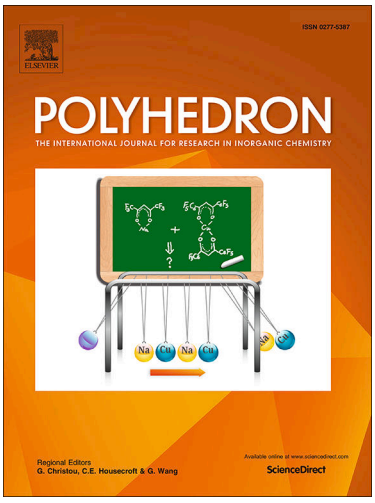

Competitive behavior of nitrogen based axial ligands in the oxovanadium(IV)-salen catalyzed sulfoxidation of phenylmercaptoacetic acid

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Competitive behavior of nitrogen based axial ligands in the oxovanadium(IV)-salen catalyzed sulfoxidation of phenylmercaptoacetic acid

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ABSTRACT

The sulfoxidation of twelve phenylmercaptoacetic acids (PMAA) by H_2O_2 catalyzed by three oxovanadium(IV)-salen complexes, having varied substituents on PMAA and salen with regard to their position, size and inductive effect, has been performed spectrophotometrically in 100% acetonitrile medium. Three nitrogen bases (NB), pyridine (Py), imidazole (ImH) and 1-methylimidazole (MeIm), were used as axial ligands. It has been found that the rate of sulfoxidation is not only tuned by the substituents on PMAA and salen, but it is also varied by the addition of nitrogen bases. The observed order of retardation found among the different nitrogen bases is ImH > MeIm > Py. The rate of reaction decreases with the increase in concentration of the NB axial ligands. The strongly binding ImH shows the least reactivity. Hydroperoxovanadium(V)-salen has been proposed as the sole active oxidizing species. A detailed mechanistic study reveals that the low rate constant values in the presence of the nitrogen base is due to the existence of competition of NB with H_2O_2 and PMAA during the formation of active species and the coordination of PMAA with active species, respectively. Both electron donating and electron withdrawing substituents on PMAA retard the sulfoxidation rate significantly. The Hammett correlation between the rate constants and substituent constants shows a non-linear concave downward curve which is explained by the existence of two different rate determining steps within the same mechanism; coordination of PMAA with the active species for electron withdrawing substituents and transfer of oxygen to PMAA for electron donating substituents. All the experimental observations are explained by proposing a suitable mechanism.

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***Keywords*:** Sulfoxidation, oxovanadium(IV)-salen, phenylmercaptoacetic acid, downward Hammett plot, axial ligand, nitrogen base

***Abbreviations*:** PMAA, phenylmercaptoacetic acid; PSAA, phenylsulfinylacetic acid; EWG, electron withdrawing group; EDG, electron donating group; r, correlation coefficient; ImH, imidazole; MeIm, 1-methylimidazole; Py, pyridine; NB, nitrogen bases; AN, acetonitrile; RDS, rate determining step.

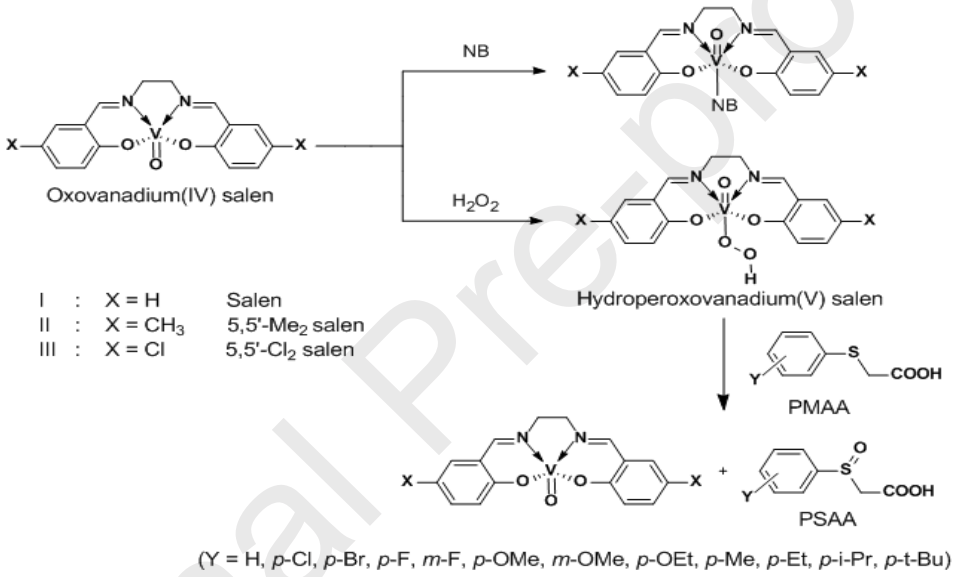
1. Introduction

Oxovanadium catalyzed organic reactions constitute a vital and powerful role, not only in chemistry but also in biochemistry and biomedical sciences [1,2]. Reactions catalyzed by oxovanadium species attract a lot of attention in biological systems because of their participation in enzyme catalyzed processes such as halo peroxidases [3] and nitrogenases [4,5]. These reactions are characterized by very high selectivity, high yield and proceed under mild conditions. As the oxovanadium complexes generally exist in the IV and V oxidation states and possess excellent biological activity, they are being utilized as antituberculosis, antibacterial and antifungal agents [6,7] and to suppress tumor growth [8,9]. Further, oxovanadium complexes with an N_2O_2 donor environment possessing chemo preventive properties have been employed to reduce blood glucose levels by enhancing insulin secretion [10,11], for the treatment of obesity and hypertension [12] and as anticancer [13,14] and anti-HIV [15] drugs.

The structural similarities of the ligating groups of the salen complexes with metalloproteins and enzymes are responsible for their broad range of applications. Considering their applications in areas such as catalysis across a wide range of transformations [16-18], pronounced biological applicability along with biocompatibility varying from bio-related nanotechnology to biosensors [19,20], biomedical sciences ranging from enzyme models to therapeutics and drug development [1,9] and materials science [21-23], many research articles and reviews have been published. Vanadium salen complexes are widely explored as electrochemical sensors for sensing metal ions, biomolecules, cell organelles and pharmaceuticals. The appearance of several recent reviews [16,23-27] addressing exclusively the

potential use of vanadium salen complexes substantiate the importance of vanadium salen complexes.

Different mechanisms, namely electrophilic attack of a sulfur atom on the nucleophilic peroxo oxygen atom [28], S_N^2 type oxygen transfer [29-32], direct oxygen transfer [33-35] and single electron transfer [36-41], have been proposed by our laboratory recently for sulfoxidation reactions on the basis of spectral and kinetic evidence. In continuation, this paper is dedicated to the study of mechanistic aspects covering the effect of added nitrogen bases and electronic modification of the substituents on the sulfoxidation of PMAA by H_2O_2 catalyzed by oxovanadium(IV)-salen complexes. The overall reaction scheme is represented in Scheme 1.



Scheme 1. Overall reaction scheme.

This study has gained more importance due to high synthetic utility of such a type of vanadium Schiff base complex in the synthesis of chiral sulfoxides in good yield with high enantioselectivity. Coletti et al. [42] reported > 90 % sulfoxide yield during the oxidation of sulfides catalyzed by di and tetra substituted salophen and salen oxo vanadium complexes. 60-94 % yield of sulfoxide has been reported in the sulfoxidation of thioanisoles catalyzed by vanadium salen complexes [43] and vanadium Schiff base complexes derived from salicylaldehyde analogues and amino alcohols [44-47]. More than 90 % sulfoxide yield has been reported for the oxidation of sulfides catalyzed by a vanadium Schiff base derived from salicylaldehyde and *tert*-leucinol [48-50]. Besides the advantage of the high yield of sulfoxide in

these vanadium Schiff base catalyzed sulfoxidation, the over oxidation of sulfoxide to sulfone were also not observed.

2. Experimental section

2.1. Materials

Salicylaldehyde, 5-methyl and 5-chloro salicylaldehydes and vanadyl sulfate were purchased from Alfa Aesar and used as supplied. Thiophenols were purchased from Sigma Aldrich. HPLC-grade acetonitrile (Merck) and 30 % H_2O_2 were used as received without further purification. H_2O_2 was standardized by iodometric titration. All other chemicals used were of analytical reagent grade. The nitrogenous bases (NB), imidazole (ImH), 1-methyl imidazole (MeIm) and pyridine (Py), were obtained from Merck and used without further purification, except Py which was distilled over KOH before use.

2.2. Preparation of the phenylmercaptoacetic acids

Twelve phenylmercaptoacetic acids (Scheme 1) with different substituents, viz. H, *p*-Cl, *p*-Br, *p*-F, *m*-F, *p*-OMe, *m*-OMe, *p*-OEt, *p*-Me, *p*-Et, *p*-i-Pr and *p*-t-Bu, were used in this work. They were prepared using a standard procedure by the condensation of the corresponding thiophenols with chloroacetic acid in alkaline medium [35,51]. The purity of the PMAAs was checked using their melting points and LCMS spectra, which were found to agree with the literature values. The LCMS analysis of each PMAA on a HPLC coupled Agilent ion trap mass spectrometer using an inestsil-ODS-3V column of the size 4.6 × 250 mm confirmed the presence of a single species.

2.3. Synthesis of the oxovanadium(IV)-salen complexes

The oxovanadium(IV)-salen complexes (**I-III**) were prepared following the literature procedure [52,53], starting from the appropriately substituted salen ligands and $VOSO_4.5H_2O$. The salen ligands were prepared by condensing the substituted salicylaldehydes with ethylene diamine [54].

2.4. General kinetic studies

The kinetic runs were carried out under atmospheric conditions in a double beam BL 222 Elico UV-vis Biospectrophotometer. An inbuilt program was used to gather the absorbance

values at the desired wavelength periodically. The reactions were carried out in 100 % acetonitrile medium under pseudo-first order conditions with an excess of the PMAA concentration over the oxidant, NB and catalyst concentrations. In all the kinetic runs, the concentration of NB was kept over the concentration of the catalyst and below that of H_2O_2. The progress of the reaction was followed through the changes in the UV-visible spectra, by monitoring the decrease in absorbance of the salen complex at an appropriate wavelength: 363 nm for complex **I**, 376 nm for complex **II** and 373 nm for complex **III**. In a typical run, the reactions were started quickly by injecting freshly prepared standard H_2O_2 into the reaction mixture containing PMAA, the oxovanadium(IV)-salen complex and the nitrogen base in a quartz cuvette at zero time. A representative case of absorption change with time is presented in Fig. 1. As most of the pseudo first order plots have an initial induction period, the pseudo-first order rate constants (k_1) were calculated from the slope of the linear potion of the plots, where the OD decreases steadily after the induction period, using the equation, $k_1 = 2.303 \times$ slope. The precision of the rate constant is given in terms of 95 % confidence limit of the student's t-test.

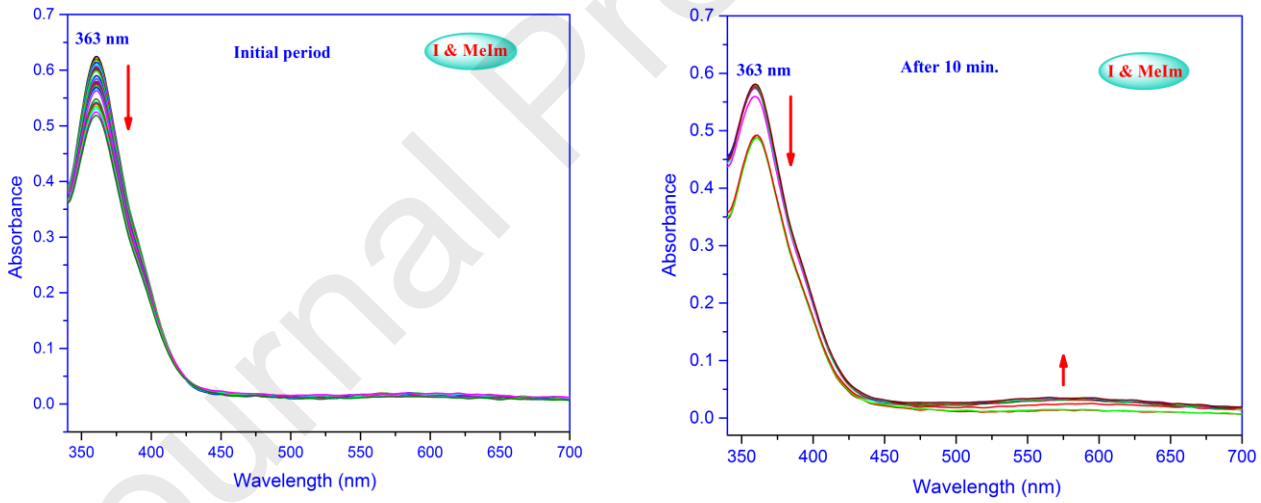


Fig. 1. Absorption spectral changes between 350 and 700 nm with time
[PMAA] = 5.0×10^{-2} M; [H_2O_2] = 5.0×10^{-3} M; [**I**] = 5.0×10^{-5} M; [MeIm] = 2.0×10^{-4} M;
Solvent = 100 % AN; Temp. = 30 °C.

Formation of PSAA was identified as the only product of the reaction by GC-MS and FT-IR spectral methods. It is important to note that under the experimental conditions no over oxidation of the product PSAA was achieved. The experimental procedure for the analysis and characterization of the product (Supporting information) was in accordance with our latest

publication on the sulfoxidation of PMAA in the absence of nitrogen bases [33]. It was also confirmed by GC-MS that sulfoxide is the sole product in all the substituted PMAAs, containing both electron donating and electron withdrawing substituents, thus eliminating deeper oxidation in all cases.

3. Results

3.1. Spectral observation

The electronic spectra of oxovanadium(IV)-salens **I**, **II** and **III** have an absorption maxima at 363, 376 and 373 nm respectively, which arise as a result of ligand to metal charge transfer [42]. Addition of PMAA or H_2O_2 to the salen complex during the reaction does not alter the absorption of these peaks. Similarly, addition of the NB axial ligand to the reaction mixture does not modify either the λ_{max} value or the intensity of the peak. In the majority of cases, the addition of axial donor ligands, a nitrogen base or oxide ligand, to salen/porphyrin complexes causes a significant red shift in the λ_{max} value [34-36,53,55-58] or a change in the intensity of the peak [59]. In these reactions, formation of a 1:1 adduct between the complex and the axial ligand has been identified as the active oxidizing species. From the above observations, it is obvious to conclude that in the present oxidation, adduct formation between the oxovanadium-salen complex and the nitrogen base is unambiguously not the active species.

Another spectral observation noted in the kinetic runs is that the absorbance of the complex remains the same during the initial period of a reaction for certain time. This is also reflected in the pseudo first order plots where an initial well defined induction period exists for a definite period of time before a gradual decrease in the absorbance of the complex begins. The existence of an induction period unambiguously indicates that the active catalytic species is slowly generated in the reaction mixture after mixing all the reagents. The length of the induction period is found to decrease with an increase in temperature and concentrations of PMAA, salen complex and H_2O_2. On the addition of the axial ligands ImH, MeIm and Py, the induction period begins to increase with concentration (Fig. 2).

One more salient feature observed during the course of the reaction is the delayed appearance of a new broad peak with an increase in intensity at around 570 nm (Fig. 1), followed by a decrease in its intensity. Actually this peak corresponds to the d-d transition of a vanadium(IV) complex, which is invisible in the absence of H_2O_2 due to its low intensity. When

H_2O_2 is added, an increase in intensity appears in a sluggish manner and its rate of increase depends on time and the increase in concentrations of both H_2O_2 and salen complex. This strongly advocates the conversion of the oxovanadium(IV)-salen complex to a new species.

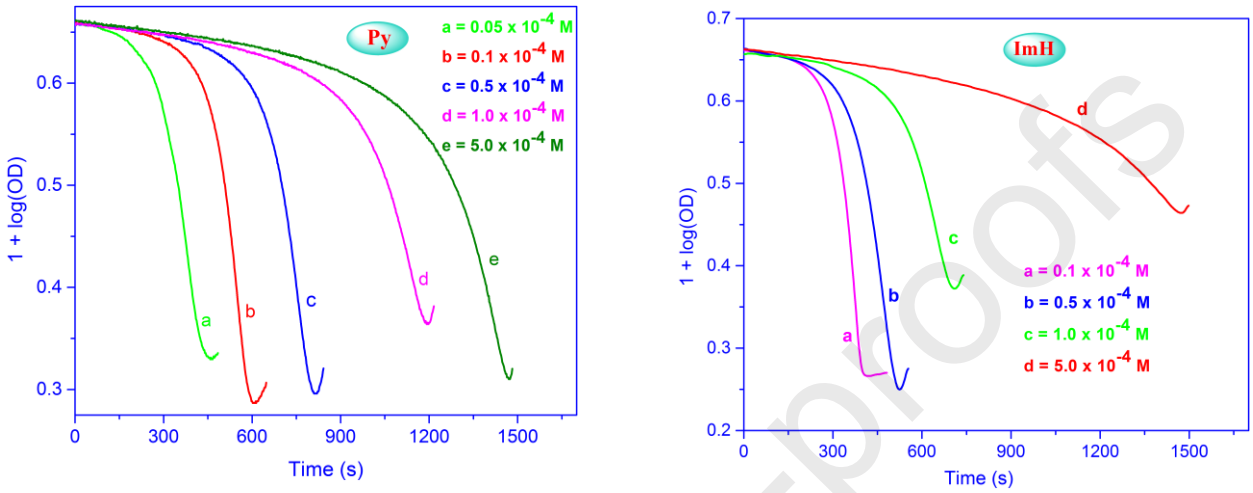


Fig. 2. Pseudo first order plots for NB variation with complex **II**
[PMAA] = 5.0×10^{-2} M; [H_2O_2] = 5.0×10^{-3} M; [**II**] = 5.0×10^{-5} M; Solvent = 100 % AN; λ_{max} = 376 nm; Temp. = 30 °C.

3.2. Kinetic results

The reaction was carried out at different PMAA concentrations in the range 2×10^{-2} M to 15×10^{-2} M, keeping all other conditions unchanged. It is noted that the pseudo first order rate constant increases with the increase in concentration of PMAA. The non-integral slope value observed in the plot of log k_1 *vs* log [PMAA] supports the fractional order dependence of PMAA. This is also verified by the inconstancy of the second order rate constants (k_2), calculated using $k_2 = k_1/[PMAA]$. The plot of $1/k_1$ against 1/[PMAA] was found to be linear (Fig. 3), having an intercept value at the y-axis which confirms not only the fractional order dependence of PMAA but also indicates that PMAA coordinates with any one of the reagents in a reversible step during the reaction. The values of the pseudo first order and overall rate constants as a function of PMAA are collected in Table 1. The overall rate constants (k_{ov}) were calculated using the expression $k_{ov} = k_1/[PMAA]^n$, where n is the order of the reaction with respect to PMAA.

The relative high values of the Michaelis-Menten constant (K_M) derived from $1/k_1$ against 1/[PMAA] plots (Table 2) indicate that the coordination of PMAA with the other reagent is weak

in nature. The Michaelis-Menten constants obtained with different complexes are found to be independent of the nature of the nitrogen base. This signals a clear indication that the coordination of PMAA with the oxovanadium complex is not influenced by the nature of the NB.

Table 1
Effect of [PMAA] on the rate constants in the presence of nitrogen bases.

10^2 [PMAA] (M)	Py		MeIm		ImH	
	$10^4 k_1$ (s^{-1})	$10^3 k_{ov}$ [$(M^{-1})^n s^{-1}$)]	$10^4 k_1$ (s^{-1})	$10^3 k_{ov}$ [$(M^{-1})^n s^{-1}$)]	$10^4 k_1$ (s^{-1})	$10^3 k_{ov}$ [$(M^{-1})^n s^{-1}$)]
			I			
2.0	0.97 ± 0.01	1.83 ± 0.02	0.66 ± 0.01	1.24 ± 0.02	0.43 ± 0.01	0.82 ± 0.02
5.0	1.89 ± 0.02	1.79 ± 0.02	1.17 ± 0.02	1.12 ± 0.02	0.81 ± 0.03	0.78 ± 0.03
7.5	2.57 ± 0.03	1.80 ± 0.02	1.67 ± 0.02	1.17 ± 0.01	0.99 ± 0.02	0.70 ± 0.01
10	3.14 ± 0.04	1.77 ± 0.02	2.16 ± 0.05	1.22 ± 0.03	1.38 ± 0.02	0.78 ± 0.01
15	4.45 ± 0.06	1.85 ± 0.03	3.02 ± 0.03	1.26 ± 0.01	2.02 ± 0.03	0.85 ± 0.01
			II			
2.0	2.26 ± 0.01	3.84 ± 0.02	1.78 ± 0.02	3.07 ± 0.03	1.32 ± 0.01	2.26 ± 0.02
5.0	4.61 ± 0.02	4.03 ± 0.02	3.42 ± 0.02	3.03 ± 0.02	2.57 ± 0.02	2.26 ± 0.02
7.5	6.49 ± 0.02	4.23 ± 0.01	4.58 ± 0.03	3.02 ± 0.02	3.62 ± 0.03	2.37 ± 0.02
10	7.58 ± 0.03	4.01 ± 0.02	5.85 ± 0.03	3.13 ± 0.02	4.23 ± 0.03	2.25 ± 0.02
15	9.44 ± 0.05	3.73 ± 0.02	7.54 ± 0.04	3.00 ± 0.02	5.68 ± 0.07	2.25 ± 0.03
			III			
2.0	0.43 ± 0.01	0.82 ± 0.02	0.24 ± 0.01	5.57 ± 0.02	0.17 ± 0.01	0.41 ± 0.02
5.0	0.81 ± 0.01	0.78 ± 0.01	0.52 ±0.02	5.93 ± 0.02	0.36 ± 0.03	0.41 ± 0.04
7.5	0.94 ± 0.02	0.70 ± 0.02	0.72 ± 0.03	5.96 ±0.03	0.51 ± 0.02	0.42 ± 0.02
10	1.38 ± 0.03	0.79 ± 0.02	0.87 ± 0.02	5.68 ± 0.01	0.63 ± 0.03	0.41 ± 0.02
15	2.02 ± 0.06	0.85 ± 0.03	1.18 ± 0.03	5.54 ± 0.01	0.84 ± 0.05	0.40 ± 0.02

$[H_2O_2]$ = 2.0 × 10^{-3} M; [**I**] = [**II**] = [**III**] = 2.0 × 10^{-5} M;

[Py] = [MeIm] = [ImH] = 2.0 × 10^{-4} M; Solvent = 100 % AN; Temp. = 30 °C.

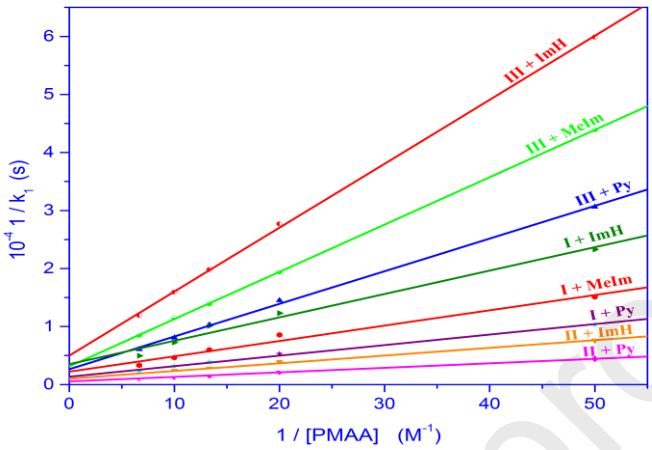


Fig. 3. Plot of $1/k_1$ *vs* 1/[PMAA] for the reactions with the NBs
(General conditions as in Table 1)

Table 2
Michaelis-Menten constants for the reactions of PMAA with different complexes and NBs.

Complex	K_M value		
	Py	MeIm	ImH
I	0.133	0.117	0.115
II	0.141	0.121	0.121
III	0.212	0.260	0.221

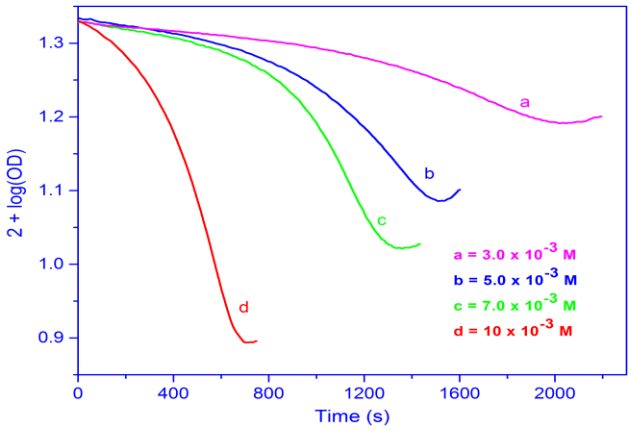


Fig. 4. Pseudo first order plot for H_2O_2 variation with Py and complex **I**. [PMAA] = 10 × 10^{-2} M; [**I**] = 2.0 × 10^{-5} M; [Py] = 2.0 × 10^{-4} M; Solvent = 100% AN; λ_{max} = 363 nm; Temp. = 30 °C.

The dependence of the reaction rate on H_2O_2 in the presence of ImH, MeIm and Py was studied by measuring the rate constants at different [H_2O_2]. As the concentration of H_2O_2 increases, the induction period gradually decreases (Fig. 4) and the rate of the reaction increases (Table S1). Even though the pseudo first order rate constant increases with the increase in [H_2O_2], the observed excellent pseudo first order plots ($r > 0.995$) clearly show that the order with respect to H_2O_2 is one. The observed increase in reaction rate and decrease in induction period with [H_2O_2] is visualized by the easy formation of active species with increasing concentrations of H_2O_2.

3.3. Relative reactivity of the catalysts

Table 3
Effect of [catalyst] on the reaction rate.

10^5 [complex] (M)	10^3 k_1 (s^{-1})		
	Py	MeIm	ImH
	I		
1.0	1.52 ± 0.02	1.06 ± 0.01	0.89 ± 0.01
2.0	2.87 ± 0.02	2.11 ± 0.02	1.74 ± 0.02
5.0	4.26 ± 0.04	3.48 ± 0.03	2.60 ± 0.03
7.0	6.15 ± 0.05	5.72 ± 0.04	4.32 ± 0.03
10	8.76 ± 0.07	7.04 ± 0.06	6.29 ± 0.05

	II		
1.0	1.63 ± 0.02	1.22 ± 0.03	1.03 ± 0.01
2.0	3.27 ± 0.02	2.69 ± 0.02	2.48 ± 0.01
5.0	7.19 ± 0.05	6.48 ± 0.03	4.22 ± 0.02
7.0	11.8 ± 0.08	9.36 ± 0.06	7.64 ± 0.04
10	15.2 ± 0.11	13.8 ± 0.09	11.0 ± 0.08
	III		
1.0	0.17 ± 0.01	0.12 ± 0.01	0.07 ± 0.01
2.0	0.43 ± 0.01	0.38 ± 0.02	0.24 ± 0.01
5.0	0.56 ± 0.02	0.45 ± 0.01	0.38 ± 0.01
7.0	0.71 ± 0.01	0.62 ± 0.02	0.51 ± 0.02
10	0.86 ± 0.03	0.74 ± 0.02	0.60 ± 0.01

[PMAA] = 10×10^{-2} M; [H_2O_2] = 1.0×10^{-2} M; [Py] = [MeIm] = [ImH] = 2.0×10^{-4} M; Solvent = 100 % AN; Temp. = 30 °C.

Realizing the importance of the electronic effect of the substituents, the reactivity of three salen complexes having different substituents was compared. The rate constants obtained with three catalysts at different concentrations in the presence of ImH, MeIm and Py are presented in Table 3. It is observed that the pseudo-first order rate constant increases with the increase in concentration of the oxovanadium(IV)-salen complex in all cases, irrespective of the nature of the nitrogen base. The data show that the introduction of an electron donating group in the salen moiety (**II**) enhances the catalytic activity, while an electron withdrawing group (**III**) retards the reaction rate compared to the unsubstituted oxovanadium(IV)-salen complex (**I**).

3.4. Influence of axial ligands

In the literature it has been shown that additive axial ligands not only affect the catalytic activity of the catalyst in oxygenation reactions but also influence the product selectivity [54,60,61], stereoselectivity [62] and enantioselectivity [55,63]. To better understand the influence of axial ligands on the catalytic activity of oxovanadium(IV)-salen, the reaction was carried out with three nitrogen bases, Py, ImH and MeIm, having different π-donating abilities. The calculated pseudo first order rate constants in the presence of the nitrogen bases with increasing amounts up to 5×10^{-4} M are presented in Table 4. The determination of the rate constant is restricted to the nitrogen base concentrations mentioned in the Table 4 because beyond 5×10^{-4} M no appreciable change in rate constant was observed. An examination of the

results reveal that the reaction rate is strongly retarded by all the three nitrogen bases in their lower concentration range, whilst almost saturation is attained at higher concentrations [Fig. 5].

Table 4
Influence of nitrogen bases on the reaction rate

10^4 [NB] (M)	Py		MeIm		ImH	
	$10^4\,k_1$ (s^{-1})	$10^3\,k_{ov}$ [$(M^{-1})^n\,s^{-1}$]	$10^4\,k_1$ (s^{-1})	$10^3\,k_{ov}$ [$(M^{-1})^n\,s^{-1}$]	$10^4\,k_1$ (s^{-1})	$10^3\,k_{ov}$ [$(M^{-1})^n\,s^{-1}$]
			I			
0	41.0 ± 0.05	39.0 ± 0.05	41.0 ± 0.05	39.0 ± 0.05	41.0 ± 0.05	39.0 ± 0.05
0.05	36.9 ± 0.06	35.1 ± 0.06	29.0 ± 0.04	27.6 ± 0.04	23.1 ± 0.04	22.2 ± 0.03
0.1	26.2 ± 0.03	25.0 ± 0.03	25.3 ± 0.05	24.1 ± 0.05	18.9 ± 0.03	18.2 ± 0.03
0.3	20.3 ± 0.04	19.3 ± 0.04	13.6 ± 0.03	13.0 ± 0.03	10.4 ± 0.02	10.0 ± 0.02
0.5	18.6 ± 0.03	17.7 ± 0.03	7.94 ± 0.04	7.56 ± 0.04	5.32 ± 0.01	5.12 ± 0.01
1.0	14.2 ± 0.04	13.5 ± 0.04	6.17 ± 0.01	5.88 ± 0.01	3.78 ± 0.03	3.63 ± 0.03
2.0	9.79 ± 0.03	9.32 ± 0.03	4.47 ± 0.02	4.26 ± 0.02	2.97 ± 0.02	2.86 ± 0.02
3.0	7.14 ± 0.02	6.80 ± 0.02	3.89 ± 0.01	3.70 ± 0.01	2.56 ± 0.01	2.46 ± 0.01
5.0	6.32 ± 0.01	6.02 ± 0.01	2.76 ± 0.02	2.63 ± 0.02	2.01 ± 0.01	1.93 ± 0.01
			II			
0	93.7 ± 0.06	82.2 ± 0.05	93.7 ± 0.06	82.2 ± 0.05	93.7 ± 0.06	82.2 ± 0.05
0.05	81.7 ± 0.08	71.7 ± 0.07	72.3 ± 0.06	64.0 ± 0.05	63.3 ± 0.05	55.5 ± 0.04
0.1	72.3 ± 0.06	63.4 ± 0.05	59.6 ± 0.05	52.7 ± 0.04	40.8 ± 0.04	35.8 ± 0.04
0.3	53.5 ± 0.07	46.9 ± 0.06	45.2 ± 0.04	40.0 ± 0.04	34.3 ± 0.05	30.1 ± 0.04
0.5	41.9 ± 0.03	36.8 ± 0.03	37.7 ± 0.05	33.4 ± 0.04	26.8 ± 0.04	23.5 ± 0.04
1.0	33.6 ± 0.05	29.5 ± 0.04	22.9 ± 0.04	20.3 ± 0.04	18.6 ± 0.03	16.3 ± 0.03
2.0	25.1 ± 0.04	22.0 ± 0.04	14.3 ± 0.03	12.7 ± 0.03	9.92 ± 0.03	8.70 ± 0.03
3.0	17.8 ± 0.02	15.6 ± 0.02	11.8 ± 0.04	10.4 ± 0.04	8.40 ± 0.02	7.37 ± 0.02
5.0	14.0 ± 0.01	12.3 ± 0.01	10.2 ± 0.02	9.03 ± 0.02	7.20 ± 0.02	6.32 ± 0.02
			III			
0	9.68 ± 0.03	11.1 ± 0.03	9.68 ± 0.03	11.1 ± 0.03	9.68 ± 0.03	1.11 ± 0.03
0.05	7.82 ± 0.03	8.99 ± 0.03	7.11 ± 0.04	8.17 ± 0.05	6.36 ± 0.02	7.31 ± 0.02

0.1	6.83 ± 0.02	7.85 ± 0.02	6.23 ± 0.03	7.16 ± 0.03	5.54 ± 0.03	6.37 ± 0.03
0.3	5.49 ± 0.03	6.31 ± 0.03	4.99 ± 0.01	5.74 ± 0.01	4.01 ± 0.02	4.61 ± 0.02
0.5	4.68 ± 0.02	5.38 ± 0.02	4.09 ± 0.02	4.70 ± 0.02	3.24 ± 0.01	3.72 ± 0.01
1.0	3.69 ± 0.01	4.24 ± 0.01	3.28 ± 0.02	3.77 ± 0.02	2.34 ± 0.03	2.69 ± 0.03
2.0	2.87 ± 0.02	3.30 ± 0.02	2.10 ± 0.01	2.41 ± 0.01	1.85 ± 0.01	2.13 ± 0.01
3.0	2.27 ± 0.01	2.61 ± 0.01	1.91 ± 0.01	2.20 ± 0.01	1.31 ± 0.01	1.51 ± 0.01
5.0	1.98 ± 0.01	2.28 ± 0.01	1.59 ± 0.01	1.83 ± 0.01	1.10 ± 0.01	1.26 ± 0.01

[PMAA] = 5.0×10^{-2} M; [H_2O_2] = 5.0×10^{-3} M; [**I**] = [**II**] = [**III**] = 5.0×10^{-5} M;
Solvent = 100 % AN; Temp. = 30 °C.

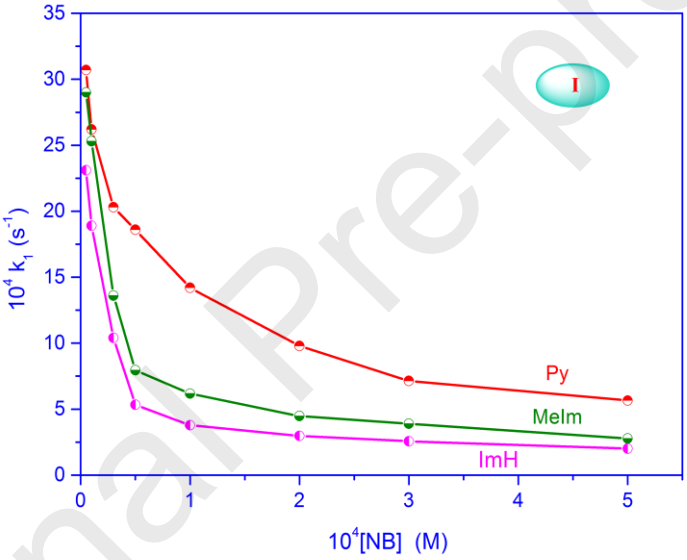


Fig. 5. Variation of the pseudo first-order rate constant with [NB]
(General conditions as in Table 4)

The observed decrease in rate constant with the increase in concentration of the axial ligand is probably due to the partial formation of inactive species, [O=V(salen)NB] [59] or [O=V(salen)$(NB)_2$] [53,60,64]. The formation of these species decreases the concentration of high valent active species in the reaction medium, which is a precursor required to transfer an oxygen atom to PMAA. The decrease in the reaction rate by the addition of a nitrogen base in the present case is in agreement with the results already reported for the oxidation of thiodiglycollic acid by an iron(III)-salen complex [59], manganese(III)-salen catalyzed H_2O_2 oxidation of sulfides [65,66], oxygenation of hydrocarbons catalyzed by metalloporphyrins [67],

molybdenum(IV)-Schiff base catalyzed epoxidation of olefins by t-butyl hydroperoxide [68], epoxidation of olefins by iodosylarenes [69], sodium periodate [70] catalyzed by manganese(III) porphyrin and the epoxidation of olefins by Mn(III) oxazoline complexes [64] in the presence of nitrogenous bases. Binding of the nitrogen base with the metal center of the catalyst, which restricts the attack of reactants on the free coordination site of the catalyst, was identified as the major cause for the observed rate inhibition in the above cases. The coordination of NB with the reactive site of the oxo(salen)iron complex in the oxidation of phenyl methyl sulfides [71] and iron-porphyrin during epoxidation of olefin [72] completely prevent the reactivity.

Among the three nitrogen bases used, ImH exhibits the highest activity towards rate retardation. The rate constants in Table 4 clearly indicate that the observed effect of rate retardation shown among the different NBs is in the order: ImH > MeIm > Py. Hence, the order of reactivity among the NBs is Py > MeIm > ImH. This order seems to be directly related to the π-donating ability of these nitrogen donors. The ligand with the stronger π-donating capability seems to play a greater retarding effect on the rate constant. In the majority of NB mediated reactions, where the NB acts as a cocatalyst, the reverse order of reactivity has been observed, i.e. ImH accelerates the reaction to a greater extent than MeIm and Py. The observed order of reactivity, ImH > MeIm > Py, in the epoxidation of olefins [61,64,53,73,74], oxidation of alcohol and oximes [75], and decarboxylation of carboxylic acids [76] has been explained by the increase in electron density on the metal center of the catalyst to a greater extent by a proximal and distal effect of ImH. In all these cases, NBs accelerate the reaction rate by coordination with the catalyst. However, the reverse order of reactivity observed in the sulfoxidation reaction [34,59], Py > MeIm > ImH, was explained by strong binding of ImH with the active site of the reactive species that restricts the binding of substrate, which is an essential step for a reaction to take place.

3.5. Substituent effects

To gain more information on the electronic sensitivity of the substituents towards the reaction center, the reactions between oxovanadium(IV)-salen complex (**I**) and twelve PMAAs having different electron releasing and electron withdrawing substituents were investigated in the presence of Py, ImH and MeIm and the consolidated kinetic data are listed in Table 5. It is noted that both electron donating and electron withdrawing substituents on PMAA decrease the rate of

the reaction considerably and the unsubstituted PMAA is the most reactive species in this series. The Hammett correlation of the electronic effect of the substituents unveiled a deviation from linearity. The non-linear concave downward type Hammett plot observed [Fig. 6] is a composite of two straight lines, one with a positive slope for EDGs falling on the one side of the curve and the other with a negative slope for EWGs on the other side. Such a type of non-linear downward Hammett plot, observed earlier [33], has been explained by a change in the rate determining step/transition state upon changing the substituents.

The observed high ρ values with NBs (Table 5) prove that the reaction center is more susceptible to electronic variation. It is pertinent to note that with NB the ρ value is found to be almost constant, irrespective of temperature and the nature of the nitrogen base. In the absence of NBs, the ρ value for the same reaction was found to increase with temperature [33].

Table 5
Overall rate constants and thermodynamic parameters for the reactions of PMAAs with complex **I** in the presence of nitrogen bases.

PMAA	$10^3\, k_{ov}$ $[(M^{-1})^n\, s^{-1})]$			$\Delta^{\ddagger}H$ (kJ mol^{-1})	$-\Delta^{\ddagger}S$ (J K^{-1} mol^{-1})
	20 °C	30 °C	40 °C		
			Py		
m-F	0.543 ± 0.01	0.740 ± 0.01	0.964 ± 0.01	19.3 ± 1.1	88.3 ± 3.7
p-Br	0.862 ± 0.01	1.26 ± 0.01	1.66 ± 0.01	22.0 ± 0.7	75.1 ± 2.6
p-Cl	1.12 ± 0.01	1.57 ± 0.02	2.24 ± 0.02	23.7 ± 0.8	67.4 ± 2.9
m-OMe	2.74 ± 0.02	3.94 ± 0.02	5.47 ± 0.02	23.7 ± 0.4	59.9 ± 1.4
p-F	4.64 ± 0.02	7.06 ± 0.02	9.61 ± 0.02	25.4 ± 0.2	49.8 ± 0.8
H	6.78 ± 0.02	9.32 ± 0.03	13.4 ± 0.05	23.7 ± 0.3	52.5 ± 0.9
p-^{i}Pr	1.95 ± 0.02	2.81 ± 0.03	3.93 ± 0.02	24.6 ± 0.7	59.5 ± 2.6
p-Et	1.78 ± 0.02	2.30 ± 0.03	3.12 ± 0.03	19.3 ± 0.8	78.7 ± 2.9
p-Me	1.59 ± 0.01	2.03 ± 0.02	3.01 ± 0.03	21.9 ± 0.7	70.8 ± 2.6
p-t-Bu	1.35 ± 0.01	1.96 ± 0.02	2.67 ± 0.03	23.7 ± 0.7	65.7 ± 2.6
p-OEt	0.720 ± 0.01	1.06 ± 0.01	1.55 ± 0.01	27.2 ± 0.7	58.9 ± 2.6
p-OMe	0.578 ± 0.005	0.863 ± 0.005	1.26 ± 0.005	27.2 ± 0.5	60.9 ± 1.8
ρ_{EWS}	-3.43 ± 0.23	-3.4 ± 0.20	-3.57 ± 0.23		

r	0.991	0.993	0.992		
ρ_{EDS}	3.96 ± 0.20	3.80 ± 0.22	3.80 ± 0.21		
r	0.994	0.992	0.992		
		MeIm			
m-F	0.251 ± 0.005	0.349 ±0.005	0.465 ±0.01	21.1 ± 1.4	88.7 ± 4.9
p-Br	0.438 ± 0.01	0.623 ±0.01	0.859 ±0.01	22.8 ± 1.3	77.9 ± 4.6
p-Cl	0.510 ± 0.01	0.729 ±0.01	1.03 ± 0.02	24.6 ± 1.3	70.8 ± 4.6
m-OMe	1.28 ± 0.01	1.76 ± 0.02	2.48 ± 0.03	22.8 ± 0.8	69.3 ± 2.8
p-F	2.00 ± 0.02	2.99 ± 0.02	4.44 ± 0.03	28.1 ± 0.6	47.7 ± 2.1
H	3.02 ± 0.02	4.26 ± 0.02	6.28 ± 0.02	25.4 ± 0.4	53.2 ± 1.4
p-^{i}Pr	0.917 ± 0.01	1.30 ± 0.02	1.88 ± 0.03	24.5 ± 1.1	66.1 ± 3.9
p-Et	0.822 ± 0.01	1.08 ± 0.02	1.48 ± 0.03	19.3 ± 1.1	85.0 ± 3.9
p-Me	0.717 ± 0.01	0.969 ± 0.01	1.39 ± 0.02	22.8 ± 1.0	74.3 ± 3.5
p-t-Bu	0.597 ± 0.01	0.792 ± 0.01	1.15 ± 0.01	22.8 ± 1.0	75.8 ± 3.5
p-OEt	0.330 ± 0.005	0.496 ± 0.01	0.758 ± 0.01	29.0 ± 1.2	59.5 ± 4.2
p-OMe	0.289 ± 0.005	0.399 ± 0.005	0.603 ± 0.005	25.4 ± 1.0	72.9 ± 3.5
ρ_{EWS}	-3.32 ± 0.17	-3.38 ± 0.18	-3.49 ± 0.18		
r	0.995	0.995	0.995		
ρ_{EDS}	3.84 ± 0.18	3.82 ± 0.14	3.78 ± 0.16		
r	0.994	0.997	0.996		
		ImH			
m-F	0.158 ± 0.003	0.222 ± 0.005	0.299 ± 0.005	22.0 ± 1.4	89.6 ± 4.9
p-Br	0.296 ± 0.005	0.384 ± 0.01	0.518 ± 0.01	19.3 ± 1.6	93.6 ± 5.6
p-Cl	0.382 ± 0.01	0.502 ± 0.01	0.685 ± 0.01	20.2 ± 1.5	88.5 ± 5.2
m-OMe	0.886 ± 0.01	1.24 ± 0.02	1.63 ± 0.02	21.1 ± 1.0	78.1 ± 3.5
p-F	1.37 ± 0.02	1.92 ± 0.02	2.39 ± 0.03	18.5 ± 0.9	83.3 ± 3.1
H	1.95 ± 0.02	2.86 ± 0.02	4.15 ± 0.03	26.3 ± 0.6	53.8 ± 2.1
p-^{i}Pr	0.622 ± 0.01	0.810 ± 0.02	1.13 ± 0.02	20.2 ± 1.4	84.3 ± 4.9
p-Et	0.535 ± 0.01	0.696 ± 0.01	0.937 ± 0.02	19.3 ± 1.3	78.7 ± 4.5
p-Me	0.483 ± 0.01	0.653 ± 0.01	0.886 ± 0.01	20.2 ± 1.2	86.4 ± 4.2

p-t-Bu	0.403 ± 0.005	0.575 ± 0.01	0.826 ± 0.01	24.6 ± 1.1	72.8 ± 3.8
p-OEt	0.224 ± 0.005	0.335 ± 0.005	0.482 ± 0.01	27.2 ± 1.4	68.7 ± 4.9
p-OMe	0.180 ± 0.002	0.261 ± 0.002	0.398 ± 0.005	27.2 ± 0.8	70.7 ± 2.8
ρ_{EWS}	-3.33 ± 0.17	-3.41 ± 0.21	-3.42 ± 0.21		
r	0.994	0.992	0.992		
ρ_{EDS}	3.83 ± 0.20	3.82 ± 0.18	3.76 ± 0.22		
r	0.993	0.994	0.992		

[PMAA] = 5.0×10^{-2} M; [H_2O_2] = 5.0×10^{-3} M; [**I**] = 5.0×10^{-5} M;
[Py] = [MeIm] = [ImH] = 2.0×10^{-4} M; Solvent = 100 % AN.

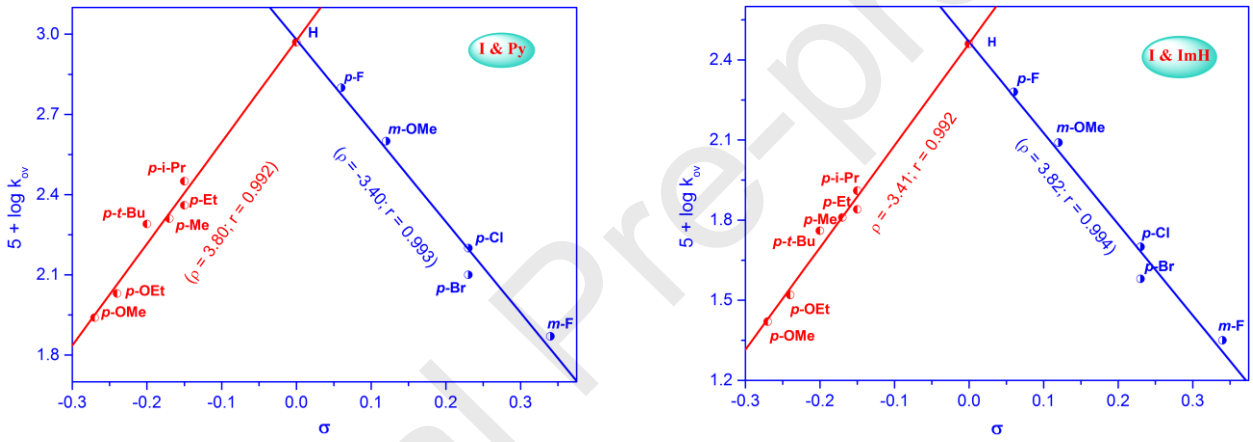


Fig. 6. Hammett plots for the reactions at 30 °C
(General conditions as in Table 5)

3.6. Thermodynamic parameters

The sulfoxidation reaction of PMAA with the three complexes in the presence of nitrogen bases was studied at three different temperatures and the thermodynamic parameters, viz. enthalpy ($\Delta^{\ddagger}H$) and entropy ($\Delta^{\ddagger}S$) of activation, were evaluated from the slope and intercept of Eyring's plot of log (k_2/T) vs. 1/T (Fig. 7) and the values are presented in Tables 5 and 6.

Table 6
Overall rate constants and thermodynamic parameters with complexes **II** and **III.**

NB	10^3 k_{ov} $[(M^{-1})^n s^{-1})]$	$\Delta^{\ddagger}H$	$-\Delta^{\ddagger}S$

	20 °C	30 °C	40 °C	(kJ mol^{-1})	(J K^{-1} mol^{-1})
			II		
Py	13.9 ± 0.03	22.0 ± 0.04	34.3 ± 0.05	32.5 ± 0.1	38.7 ± 0.4
MeIm	8.27 ± 0.02	12.7 ± 0.03	19.8 ± 0.04	30.7 ± 0.2	46.1 ± 0.7
ImH	5.68 ± 0.02	8.70 ± 0.03	13.5 ± 0.03	30.7 ± 0.2	49.2 ± 0.7
			III		
Py	2.52 ± 0.01	3.30 ± 0.02	4.29 ± 0.02	17.6 ± 0.4	100 ± 1.4
MeIm	1.92 ± 0.01	2.41 ± 0.01	3.20 ± 0.02	16.7 ± 0.5	105 ± 1.8
ImH	1.63 ± 0.01	2.13 ± 0.01	2.83 ± 0.01	18.4 ± 0.5	101 ± 1.8

[PMAA] = 5.0 × 10^{-2} M; [H_2O_2] = 5.0 × 10^{-3} M; [**II**] = [**III**] = 5.0 × 10^{-5} M; [Py] = [MeIm] = [ImH] = 2.0 × 10^{-4} M; Solvent = 100% AN.

An inspection of the data reported in Tables 5 and 6 seems to indicate that both the enthalpy and entropy of activation are found to be almost constant, irrespective of the nature of PMAA and NB, but they do depend on the substituent present on the vanadium complex.

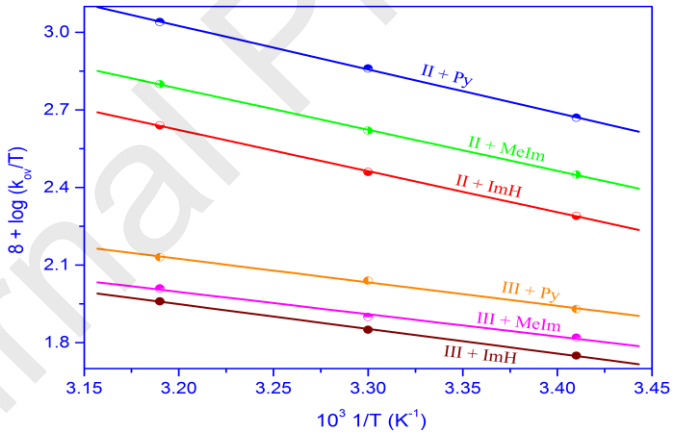


Fig. 7. Eyring's plots for the reactions

When the $\Delta^{\ddagger}H$ values of different PMAAs are plotted against the $\Delta^{\ddagger}S$ values, no linear correlation (r = 0.81) is obtained. On the other hand, an excellent linear Exner's plot (r = 0.997) is obtained when logarithm of the overall rate constants at two extreme temperatures are plotted (Fig. 8). The excellent correlation obtained in the Exner's plot. along with almost constant $\Delta^{\ddagger}H$ and $\Delta^{\ddagger}S$ obtained with all substituted PMAAs (Table 5), lead to the conclusion that there is no change in the reaction mechanism or the transition state with respect to the substituents on

PMAA. Hence, the observed downward Hammett correlation could be explained by invoking a mechanism having a shift in the RDS within a single reaction pathway.

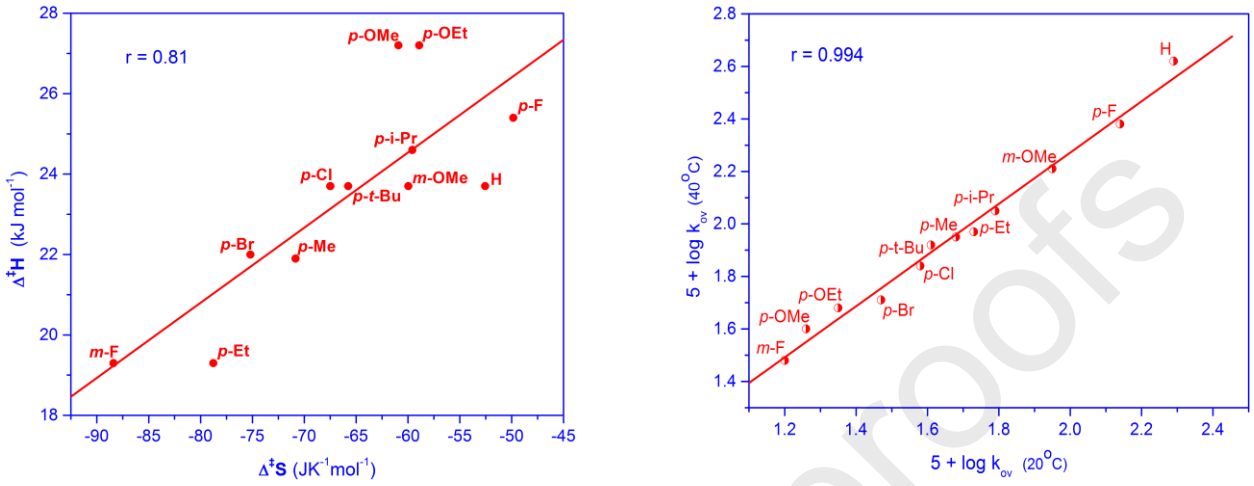


Fig. 8. $\Delta^{\ddagger}S$ *vs* $\Delta^{\ddagger}H$ and Exner's plots for the reactions of PMAAs with **I** in the presence of Py.

4. Discussion

4.1. Active species

Various reactions catalyzed by metallosalen and metalloporphyrin ligands have shown that nitrogen bases behave differently with different catalysts and under different reaction conditions. In the majority of cases, the NB coordinates with the catalyst/oxidant by a proximal effect to form high valent metal oxo-NB species, which are considered as the active oxidizing species that transfers oxygen to the substrate. Reactions which involve the formation of such precursors normally show rate acceleration [64,77,78] or marked improvement in product yield [61,73,79]. The enhancement in the catalytic power of the catalyst as a result of reinforcement of proximal electron donation by axially coordinated NB was suggested during the oxidation [67,80,81], epoxidation [82-84] and sulfoxidation [34,60,85] reactions. Formation of NB ligated active species with the catalyst was confirmed by a shift in the absorption spectra, change in the color of the solution along with EPR and ESI-MS spectral data. The coordination of Py with the vanadium atom of the pyrazolyl-V(III) catalyst used for ethylene polymerization was confirmed by crystal structure analysis [86]. Coordination of ImH/MeIm with an iron(III) salen complex during aniline oxidation by H_2O_2 was concluded by ESI-MS spectra [58]. The nitrogen bases are

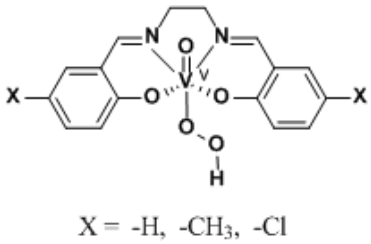
generally presumed to bind at a site trans to the oxo group [87,88] and weaken the M-O bond of the oxo species by donating electron density to the metal atom [62,64].

In some cases, where the adduct formed between the NB and the catalyst is not the active species, the NB blocks the vacant site of the catalyst by weak coordination prior to the coordination of oxidant/substrate. In such cases, retardation in the rate constant or product yield is observed [55,59,70]. It is interesting to note that even the reactions where rate acceleration was observed at a low concentration of the NB, rate retardation was reported at higher concentrations of NB [60,64]. This observation has been explained by the increase in concentration of the bis NB ligated species that do not have any vacant sites for coordination of the oxidant/substrate.

Previously, in various oxygenation reactions catalyzed by oxovanadium(IV) complexes in the absence of NB, a newly formed high valent oxoperoxovanadium moiety has been proposed as the sole reactive species. The gradual appearance of new broad peak followed by a decrease in intensity corresponds to a d-d transition; this peak was observed at around 560 nm in the asymmetric oxidation of sulfides to sulfoxides [89], at 590 nm in the oxidation of phenols [90], at 572 nm in the oxidation of tertiary amines [91], and at 610 and 560 nm in the oxidations of PSAA [28] and PMAA [33] during the course of the reaction catalyzed by Schiff base oxovanadium(IV) and (V) complexes, and was taken as evidence for the formation of hydroperoxovanadium(V) as the new active species. The existence and involvement of hydroperoxovanadium(V) as the reactive species in the reactions of oxovanadium(IV)-salophen and salen complexes was confirmed by IR, ^{51}V NMR and theoretical studies [42].

Based on the above facts and discussion, it is concluded that the active oxidizing species in the present study may be either the adduct formed between NB and oxovandium(IV)-salen or hydroperoxovanadium(V)-salen species. The absence of an observable change in the characteristic peak of oxovanadium(IV)-salen with NB, either in λ_{max} or intensity, observed retardation effect with an increase in [NB] (Table 4), appearance of a new peak with an increase in intensity followed by its decay at 570 nm with time during the reaction (Fig. 1), precisely at the same position as that in the absence of NB [33], and the coincidence of the λ_{max} value of the newly formed peak exactly in the same range as that of other reported values for the reactions where hydroperoxovanadium(V) is involved as the active species [28,89-91] not only confirm hydroperoxovanadium(V) (Fig. 9) is the sole active species for the sulfoxidation but also eliminate the involvement of a 1:1 salen-NB adduct (**C$_3$**) as the active oxidizing species under

these reaction conditions. The non-existence of the reaction without the combination of oxovanadium(IV)-salen and H_2O_2 also emphasizes the importance of both H_2O_2 and salen in the generation of active species and the involvement of hydroperoxovanadium(V)-salen in the reaction.

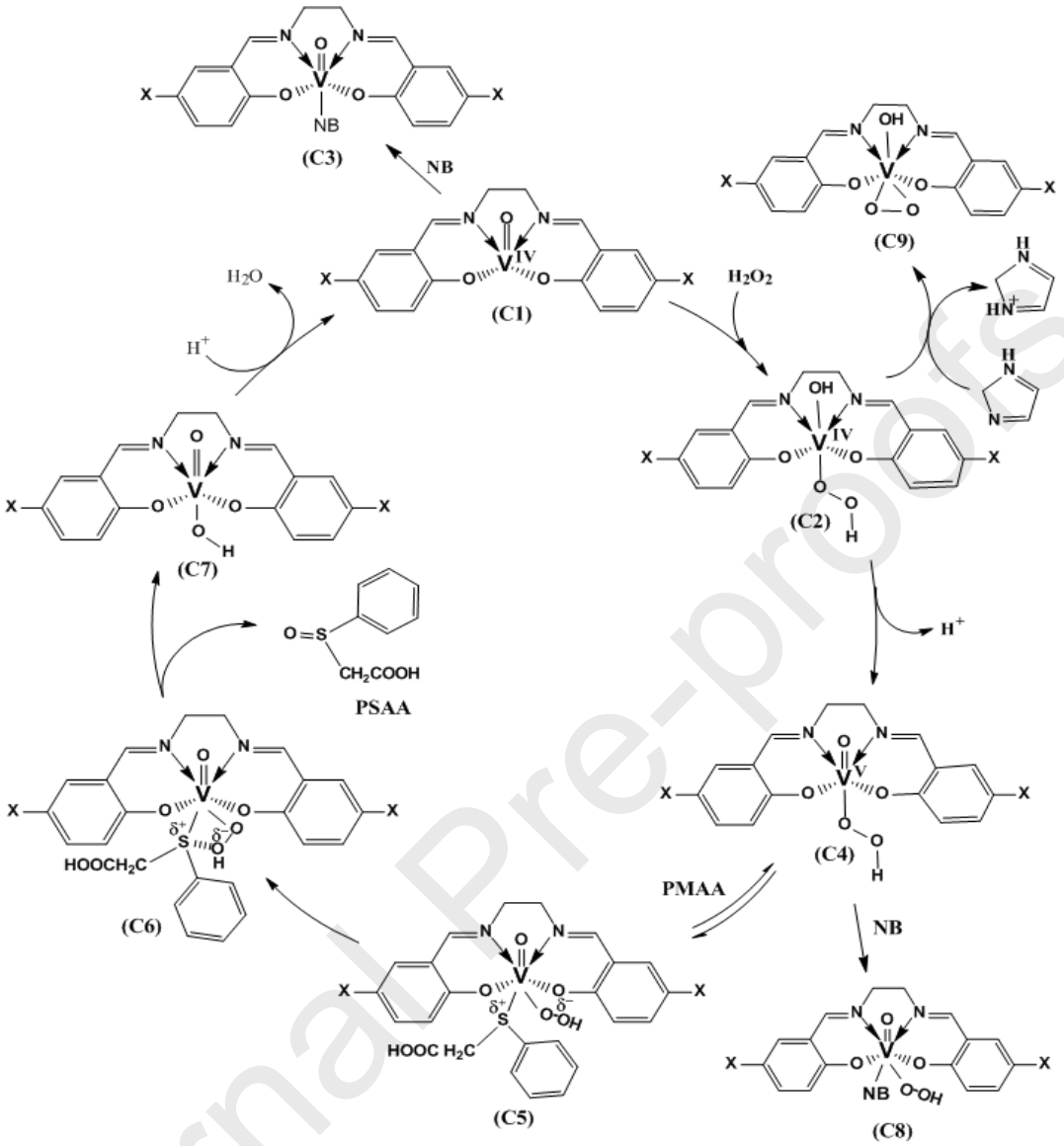


X = -H, -CH_3, -Cl

Fig. 9. Structure of hydroperoxovanadium(V)-salen.

4.2. Mechanism

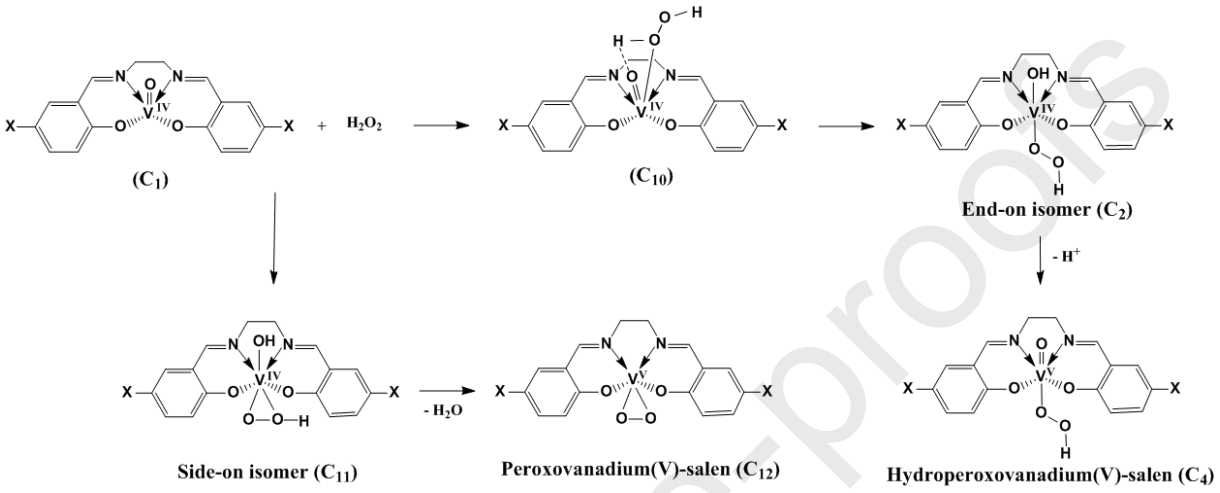
Based on the spectral observations, kinetic results, analysis of facts concerning the nature of active species, low reactivity of PMAAs having electron donating and withdrawing substituents and the retarding effect exerted by axial nitrogenous ligands, the following mechanism with two different rate determining steps (Scheme 2) representing a possible catalytic cycle of the oxovanadium complex is proposed.



Scheme 2. Overall mechanism for the sulfoxidation.

It is proposed that the first step in the mechanism involves the activation of the O-O group by transferring a proton from H_2O_2 to the oxo group of vanadium(IV)-salen complex (**C_1**), with simultaneous binding of the hydroperoxo moiety to the vanadium center to form a vanadium(IV) species (**C_2**). If the conversion of **C_1** to **C_2** takes place via an intermediate (**C_{10}**), in which H_2O_2 is bound apically in an end-on fashion, then the end-on vanadium(IV) species (**C_2**) is formed. On the other hand, if H_2O_2 is coordinated to vanadium in a side-on fashion, then the side-on isomer (**C_{11}**) is formed. Side-on peroxo formation is strongly accelerated by acid-base catalysts. In the side-on isomer, both peroxo oxygen atoms are coordinated to the vanadium

center. It has been shown that both end-on (**C2**) and side-on (**C11**) isomers are isoenergetic. As they are relatively unstable [92,93], they are readily converted into hydroperoxovanadium(V)-salen (**C4**) and peroxovanadium(V)-salen (**C12**) by losing a proton and water molecule, respectively.



Scheme 3. Scheme for O-O activation and active species formation.

Thus, the possible oxidizing species in the reaction is either the end-on species, hydroperoxovanadium(V)-salen (**C4**), or the side-on species, peroxovanadium(V)-salen (**C12**). Balcells et al. [94] have shown by theoretical calculation that these two forms are interconvertible as they have an energy difference within a span of 5 kcal/mol. The existence of a rapid equilibrium between these two species is evidenced from a ^{51}V NMR spectral study [95]. Further, attempts to isolate these active species were unsuccessful. Thus it has been inferred that both forms are feasible candidates for the active form of the catalyst. The choice amongst them, hydroperoxo or peroxo, as the active species depends on the reaction conditions, catalyst and substrate.

Although peroxovanadium(V)-salen (**C12**) has been proposed as the active species for the epoxidation of cyclohexene catalyzed by vanadium porphyrin complexes [96] and halide oxidation catalyzed by vanadium haloperoxidases [93], the involvement of the hydroperoxo form in most sulfoxidation reactions [42,45,54,94,97,98] is in agreement with our proposal. The involvement of hydroperoxovanadium(V)-salen (**C4**) as the active species is supported by the substituent effect shown in salen complexes. It is pertinent to note that an EDG on

oxovanadium(IV)-salen increases the electron density on the vanadium center and thereby increases the nucleophilicity of the oxovanadium active species. Even though this effect disfavors the attack of PMAA with **C₄** to form **C₅**, the increase in rate with an EDG on **C₁** clearly indicates the importance of O-O activation and active species formation in this reaction over attack of PMAA with the active species. An EDG on the salen complex favors the polarization of the oxovanadium bond in **C₁** and thereby facilitates the formation of **C₄** by the attack of H_2O_2. The easy formation of active species with EDGs on the salen complex has been verified by the decrease in magnitude of the induction period. The reverse explanation can be applied to EWGs on the salen complex for the observed rate retardation effect and increase in induction period. The significant role of active species generation in this reaction is also evidenced from the retardation effect shown by increase in concentration of NB (Table 4).

On the basis of the mechanism proposed for the sulfoxidation reactions catalyzed by hypervalent oxosalen species [34-36,99,100], an electrophilic attack of the vanadium atom of the active species, hydroperoxovanaium(V) species (**C₄**) on the sulfur atom of PMAA, leading to the formation of **C₅** in a reversible process, is proposed for this reaction. This results in the development of a partial positive charge on the coordinated sulfur atom and a negative charge on the hydroperoxyl oxygen atom. The reverse nature of the step is suggested on the basis of the observed Michaelis-Menten kinetics with PMAA. A similar sulfoxidation intermediate (**C₅**) has been postulated in the sulfoxidation of disulfide [94], methyl phenyl sulfides [45] and PMAA [33] catalyzed by oxovanadium(IV)-Schiff base complexes. The formation of intermediate **C₅** is affected by structural changes in PMAA and presumably influences the rate determining step. This view is apparently in agreement with our experimental results that both EDGs and EWGs on PMAA decrease the sulfoxidation rate. The observed retardation effect with EDGs and EWGs (Table 5) indicates that the formation of **C₅** from **C₄** is not a common rate determining step for both types of substituents. The observed downward non-linear Hammett plot with an opposite sign of the reaction constant (ρ) for EDGs and EWGs (Fig. 6) is in agreement with a change in the rate determining step or a change in the transition state with the change in the nature of the substituent. The observed constant thermodynamic parameters, $\Delta^{\ddagger}H$ and $\Delta^{\ddagger}S$, in all the substituted PMAAs (Table 5) are a clear indication that two different transition states are not involved in the reaction and supports two different rate determining steps for the donor and acceptor substituents.

It is seen that an EWG on PMAA pulls electron density from the sulfur atom and thus reduces the nucleophilic character of PMAA. As a result, the reactive species (**C4**) finds it difficult to electrophillically attack the sulfur atom of PMAA and disfavors the formation of the intermediate **C5**. Not only that, EWGs also tend to increase the positive charge on the sulfur atom of **C5** which results in the destabilization of **C5** and also facilitates the conversion of **C5** into **C6** in a fast manner. The above discussion leads us to conclude that the formation of **C5** from **C4** in a reversible step is the rate controlling step for PMAAs containing EWGs. The appearance of a positive charge at the reaction center of PMAA in the rate controlling step is evidenced from the observed negative ρ value in the portion of the Hammett plot containing EWGs (Table 5 and Fig. 6).

The nucleophilic character of PMAA is strongly reduced as a result of coordination of PMAA with the vacant site of the vanadium center (**C4** to **C5**). Subsequently, a four membered cyclic intermediate (**C6**) is formed by the coordination of the peroxo oxygen atom with PMMA through the coordinated sulfur atom. This coordination is favored by EWGs on PMAA, while EDGs make the coordination more difficult. Further, EDGs on the PMAA preclude the transfer of oxygen to the sulfur atom in the intermediate **C6** by increasing the charge density on the sulfur atom, i.e. disfavoring the disproportionation of **C6** into the products PSAA and **C7**. The transfer of oxygen to the sulfur atom in the slow rate determining step for EDGs is evidenced by the decrease in the rate constant with the increase in electron donating ability of the substituents and the observed positive ρ value with EDGs in the Hammett correlation. Thus, the break at the unsubstituted PMAA in the Hammett plot (Fig. 6) is in strong favor for a change in the rate determining step in a multi stage mechanism as a function of the substituents on PMAA. The process of formation of PSAA in a multistage mechanism is confirmed by the absence of isobestic points during the course of the reaction (Fig. 1). The existence of an excellent linear Exner's plot (Fig. 8) with EDGs and EWGs in the same line rules out the operation of two different mechanisms in this reaction series.

The observed non-linearity in the plot of log k_{ov} against oxidation potential of PMAAs (Fig. 10) firmly rules out the operation of a single electron mechanism as proposed in many salen mediated reactions, viz. oxidation of organic sulfides [101] and anilines [102] by chromium(V) complexes, H_2O_2 oxidation catalyzed by iron(III)-salen complexes [103] and phenols catalyzed by oxovanadium(IV)-salen [90].

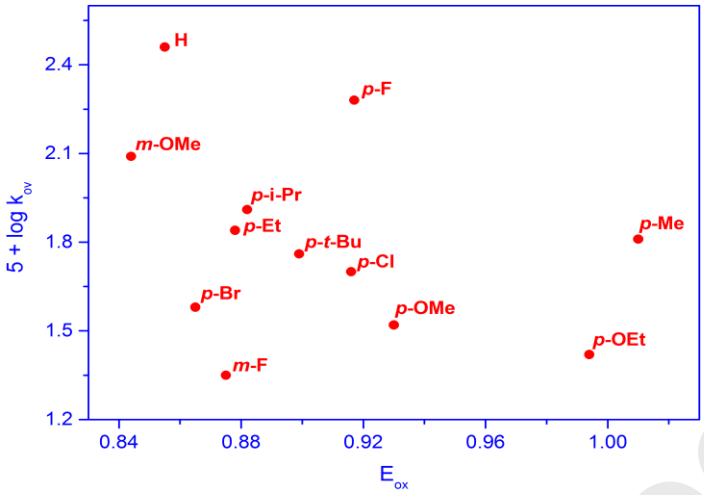


Fig. 10. Plot of log k_{ov} against E_{ox} potential of PMAA for the reaction with **I** and ImH.

4.3. Role of the nitrogen base and reactivity

A comparison of the rate constants with and without nitrogen bases (Table 4) indicates that NBs deteriorate the catalytic activity of oxovanadium(IV)-salen complexes. According to Scheme 2, two vacant sites on the vanadium atom are essential for the formation of high valent oxidizing species and the transfer of oxygen from the active species to PMAA. If any one of the sites is occupied by any additives then the rate of the reaction might be decreased. The observed decrease in reactivity in the presence of NB is better explained by the concomitant formation of an adduct (**C_3**) between the catalyst (**C_1**) and NB by weak coordination as a competitive reaction, simultaneous and parallel to the formation of active species (**C_4**); not only that, it also emphasizes the crucial importance of free coordination sites on the oxosalen complex for a smooth reaction to take place. Weak coordination of NB with the salen complex is confirmed by the absence of any shift in the absorption and intensity of the peak for **C_1**. The coordination of NB prevents the coordination of H_2O_2 with the catalyst by restricting the free coordination site. As a result, the formation of active species (**C_4**) and binding of PMAA with active species to form **C_5** become difficult, which are essential steps for the sulfoxidation to take place.

The interesting aspect gathered from the kinetic profiles reported in Fig. 2 is that the induction period increases with an increase in the concentration of the NBs. This unambiguously proves the existence of competition between the NB and H_2O_2 in coordinating with oxovanadium(IV)-salen to form inactive species (**C_3**) and active species (**C_4**), respectively. The

simultaneous existence of competition between two reactions is confirmed from the fact that NBs are found only to slow down the reactivity but not completely inhibit the reaction. As the concentration of the NB increases, the fraction of the salen complex (**C_1**) utilized for the formation of unreactive species increases. Even though there is a competition between H_2O_2 and NBs to form a six coordinated vanadium complex, apparently due to less steric hindrance around the terminal oxygen atom of H_2O_2, the attachment of H_2O_2 to the vanadium center through the terminal peroxo oxygen atom is more facile and dominant compared to the attack of the NB.

The occurrence of competition between H_2O_2 and NBs is further substantiated from the order of reactivity noted among different NBs. Imidazole, being a strong π donor, binds with the vanadium atom of the complex more preferentially, which prevents the formation of the active species (**C_4**) more effectively and is followed by the highest retardation rate among all the NBs. As Py has a weak π donating ability, its possibility to bind with the salen complex is faint. This results in easy formation of the active species (**C_4**) in the presence of Py, showing a low retardation effect as compared to ImH and MeIm.

In addition to the competition between NBs and H_2O_2 towards **C_1**, the probability of competition amongst NBs and PMAA through **C_4** leading to the formation of **C_8** and **C_5** respectively cannot be ruled out and that may be one of the reasons for the observed retardation effect with NBs. In some reactions, coordination of the NB with the active species that compete and prevent the binding of substrate was given as explanation for the observed retardation effect with the NB [59,70]. In fact, coordination with two sites of the metal center connected with HOO- and the NB in salen complexes was considered as the dominant form in the presence of H_2O_2 and the NB [77,79].

The least reactive rate observed with ImH also demonstrates the existence of distal hydrogen bonding, -N-H-----B, that is possible only for ImH. This interaction naturally increases the binding ability of ImH by shifting electron density from the free base (B) to the coordinated base. The increasing binding ability of ImH towards different catalysts by such a type of hydrogen bonding is already advocated in many cases [53,64,104]. Another reason for ImH's higher rate retardation effect may be due to the ability of ImH to convert the catalyst into a catalytically inactive bisligated species, by consuming a portion of the catalyst [53,67,74,105]. Beside the above mentioned effects, the added nitrogen bases also prevent the formation of hydroperoxovanadium(V) salen (**C_4**) by the preferential removal of a hydrogen atom from

coordinated H_2O_2 in **C_2**. As a consequence, instead of forming the active species (**C_4**) from **C_2**,, a less active cyclic peroxo species (**C_9**) is formed in the catalytic cycle. The existence of the cyclic peroxo species in acetonitrile medium has been proved by Coletti et al. [42] using theoretical studies. Proton abstraction from a peroxo group coordinated with a metal atom by imidazole has been advocated during the oxidation of hydrocarbons by H_2O_2 catalyzed by Mn-porphyrins [106], oxidation of sulfides to sulfoxides by UHP using Mn(III)-oxazoline complexes [107] and in the oxidation of olefins and sulfides catalyzed by a manganese(III)-tridentate Schiff base complex using UHP as the oxidant [74].

5. Conclusions

This study describes the influence of nitrogen bases, such as imidazole, 1-methyl imidazole and pyridine, on the selective sulfoxidation of several phenylmercaptoacetic acids to phenylsulfinylacetic acids, catalyzed by oxovanadium(IV)-salen complexes. The findings prove that axial ligation of the nitrogen bases to the vanadium atom of salen to form 1:1 adducts compete with the formation of active hydroperoxovanadium(V) species, which results in a decrease in the rate of sulfoxidation. The observed order of retardation ImH > MeIm > Py has been explained on the basis of proximal and distal interactions of the nitrogen bases with the oxovanadium(IV)-salen complex. A weak π donor with the lowest binding ability with the salen complex has the highest catalytic effect in this reaction. Vanadium salen complexes with electron donating substituents on the phenyl group are found to be more effective catalysts than those with electron withdrawing substituents. The reaction between PMAA, H_2O_2, the oxovanadium(IV)-salen complex cocatalyzed by nitrogen bases has been retarded by both electron donors and electron acceptors in the *p*- and *m*-positions of PMAA. The observed downward Hammett plot has been rationalized by a change in the rate determining step from addition of PMAA to the active species with electron withdrawing substituents to transfer of oxygen to PMAA with electron donating substituents within the same mechanism. The sulfoxidation of PMAA to yield PSAA, a challenging compound in pharmaceutical chemistry, can lead to the future use of this compound in medicinal industry.

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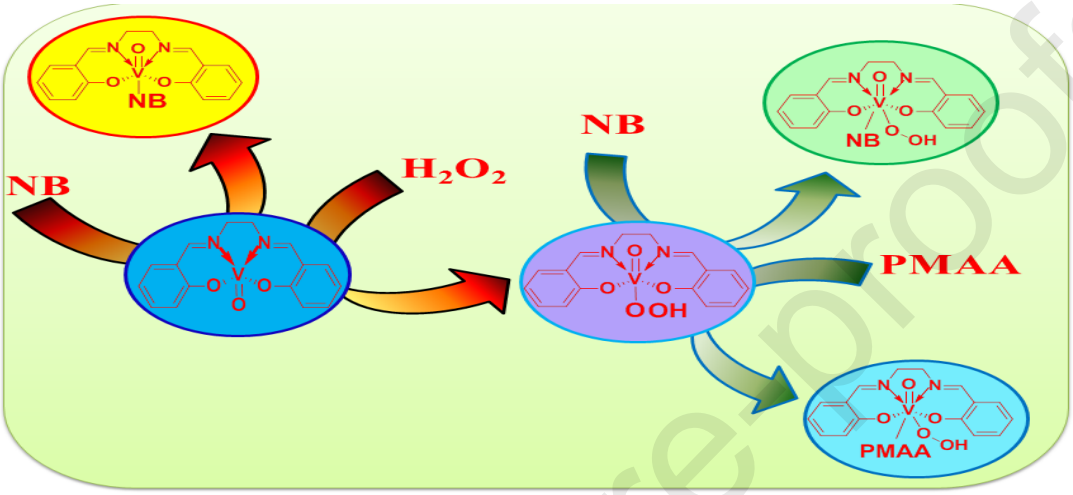
Graphical abstract –synopsis

The sulfoxidation of phenylmercaptoacetic acids (PMAA) catalysed by oxovanadium(IV)-salen complexes is retarded by the addition of the nitrogen based ligands pyridine, imidazole and 1-methylimidazole. A suitable mechanism involving hydroperoxovanadium(V)-salen as the active oxidizing species is proposed. The observed non-linear downward Hammett plot is rationalized by two different rate determining steps within a single mechanism.



HIGHLIGHTS

- Nitrogen bases retard the sulfoxidation rate of phenylmercaptoacetic acid by H_2O_2
- Hydroperoxovanadium(V)-salen is identified as the active oxidizing species
- The competition of nitrogen bases with H_2O_2 and substrate causes a rate retardation
- The order of retardation ImH > MeIm > Py is explained by proximal and distal effects
- The downward Hammett plot indicates a change in the rate determining step with the same mechanism

P. SUBRAMANIAM: Conceptualization, Supervision, Investigation.

C. KAVITHA: Methodology, Writing- Reviewing and Editing, Writing- Original draft preparation.