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ROLE OF NITROGEN BASES IN THE OXOVANADIUM(IV)-SALOPHEN CATALYZED OXIDATION OF PHENYLSULFINYLACETIC ACIDS BY HYDROGEN PEROXIDE AND THE NON-LINEAR HAMMETT CORRELATION

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A B S T R A C T

The oxidative decarboxylation of phenylsulfinylacetic acid (PSAA) and substituted PSAAs by H_2O_2 in the presence of oxovanadium(IV)-salophen complex has been studied spectrophotometrically in 100% acetonitrile medium under the influence of nitrogen bases like pyridine (Py), imidazole (ImH) and 1-methylimidazole (MeIm). Kinetic results reveal that the reaction rate is strongly retarded by nitrogen bases and highly sensitive to the nature of base. Among the three nitrogen bases used, MeIm with a strong π-donating ability shows the highest retarding effect on rate with oxovanadium(IV)-salophen complex. The reaction involving hydroperoxo species and an electrophilic attack of sulfur atom of PSAA on the nucleophilic peroxo oxygen of the vanadium complex is proposed as the mechanistic pathway. The linear Yukawa-Tsuno plot demonstrates that the ground state stabilization of PSAAs through resonance interaction is the cause for the observed non linearity in the Hammett plot.

Abbreviations: PSAA, phenylsulfinylacetic acid; EWG, electron withdrawing group; EDG, electron donating group;Py, pyridine; ImH, imidazole; MeIm, 1-methylimidazole.

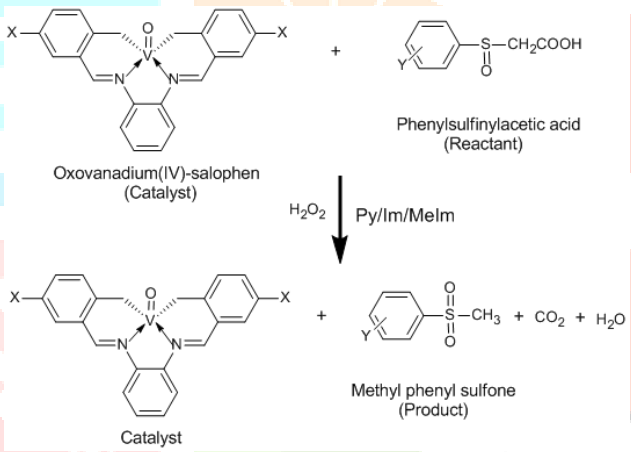
Keywords: oxovanadium(IV)-salophen, phenylsulfinylacetic acid, non-linear Hammett, oxidative decarboxylation, nitrogen base

1. INTRODUCTION

In the recent years, vanadium species have been extensively studied for energy conversion in photovoltaic solar cells and fuel cells; and in biological systems owing to their multivalent oxidation states,excellent interactions with molecules or ions and superior catalytic properties (Liu, Minsu, et al. 2017).Coordination of vanadium(V) species with oxygen/nitrogen compounds forms bioinorganic catalysts where the coordination environment is similar to that of the prosthetic groups present in the enzymes and vanadate dependent peroxidases. The use of vanadium in human is recommended in the case of pathological conditions such as malnutrition, anemia, tuberculosis and diabetes (Correia, I., et al., 2004). Oxovanadium catalyzed reactions constitute a vital and powerful role, not only in chemistry but also in biomedical and environmental sciences (Pessoa, J.C. and Correia, I., 2019).Oxovanadium species exist in IV and V oxidation states possess excellent biological activity; and utilized as antituberculosis, antibacterial, antifungal, antitumor and anti-HIV drugs.Further, oxovanadiumspecies with an N_2O_2 donor environment possessing chemo preventive properties were employed to reduce the blood glucose levels by enhancing insulin secretion (Crans, Debbie C., et al. 2011) and for the treatment of obesity and hypertension (Correia, Isabel, et al. 2004).The structural similarities of the salen/salophen vanadium complexes with metalloproteins and enzymes are responsible for their broad range of catalytic applications for a wide range of transformations (McCaffrey, V.P., et al., 2021, Kargar, Hadi, et al. 2021.,Kargar, Hadi, et al. 2021).Salophen ligand which readily combines with vanadium salts to form oxovanadium complexes show binding property with proteins (Kamyabi, M.A. et al., 2008). The oxovanadiumcation, $[O=V(IV)]^+$ readily interacts with amine, amide, hydroxyl, imidazole, thiolate and carboxylate functionalities of proteins.

Oxidative decarboxylation plays an important role in biological systems, organic synthesis and drug metabolism. In humans, oxidative decarboxylation continually produces carbon dioxide in all live tissues during metabolism. Oxidative decarboxylationtakes place in the mitochondrial membrane in conjunction with electron transport and oxidative phosphorylation provides the basis of human cell respiration. Anti-inflammatory drugs such as indomethacin and ibuprofen are decarboxylated during metabolism by cytochrome p-450 in vivo and the carbon dioxide released was found to reduce pain (Komuro, M., et al., 1995). Organosulfur compounds widely distributed in food are found to possess antiseptic, antibiotic, antithrombotic and antioxidant activities (Fang, Y, et al., 2022). In the present oxidative decarboxylation study, phenylsulfinylaceticacid(PSAA), a sulfoxide containing chelating agent is oxidized and decarboxylated to methyl phenyl sulfone. The chemistry of sulfones has been explored due to their antimicrobial (Dixit, Y, et al., 2008), anticancer (Al-Said, M.S., et al., 2012), anti-HIV (Meadows, D.C., et al., 2007) antimalarial (Lee, P.J., 2009) and anti-inflammatory (Shaaban, O.G., et al., 2013) therapeutic activities. Hence the oxidation of organic sulfur compounds has been the subject of extensive studies in recent years.

Nitrogen donors have long been used as axial ligands to mimic the function of axial cysteine thiolate or histidine imidazole in natural metallo proteins (Dolphin, D., et al.,1997). Nitrogen bases like pyridine (Py), imidazole (Im) and their derivatives exhibit various types of biological activities *viz.*, antimicrobial, analgesics, anticancer, antidiabeticetc (Shalini, K., et al., 2010). The reactivity of metal - salen complexes can be tuned (Collman, J.P., et al., 2004.] by adding donar ligands ligands in the reaction mixture.Addition of pyridine (Py), imidazole (Im) or 1-methylimidazole (MeIm) to metal-salen related complexes significantly lowers the oxidation potential by coordination with the metal ion which results in altering the electrochemical properties and their reactivity (Kalow, J.A. and Doyle, A.G., 2011).Realizing the importance of vanadium species in biological studies, it is worthwhile to study the influence of nitrogen bases on the reaction rate towards oxidative decarboxylation. Several studies on sulfoxidation reactions involving different mechanisms; namely electrophilic attack of a sulfur atom on the nucleophilicperoxo oxygen atom (Jeevi Esther Rathnakumari,R., et al. 2016) S_N2 type oxygen transfer, direct oxygen transfer (Kavitha, C. and Subramaniam, P., 2020 &Kavitha, C et al. 2020, Subramaniam, P., et al. 2016) and single electron transfer (Sugirtha Devi, S et al 2016, Janet Sylvia Jaba Rose,J.,et al 2016, Balakumar, P., et al 2012, P. Subramaniam et al., 2016), have been reported. This paper reveals the effect of nitrogen bases like Py, Im and MeIm on the oxidative decarboxylation of substituted PSAAs by H_2O_2 catalyzed by oxovanadium(IV) salophen complex (**I**). The overall reaction scheme is represented in Scheme 1.



Scheme 1: Complex : X = H (**I**)

PSAA :Y = H; *p*-Cl; *m*-Cl; *p*-F ; *p*-Br ; *p*-Me; *p*-OEt; *p*-OMe.

2. EXPERIMENTAL

2.1. Materials And Methods

Salicylaldehyde, 1,2-benzenediamine,$VOSO_4.5H_2O$, methanol, ethanol, H_2O_2 and acetonitrile were analytical grade, the nitrogenous bases (N-bases) used were pyridine (Py), imidazole and 1-methyl imidazole (MeIm) were purchased from Sigma-Aldrich and were used as received. .

A double beam BL 222 Elico UV–vis bio spectrophotometer with an inbuilt thermostat was employed to record the absorption spectra of oxovanadium(IV)-salophen complex. LC-MS was performed on a HPLC coupled Agilent ion trap mass spectrometer. Mass spectrometry was done using APCI (+) ionization technique. GC-MS data were acquired using Thermo GC-Trace ultra Ver: 5.0, Thermo MS DSQ II mass spectrometer. Infrared spectrum of the product was recorded using KBr pellet on a JASCO FT/IR-410 spectrophotometer.

2.2. Preparation of phenylsulfinylacetic acids

Phenylsulfinylacetic acid and its meta- and para-substituted acids were prepared from the corresponding phenylmercaptoacetic acids by controlled oxidation with an equimolar amount of hydrogen peroxide as reported in the previous paper (Jeevi Esther Rathnakumari, R. et al. 2016).The purity of the PSAAs was checked using their melting points.The purity of PSAAs and the presence of single entity were also confirmed by LC-MS analysis.

2.3. Synthesis of the oxovanadium(IV)-salophen complex

The synthesis of the oxovanadium(IV)-salophen complex was accomplished by following the literature procedure as mentioned earlier(Jeevi Esther Rathnakumari, R. et al. 2016).oxovanadium(IV)-salophen complex synthesized was characterized by UV-vis, FT-IR and mass spectral techniques.

2.4. Kinetic studies

The kinetic study for the reaction of PSAA and substituted PSAAs with H_2O_2 and oxovanadium(IV)-salophen complex in the presence of nitrogen bases was carried out in 100% acetonitrile medium under pseudo first-order conditions with excess of PSAA concentration over the oxidant as well as complex concentrations. The progress of the reaction was followed spectrophotometrically by monitoring the decrease in absorbance of the salophen complex at an appropriate wavelength of 396nm using a double beam BL 222 Elico UV-vis spectrophotometer.The kinetics of the reaction was studied for different variations of the reactants, oxovanadium(IV)-salophen complex, PSAA and H_2O_2 at various initial concentrations keeping the other reaction conditions as constant.The pseudo first order rate constants were calculated from the slope of linear plots of log OD versus time. The second order rate constants were calculated by dividing the pseudo first order rate constants with the concentration of PSAA. The error in the rate constants was calculated according to 95% of the student'st-test.

2.5. Product analysis

The experimental procedure for the analysis and characterization of the product was in accordance with our previous publication on the oxidative decarboxylation of PSAA in the absence of nitrogen bases (Jeevi Esther Rathnakumari, R.et al.2016).Formation of methyl phenyl sulfone was identified as the only product of the reaction by FT-IR and GC-MS. The FT-IR spectrum shows strong bands at 1148 cm^{-1} and 1290 cm^{-1},characteristic of symmetric and asymmetric stretching vibrations, respectively of $–SO_2–$ group and confirms the formation of sulfone as the product.This is further confirmed by the appearance of the parent peak at m/z = 156 in the GC-MS spectrogram.

3. RESULTS

3.1. Spectral studies and active species

Oxovanadium(IV) salophen complex (**I**) has an absorption maximum at 396 nm, which arises due to ligand to metal charge transfer transition (LMCT). When a nitrogen base or PSAA or both of them together are added to the complex, no substantial shift in the absorption maxima or increase in the absorbance of the oxovanadium(IV)-salophen complex is observed. In a majority of the oxidation studies involving salen/porphyrin complexes, the addition of axial donar ligands, nitrogen base or oxide ligand causes a significant red shift in the λ_{max} value (Aslam, Adhem Mohamed, et al. 2011) or a change in the intensity of the peak (Subramaniam, Perumal, et al. 2014). In these cases, formation of 1:1 adduct between the complex and the axial ligand has been identified as the active oxidizing species. Thus, it has been concluded that in the present oxidation, adduct formation between the oxovanadium-salophen complex and the nitrogen base is unambiguously not the active species.

Another spectral observation noted in the kinetic runs is that addition of H_2O_2 at a higher concentration to the complex shows an initial increase in the intensity of a new broad absorption peak around 610 nm after certain time interval followed by decrease in absorbance during the course of time, as observed in the absence of nitrogen bases (Jeevi Esther Rathnakumari, R.et al. 2016). This observation clearly indicates the formation of a new vanadium intermediate species in the reaction mixture. This is also supported by the fact that neither oxovanadium(IV)- salophen complex alone nor hydrogen peroxide alone oxidizes the PSAA in acetonitrile medium, but the reaction proceeds smoothly only in the combination of these two. Similar spectral change of a new weak broad band followed by its decrease in intensity of absorbance, has been taken as an evidence for the formation of hydroperoxovanadium(V) species in the oxidation of sulfides, phenols (Ramdass, A. et al 2015) tertiary amines (Mathavan, Alagarsamy, et al. 2015) and sulfoxidation of phenylmercaptoacetic acids in the absence and presence of N-bases (Kavitha, C. and Subramaniam, P., 2020&Kavitha, C et al. 2020).

An interesting observation noted in the kinetic studies with complex (**I**) in the presence of nitrogen bases is an initial well defined induction period for a definite period of time followed by a gradual decrease in absorbance.The induction period and initial time taken for the decrease in OD are found to decrease with an increase in temperature and concentration of the substrate and hydrogen peroxide(Fig.1). The decrease in induction period observed with temperature in the reaction may be due to the easy formation of the active hydroperoxovanadium(V) species at high temperature.

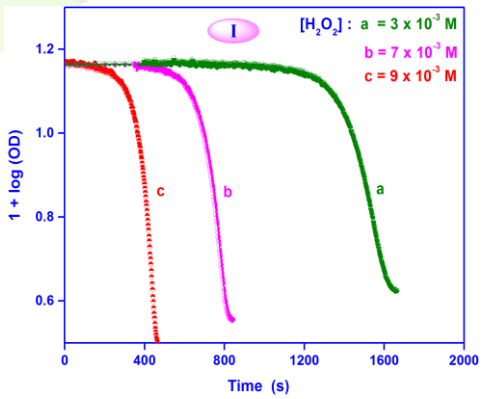


Fig.1 Pseudo first-order plots at different $[H_2O_2]$. [PSAA] = 7.0 ×10^{-2} M; [**I**] = 5.0 × 10^{-5} M; [Py] = 5.0 × 10^{-4} M.

3.2. Effect of PSAA and hydrogen peroxide

The reaction is carried out at different PSAA concentrations in the range of 0.03 M to 0.15 M. The reaction is found to exhibit first-order dependence on PSAA as evidenced from the constant second-order rate constants observed at different [PSAA] (Table 1), unit slope values obtained from the plots of log k_1*vs.* log [PSAA] (Fig. 2) and the observed linear plots between k_1 and [PSAA] passing through the origin for the oxovanadium(IV)- salophen complex in the presence of nitrogen bases.

Table 1. Effect of [PSAA] on the reaction rate in the presence of nitrogen bases.

10^1 [PSAA] (M)	Py		Im		MeIm	
	$10^3\,k_1\,(s^{-1})$	$10^2\,k_2\,(M^{-1}s^{-1})$	$10^3\,k_1\,(s^{-1})$	$10^2\,k_2\,(M^{-1}s^{-1})$	$10^3\,k_1\,(s^{-1})$	$10^2\,k_2\,(M^{-1}s^{-1})$
			I			
0.3	1.31 ± 0.02	4.37 ± 0.67	1.08 ± 0.05	3.60 ± 1.6	0.208 ± 0.04	0.693 ± 1.3
0.7	2.80 ± 0.01	4.00 ± 0.14	2.40 ± 0.08	3.43 ± 1.1	0.532 ± 0.07	0.760 ± 1.0
1.0	4.00 ± 0.05	4.00 ± 0.50	3.24 ± 0.12	3.24 ± 1.2	0.785 ± 0.03	0.785 ± 0.3
1.5	6.50 ± 0.08	4.33 ± 0.53	5.51 ± 0.20	3.67 ± 1.3	1.13 ± 0.06	0.753 ± 0.4

[**I**] = 3.0×10^{-4} M; Temp. = 30 °C; Solvent = 100% CH_3CN; [N-base] = 5.0×10^{-4} M; $[H_2O_2] = 3.0 \times 10^{-3}$ M

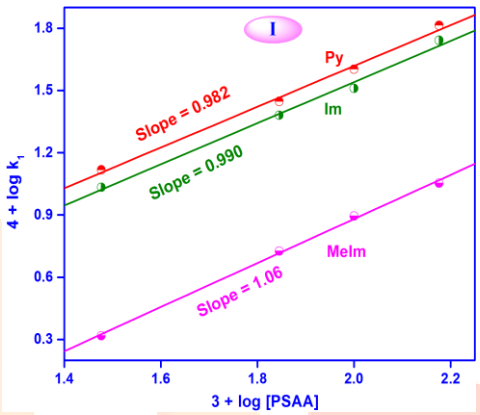


Fig.2 Plot of log k_1 *vs*. log [PSAA] variation.

Kinetic runs were carried out with different concentrations of H_2O_2 in the presence of nitrogen bases and the observed kinetic data are given in Table 2.The first-order dependence of rate on H_2O_2 is evidenced from the linear portion observed in the plot of log (OD) *vs*. time after a period of induction time (Fig.1). However, it is observed that with the increase in concentration of H_2O_2, there is a significant increase in the pseudo first-order rate constant. Beyond a particular concentration of H_2O_2, the reaction rate begins to decrease.

Table 2. Effect of $[H_2O_2]$ on the rate of reaction in the presence of nitrogen bases.

10^3 $[H_2O_2]$ (M)	Py $10^3\,k_1\,(s^{-1})$	Im $10^3\,k_1\,(s^{-1})$	MeIm $10^3\,k_1\,(s^{-1})$
I			
1.0	0.924 ± 0.03	0.387 ± 0.01	0.102 ± 0.02
3.0	1.72 ± 0.02	0.825 ± 0.03	0.577 ± 0.04
5.0	2.48 ± 0.04	1.74 ± 0.05	1.10 ± 0.06
7.0	3.30 ± 0.08	2.88 ± 0.04	1.79 ± 0.08
9.0	4.21 ± 0.03	3.76 ± 0.06	2.62 ± 0.01
11.0	3.71 ± 0.02	2.95 ± 0.02	1.99 ± 0.03

[PSAA] = 7.0×10^{-2} M; [**I**] = 5.0×10^{-5} M; Temp. = 30 °C; [N-base] = 5.0×10^{-4} M; solvent = 100 % CH_3CN.

3.4. Influence of nitrogen bases

To evaluate the effect of nitrogen bases on the reaction rate, the reactions of PSAA and H_2O_2 with the complex **I** was carried out in the presence of nitrogen bases *viz*., Py, Im and MeIm at different concentrations and the observed pseudo first-order rate constants are presented in Table 3 and the representative plot is shown in Fig.3. Kinetic results reveal that the reaction rate is highly sensitive to the nature of base and is strongly retarded by all the three nitrogen bases. The determination of rate constant is restricted only to the given concentration range of nitrogen bases because beyond this range, the reaction is too slow to measure. The reason for the profound rate retardation observed with N-base may be due to the prevention of the active hydroperoxo species generation. Among the three nitrogen bases, MeIm shows the highest rate retardation with the complex **I.** The rate constants in Table 3 clearly show that the observed order of retardation among the three different N-bases is Py>Im>MeIm .

Table 3. Influence of nitrogen bases on the reaction rate.

10^3 [N-base] (M)	10^3 k_1 (s^{-1})		
	Py	Im	MeIm
I			
0	3.58 ± 0.11	3.58 ± 0.11	3.58 ± 0.11
0.50	3.30 ± 0.08	2.88 ± 0.04	1.79 ± 0.08
0.75	2.68 ± 0.02	2.24 ± 0.25	1.03 ± 0.09
1.0	2.01 ± 0.21	1.62 ± 0.20	0.834 ± 0.05
2.5	0.819 ± 0.21	0.791 ± 0.02	0.401 ± 0.06
3.5	0.523 ± 0.07	0.488 ± 0.04	0.298 ± 0.03
5.0	0.287 ± 0.05	0.251 ± 0.06	0.159 ± 0.01

[PSAA] = 7.0×10^{-2} M; [H_2O_2] = 7.0×10^{-3} M; [**I**] = 5.0×10^{-5} M; Temp. = 30 °C; solvent = 100% CH_3CN.

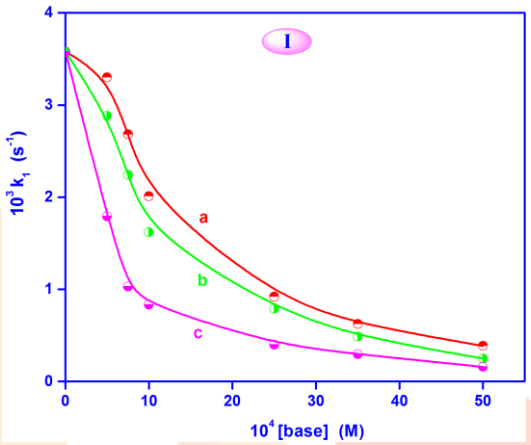


Fig. 3. Variation of pseudo first-order rate constant with [N-base].
[PSAA] = 7.0×10^{-2} M; [H_2O_2] = 7.0×10^{-3} M; [**I**] = 5.0×10^{-5} M; a = Py, b = Im, c = MeIm.

3.5. Effect of substituents and linear free energy relationship

In order to understand the nature of transition state and the extent of charge transfer, several *para*- and *meta*- substituted PSAAs were utilized to carry out the reaction with H_2O_2 in the presence of theoxovanadium(IV) salophen complex (**I**) and the bases Py, Im and MeIm (Table 4). The substituent effect was also studied at three different temperatures 25, 30and 35°C with the complex . The observed data show that the reaction is sensitive to the change of substituents in the phenyl ring of PSAA. It is interesting to note that EWG in PSAA accelerates the rate of the reaction while the EDG retards the reaction rate. The kinetic data analyzed using Hammett equation show a nonlinear downward curvature with two distinct lines for groups comprising of electron withdrawing and electron donating substituents converging at the parent compound (Fig. 4) as observed earlier (Jeevi Esther Rathnakumari, R.et al. 2016) which has been explained on the basis of ground state stabilization of the substrates possessing EDG.

Table 4. Second-order rate constants and thermodynamic parameters for the reactions of PSAAs with complex **I** in the presence of nitrogen bases.

X	10^2 k_2 (M^{-1} s^{-1})			$\Delta^{\ddagger}H$ (kJ mol^{-1})	$\Delta^{\ddagger}S$ (JK^{-1} mol^{-1})
	25°C	30°C	35°C		
			Py		
p-Cl	12.5 ± 0.5	15.3 ± 0.32	22.5 ± 1.1	42.2 ± 2.8	-121 ± 6.5
m-Cl	14.0 ± 0.8	16.9 ± 0.10	25.2 ± 0.62	42.0 ± 2.1	-121 ± 7.9
p-F	10.2 ± 0.56	13.6 ± 0.90	18.2± 0.80	44.2 ± 1.6	-116 ± 8.1
p-Br	12.2 ± 0.6	15.1 ± 0.20	23.4 ± 1.0	46.9 ± 2.2	-106 ± 5.4
H	9.80 ± 0.41	12.6 ± 0.53	15.8 ± 1.2	33.9 ± 2.6	-151 ± 4.9
p-Me	6.76 ± 0.26	8.76 ± 0.44	10.2 ± 0.3	28.9 ± 2.0	-171 ± 5.8
p-OEt	6.17 ± 0.80	7.59 ± 0.62	7.94 ± 0.51	16.8 ± 1.2	-212 ± 9.6
p-OMe	4.90 ± 0.30	5.90 ± 0.09	6.31 ± 0.22	16.6 ± 1.8	-214 ± 10.2
ρ_{EWG}	0.436 ± 0.05	0.333 ± 0.02	0.540 ± 0.03		
r	0.996	0.995	0.961		

ρ_{EDG}	0.691 ± 0.06	0.920 ± 0.03	1.16 ± 0.02		
r	0.991	0.999	0.995		
			Im		
p-Cl	12.5 ± 0.32	14.5 ± 0.15	20.1 ± 0.09	33.6 ± 3.1	-150 ± 8.3
m-Cl	13.8 ± 0.06	16.9 ± 0.41	23.2 ± 0.03	37.0 ± 2.8	-138 ± 10.1
p-F	10.9 ± 0.13	13.3 ± 0.24	17.8 ± 0.19	35.1 ± 3.3	-146 ± 9.9
p-Br	12.6 ± 0.41	15.0 ± 0.32	20.9 ± 0.28	36.1 ± 4.2	-142 ± 2.9
H	9.30 ± 0.18	11.6 ± 0.09	14.8 ± 0.05	33.0 ± 2.1	-154 ± 7.2
p-Me	5.65 ± 0.02	6.92 ± 0.06	9.22 ± 0.10	34.7 ± 1.8	-152 ± 8.7
p-OEt	4.09 ± 0.05	5.04 ± 0.02	6.31 ± 0.08	30.4 ± 1.2	-169 ± 9.2
p-OMe	2.18 ± 0.03	2.88 ± 0.04	4.20 ± 0.07	46.6 ± 2.6	-121 ± 3.0
ρ_{EWG}	0.429 ± 0.01	0.398 ± 0.02	0.474 ± 0.06		
r	0.967	0.975	0.970		
ρ_{EDG}	1.45 ± 0.04	1.48 ± 0.02	1.48 ± 0.06		
r	0.994	0.995	0.985		
			MeIm		
p-Cl	10.1 ± 0.13	13.2 ± 0.11	20.4 ± 0.18	50.5 ± 2.5	-95.0 ± 4.1
m-Cl	10.5 ± 0.21	13.6 ± 0.13	22.6 ± 0.16	56.2 ± 3.2	-75.1 ± 3.9
p-F	8.34 ± 0.08	10.6 ± 0.03	15.9 ± 0.10	46.3 ± 2.1	-110 ± 8.8
p-Br	10.9 ± 0.12	12.9 ± 0.08	20.2 ± 0.15	44.4 ± 3.0	-115 ± 1.3
H	7.98 ± 0.04	9.68 ± 0.02	12.3 ± 0.11	30.4 ± 2.2	-164 ± 6.2
p-Me	3.00 ± 0.01	4.54 ± 0.03	6.50 ± 0.08	56.4 ± 3.8	-84.8 ± 5.4
p-OEt	2.14 ± 0.06	2.58 ± 0.02	3.97 ± 0.04	44.5 ± 3.1	-128 ± 7.3
p-OMe	0.980 ± 0.02	1.21 ± 0.03	1.82 ± 0.03	44.7 ± 2.8	-134 ± 10.2
ρ_{EWG}	0.341 ± 0.03	0.413 ± 0.01	0.672 ± 0.02		
r	0.968	0.960	0.956		
ρ_{EDG}	2.40 ± 0.11	2.30 ± 0.09	1.97 ± 0.06		
r	0.999	0.988	0.987		

[PSAA] = 5.0×10^{-2} M; [H_2O_2] = 5×10^{-3} M; [Py] = [Im] = [MeIm] = 5×10^{-4} M;
[**I**] = 3×10^{-4} M; Temp. = 30 °C; solvent = 100 % CH_3CN.

The results reveal that the reaction is fairly susceptible to EWGs with small positive ρ values (0.287 to 0.672) while the EDGs are found to exert a higher effect on the reaction rate as indicated by the fairly high positive ρ values (0.691 to 2.40). The values of ρ obtained for the oxovanadium(IV)-salophen complex with three nitrogen bases are given in Table4. The positive ρ values indicate the electrophilic behavior of PSAA towards the oxidant in the reaction.

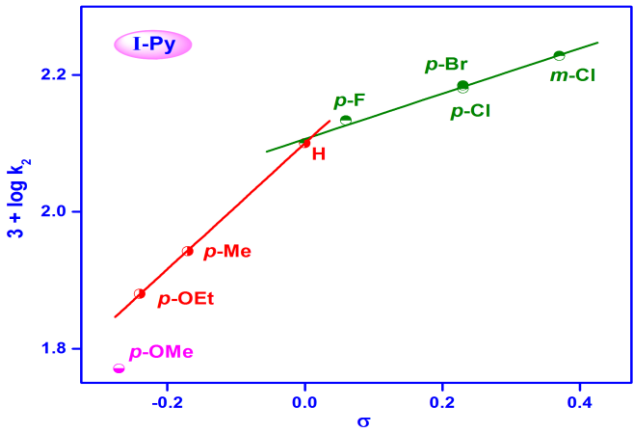


Fig. 4. Hammett plot for the reaction between PSAAs and H_2O_2 with complex **I**.

[PSAA] = 5.0×10^{-2} M; [H_2O_2] = 5.0×10^{-3} M; [**I**] = 3.0×10^{-4} M;[N-base] = 5.0×10^{-4} M; solvent = 100 % CH_3CN; T = 30°C.

3.6. Influence of temperature and thermodynamic parameters

The kinetic data for the reactions of PSAAs and H_2O_2 at 25, 30 and 35 ºC with complex **I** in the presence of N-bases (Table 4) show a linear increase in the rate of oxidation with temperature. The thermodynamic parameters, $\Delta^{\ddagger}H$ and $\Delta^{\ddagger}S$ evaluated from the slope and intercept of the linear Eyring′s plots (Fig. 5) are shown in Table 4. The entropy of activation is found to be negative and the enthalpy of activation is small. The positive $\Delta^{\ddagger}H$ values suggest that the reaction is endothermic in nature. A plot of $\Delta^{\ddagger}H$ *vs.* $\Delta^{\ddagger}S$ for the reactions of PSAAs and H_2O_2 with **I** in the presence of pyridine is shown in Fig. 6. The linear isokinetic relation between $\Delta^{\ddagger}H$ and $\Delta^{\ddagger}S$ reveals that all PSAAs follow the same mechanism.

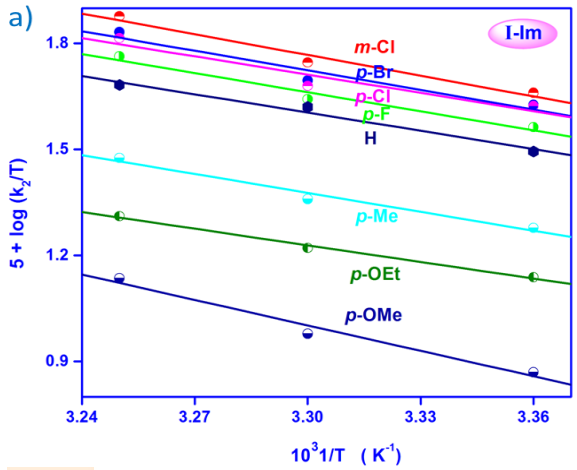


Fig. 5. Eyring′s plots for the reactions of PSAAs and H_2O_2 in the presence of complex and N-base; General conditions as in Table 4

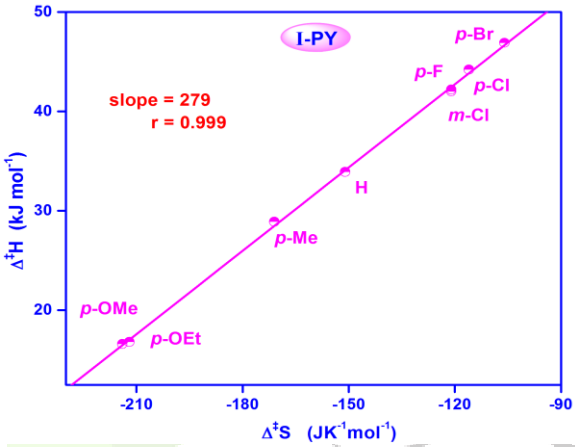


Fig.6. Plot of $\Delta^{\ddagger}H$ *vs.* $\Delta^{\ddagger}S$ for the reactions with **I** in the presence of Pyridine.

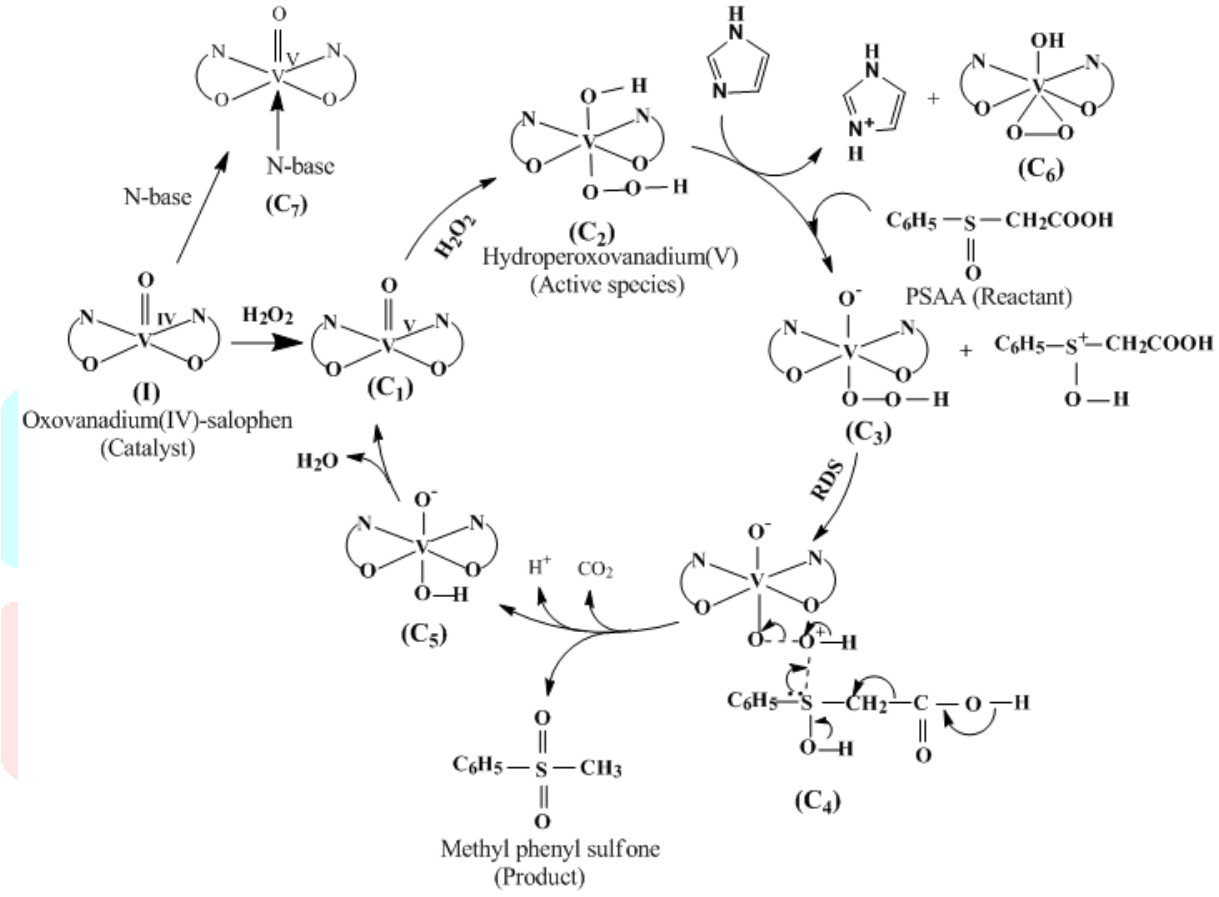
4. DISCUSSION

4.1. Mechanism

The reaction involving hydroperoxo species formation is proposed as the mechanistic pathway for the reaction in the presence of N-base amidst the retarding forces of bases. It is proposed that in the first step, oxovanadium(IV)-salophen complex is oxidized to oxovanadium(V) salophen (**C_1**) that further reacts with another molecule of hydrogen peroxide in the second step to form the active species, hydroperoxovanadium(V)-salophen (**C_2**). As the active species (**C_2**) contains the acidic hydroxyl group, it readily releases a proton and transforms into the intermediate (**C_3**). The proton released from **C_2** polarizes the sulfoxide group of PSAA, rendering sulfur electrophilic in nature. The behaviour of sulfoxide in a reaction can be ascertained from the sign of the ρ value from the Hammett correlation. Usually negative ρ value for nucleophilic sulfoxides(Jayaseeli, A.M.I. and Rajagopal, S., 2009) and positive ρ value for electrophilic sulfoxides(Rajagopal, S., et al. 1991).have been reported in reactions with different substituents. In the present study from the observed positive ρ values for both electron donating and electron withdrawing groups of PSAA in the Hammett correlation, it is concluded that PSAA behaves as an electrophile. On this basis, an electrophilic attack of sulfur atom of PSAA on the peroxonucleophilic oxygen, leading to the formation of the transition state (**C_4**) in a slow rate determining step is proposed for the reaction. Along with these main steps in the catalytic cycle, two other reactions are also possible in the presence of N-bases. Oxovanadium(IV)- salophen complex combines with the nitrogen base to form the 1:1 oxovanadium(IV) salophen-nitrogen base adduct (**C_7**) which competes with the formation of active vanadium peroxo species (**C_2**). In addition, the N-base abstracts a proton from the active hydroperoxo oxidizing species (**C_2**) and transforms to a less active cyclic peroxo species (**C_6**) in the catalytic cycle. Based on the above facts, Scheme 2 has been proposed for the oxovanadium(IV)-salophen catalytic oxidation of PSAA by H_2O_2 in the presence of nitrogen bases.

The proposed rate determining step (RDS) is in consistence with the observed substituent effect i.e., increase in rate with EWG in PSAA and decrease in rate with EDG in PSAA. EDG in the phenyl ring of PSAA makes sulfur less electropositive and thus slows down the electrophilic attack of PSAA on the nucleophilic oxygen, whereas the EWG in the phenyl ring of PSAA makes sulfur atom more electropositive and thereby facilitates the electrophilic approach of sulfur towards the nucleophilicperoxo oxygen. A similar nucleophilic oxygen transfer from the active hydroperoxide to electropositive sulfur atom has been proposed in the vanadium-Schiff base catalyzed sulfoxidation (Jeong, Y.C., et al. 2009). The intermediate (**C_4**) then undergoes fast internal oxygen atom transfer leading to the formation of methyl phenyl sulfone with the regeneration of oxovanadium(V) complex. The regeneration of oxovanadium(V)-salophen complex has been confirmed during the product analysis.

The observed decrease in reaction rate at high concentrations of hydrogen peroxide may be visualized by the conversion of vanadium complex into inorganic peroxovanadate. In addition to that, the rate of reaction increases with increase in concentration of oxovanadium(IV)-salophen complex in the presence of N-base. This may be due to the increase in concentration of active hydroperoxo species and the decrease in percentage conversion into inactive diperoxo vanadate, with increase in concentration of complex.



Scheme 2. Mechanistic pathway for the oxovanadium(IV) salophencatalysed oxidation of PSAA by H_2O_2 in the presence of N-bases.

4.2 Effect of nitrogen bases and reactivity

Covalently attached axial ligand 'tails' are commonly employed in functional biomimetic modeling (Collman, James P., et al.1999) and alkene epoxidation catalysis (Banfi, S., et al. 1990). It has been proved that one molecule of added ligand enters into the coordination sphere of oxo(salen)chromium(V) prior to the reaction with the substrate (Srinivasan, K. and Kochi, J.K., 1985). In the Mn^{III}(salen) catalysedepoxidation of olefins (Bahramian, B., et al. 2006) coordination of 1-MeIm with the sixth coordination site of oxoMn^{V}(salen) intermediate has been proposed as the active species. Abbo et al. 2013 have confirmed the coordination between the N-pyridine moiety and the vanadium metal ion in the crystal structure of pyrazolyl-pyridine V(III) complex, that was used as a catalyst for ethylene polymerization. The rate enhancement observed with axial ligands in the oxidation and epoxidation reactions,involving salen as catalyst Srinivasan, K., et al., 1986) was explained on the basis of easy transfer of oxygen atom from oxo(salen) intermediates to the substrate, facilitated by the binding of donor ligands to salen.

In all the above rate acceleration reactions in the presence of added ligands where 1:1 adduct was identified as the active oxidizing species, a shift in the λ_{max} and change in OD were observed. In the present study, from the kinetic data (Table 3) it is observed that rate constants in the presence of N-bases decreases, indicating that the N-bases impede the catalytic activity of oxovanadium(IV)-salophen complex. The observed rate retardation along with no shift in λ_{max} and unchanged OD values of complexes with nitrogen bases in the present case, unambiguously ruled out the adduct formation between oxovanadium(V)-salophen and nitrogen base as the active species.

However, binding of nitrogen base to the complex was identified as the major cause for rate retardation in the following cases. Decrease in the rate of sulfoxidation of thiodiglycolic acid with axial ligands Py, Im and MeIm in $[Fe(III)salen]^+$ reaction was explained on the basis of 1:1 adduct formation between $[Fe(III)salen]^+$ and N-base. It has been concluded that coordination of nitrogen base with salen complex prevents the binding of substrate with $[Fe(III)salen]^+$. The binding of Im with the reactive site of the complex was given as the explanation for the absence of oxygenation reaction between methyl phenyl sulfide and oxo(salen)iron complex in the presence of Im(Sivasubramanian, V.K., et al 2002). In the Mn^{III}(salen) catalysed H_2O_2 oxidation of diphenylsulphide(Chellamani,A. and Alhaji, N.M.I., 2009)and methyl phenyl sulfide(Chellamani et al. 2007) have shown that nitrogen bases bind irreversibly and strongly at the metal centre of the reactive species which prevents the binding of sulphides to the reactive species, that is an essential condition for the oxidation reaction to proceed. The low rate constant value in oxovanadium(IV)-salen catalyzed sulfoxidation of phenylmercaptoacetic acids (PMAA) by hydrogen peroxide in the presence of the nitrogen base, has been attributed to the competition of nitrogen base with H_2O_2 and PMAA during the formation of active species and the coordination of PMAA with active species.

On the basis of the above discussions, it has been concluded that the observed rate retardation with nitrogen base in the present study, is due to the formation of a 1:1 oxovanadium(IV) salophen-nitrogen base adduct (**C_7**) in small amount (Fig.7) which competes with the formation of active vanadium peroxo species (**C_2**).

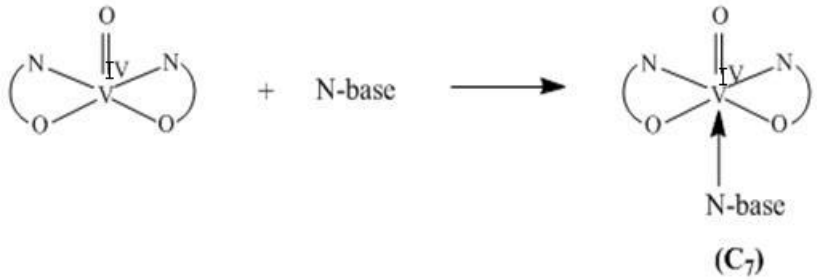


Fig. 7. Formation of nitrogen base adduct with complex.

As there is a competition between the peroxo species formation (**C_2**) and the 1:1 adduct formation (**C_7**) in the reaction mixture, nitrogen bases restrict the free coordination site of oxovanadium(IV)-salophen that would be required for binding of H_2O_2 and for the generation of active species for the reaction to take place. Hence, the observed decrease in reaction rate with increase in nitrogen base concentration, can be explained on the basis of prevention of binding of H_2O_2 with oxovanadium(IV)-salophen by nitrogen bases.

In the study of proximal effect of nitrogen donor ligands during the epoxidation of olefins by the NaOCl/Mn(III) porphyrin(Meunier, Bernard, et al. 1988),Im has been shown as better axial ligand than Py in enhancing the catalytic activity. In the present study also strong π donating ligands like Im and MeIm have higher retarding effect than less π donating pyridine ligand. This gives a direct evidence that Im and MeIm can form adduct with oxovanadium(IV) salophen complex more easily than Py which prevents the formation of active hydroperoxo vanadium complex to a greater extent and leads to a higher retardation in reaction rate. The increase in retarding effect with increase in concentration of N-base may be due to the decrease in concentration of active hydroperoxovanadium(V) species.

It is interesting to note that among the three nitrogenous bases investigated, MeIm with a strong π-donating ability (Bagherzadeh, Mojtaba, et al. 2008) shows the highest retarding effect on rate in the oxovanadium(IV) salophen complex. MeIm has higher binding ability than Im with the low electron density vanadium atom of the complex and shows less reactivity by preventing the attack of H_2O_2 on complex. Further, as Py has the weakest π-donating ability among different nitrogenous bases used (Safo, Martin K., et al. 1992). Py has the least binding ability and shows higher reactivity.Thus the observed order of reactivity among the N-bases is found to be Py>Im>MeIm. This observed order of reactivity gives an additional evidence for the proposal that the binding of the N-base with the vanadium atom of the salophen complex is the major cause for rate retardation.

Another possible reason for the rate retardation with nitrogenous bases is, the conversion of more active hydroperoxo oxidizing species (**C_2**) to less active cyclic peroxo species (**C_6**) in the catalytic cycle, by the abstraction of proton from the active hydroperoxo vanadium species. The possibility of existence of the cyclic peroxo species in acetonitrile medium has been proposed by (Colettiet al 2012). using theoretical studies. The less active cyclic peroxo intermediate species hinders the oxidation of PSAA by hydroperoxovanadium(V) species and causes a further retardation in rate, in addition to the retardation of rate caused due to the formation of adduct. Proton abstraction from metal coordinated H_2O_2 by N-base has also been proposed in the catalytic oxidation of sulfides to sulfoxides by UHP using Mn(III)-oxazoline complexes, in the presence of imidazole (Bagherzadeh, M., et al. 2008)and in the oxidation of olefins and sulfides, catalysed by Manganese(III)-tridentate Schiff base complex using UHP as oxidant (Rayati, S. and Nejabat, F., 2016). Thus the observed order of reactivity in the presence of nitrogen base unambiguously supports the proposed scheme of mechanism.

4.3. Nonlinear Hammett plot and Ground state stabilization of PSAAs

In the present study, stabilization of the ground state of PSAA through resonance interaction, on changing the substituents from electron withdrawing to electron releasing is proposed to explain the apparent curvature in the Hammett plots as reported earlier (Jeevi Esther Rathnakumari, R.et al.2016). The resonance interaction between the electron donating substituent and the thionyl functionality is represented in Fig. 8.

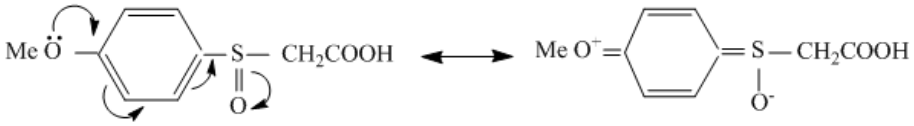


Fig. 8. Ground state stabilization of PSAA.

The presence of such resonance structures in electron releasing groups, stabilizes the GS of PSAA causing decrease in reactivity [Um, I.H., et al 2019 &Alenzi, R.A., et al 2020]. The above argument is supported by the significant positive deviation observed in the Hammett plot as the substituent becomes a stronger EDG (Fig.4). Accordingly, a large ρ value can be expected for EDG when compared with EWG. In fact, the ρ value increases from 0.672 for those with EWG to 2.40 with EDG. Thus, the deviation from Hammett correlation is considered as the evidence for ground state stabilization by EDG.To ascertain the validity of the above argument, the rate data have been treated with the Yukawa-Tsuno equation (Tsuno, Y. and Fujio, M., 1999).

$$\log (k_X / k_H) = \rho [\sigma^o + r (\sigma^+ - \sigma^o)]$$

The term $(\sigma^+ - \sigma^o)$ is the resonance substituent constant, while the 'r' value is a parameter characteristic of the extent of resonance contribution. The observed linear Yukawa-Tsuno plots (Fig.9) for the reactions under study and almost unit 'r' values obtained suggest that resonance interaction is relatively significant. The linear Yukawa-Tsuno plots not only confirm a common mechanism for all PSAAs but also prove that the ground state stabilization of PSAAs through resonance interaction is the cause for the observed non linearity in the Hammett plot.

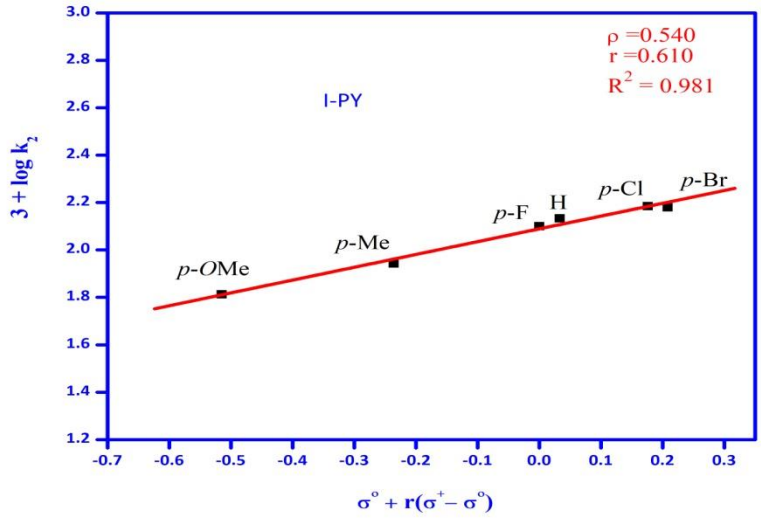


Fig. 9. Yukawa-Tsuno plots for the reactions of complex **I** at 30 ^oC in the presence of N-base

CONCLUSION

The influence of nitrogen bases such as pyridine, imidazole and 1-methyl imidazole on the oxidative decarboxylation of several phenylsulfinylacetic acids to methylphenylsulfone by H_2O_2, catalyzed by oxovanadium(IV)-salophen complex has been studied. The findings show that nitrogen base forms a 1:1 oxovanadium(IV)-salophen-nitrogen base adduct, which competes with the formation of active vanadium peroxo species. Also it converts the more active hydroperoxo oxidizing species to less active cyclic peroxo species in the catalytic cycle and thus causes an impeding effect in the reaction. The observed order of reactivity among the N-bases, Py>Im>MeIm with the complex has been explained on the basis of π-donating ability of the N-bases. A suitable mechanism involving hydroperoxovanadium(V)-salophen as the active oxidizing species has been proposed for the reaction. The linear Yukawa-Tsuno plots and non linear Hammett plots prove the ground state stabilization of PSAAs through resonance interaction. While vanadium catalysts can offer competitive reactivity to those of developed metals, additional work toward the understanding of structure−activity relationships is needed, requiring more integrated and comprehensive comparisons of catalytic systems containing vanadium.

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