Co(II) to Co(III) is achieved in less than 10 s. The intensity of the three peaks corresponding to cobalt(II)–salen decreases and becomes a single peak at 376 nm (for complex **I**) on adding H_2O_2. The obvious decrease in the absorbance at λ_{max} = 489 nm (d–d) indicates that cobalt ion attains +3 state [48]. The similar behavior is observed with the Co(II) complexes carrying substituted salen ligands (**II–V**) also. The spectral changes observed for complex **V** are shown in Fig. S7.

In principle one electron oxidation of Co(II)–salen complex could afford either metal–ligand radical Co^{II}–(salen$^{.+}$) or (Co^{III}–salen) complex according to Eq (1).

$$[Co^{II} - salen] + oxidant \rightleftharpoons [Co^{II} - salen^{.+}] \text{ or } [Co^{III} - salen] \qquad (1)$$
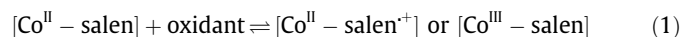
Determining the electronic structure of one electron oxidized Co(II)–salen complexes is of prime importance to understand the catalytic pathway and mechanism of the reaction [3c,49]. Recent studies show that the absorption in the whole visible region as well as an intense absorption band at >900 nm indicate the formation of [Co^{II}–(salen$^{.+}$)] as the oxidized product of [Co^{II}–salen] complex [32]. As shown in Fig 1 there is no significant absorption at >600 nm for [Co^{II}–salen] in the presence of H_2O_2 which compels us to conclude that [Co^{III}–salen] complex is the catalyst for the catalysed oxidation of organic sulfides.
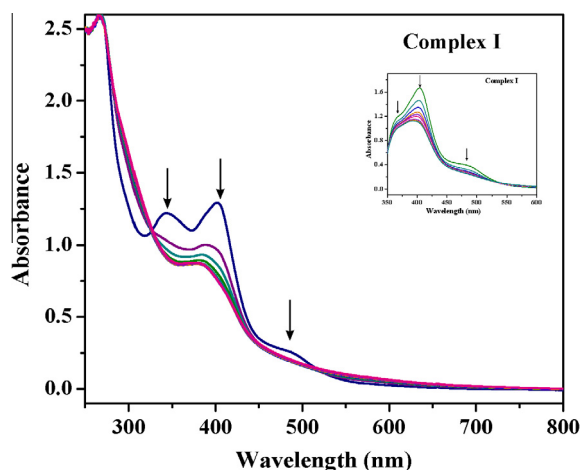
3.3. Kinetic studies

The *in situ* generated cobalt(III)–salen complexes catalyze the H_2O_2 oxidation of organic sulfides. When phenyl methyl sulfide is injected into the reaction mixture, there is a substantial shift in λ_{max} towards red region and also there is increase in intensity. For parent cobalt(III)–salen (**I**), the λ_{max} value shifts from 376 to 383 nm. The increase in the absorbance (OD) is to the extent of 0.1–0.3 depending on the nature of the substituents in the salen ligand (Fig. S8). The increase in the absorption intensity is instantaneous and decreases fast with time. The rate of the reaction is measured following the decay of absorbance of the complex at appropriate wavelength (λ_{max}) with time intervals of 5 min at 298 K. The sample spectral changes with time are shown in Figs. 2 and S9.

When we monitored the progress of the reaction spectrophotometrically, an induction period of about 20–30 min was observed followed by decrease in the intensity at the appropriate λ_{max}. It is evident from Fig. 3 that there is negligible change in OD initially for about 25 min and then there is a linear decrease in log OD with time.

It is interesting to point out that similar induction periods have been observed for the Co(II)–salen complexes catalyzed O_2 oxygenation of cyclohexane [50]. The induction period is used for the generation of the active oxidant species [Co(III)–(salen)–OOH]. It is generally accepted that co-coordinated peroxy complexes are the active oxygen transfer species formed during propagation of the oxidation reactions catalyzed by Co complexes [50].

The inset in Fig. 3 shows the linear part of the plot signifying the first order kinetics of the reaction on the oxidant. The rate measurement is followed for the linear part of the plot giving the appropriate range for measurement of rate constant using the inbuilt program Win Aspect. The first order rate constant, k_1, values measured for seven *para*-substituted aryl methyl sulfides catalyzed by cobalt(III)–salen complexes **I** and **II** are tabulated in Tables S2 and S3.

The influence of substrate concentration on the rate of reaction is studied by measuring the rate of the reaction at different [substrate]. The kinetic results are shown in Tables S2 and S3 and in Fig. 4. These results indicate that the rate of the reaction increases with increase in [substrate] and attains saturation at high [substrate]. The inference from the saturation kinetics is that the substrate binds to the oxidant before the rate controlling step. The binding of substrate with the oxidant is evident with an initial
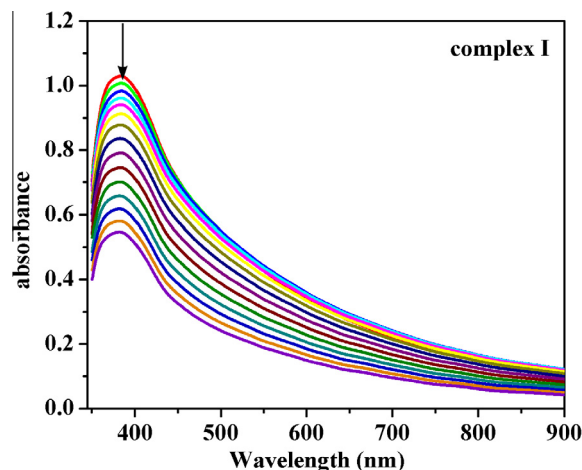

Fig. 1. UV–Vis spectral changes observed for complex **I** in the presence of H_2O_2 in 90% CH_3CN and 10% DCM at 298 K. [**I**] = 2×10^{-4} M, [H_2O_2] = 5×10^{-3} M.

Fig. 2. Change of absorbance of **I**–H_2O_2 system with time in the presence of C_6H_5SMe (**1**). [**I**] = 2×10^{-4} M, [H_2O_2] = 5×10^{-3} M, [**1**] = 4×10^{-3} M.
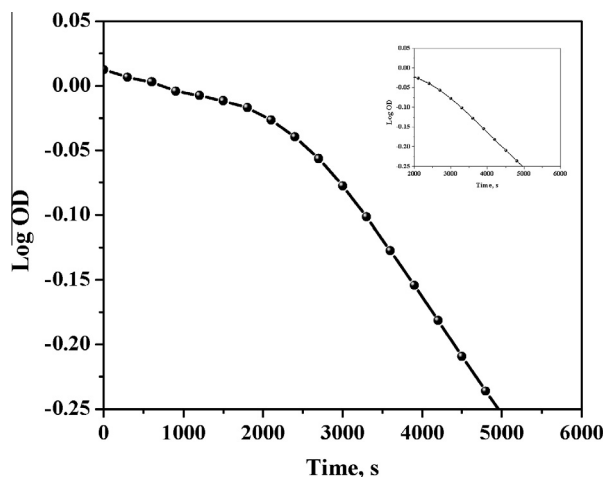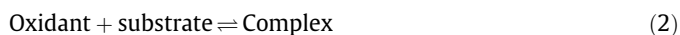
Fig. 3. Log OD vs time plot. [I] = 2×10^{-4} M, [H_2O_2] = 5×10^{-3} M, [1] = 2×10^{-3} M.

Table 1
Rate constants 10^4 k, s^{-1} for the cobalt(III)–salen catalyzed H_2O_2 oxidation of p-$XC_6H_4SCH_3$ in 90% CH_3CN-10% DCM at 298 K.

X=	I	II	III	IV	ρ	r	V
H	3.30	4.90	1.98	1.93	0.4	0.98	1.40
OCH$_3$	5.90	7.60	3.40	3.30	0.4	0.97	2.30
CH$_3$	5.50	6.40	2.90	2.70	0.4	0.97	2.10
F	2.30	3.60	0.99	0.92	0.7	0.97	0.91
Cl	2.70	3.00	1.00	0.93	0.6	0.98	0.90
Br	2.12	2.90	0.91	0.88	0.6	0.97	0.85
NO$_2$	0.72	1.20	0.40	0.39	0.5	0.97	0.35
ρ	−0.9	−0.8	−1.0	−0.9	–	–	−.0.9
r	0.98	0.99	0.97	0.97	–	–	0.97

Table 2
Michaelis–Menten constants, $10^3 K_M$ obtained from Michaelis–Menten kinetics of cobalt(III)–salen complexes catalyzed H_2O_2 oxidation of p-$XC_6H_4SCH_3$ in 90% CH_3CN-10% DCM system at 298 K.

X=	I	II	III	IV	V
H	9.50	18.1	19.6	19.2	6.20
OCH$_3$	6.50	8.10	13.6	17.0	4.80
CH$_3$	9.80	12.2	14.5	14.5	5.80
F	6.40	7.00	19.2	20.4	8.90
Cl	12.9	4.80	20.8	16.2	8.50
Br	13.0	8.40	15.1	11.2	9.50
NO$_2$	35.0	15.5	12.7	9.50	13.5

increase in the absorbance (OD) of oxidant on the addition of substrate (Fig. S8).

Thus the redox reaction proceeds through Michaelis–Menten kinetics which can be treated through Eqs. (2) and (3).

$$\text{Oxidant} + \text{substrate} \rightleftharpoons \text{Complex} \qquad (2)$$

$$\text{Complex} \xrightarrow{k} \text{Product} \qquad (3)$$

from these equations the rate law can be derived and the rate expression is given by Eq. (4).

$$k_1 = k_{obs} = k[\text{substrate}]/(K_M + [\text{substrate}]) \qquad (4)$$

The inverse of Eq. (4) becomes Eq. (5)

$$1/k_1 = (1/k) + (K_M/k[\text{substrate}]) \qquad (5)$$

when $1/k_1$ is plotted against 1/[substrate], linear plots are obtained with finite intercepts. A sample plot is shown in Fig. S10. From the slope and intercept values, k and K_M have been evaluated and are given in Tables 1 and 2.

3.4. Substituents effects

The data provided in Table 1 give a clear picture on the substituent effect. The substituents present in 5,5′-positions of salen
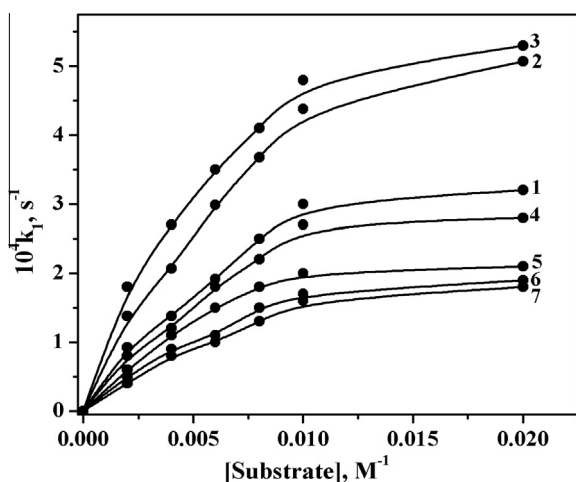
ligand and the aryl moiety of ArSMe influence the rate of the reaction enormously. The rate of the reaction is enhanced by the introduction of electron donating substituents in the phenyl ring of PhSMe and the rate is retarded by electron withdrawing substituents in the same moiety. The opposite effect is noticed when the substituents are introduced in the 5,5′-positions of salen ligand. In order to understand the extent of charge separation in the transition state of the reaction, the rate constant values collected in Table 1 are analyzed in terms of the Hammett equation [51] (Eq. (6)).

$$\log k/k_0 = \sigma\rho \qquad (6)$$

where k_0, the rate constant when X = H, k, the rate constant when X = substituents, ρ = reaction constant, σ = substituent constant.

The correlation of log k values of phenyl methyl sulfides with Hammett sigma constant is good (Figs. 5 and S11) and the reaction constant (ρ) values range from −0.8 to −1.0 for different cobalt(III)–salen complexes. The correlation is not improved if

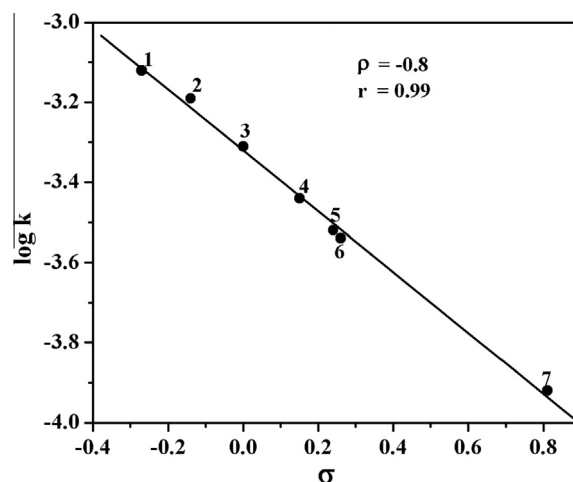**Fig. 4.** Plot of k_1 vs [substrate] for a reaction catalyzed by complex **II**.

Fig. 5. Hammett plot for the H_2O_2 oxidation of ArSMe catalyzed by **II**.

sigma+/sigma− values are used instead of sigma ($r = 0.96$, $n = 7$, $\rho^+ = -0.7$ for complex **I**).

The effect of introducing substituents in the salen ligand of cobalt(III)–salen complex on the rate of oxidation of phenyl methyl sulfides is also investigated and the rate data are collected in Table 1. These kinetic data are also treated using Hammett equation by plotting log k versus 2σ (Fig. 6). The ρ value is positive and it is in the range of +0.4 to +0.7.

Jayaseeli and Rajagopal [2e] followed the iron(III)–salen ion catalyzed H_2O_2 oxidation of organic sulfides based on spectrophotometric measurements. H_2O_2 is used as oxidant and the active oxidant, oxo iron radical cation is generated *in situ* with iron(III)–salen complexes. At this juncture, it is worth mentioning that the H_2O_2 oxidation reactions are attractive because of its eco-sustainability. Sivasubramanian et al. [2h] separated the [oxo(salen)iron] ion on treating iron(III)–salen complexes with PhIO and followed the kinetics of oxidation of sulfides. Michaelis–Menten saturation kinetics are observed when H_2O_2 as well as PhIO are used as oxidants. The ρ value obtained for the iron(III)–salen ion catalyzed H_2O_2 oxidation of seven *para*-substituted methyl phenyl sulfides is -1.5. Interestingly similar ρ value was obtained when PhIO was used as the oxidant for the oxidation of nine *para*-substituted methyl phenyl sulfides. In this present work, the Michaelis–Menton kinetics was followed for the 5,5′-substituted cobalt(III)–salen complexes catalyzed H_2O_2 oxidation of para substituted methyl phenyl sulfides. The reaction constant, ρ, value lies between -0.8 and -1.0 for Co(III)–salen catalyzed oxidation. The reported ρ value is -0.85 for the kinetics of Mn(III)–salen complexes catalyzed oxidation of aryl methyl sulfides with hydrogen peroxide [52]. The ρ values obtained for the Cr(III)–salen catalyzed oxidation of sulfides ranges between -1.5 and -1.8 [2g,2i,53]. The comparison of ρ values observed with different metal–salen complexes indicates that the reaction constant observed with cobalt–salen complexes is comparable with the value reported on the Mn(III)–salen catalyzed reaction but less compared to Fe(III)– and Cr(III)–salen complexes. The inference from this comparison is that though the electrophilicity of Co(III)–salen ion is comparable with Mn(III)–salen but less compared to Fe(III)– and Cr(III)–salen ions. This is also evident from the ρ values observed with these complexes when the effect of changing the substituent in the salen ligand is tested on the catalytic activity of the sulfoxidation reaction. As the magnitude of ρ is related to the development of charge during the rate determining step, mechanisms can be devised based on this information.
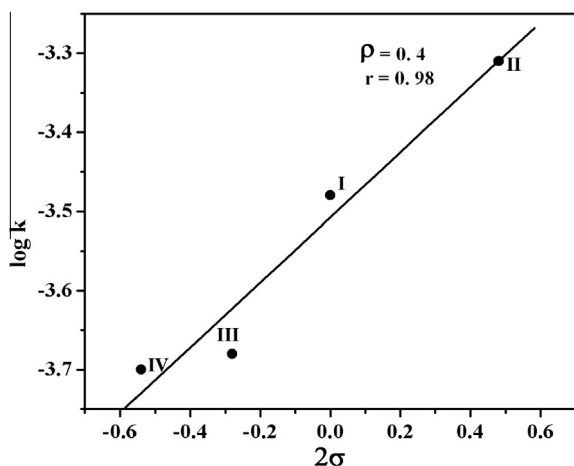

Fig. 6. Hammett plot for the H_2O_2 oxidation of **1** catalyzed by cobalt(III)–salen complexes **I–IV**.

3.5. Product analysis

In order to analyze the products formed during the course of the reaction, FT-IR and ^{1}H NMR techniques have been used. FT-IR analysis of the product obtained from the oxidation of MPS shows S=O stretching frequency at 1049 cm^{-1}, indicating the formation of sulfoxide from sulfide. There is a band at 692 cm^{-1} corresponding to C–S stretching frequency. Since there is no stretching frequency at 1150 cm^{-1} corresponding to sulfone, we understand that sulfide is not oxidized to sulfone under the present experimental conditions. The product analysis study demonstrates that sulfoxide is the only product formed under the present reaction conditions.

When ^{1}H NMR spectral study is used for the product analysis, it also gives similar results as observed with FT-IR study. From the available literature, it is known that the methyl groups of $C_6H_5SCH_3$, $C_6H_5S(O)CH_3$ and $C_6H_5S(O_2)CH_3$ in deuterated solvents show distinctive peaks at δ 2.4, 2.72 and 3.08 ppm respectively [54]. In the present study, CDCl$_3$ is used as the solvent.

The ^{1}H NMR peak obtained at 2.7 ppm (Fig. S12) is a strong evidence for the selective oxidation of sulfide to sulfoxide. The aromatic protons appear as multiplets centered at 7.2 and 7.3 ppm for sulfide and at 7.6 and 7.7 ppm for sulfoxide respectively [55]. These studies strongly confirm that the major product of the reaction is the corresponding sulfoxide.

The percentage yield of the products obtained during the course of the reaction is carried out based on GC analysis as well as NMR spectral data. The results obtained in the H_2O_2 oxidation of seven para substituted phenyl methyl sulfides in the presence of complex **I** are given in Table 3 and sample GC–MS spectrum is shown in Supporting information (Fig. S13). It is evident that the percentage yield lies in the range 50–64% in accordance with the effect of substituents on the reactivity of the reaction. Organic sulfides carrying electron donating substituents in the aryl moiety form higher yield compared to electron withdrawing substituents. The turnover number (TON) calculated from the percentage yield obtained from different organic sulfides is in the range of 10–13.
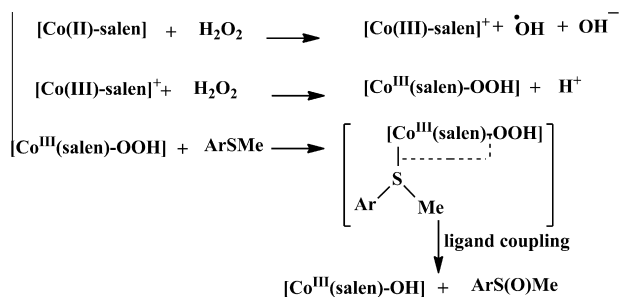
3.6. Mechanism of the reaction

The initial reaction between Co(II) and H_2O_2 leads to the formation of Co(III) which catalyzes the H_2O_2 oxidation of organic sulfides. Co(III) ion reacts with H_2O_2 to produce cobalt(III)–hydro peroxide adduct [Co^{III}–OOH] similar to compound 0 in iron(III) catalyzed oxidation reaction [2e]. After the formation of [Co^{III}–OOH], the nature of its interaction with organic sulfides is speculative. Whether [Co^{III}–OOH] itself is the active oxidant or short lived radicals ·OH and ·OOH generated from the adduct are the active oxidant is not understood at this stage.

When the substrate phenyl methyl sulfide is added to [Co^{II}–salen]–H_2O_2 system there is an initial increase in OD at 383 nm (corresponding to Co(III)) indicating the binding of substrate with the oxidant. Thus the initial step involves the binding of substrate to the oxidant similar to enzyme catalyzed reaction. After the formation of oxidant–substrate complex the product

Table 3
Percentage yield of sulfoxide formed from the complex **I** catalyzed H_2O_2 oxidation of p-XC$_6$H$_4$SCH$_3$.

X	Sulfoxide (yield%)
H	60
OCH$_3$	64
CH$_3$	62
F	53
Cl	55
Br	52
NO$_2$	50

$$[Co(II)\text{-salen}] \ + \ H_2O_2 \ \longrightarrow \ [Co(III)\text{-salen}]^+ + \ \overset{\bullet}{O}H \ + \ OH^-$$

$$[Co(III)\text{-salen}]^+ + \ H_2O_2 \ \longrightarrow \ [Co^{III}(salen)\text{-}OOH] \ + \ H^+$$

Scheme 1. Mechanism for the [Co(III)–salen]⁺ catalyzed H₂O₂ oxidation of organic sulfides.
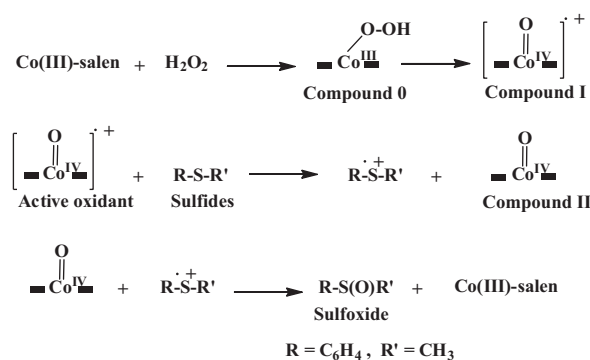
Scheme 2. Electron transfer mechanism for the [Co(III)–salen]⁺ catalyzed H₂O₂ oxidation of organic sulfides.

sulfoxide is formed through oxygen atom transfer from the oxidant to the substrate via the ligand coupling mechanism as shown in Scheme 1.

In this proposal both –OOH and ArSMe serve as ligands for Co^{III} and oxygen atom transfer takes place through ligand coupling reaction. The importance of this ligand coupling reaction has been extensively advocated by Oae and co-workers [36b]. We have proposed such ligand coupling mechanism for the picolinic acid catalyzed Cr(VI) oxidation of organic sulfides [56]. We also wish to propose alternative mechanism for this [Co^{III}–salen] catalyzed oxidation. After the formation of [Co^{III}(salen)–OOH] it may form [oxo(salen)cobalt(IV)] as the active oxidant similar to compound **I** type species postulated for iron(III)–salen and iron(III)–porphyrin catalysed H₂O₂ oxidation of organic substrates [2e,57]. This active species can oxidize organic sulfides through electron transfer mechanism. The mechanism for iron(III)–salen ion catalysed H₂O₂ oxidation of sulfides via active oxidant species [Fe^{IV}=O(salen)]·⁺ followed by electron transfer (ET) was proposed by Rajagopal and coworkers [2e]. In a similar way, the reactive species [Co^{IV}=O(salen)]·⁺ formed from [Co^{III}(salen)–OOH] combines with the substrate to form the oxidant–substrate complex. After the formation of this oxidant–substrate adduct the reaction proceeds through a series of electro transfer processes. In the first step the electron transfer from the substrate to the oxidant results in the formation of compound **II** and sulfide radical cation. The compound **II** and sulfide radical cation produce the corresponding sulfoxide and Co^{III}–salen complex as shown in Scheme 2.

4. Conclusion

The oxidation of aromatic sulfides with H₂O₂ catalysed by cobalt(II)–salen complexes is an eco-friendly efficient method for the synthesis of sulfoxide. Cobalt(III)–salen complexes are

generated *in situ* from cobalt(II)–salen complexes using H₂O₂ as the oxidant. The reaction follows Michaelis–Menten kinetics and the rate is highly sensitive to the change of substituent in the salen moiety of Co(III) complex and aryl moiety of ArSMe. The product analysis study using FT-IR and NMR techniques shows that aryl methyl sulfides are selectively oxidized to the corresponding sulfoxides under the present experimental conditions. Based on these spectral, kinetic and product analysis study, two possible mechanisms have been proposed.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.poly.2015.07.020.

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