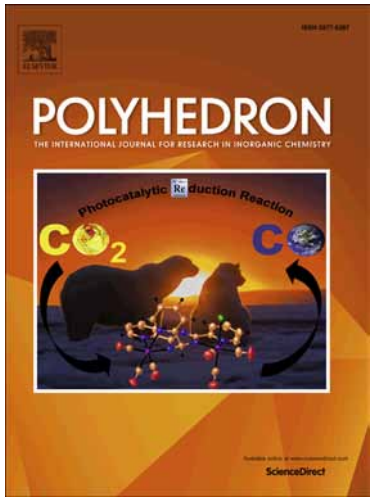

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Modulation of catalytic activity by ligand oxides in the sulfoxidation of phenylmercaptoacetic acids by oxo(salen)chromium(V) complexes

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A B S T R A C T

Mechanism of sulfoxidation of eleven para-substituted phenyl mercaptoacetic acids (PMAAs) by three oxo(salen)chromium(V)$^{+}$ PF_6^{-} complexes in the presence of different ligand oxides (LOs) such as triphenylphosphine oxide, pyridine N-oxide and 4-picoline N-oxide have been studied spectrophotometrically in 100 % acetonitrile medium. Spectral and kinetic profiles establish the formation of adduct, O=Cr(V)(salen)$^{+}$-LO as the reactive intermediate in the catalytic cycle. The rate of sulfoxidation is found to be enhanced significantly by the addition of LOs and introduction of substituent in PMAA and salen complex. Both electron-releasing and electron-withdrawing substituents in the substrate and oxidant facilitate the rate of sulfoxidation. Correlation with Hammett constants yields a non-linear concave upward curve. Based on the experimental results and substituent effects two different mechanisms, a direct oxygen atom transfer (DOT) for PMAAs with electron withdrawing substituents and single electron transfer for PMAAs with electron donating substituents have been postulated.

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Abbreviations: PMAA, phenylmercaptoacetic acid; PSAA, phenylsulfinylacetic acid; salen, N,N'-bis(salicylidene)-ethylenediaminato; LO, ligand oxide; TPPO, triphenylphosphine oxide; PyO, pyridine N-oxide; PicNO, picoline N-oxide; SET, single electron transfer

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Keywords: Oxo(salen)chromium(V); Phenylmercaptoacetic acid; Sulfoxidation; Non-linear Hammett plot; Ligand oxide.

1. Introduction

Sulfur is an essential element to life and a key component in fats, body fluids, bones and proteins [1,2]. The study on the oxidation of organic sulfide moiety is important because of the central role of sulfides in living organisms and their ability to act as antioxidant. The antioxidant activity of sulfides could be ascribed partly to their ease of oxidation to form sulfoxide [3]. The sulfide moiety in biological systems is more prone to oxidation and such sulfide oxidation has received a detailed examination to understand the underlying mechanism [4–7].

Selective oxygenation of sulfide to sulfoxide is one of the most interesting routes for the production of synthetic intermediates in the construction of biologically and pharmaceutically active molecules [8,9]. Phenylmercaptoacetic acid (PMAA) and its derivatives are one among organic sulfides widely used in the fields of medicine [10] and biology [11]. Selective oxidation of PMAA and substituted PMAAs by metals [12–15], metal complexes [16–19], N-halo compounds [20–26], halo chromates [27–29], peroxocompounds [30–32], sodium perborate [33–36] and percarbonate [37] have been extensively studied. In these reactions S_N^2 type mechanism with the formation of electron deficient sulfonium ion intermediate or single electron transfer mechanism (SET) with the formation of sulfur radical cation intermediate has been proposed. Though phenylsulfinylacetic acid was reported as the sole product in most of the reactions, thiophenol [28,36], α-hydroxyphenylmercaptoacetic acid [19] and disulfide [12,14] were also identified as products in some cases.

Oxidation of organic sulfur compounds such as sulfides, sulfoxides and thioacids etc., using transition metal complexes either as an oxidant or as a catalyst is an area of current interest. In this way, synthetic organic ligands viz. Schiff's bases [38,39], porphyrin [40–42] and phthalocyanine [43] have been recently employed in the development of synthetic metal complexes in order to mimic the reactivity of metallo enzymes. In the past three decades, relatively long lived chromium(V) intermediates formed with various chelating agents have been detected both *in vivo* and *in vitro*. Since Cr(V) intermediates are more labile and reactive these are considered to be the key species in Cr(VI) carcinogenesis. Of the biomimetic Cr(V) complexes studied, the chromium(V)-salen complex chosen for the present study mimics Cr(V)-peptide complexes that were formed during intracellular reoxidation of Cr(III)-peptide complexes [44].

Several donor ligands have been employed in porphyrin and salen catalysed reactions to enhance the turnover rates and product selectivity [45,46]. The added donor ligands directly coordinate with metal centre of the porphyrin and salen complexes thereby enhancing their oxidizing ability by decreasing the oxidation potential of the metal complexes [47]. In recent years we have made systematic attempts to explore different mechanistic pathways in the oxidation of organic sulfur compounds using Cr(VI) [48–51], Fe(III) complexes [52–55], Cr(V) complexes [56,57] and V(IV) complexes [58] under different conditions. In continuation of our progress, we carried out a systematic study on the oxidation of eleven para substituted PMAAs with three [oxo(salen)chromium(V)]$^{+}$ ions (**Ia-Ic**) in the presence of three donor ligand oxides viz. triphenylphosphine oxide (TPPO), picoline N-oxide (PicNO) and pyridine N-oxide (PyO) (Chart 1) and the results are discussed in this report.

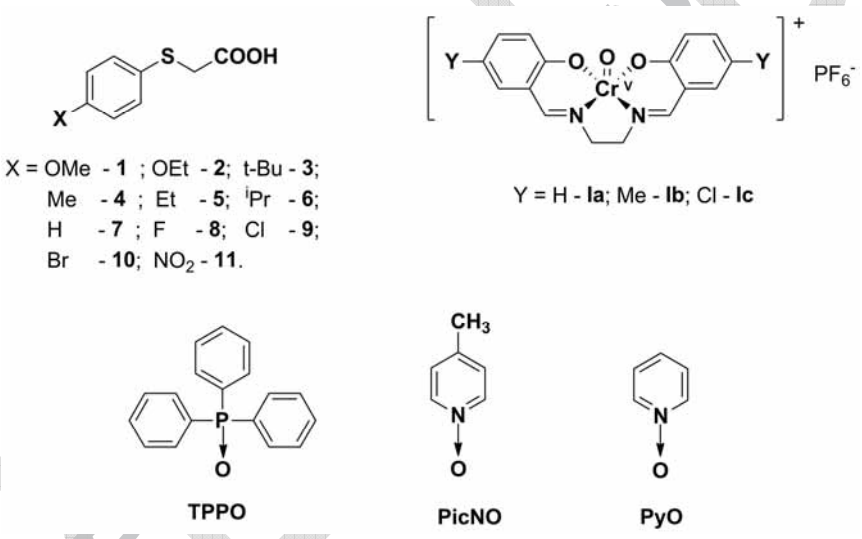


Chart 1. Structures of phenylmercaptoacetic acids (**1-11**), [oxo(salen)chromium(V)]$^{+}PF_6^{-}$ (**Ia-Ic**) and ligand oxides.

2. Experimental

2.1. Materials

Salicylaldehyde, 5-methyl and 5-chloro salicylaldehydes and triphenylphosphine oxide were purchased from Alfa Aeser and used as such. The chemicals $CrCl_3 \cdot 6H_2O$, pyridine N-oxide, picoline N-oxide and substituted thiophenols were purchased from Sigma-Aldrich. Pyridine and thiophenol were purchased from SD fine. HPLC-grade acetonitrile (Merck) was used as the solvent without further purification.

2.2. Preparation of phenylmercaptoacetic acids

PMAAs were prepared by established procedure by the condensation of the corresponding thiophenols with chloroacetic acid in alkaline medium [59]. The *p*-nitrophenylmercaptoacetic acid was prepared by a different procedure as advocated by Srinivasan et al. from *p*-chloronitrobenzene and thioglycollic acid [60]. The purity of PMAAs was checked by determining their melting points and comparing them with literature values [60]. Iodosobenzene was prepared from (diacetoxyiodo)benzene by a standard procedure [61].

2.3. Preparation of (salen)chromium(III) chloride complexes

Chromium(III) chloride hexahydrate (2.5 g, 0.01 M) dissolved in distilled water was reduced to chromium(II) chloride by zinc amalgam under deaerated condition by passing nitrogen gas. The blue solution of chromous chloride formed was added to a suspension of salen ligand (2.15 g, 0.008 M) in acetone under nitrogen atmosphere. The dark-brown solution was allowed to reflux in the presence of air for 2 h. The solvent was removed in vacuum, the residue was suspended in water and allowed to stir for 2 h in the presence of air. The yellowish-brown material was collected by filtration, redissolved in CH_2Cl_2 (60 mL) and washed with saturated NH_4Cl and then with aqueous NaCl. The organic phase was separated and dried over Na_2SO_4 and concentrated under reduced pressure to afford the (salen)chromium(III) chloride complex.

2.4. Preparation of (salen)chromium(III) hexafluorophosphate complexes

Equimolar solutions of (salen)chromium(III) chloride in methanol-water mixture and ammonium hexafluorophosphate in minimum amount of water were mixed together with stirring for 4 hours and kept aside. The formed orange crystal after 2 days were filtered through pump, washed with water, diethyl ether and dried in vacuum.

2.5. Preparation of [oxo(salen)chromium(V)]$^+$ ions

The solutions of [oxo(salen)chromium(V)]$^+$ (**Ia**), [oxo(5,5'-dimethylsalen)-chromium(V)]$^+$ (**Ib**) and [oxo(5,5'-dichlorosalen)chromium(V)]$^+$ (**Ic**) ions with PF_6^- counterion were prepared by the oxidation of corresponding orange coloured

$[Cr^{III}(salen)]^{+}PF_6^{-}$ complexes with slight excess of iodosobenzene [62] in acetonitrile. The dark green coloured solutions of [oxo(salen)chromium(V)]$^{+}$ ions formed were filtered to remove the excess of iodosobenzene and used for the kinetic study after dilution. The purity of the $Cr^{III}(salen)]^{+}PF_6^{-}$ and [oxo(salen)chromium(V)]$^{+}$ ions were checked by comparing their absorption spectra with the previous reports [63,64].

2.6. Kinetic measurements

The kinetic study of PMAA and substituted PMAAs with [oxo(salen)chromium(V)]$^{+}$ ions in the presence of TPPO, PyO and PicNO was carried out in acetonitrile medium under pseudo-first order conditions with excess of PMAA concentration over the [oxo(salen)chromium(V)]$^{+}$ ion. The reactions were started by quickly injecting [oxo(salen)chromium(V)]$^{+}$ ion in to a solution of PMAA and LO in varying concentrations in such a way that in each run the total volume was maintained as 5 cc. The reaction was followed by measuring the decrease in absorbance of oxo(salen)Cr(V)–LOs adduct at the appropriate wavelength. To follow the progress of the reaction and to record the absorption spectra of [oxo(salen)chromium(V)]$^{+}$ ions and the adduct formed between [oxo(salen)chromium(V)]$^{+}$ ion and LO, double beam BL 222 Elico UV–vis bio spectrophotometer was employed.

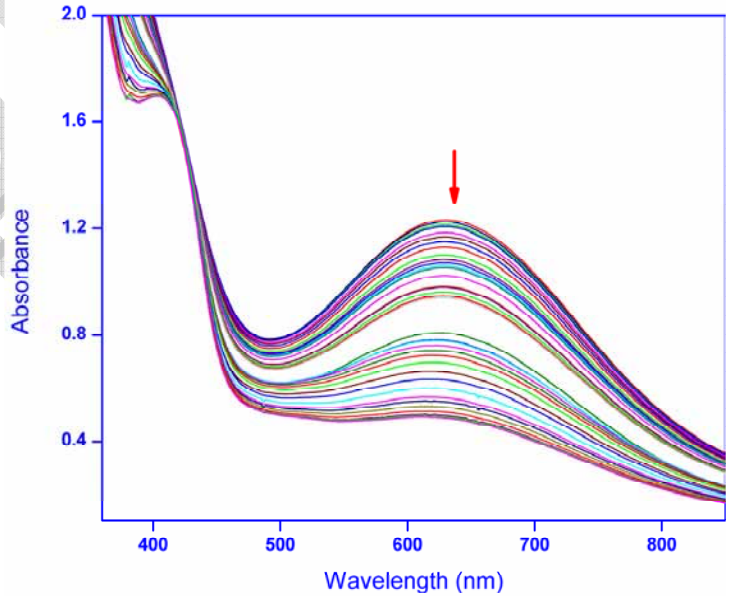


Fig. 1. The absorption spectral change for the reaction between PMAA and **Ia** in the presence of TPPO. [PMAA] = 1×10^{-1} M; [**Ia**] = 5×10^{-4} M; [TPPO] = 5×10^{-3} M; temp. = 303 K; solvent = 100% CH_3CN.

The representative plot showing decrease in absorbance with time for the reaction between PMAA and **Ia** in the presence of TPPO is shown in the Figure 1. The pseudo-first order rate constants were calculated from the slope of linear plots of log OD *vs.* time and the overall rate constants were obtained by using the expression $k_{ov} = k_1 / [PMAA]^n$, where n is the order with respect to PMAA. The error in the rate constants are given in accordance to 95 % student's t-test.

2.7. Binding constant

The binding constant values for the adduct formed between the complexes (**Ia-Ic**) and LOs were determined by spectral titration method using UV-vis spectroscopy. Typically 5.0 × 10^{-4} M solution of the $[oxo(salen)Cr(V)]^+$ ion in CH_3CN was titrated against successive addition of a standard solution of the LO without changing the total volume. Upon increase in [LO], the absorption spectrum of the $[oxo(salen)Cr(V)]^+$ ion showed increase in λ_{max} value along with the enhancement in the extinction coefficient. Similar results were obtained for all LOs and complexes.

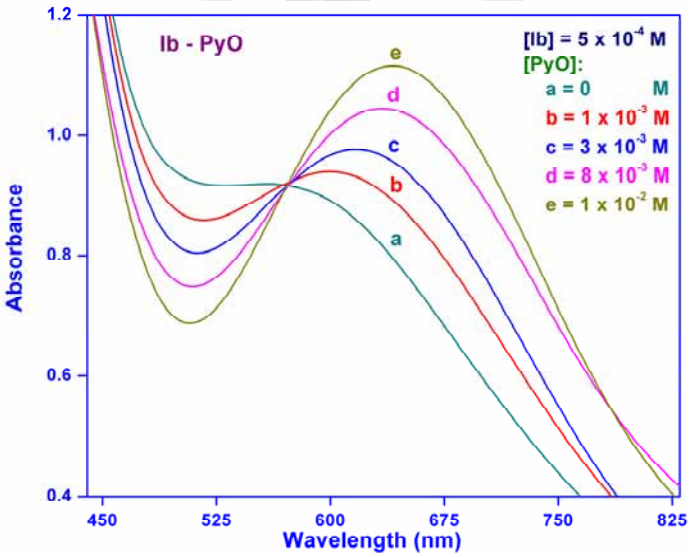


Fig. 2. Absorption spectral changes during the spectral titration between **Ib** and PyO.

The Figure 2 shows the absorption spectral changes observed during the spectral titration of **Ib** with PyO. The existence of isobestic point in the spectral titration curves of $[oxo(salen)Cr(V)]^+$ ions with all LOs provides a direct proof for the binding of one equivalent

of LO with the [oxo(salen)Cr(V)]$^+$ ion in a reversible process. From the absorbance at different concentrations of LOs at the appropriate λ_{max}, the binding constant values were calculated using the modified Bensi-Hildebrand equation (1).

$$\frac{[complex]\,[LO]}{\Delta(OD)} = \frac{[complex] + [LO]}{\Delta\varepsilon} + \frac{1}{K_f\,\Delta\varepsilon} \qquad (1)$$

where Δ(OD) and $\Delta\varepsilon$ are the difference in the absorption intensity and molar extinction coefficient of the complex in the presence and absence of LO. From the ratio of the slope to y-intercept in the linear plot of [complex] [LO] / Δ(OD) vs. [complex] + [LO], the binding constant, K_f can be calculated and the values are given in Table S1.

2.8. Product analysis

A mixture of PMAA (2 mM), [oxo(salen)chromium(V)]$^+$ ion (2 mM) and PyO (0.2 mM) in 100% CH_3CN was stirred well till the completion of the reaction. The solvent was evaporated under reduced pressure. The residue was extracted with chloroform and dried over anhydrous sodium sulfate. After the removal of chloroform under reduced pressure, the residue was analyzed by FT-IR spectroscopy and LC-MS technique. The IR spectrum of product was found to be similar to that of phenylsulfinylacetic acid (PSAA) and the observed FT-IR (KBr, cm^{-1}) frequencies are: 3421 ν_{str} (OH), 2983 ν_{str} (CH_2), 1725 ν_{str} (CO), 1525 ν_{str} (C=C), 1346 ν_{ben} (CH_2), 1025 ν_{str} (SO) and 854 ν_{ben} (Ar-H) (Fig. S1). The HPLC chromatogram has only one major peak. The peak eluted at wavelength of 254 nm and at the retention time of 5.562 min. has an overall area of 95.5 %. This clearly shows that the product contains only one component. The peak eluted in LC-MS of the product at the retention time of 5.604 min. ionizes in APCI (-) mode at m/z = 183.1 (Fig. S2) confirmed the formation of PSAA as the only product. The UV-vis spectrum of the reaction mixture after completion of the reaction was identical with that of [(salen)Cr(III)]$^+$ ion. These observations confirm that PMAA and [oxo(salen)chromium(V)]$^+$ are converted into PSAA and [(salen)Cr(III)]$^+$ respectively and are the only products of the reaction.

3. Results

3.1. Spectral studies

The electronic spectrum of [oxo(salen)chromium(V)]$^+$ ion (**Ia-Ic**) in acetonitrile medium has absorption maximum at 560, 557 and 584 nm respectively corresponding to d-π*

charge-transfer transition [65]. Addition of ligand oxides such as TPPO, PicNO and PyO to the solution of [oxo(salen)chromium(V)]$^+$ causes an immediate colour change from dark green-black to emerald green, a significant red shift in the λ_{max} and increase in absorbance in the absorption maxima. Moreover, upon successive addition of incremental amounts of donor ligands to the complexes, an increase in OD is observed. This shift in λ_{max} value depends upon the nature of LO and nature of substituent in the complex and is found to be in the range of 46 - 85 nm. The observed λ_{max} value of complexes (**Ia-Ic**) in the absence and presence of LOs are listed in the Table 1. Maximum red shift is observed for the complex **Ib** with PicNO and a minimum red shift is noticed in **Ic** with PicNO and PyO. Similar shift of λ_{max} value for the complexes with LO has been observed by Samsel et al. [66], Venkataramanan et al. [67] and Srinivasan and Kochi [68]. They explained the spectral changes on the basis of the formation of adduct between [oxo(salen)Cr(V)]$^+$ and LO. Contradictorily, addition of donor ligand during the oxidation of organic sulfides by sodium hypochlorite catalyzed by (salen)Mn(III) [69] and the oxidation of PMAAs by oxo(salen)Mn(V) complexes [16] no change in the absorption spectrum of the complex was noted.

Table 1. Absorption maxima of complexes in the presence and absence of ligand oxides

Complex	λ_{max} (nm)			
	Without additive	TPPO	PicNO	PyO
Ia	560	627	608	612
Ib	557	640	642	620
Ic	584	645	630	630

3.2. Kinetic results

The sulfoxidation reaction is first-order with respect to [oxo(salen)chromium(V)]$^+$ ion as evidenced from the linearity of log OD vs. time plots (Fig. S3) and the constant value of pseudo-first order rate constants calculated at various concentrations of the complex (Table S2). Though the pseudo-first order rate constants (k_1) increase with increase of PMAA concentration (Table S2 and Fig. S4), the second order rate constants evaluated using the expression $k_2 = k_1/[PMAA]$ are not constant. This along with fractional slope values (Table S3) obtained from the plots of log k_1 vs. log [PMAA] (Fig. S5) indicate a fractional order

dependence on PMAA. The operation of Michaelis-Menten kinetics [70] is confirmed from the excellent linear plots of $1/k_1$ vs. 1/[PMAA] having positive slopes without passing through the origin (Fig. S6). The Michaelis-Menten constants (K_M) calculated from the slope and intercept values of the Michaelis-Menten plots are listed in Table S4. The observed constant Michaelis-Menten value for each LO with different complexes shows that the binding of PMAA with [oxo(salen)chromium(V)]$^+$-LO adduct is independent of the nature of the substituents in the complex. The non-saturation obtained at high concentrations of PMAA and the observed high K_M values indicate that the binding of PMAA is weak in nature. The weak binding of PMAA with complex is further evidenced from the non occurrence of any spectral change upon the addition of PMAA either to the complex alone or along with LOs. Similar kinetic results have been noticed for all PMAAs with all complexes.

3.3. Effect of donor ligand oxides

In order to find the effect of donor ligands on sulfoxidation, the reaction was carried out in the presence of three donor ligand oxides *viz.* TPPO, PicNO and PyO. Addition of these donor ligands show that the rate constant increases with increase of LO concentration, reaches maximum and then attains saturation at higher concentration of LO. The rate constants at different concentrations of LOs are given in Table 2. The kinetic data show that the rate of sulfoxidation in the presence of LO is about 50-150 times higher than its absence. The order of reactivity among the LOs is PyO > PicNO > TPPO and more specifically the rate is about one and half times higher in the presence PicNO and about two and half times higher in the presence of PyO than that in the presence of TPPO. The highest reactivity in the presence of PyO is due to the easy formation of the oxidizing species, O=Cr(salen)-PyO (**C_1**) as evidenced from its higher binding constant value. The strong binding of PyO weakens the Cr-O oxo bond assisting the rate enhancement enormously. The observed least reactivity in the presence of TPPO is due to the least binding of TPPO with the complex.

Gilheany and co-workers [71] have shown that the rate of ligation of bulky ligands with [oxo(salen)chromium(V)]$^+$ is lower than expected which is substantiated by lower reduction potential of O=Cr(V)-TPPO adduct than O=Cr(V)-PyO [44]. Similar acceleration of rate was observed in the oxidation of olefins [66] and organic sulfides [67,72] by oxo(salen)chromium(V) complexes and in (salen)Mn(III) catalysed epoxidation of olefins [73].

Table 2. Effect of ligand oxide concentrations on the reaction rate

10^4[LO] M	TPPO		PicNO		PyO	
	$10^3\,k_1$ (s^{-1})	$10^3\,k_{ov}$ ($(M^{-1})^n\,s^{-1}$)	$10^3\,k_1$ (s^{-1})	$10^3\,k_{ov}$ ($(M^{-1})^n\,s^{-1}$)	$10^3\,k_1$ (s^{-1})	$10^3\,k_{ov}$ ($(M^{-1})^n\,s^{-1}$)
			[a]**Ia**			
0	0.13±0.01	0.13±0.01	0.13±0.01	0.13±0.01	0.13±0.01	0.13±0.01
1.0	-	-	1.27±0.01	3.26±0.13	1.35±0.11	4.27±0.34
3.0	-	-	1.97±0.02	5.64±0.11	2.16±0.14	6.83±0.44
5.0	-	-	2.42±0.20	6.94±0.57	2.88±0.21	9.12±0.67
10	1.45±0.05	5.38±0.18	2.48±0.14	7.11±0.40	3.23±0.18	10.2±0.57
30	2.15±0.11	7.98±0.41	-	-	-	-
50	2.42±0.06	8.98±0.22	-	-	-	-
100	2.50±0.02	9.28±0.07	-	-	-	-
			Ib			
0	0.21±0.01	0.41±0.02	0.21±0.01	0.41±0.02	0.21±0.01	0.41±0.02
1.0	-	-	3.26±0.07	11.8±0.25	2.86±0.05	16.1±0.28
3.0	-	-	4.04±0.02	14.6±0.07	3.79±0.07	26.9±0.50
5.0	-	-	5.00±0.04	18.1±0.14	4.68±0.11	26.3±0.61
10	2.22±0.02	11.8±0.11	6.12±0.19	22.1±0.67	5.10±0.15	28.6±0.84
30	2.51±0.12	13.4±0.64	6.18±0.08	24.5±0.29	-	-
50	3.64±0.11	19.4±0.58	-	-	-	-
100	3.91±0.14	20.8±0.74	-	-	-	-
			Ic			
0	0.28±0.01	0.57±0.02	0.28±0.01	0.57±0.02	0.28±0.01	0.57±0.02
1.0	-	-	5.10±0.09	25.4±0.45	6.32±0.12	38.4±0.72
3.0	-	-	8.43±0.07	42.0±0.35	9.84±0.21	57.1±1.22
5.0	-	-	11.0±0.03	54.6±0.15	13.7±0.18	82.7±1.09
10	4.87±0.09	28.5±0.52	11.2±0.14	55.8±0.70	14.3±0.12	86.0±0.72
30	5.52±0.06	35.0±0.38	-	-	-	-
50	6.26±0.05	36.9±0.29	-	-	-	-
100	6.39±0.07	38.4±0.42	-	-	-	-

[**Ia**] = [**Ib**] = [**Ic**] = 5.0×10^{-4} M; Temp. = 303 K; [PMAA] = 5.0×10^{-2} M; [a][PMAA] = 0.1 M; solvent = 100 % CH_3CN; n = order w.r.t. PMAA.

The binding of oxygen of LO to the metal atom followed by weakening of M=O bond in the complex which facilitate the oxygen atom transfer to reactive center of the substrate was given as the reason for the enhancement of the reaction rate as well as product yield in the presence of donor ligand. In contrast, an opposite effect is noticed in the oxidation of aromatic amines [64] and phenols [44] with the oxo(salen)chromium(V) complexes owing to the decrease in the reduction potential of $[oxo(salen)chromium(V)]^+$ ion in the presence of LO. However, in the (salen)Mn(III) catalysed oxidation of organic sulfides by sodium hypochlorite [69], sodium metaperiodate [74] and sodium hypochlorite [75], in the oxidation of organic sulfoxides catalyzed by sodium hypochlorite [76] and in the oxygen atom transfer reaction of oxo(salen)manganese(V) complexes with PMAA [16] addition of ligand oxides has no appreciable effects on the rate of sulfoxidation reactions.

As the reaction was too fast to measure in certain cases and the decomposition of the complexes were found to be appreciable at higher concentration of LOs as shown by decrease in absorption with time, reactions were conducted in the moderate range of concentration mentioned in the Table 2. The kinetic evidence for the formation of O=Cr(V)–LO adduct is shown from the observed Michaelis-Menten kinetics with LOs (Fig. S6). The reversible formation of 1:1 adduct with strong binding nature is evidenced from the saturation kinetics observed in the plot of k_1 vs. [LO] (Fig. 3) and the low Michaelis-Menten constant (K_M) values (Table S4).

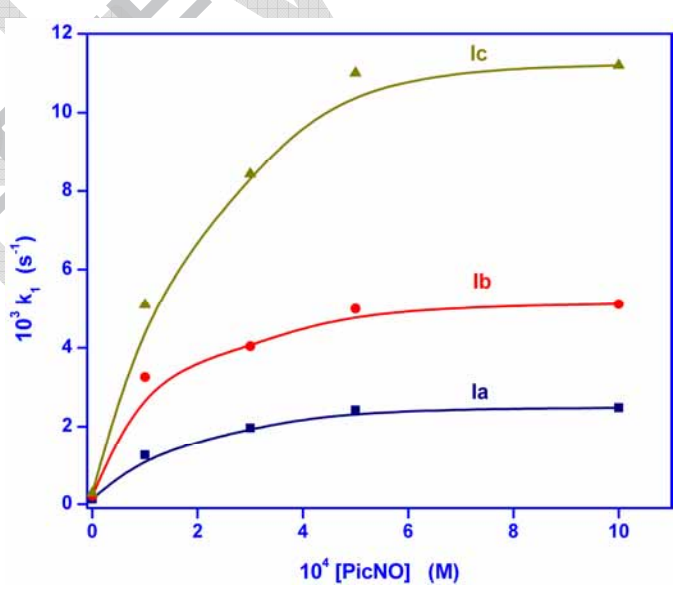


Fig. 3. Plot of k_1 vs. [PicNO] for the oxidation of PMAA by **Ia-Ic** at 303 K.

3.4. Effect of substituents

In order to probe the electronic sensitivity between the substituent and the reaction centre, three [oxo(salen)chromium(V)]$^+$ complexes and eleven PMAAs having different electron releasing and electron withdrawing substituents in the para positions were studied and the relevant kinetic data are listed in the Table 3. Interestingly both electron-releasing and electron-withdrawing substituents in the complex and PMAA enhance the rate of sulfoxidation appreciably. Insight in to the nature of the transition state was sought from the structure-reactivity correlation of Hammett [77–79]. In the Hammett correlation two intersecting linear lines with opposite slopes, a positive slope for electron withdrawing substituents and a negative slope for electron donating substituents are obtained. The unsubstituted PMAA has a minimum reactivity in the plot. Similar non-linear Hammett correlations have been reported in the oxidative decarboxylation of phenylsulphinylacetic acids by [oxo(salen)chromium(V)]$^+$ complexes in the presence of nitrogen bases [56] and iron(III)polypyridyl complexes [55], oxidation of substituted trans-cinnamic acids by pyridinium chlorochromate [80], chloramine-T [81] and acid bromate [82], oxygen-atom transfer reaction of axially ligated Mn(V)-oxo complexes [83] and stereoselective catalytic sulfoxidations mediated by titanium and zirconium trialkylanolamine complexes [84].

A high negative ρ value (-3.33 to -5.44) for electron donating substituents and comparatively low positive ρ value (2.07 to 2.55) for electron withdrawing substituents have been noticed (Table 3 and Fig. 4). The high magnitude of ρ value shows a significant charge separation in the transition state and a charge transfer between the reaction centre and substituents. Similar high ρ^- values have been reported for the oxidation of PMAAs by N-bromophthalimide (-3.22) [20], chlorosaccharin (-3.12) [21], $Cr(phen)_3^{3+}$ (-4.28) [17] and chloramine T (-2.46) [85]. On the other hand, comparatively low ρ^- values are obtained for the oxidation of PMAAs by oxo(salen)manganese(V) complexes (-1.12) [16], chromium(VI) catalysed by EDTA (-1.50) [13], peroxomonophosphoric acid (-0.996) [30] and potassium peroxodiphosphate (-0.45) [32]. Though the magnitude of ρ^- depends on the nature of LO and complex, the magnitude of ρ^+ is independent of LO as well as complex (Table 3).

Table 3. Overall rate constants for the oxidation of X-PMAA by **Ia–Ic** in presence of ligand oxides

S.No	X	$10^2 k_{ov}$ ($(M^{-1})^n s^{-1}$)								
		Ia			Ib			Ic		
		TPPO	PicNO	PyO	TPPO	PicNO	PyO	TPPO	PicNO	PyO
1	OMe	25.02±1.08	30.2±0.28	31.4±0.75	11.0±0.07	22.2±0.75	44.8±0.32	61.6±2.1	55.4±0.45	184±1.6
2	OEt	17.02±1.0	26.8±0.31	27.8±0.58	9.32±0.65	20.4±0.13	41.2±0.56	49.0±1.3	52.6±0.39	171±1.9
3	t-Bu	10.1±0.34	17.2±0.12	19.8±0.23	7.27±0.25	10.7±0.11	23.0±0.21	20.9±0.66	42.1±0.17	44.6±0.32
4	Me	7.13±0.61	14.8±0.09	16.6±0.31	5.80±0.21	9.14±0.06	18.6±0.14	16.9±0.39	28.3±0.12	40.6±0.23
5	Et	4.47±0.11	8.84±0.06	9.36±0.12	5.58±0.09	7.40±0.05	16.8±0.15	15.4±0.43	21.0±0.13	39.8±0.12
6	^{i}Pr	4.81±0.23	8.2±0.04	10.5±0.16	5.21±0.22	7.96±0.04	18.1±0.12	14.1±0.51	24.3±0.17	37.6±0.22
7	H	0.83±0.04	1.56±0.03	2.62±0.02	1.34±0.08	1.82±0.03	2.76±0.07	3.73±0.15	5.44±0.22	8.22±0.13
8	F	0.96±0.03	1.84±0.03	2.88±0.06	1.68±0.05	2.80±0.02	3.92±0.08	4.42±0.11	8.29±0.06	11.6±0.04
9	Cl	2.36±0.07	5.98±0.06	7.16±0.13	5.95±0.15	7.6±0.05	7.7±0.06	11.3±0.12	18.7±0.09	20.2±0.07
10	Br	2.96±0.03	5.82±0.07	9.68±0.08	6.28±0.12	7.9±0.04	11.7±0.09	11.8±0.18	19.5±0.12	21.2±0.13
11	NO_2	39.1±0.87	98.4±0.96	202±1.65	60.8±6.8	128.4±1.9	256±2.5	254±9.6	268.5±2.8	561±4.5
	ρ^+	2.18 ±0.08	2.33±0.09	2.48±0.08	2.11±0.18	2.33±0.08	2.55±0.17	2.39±0.05	2.07±0.02	2.37±0.15
	r	0.998	0.998	0.998	0.988	0.997	0.995	0.999	0.999	0.994
	ρ^-	-5.44±0.19	-5.19±0.27	-4.11±0.18	-3.33±0.23	-4.06±0.13	-4.48±0.28	-4.30±0.26	-3.54±0.22	-5.01±0.56
	r	0.997	0.993	0.996	0.988	0.998	0.990	0.991	0.990	0.970

[**Ia**] = [**Ib**] = [**Ic**] = 5.0×10^{-4} M; [TPPO] = 5.0×10^{-3} M; [PicNO] = [PyO] = 5.0×10^{-4} M; n = order w.r.t. PMAA; solvent = 100 % CH_3CN.

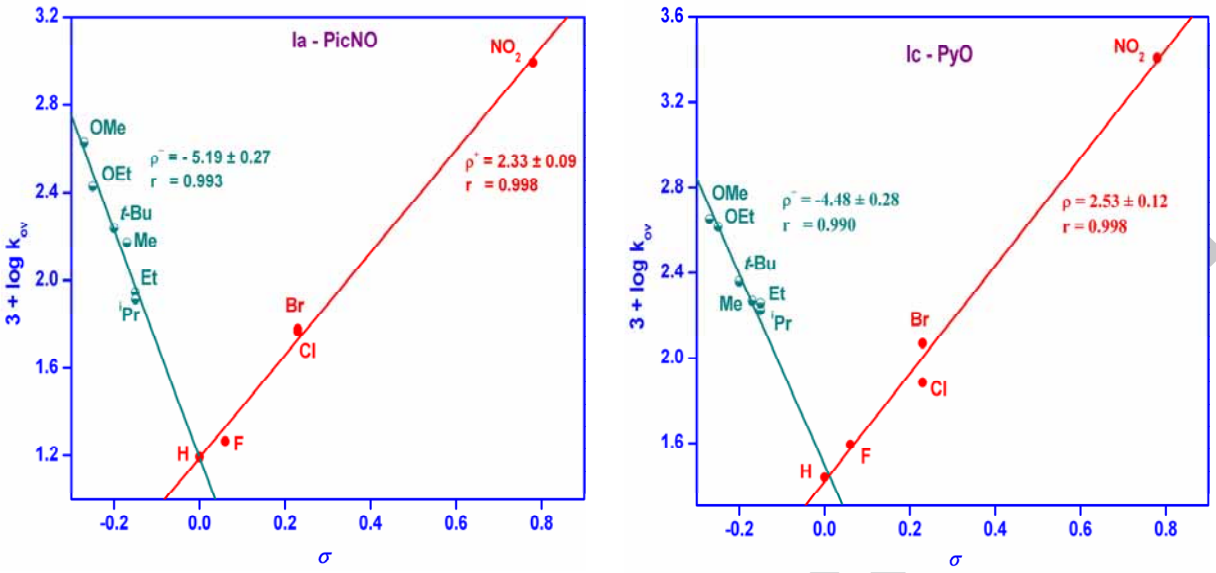


Fig. 4. Hammett plots for the sulfoxidation of X-PMAA by **Ia** and **Ic** in the presence of LO.

3.5. Effect of temperature

The oxidation of PMAA by complexes **Ia-Ic** was carried out at three different temperatures in the presence of LOs. The thermodynamic parameters, enthalpy of activation ($\Delta^{\ddagger}H$) and entropy of activation ($\Delta^{\ddagger}S$) were calculated from the Eyring's plot of log (k_{ov}/T) against 1/T (Fig. S7) and are listed in the Table S5. The enthalpy of activation ($\Delta^{\ddagger}H$) ranges from 33.9±0.24 to 57.2±0.46 kJ mol^{-1} and the entropy of activation ($\Delta^{\ddagger}S$) ranges from -111.5±3.5 to -172.8±8.5 JK^{-1} mol^{-1}. The negative $\Delta^{\ddagger}S$ values indicate that the transition state is highly ordered compared to that in the ground state. In each complex PyO has the minimum enthalpy of activation and maximum entropy of activation and TPPO has the maximum enthalpy of activation and minimum entropy of activation (Table S5). As the binding of PyO is maximum, in the transition state the number of orderly O=Cr(V)−PyO adduct species is more than the other two LO-adduct species. Consequently, a higher negative value of entropy of activation with PyO is observed.

4. Discussion

The observed color change, substantial red shift in the λ_{max} and increase in OD of the complexes upon addition of LOs can be taken as evidence for the formation of 1:1 adduct (**C_1**) between the $[(salen)Cr^{V}=O]^{+}$ ion and LO prior to the rate determining step. The evaluated binding constant values from spectral titration experiments (Table S1) also confirm

the adduct formation in the present study. Samsel et al. [66] have isolated the adduct formed between $[(salen)Cr^{V}=O]^{+}$ ion and PyO and showed from the ORTEP diagram that the LO occupies the vacant apical position in $[(salen)Cr^{V}=O]^{+}$, completing the octahedral coordination of the chromium centre. During the adduct formation it was found that the Cr atom is pulled back from the plane of ligand oxygen and nitrogen atoms by 0.27 Å and lengthened of the Cr–O bond by 0.03 – 0.04 Å.

The observed order of binding constant values among LOs is PyO > PicNO > TPPO while among the complexes it is **Ic > Ia > Ib**. From the magnitude of the binding constants it is inferred that the binding constant values are affected not only by the nature of substituents at 5 and 5′ positions of the salen ligands but also by the nature of the donor ligand oxides. The strong binding of (5,5′-dichlorosalen)chromium(V) ion (**Ic**) with LOs is intercepted by the decrease in electron density on chromium atom due to the presence of two electron attracting chlorine atoms. The low binding of **Ib** is due to the presence of electron donating methyl group at 5,5′-positions which prevents the attack of LOs. Among the LOs, PyO has maximum binding constant values as the O=Cr(V)(salen)-PyO adduct is comparatively more stable [68]. The low binding constant value for TPPO with oxo(salen)chromium(V) complexes is not only due to the steric effect of three bulky phenyl groups but also due to the decrease in electron density on the oxygen atom of TPPO by phenyl groups. The weak binding of TPPO and low stability of its adduct with the oxo(salen)chromium(V) complex was already shown by Kochi et al. [68] in the sulfoxidation by means of the spectral changes and Dalton et al. [86] in the asymmetric alkene epoxidation based on the steric hindrance of bulky TPPO.

It is pertinent to note that in the oxidation of olefins [69], organic sulfides [67] and sulfoxides [72] by Cr(V), the adduct formed between $[(salen)Cr(V)=O]^{+}$ ion and LO has been proposed as the active oxidizing species. The involvement of adduct ($\mathbf{C_1}$) as the active oxidizing species in the present case is unambiguously proved from the above discussions along with the rate acceleration observed with LOs. The absence of any spectral change during the addition of PMAAs to the reaction mixture eliminates its adduct formation with other ingredients. The absence of its binding is also confirmed from the observed high Michaelis-Menten constant values (Table S4).

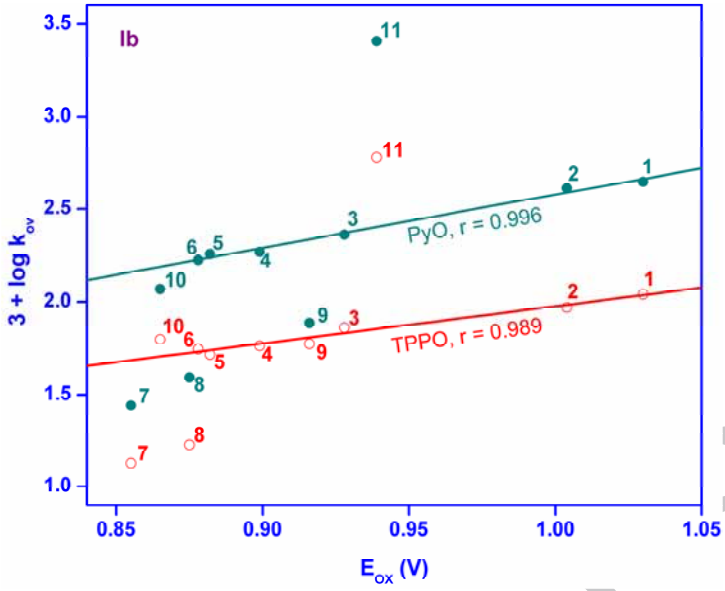
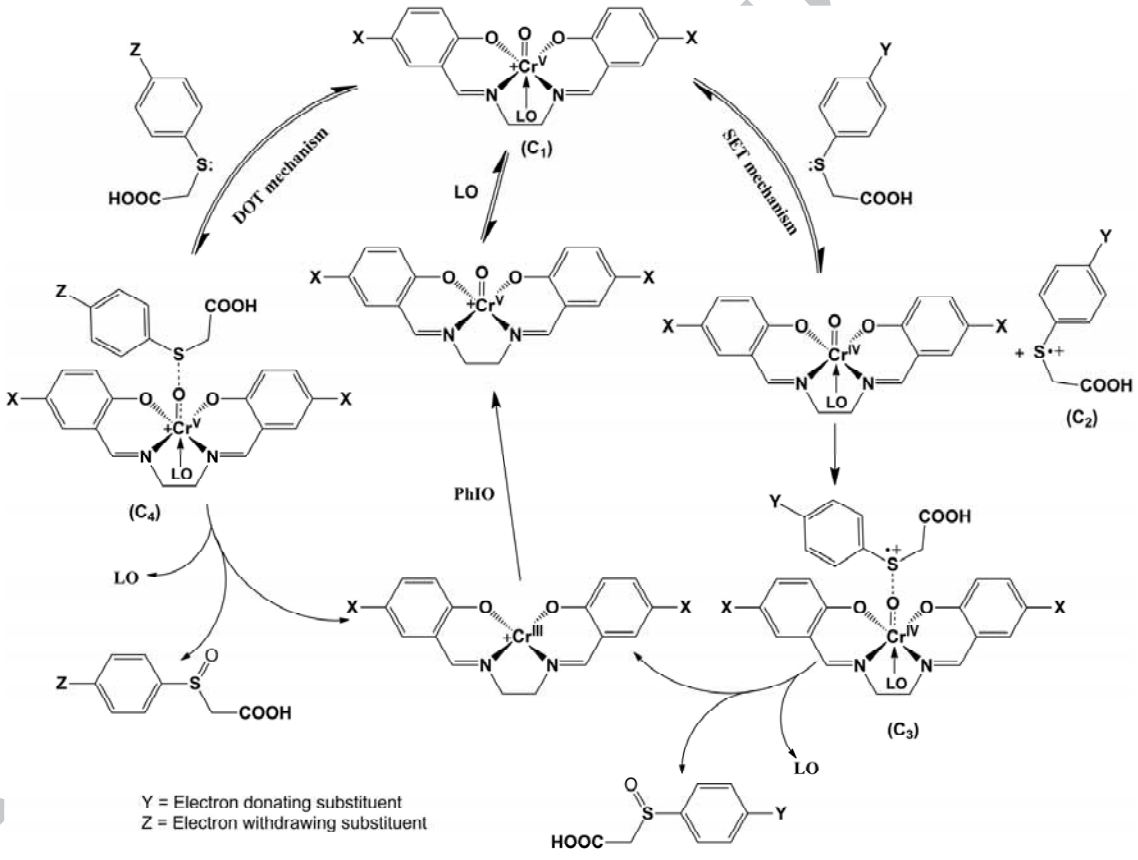


Fig. 5. Plot of log k_{ov} *vs* E_{ox} of PMAAs.

The observed substituent effect paved way to postulate a mechanism shown in Scheme 1. The non-linear Hammett behaviour in the current study can be visualized by two concurrent pathways having complementary electron demand or by two distinct rate controlling steps [87]. The observed linearity in the plot of log k_{ov} against E_{ox} potential of PMAAs (Fig. 5) with excellent correlation (r = 0.989-0.996) for electron-donating substituents and non-linearity for electron withdrawing substituents in PMAA not only rule out the operation of single electron transfer (SET) mechanism for the electron withdrawing substituents but also establish different mechanisms for electron donating and withdrawing substituents. It is worthwhile to mention here that based on the linear correlation observed between log k_2 and $E_{ox/red}$, a SET mechanism has been proposed for the oxidation of organic sulfides by oxo(salen)chromium(V) complexes [88], anilines by oxo(salen)chromium(V) [64] and H_2O_2 catalyzed by iron(III)-salen complexes [89] and phenols with oxovanadium(IV)-salen catalyzed H_2O_2 [90].

Further, operation of same mechanism involving two different rate determining steps (RDS) for electron donating and withdrawing substituents is ignored in the current study, as the Hammett plots do not show downward curvature [87]. For electron donating substituents, a more reasonable mechanism involves a single electron transfer from the PMAA to the reactive oxidizing species ($\mathbf{C_1}$) to form sulfide cation radical ($\mathbf{C_2}$) in a slow reversible rate determining step. The formation of sulfide cation radical has been well established in the

oxidation of organic sulfides by iron(III)-salen chloride [53], cobalt(III)-salen ion [91], Cr(V) [72,92] and oxo(salen)manganese(V) complexes [16]. The negative ρ value obtained for electron donating substituents in the Hammett plots also confirms the development of positive charge on the sulfur centre of PMAA at the transition state. The easy formation of intermediate ($\mathbf{C_2}$) is proved by enhancement of rate by means of increasing electron density around the sulfur centre and thereby increasing the nucleophilicity of PMAA. The electron releasing substituents not only increase the nucleophilicity of PMAA but also stabilize the intermediate $\mathbf{C_2}$ through resonance. The SET mechanism is further ascertained by enhancement of rate in the presence of electron withdrawing substituent at 5,5′-positions of the $[(salen)Cr^{V}{=}O]^{+}$ there by making it more electrophilic.



Scheme 1. Catalytic cycle for the oxo(salan)chromium(V)$^{+}$ ion

Similar rate enhancement has been noticed for the oxidative decarboxylation of PSAA by [oxo(salen)chromium(V)]$^{+}$ ion in the presence of nitrogen bases [56] and ligand oxides

[57] and for the oxidation of thioethers by manganese(V) complex, MnV(O)(TBP_8C_2) [83] where SET mechanism has been proposed. The sulfide cation radical (**C_2**) then undergoes rapid oxygen atom transfer from the oxo(salen)chromium(IV) species to PMAA through the intermediate (**C_3**). The products formed are phenylsulfinylacetic acid and the $[(salen)Cr(III)]^+$ complex. The formation of $[(salen)Cr(III)]^+$ ion as one of the products is evidenced from the change of colour from emerald-green to orange and the formation of new peaks at the λ_{max} values of 228, 285, 305, 415 nm at the end of the reaction.

If similar SET mechanism is operating in PMAAs having electron-withdrawing substituents, the rate should be decelerated as the electron withdrawing substituents diminish the electron density around sulfur centre of the PMAA. But, the observed rate enhancement, positive Hammett ρ value and non linearity in the plot of log k_{ov} vs. E_{ox} for electron-withdrawing substituents clearly demonstrate that these PMAAs do not follow SET path way and the S centre of the PMAA behaves as an electron deficient centre. So, it is conveniently assumed that these substrates follow an electrophilic path in which $[oxo(salen)chromium(V)]^+$ ion acts as a nucleophile. Consequently, the rate determination step for this path is proposed as the formation of ternary complex (**C_4**) by nucleophilic attack of the active species (**C_1**) on PMAA in a reversible manner. The electrophilicity of these PMAAs is due to the presence of phenyl ring with electron withdrawing substituents on one side of the sulfur atom and electron withdrawing carboxyl group on the other side. Electron-withdrawing substituents disseminate the electron density on the sulfur centre and also stabilize **C_4** by resonance interaction. The formation of ternary complex (**C_4**) in the rate-limiting step is further evidenced from enhancement of rate by electron donating substituents at 5,5′-positions of the $[(salen)Cr^V{=}O]^+$ ion. In the ternary complex (**C_4**) direct oxygen atom transfer takes place from oxo(salen)chromium(V) complex to PMAA with the formation of products in a fast step. Such type of mechanism involving nucleophilic attack of the oxidant in the rate determining step during sulfoxidation reaction has been proposed by Curci et al. [93] and Sawaki et al. [94]. Venkataramanan et al. [72] have shown through density functional theory (DFT) that during the formation of ternary complex between donor ligand oxide (DMSO), [oxo(salen)chromium(V)] complex and PhSMe (MPS), the substrate approaches [oxo(salen)chromium(V)] complex from the direction of oxygen atom in a perpendicular direction of the salen plane.

It is pertinent to recall that in most of the sulfide and sulfoxide reactions with oxo(salen)chromium(V) [67,95,96] and oxo(salen)manganese(V) [16,69,76] complexes, S_N2 type electrophilic attack of salen complex on substrate was proposed on the basis of the observed negative ρ reaction constant. Similar electrophilic attack of salen complex on alkenes was also proposed during epoxidation reactions based on the observed negative ρ values [66]. Again in these reactions an excellent linear correlation is observed with Hammett σ constants for both electron releasing and electron withdrawing substituents. The observed anomalous behaviour of 'V' shaped Hammett correlation and nucleophilic attack of [oxo(salen)chromium(V)]$^+$ during sulfoxidation of PMAA in the present study compared to sulfides and sulfoxides may be due to the existence of through-space interaction between the carboxyl group and sulfur atom in PMAA. Similar through-space interaction has been advocated earlier in PMAA to explain greater dependence of pKa values on the nature of substituents [97] and the low metal-ligand covalency in complexes with lanthanides [18].

5. Conclusions

The oxygenation of a series of *p*-substituted phenylmercaptoacetic acids by oxo(salen)chromium(V) complexes in the presence of different ligand oxide such as TPPO, PicNO and PyO has been studied in acetonitrile medium. Spectral and kinetic data reveal that the reactive species in this oxidation is the adduct formed between [(salen)Cr(V)=O]$^+$ ion and LO. Addition of ligand oxide to the solution of the complex causes a significant red shift and increase in absorption in the absorption maxima. The observed catalytic activity among the various LOs used in the study is PyO > PicNO > TPPO. The weakening of Cr=O bond as a result of binding of LO with metal centre of [(salen)Cr(V)=O]$^+$ is given as explanation for enhancement of rate. The novelty of the present work between [oxo(salen)chromium(V)]$^+$ and PMAAs is that the reaction is facilitated not only by electron donors but also by electron acceptors in the para- position of the PMAA as well as 5,5′-positions of salen moiety of the oxidant. A non-linear concave Hammett plots with high reactivity constant values have been observed. Two different mechanistic pathways, a SET mechanism for electron donating substituents and direct oxygen transfer mechanism for electron withdrawing substituents have been proposed for the reaction. Phenylsulfinylacetic acid is the only product formed in the reaction.

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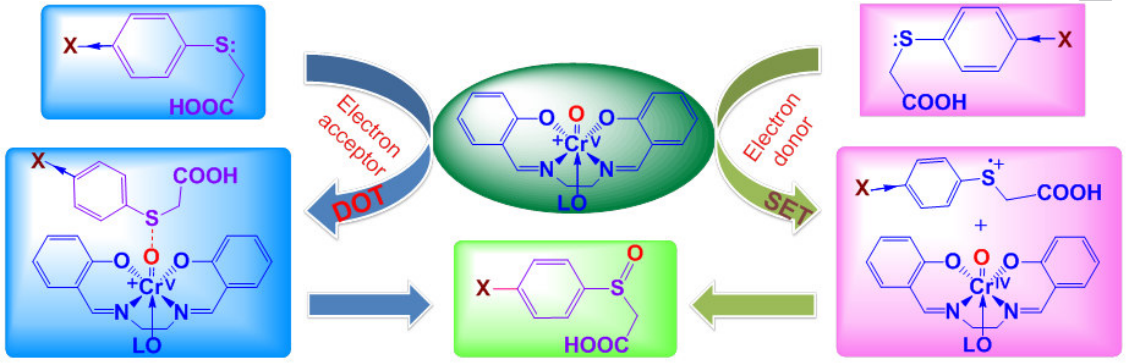
Graphical Abstract



The presence of triphenylphosphine oxide, pyridine N-oxide and picoline N-oxide in the oxidation of phenylmercaptoacetic acid by [oxo(salen)chromium(V)]$^{+}$ causes rate acceleration. Substituent effects and non-linear Hammett correlation paved way to propose a single electron transfer mechanism for electron donors and direct oxygen atom transfer mechanism for electron acceptors.