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RELATIVE REACTIVITY OF OXOVANADIUM (IV)-SALOPHEN COMPLEXES AND IMPEDING EFFECT OF NITROGEN BASES IN THE OXIDATION OF PHENYLSULFINYLACETIC ACID BY HYDROGEN PEROXIDE

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Abstract: Owing to the varied biological activities exhibited by the nitrogen bases like pyridine (Py), imidazole (Im) and methylimidazole (MeIm) the kinetic study for the reactions of PSAA with H_2O_2 catalysed by the different oxovanadium(IV)-salophen complexes were carried out in the presence of nitrogen bases like Py,Im and MeIm. The reactions were monitored spectrophotometrically in 100 % acetonitrile medium under pseudo first-order conditions with excess of [PSAA] over the oxidant and complex concentrations. Kinetic study reveals the rate of the reaction increases with increase in concentration of the complex and hydrogen peroxide whereas the rate of the reaction is strongly retarded by all the three bases.

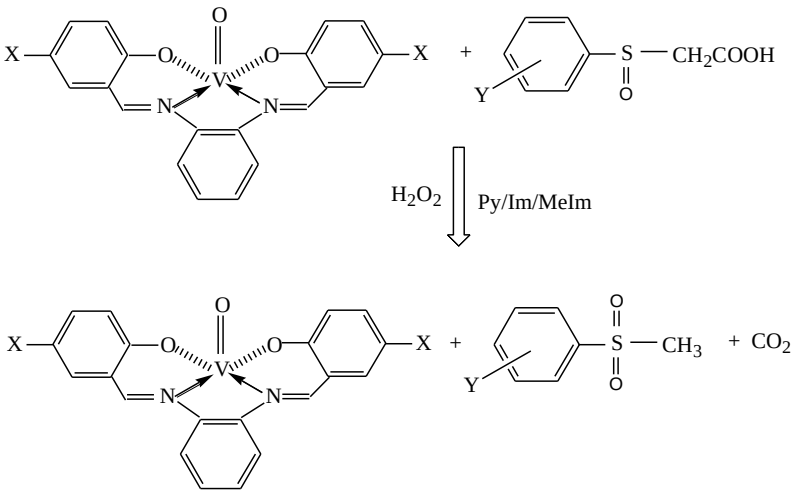
Keywords **–** Oxovanadium(IV)-salophen, phenylsulfinylacetic acids, nitrogen bases

1. INTRODUCTION

Vanadium(V) complexes with O,N coordination are regarded as bioinorganic catalysts as the prosthetic groups present in the enzymes vanadate dependent peroxidases have similar coordination environment. The use of vanadium in humans is recommended in cases of pathological conditions such as malnutrition, anemia, tuberculosis and diabetes (Correia, et al. 2004). Vanadyl compounds with different coordination modes have been designed and synthesized for their clinical use (Sakurai, et al. 2002, Liboiron, et al. 2005). Some Schiff-base complexes of oxovanadium(IV) display insulin enhancing properties (Mukherjee, et al. 2011). Salophen which is N,N'-Bis(salicylidene)-1,2-phenylenediamine is a popular symmetrical tetradendate ligand and its analogue, salen form complexes with various metal ions and these metal-salen (salophen) complexes find extensive application in catalysis and as sensor and drug. Salophen ligand readily combines with vanadium salts and forms oxovanadium complexes which show binding properties with proteins. The cation OV(IV) can potentially interact with amine, amide, hydroxyl, imidazole, thiolate and carboxylate functionalities of proteins (Gätjens, et al. 2006). VO-Salophen complex electronic structure was investigated to study the solvent polarity and Coordination ability of metal

complexes (Bertini, et al. 2015). Chromium Salophen complexes has been extensively used for carboxylation of styrene (Balas, et al. 2023).

Nitrogen bases like imidazole(Im),pyridine(Py) and their derivatives exhibit various type of biological activities *viz.*, antimicrobial, analgesics, anticancer, antidiabetic etc (Shalini, et al. 2010, Desai, et al. 2022). Addition of imidazole, 1-methyl imidazole, pyridine or pyridine-N-oxide to metal-salen complexes significantly lowers the oxidation potential by coordination with the metal and results in altering the electrochemical properties and reactivity (Kalow, et al. 2011, Bahramian, et al. 2006, Venkataramanan, et al. 2006). The reactivity of vanadium salen/salophen complexes in the sulfoxidation of PMAA (Kavitha, C., & Subramaniam, P. 2020, 2022, 2023) and PSAA (Jeevi Esther Rathnakumari, et al. 2016) using hydrogen peroxide in Acetonitrile medium have been investigated. This paper reveals the effect of substituents in the salophen moiety of oxo vanadium(IV)-salophen and the effect of nitrogen bases like Im, MeIm and Py on the oxidative decarboxylation of PSAA. The overall reaction scheme is represented as



Scheme 1: Complex : (**I**) : X = H; (**II**) : X = OCH_3; (**III**): X = CH_3 ; (**IV**) : X = Cl
PSAA : Y = H

2. EXPERIMENTAL

2.1 Materials and Methods

The materials and methods of preparation of phenylsulfinylacetic acids and the synthesis of oxovanadium(IV)-salophen complexes have been reported in the earlier paper (Jeevi Esther Rathnakumari, et al. 2016).

2.2 Kinetic Studies

The kinetic study for the reaction of PSAA with the oxo vanadium(IV)-salophen complexes 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 and complex concentrations. A double beam BL 222 Elico UV-vis spectrophotometer with an inbuilt thermostat was employed to record the absorption spectra, to measure the absorbance of the complex and also to follow the kinetics of the reaction. The reactions were started by quickly injecting the H_2O_2 into the reaction mixture containing PSAA, oxovanadium(IV)-salophen complex and the nitrogen base at zero time, in a quartz cuvette. The progress of the reaction was followed by monitoring the decrease in absorbance of the complex at the appropriate wavelength. The pseudo first order rate constants were calculated from the slope of the linear plots of log OD *vs.* time. The second order rate constants were calculated by dividing the pseudo first order rate constants with the concentration of the substrate. The error in the rate constants were given according to 95% of the student's t-test.. The absorption spectral studies and the active species formation have been reported in the previous paper (Jeevi Esther Rathnakumari, et al. 2023).

3. RESULTS

3.1 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. Representative pseudo first-order plots at different [PSAA] are represented in Fig. 1. 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 (Fig. 3) for all the four oxovanadium(IV) salophen complexes in the presence of nitrogen bases.

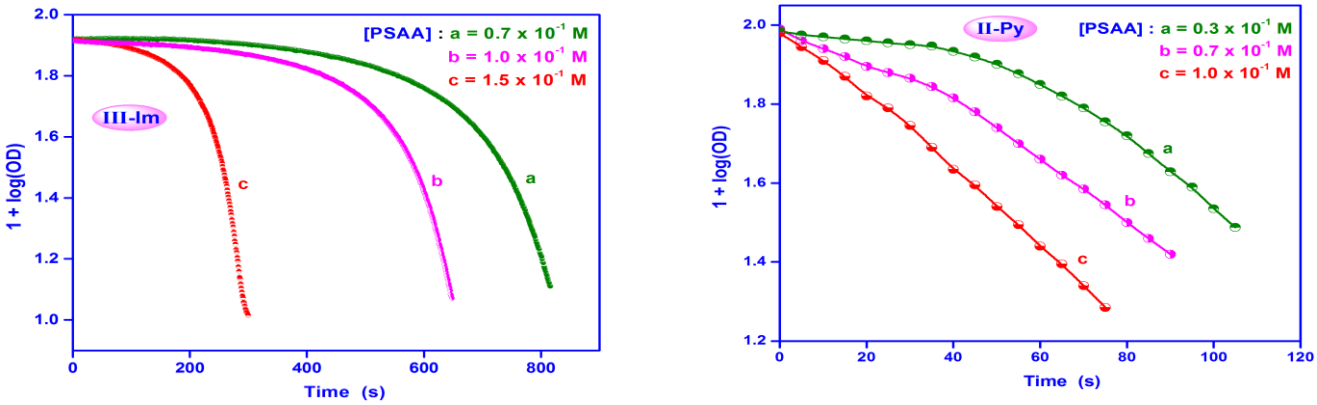


Figure 1 Log (OD) *vs.* time plots for [PSAA] variation.
$[H_2O_2] = 3.0 \times 10^{-4}$ M; **[II] = [III] =** 3.0×10^{-4} M; [N-base] = 5.0×10^{-4} M

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
			II			
0.3	6.26 ± 0.07	20.9 ± 2.3	5.12 ± 0.06	17.1 ± 0.20	5.99 ± 0.08	20.0 ± 2.6
0.7	16.1 ± 0.22	23.0 ± 3.1	11.3 ± 0.09	16.1 ± 1.3	14.1 ± 0.12	20.1 ± 1.7
1.0	23.2 ± 0.34	23.2 ± 3.4	17.8 ± 0.11	17.8 ± 1.1	21.4 ± 0.31	21.4 ± 3.1
1.5	31.4 ± 0.62	20.9 ± 4.1	25.2 ± 0.28	16.8 ± 1.9	28.5 ± 0.28	19.0 ± 1.8
			III			
0.3	3.09 ± 0.01	10.3 ± 0.33	2.22 ± 0.07	7.40 ± 2.3	2.98 ± 0.05	9.93 ± 1.6
0.7	6.85 ± 0.08	9.79 ± 1.1	5.66 ± 0.14	8.09 ± 2.0	6.81 ± 0.12	9.73 ± 1.7
1.0	9.61 ± 0.21	9.61 ± 2.1	8.11 ± 0.11	8.11 ± 1.1	9.03 ± 0.13	9.03 ± 1.3
1.5	14.9 ± 0.32	9.93 ± 2.1	13.0 ± 0.22	8.66 ± 1.5	14.1 ± 0.09	9.40 ± 0.60
			IV[a]			
0.5	0.300 ± 0.02	0.600 ± 0.40	0.223 ± 0.05	0.446 ± 1.0	0.161 ± 0.03	0.323 ± 0.60
0.7	0.460 ± 0.03	0.657 ± 0.43	0.350 ± 0.02	0.500 ± 0.28	0.250 ± 0.04	0.357 ± 0.57
1.0	0.623 ± 0.05	0.623 ± 0.50	0.447 ± 0.03	0.447 ± 0.30	0.345 ± 0.09	0.345 ± 0.90
1.5	1.01 ± 0.07	0.673 ± 0.47	0.725 ± 0.02	0.483 ± 0.13	0.515 ± 0.20	0.343 ± 1.3

[**I**] = [**II**] = [**III**] = 3.0×10^{-4} M; [**IV**] = 1.0×10^{-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; [a][N-base] = 2.5×10^{-4} M, $[H_2O_2] = 5.0 \times 10^{-3}$ M.

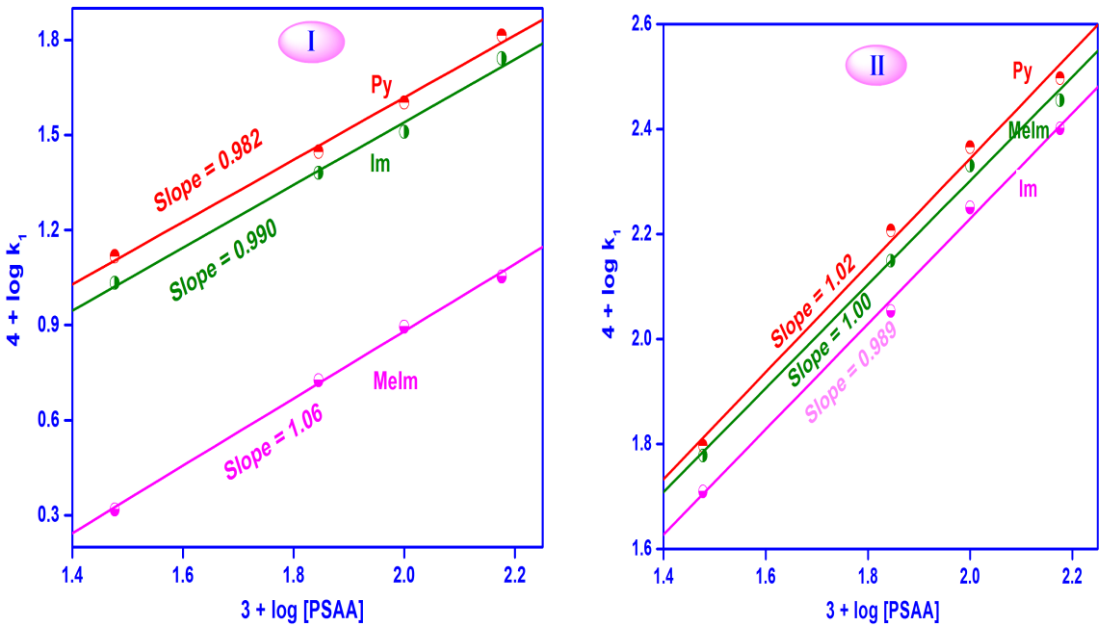


Figure 2 Plots of log k_1 *vs*. log [PSAA]. General conditions as in Table 1.

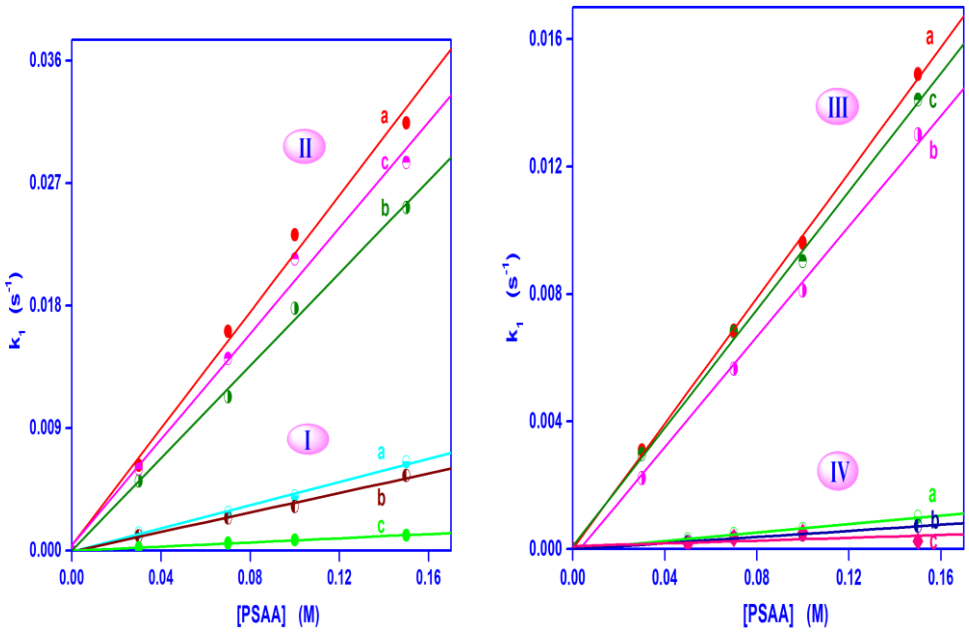


Figure 3 Plots of k_1 *vs*. [PSAA] in the presence of nitrogen bases
a = Py; b = Im; c = MeIm; General conditions as in Table 1

Kinetic runs were carried out with different concentrations of H_2O_2 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. 4). 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 the reaction rate begins to decrease for all the complexes (**I**-**IV**) (Table 2).

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
		II	
1.0	14.7 ± 0.18	10.1 ± 0.11	11.7 ± 0.23
3.0	22.8 ± 0.17	14.8 ± 0.08	17.9 ± 0.14
5.0	31.9 ± 0.61	18.1 ± 0.22	24.4 ± 0.28
7.0	41.4 ± 0.51	22.4 ± 1.1	33.0 ± 0.62
9.0	48.1 ± 0.24	37.0 ± 0.09	41.8 ± 0.16
11.0	39.2 ± 0.33	33.2 ± 0.13	36.2 ± 0.15
		III	
1.0	5.10 ± 1.1	2.94 ± 0.20	3.12 ± 0.08
3.0	6.91 ± 0.61	4.01 ± 0.14	5.23 ± 0.22
5.0	9.68 ± 0.22	7.50 ± 0.09	8.45 ± 0.15
7.0	15.7 ± 1.1	11.1 ± 0.26	13.8 ± 0.36
9.0	20.1 ± 0.09	15.1 ± 0.11	17.9 ± 0.21
11.0	17.2 ± 0.16	13.8 ± 0.22	15.4 ± 0.20
		IV[a]	
1.0	0.180 ± 0.01	0.102 ± 0.01	-
3.0	0.248 ± 0.02	0.172 ± 0.02	0.148 ± 0.04
5.0	0.434 ± 0.08	0.267 ± 0.04	0.214 ± 0.03
7.0	0.610 ± 0.03	0.416 ± 0.06	0.388 ± 0.04
9.0	0.781 ± 0.04	0.581 ± 0.03	0.479 ± 0.02
11.0	0.662 ± 0.03	0.485 ± 0.03	0.390 ± 0.01

[PSAA] = 7.0×10^{-2} M; [**I**] = [**II**] = [**III**] = [**IV**] = 5.0×10^{-5} M; Temp. = 30 °C; [N-base] = 5.0×10^{-4} M; [a][N-base] = 2.5×10^{-4} M; solvent = 100 % CH_3CN.

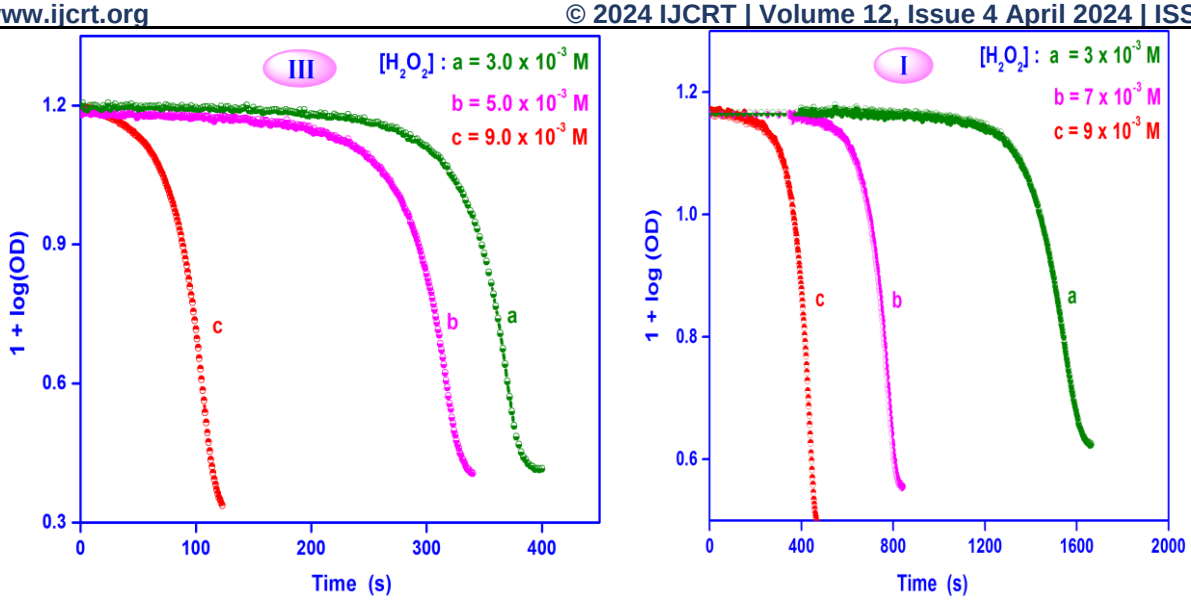


Figure 4 Pseudo first-order plots at different $[H_2O_2]$. [PSAA] = 7.0×10^{-2} M; [**I**] = [**III**] = 5.0×10^{-5} M; [Py] = 5.0×10^{-4} M.

3.2 Relative reactivity of salophen complexes

Realizing the importance of electronic and steric effects in the reactivity of salen/salophen mediated reactions, the reaction has been carried out in the presence of four salophen complexes with different substituents in the salophen moiety. The rate constants obtained with four complexes in the presence of different N-bases are presented in Table 3. It is observed that the pseudo first-order rate constant increases with increase in concentration of oxovanadium(IV) salophen complexes. The data shows that the introduction of electron donating groups (EDG) in the salophen moiety enhances the reaction rate while the electron withdrawing groups (EWG) retard the reaction rate compared to the unsubstituted oxovanadium(IV) salophen complex (**I**). The observed order of reactivity among four oxovanadium(IV) salophen complexes in the presence of different N-bases is II > III > I > IV.

Table 3 Catalytic effect of oxovanadium(IV) salophen complexes in the presence of nitrogen bases.

10^4 [complex] (M)	$10^3 k_1$ (s^{-1})		
	Py	Im	MeIm
	I		
0.25	2.26 ± 0.06	2.10 ± 0.10	1.06 ± 0.11
0.50	3.30 ± 0.08	2.88 ± 0.04	1.79 ± 0.08
1.50	7.34 ± 0.20	6.12 ± 0.20	4.98 ± 0.32
3.00	11.1 ± 0.08	10.3 ± 0.12	9.09 ± 0.25
	II		
0.25	13.8 ± 0.54	9.56 ± 0.80	11.8 ± 0.22
0.50	41.4 ± 0.51	22.4 ± 1.1	33.0 ± 0.62
1.50	54.6 ± 1.4	38.9 ± 2.1	42.6 ± 2.5
3.00	79.1 ± 2.2	54.0 ± 1.9	60.6 ± 1.3
	III		
0.25	4.79 ± 0.22	3.15 ± 0.02	3.42 ± 0.03
0.50	15.7 ± 1.1	11.1 ± 0.26	13.8 ± 0.36
1.50	22.5 ± 1.0	18.3 ± 1.2	20.9 ± 0.08
3.00	28.5 ± 0.90	24.8 ± 0.30	26.3 ± 0.11
	IV[a]		

0.25	0.509 ± 0.04	0.380 ± 0.01	0.291 ± 0.02
0.50	0.610 ± 0.03	0.416± 0.06	0.388 ± 0.04
1.50	0.784± 0.06	0.590 ± 0.04	0.522 ± 0.05
3.00	0.891 ± 0.02	0.698 ± 0.03	0.630 ± 0.01

[PSAA] = 7.0×10^{-2} M; [H_2O_2] = 7.0×10^{-3} M; Temp. = 30 °C; Solvent = 100% CH_3CN; [N-base] = 5.0×10^{-4} M; [a][N-base] = 2.5×10^{-4} M.

3.3 Influence of reaction rate by nitrogen bases

To evaluate the effect of nitrogen bases on the reaction rate, the reactions of PSAA and H_2O_2 with complexes **I-IV** are 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 4. The dependence of pseudo first-order rate constant on the concentration of the nitrogen bases for complexes **I-IV** is shown in Fig. 5.

Table 4 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
	II		
0	45.4 ± 0.19	45.4 ± 0.19	45.4 ± 0.19
0.50	41.4 ± 0.51	22.4 ± 1.1	33.0 ± 0.62
0.75	34.0 ± 0.20	15.4 ± 0.80	19.1 ± 0.42
1.0	23.4 ± 1.1	8.13 ± 0.63	11.9 ± 0.26
2.5	12.9 ± 0.25	4.19 ± 0.20	4.86 ± 0.30
3.5	7.97 ± 0.09	3.01 ± 0.18	3.78 ± 0.51
5.0	4.96 ± 0.15	1.61 ± 0.02	2.46 ± 0.08
	III		
0	28.7 ± 0.07	28.7 ± 0.07	28.7 ± 0.07
0.50	15.7 ± 1.1	11.1 ± 0.26	13.8 ± 0.36
0.75	12.4 ± 1.0	6.72 ± 0.48	10.3 ± 0.51
1.0	9.44 ± 0.32	4.24 ± 0.51	7.07 ± 0.22
2.5	5.01 ± 0.16	2.51 ± 0.62	3.72 ± 0.08
3.5	2.86 ± 0.02	1.54 ± 0.08	2.13 ± 0.06
5.0	1.60 ± 0.04	1.00 ± 0.10	1.30 ± 0.02
	IV		

0	0.646 ± 0.05	0.646 ± 0.05	0.646 ± 0.05
0.25	0.610 ± 0.03	0.416 ± 0.06	0.388 ± 0.04
0.30	0.465 ± 0.02	0.329 ± 0.04	0.309 ± 0.01
0.40	0.320 ± 0.04	0.231 ± 0.01	0.220 ± 0.02
0.50	0.258 ± 0.03	0.185 ± 0.02	0.165 ± 0.04

[PSAA] = 7.0×10^{-2} M; [H_2O_2] = 7.0×10^{-3} M; [**I**] = [**II**] = [**III**] = [**IV**] = 5.0×10^{-5} M;

Temp. = 30 ^{o}C; solvent = 100% CH_3CN

Examination of the kinetic results reveals that the reaction rate is highly sensitive to the nature of base and is strongly retarded by all the three nitrogen bases. The data in Table 4 and Fig. 5 also rule out the saturation kinetics with [N-base]. The determination of rate constant is restricted only to the concentration range of nitrogen bases mentioned in the Table 4 because beyond this range the reaction is too slow to measure. The prevention of hydroperoxo species generation may be the reason for the profound rate retardation observed with N-base.

Among the three nitrogen bases, MeIm shows the highest rate retardation with complexes **I** and **IV** while Im shows the highest rate retardation in reactions involving complex **II** and **III**. The rate constants in Table 4 clearly show that the observed order of retardation among the three different N-bases is Py > Im > MeIm with complexes **I** and **IV**, and Py > MeIm > Im with complexes **II** and **III**.

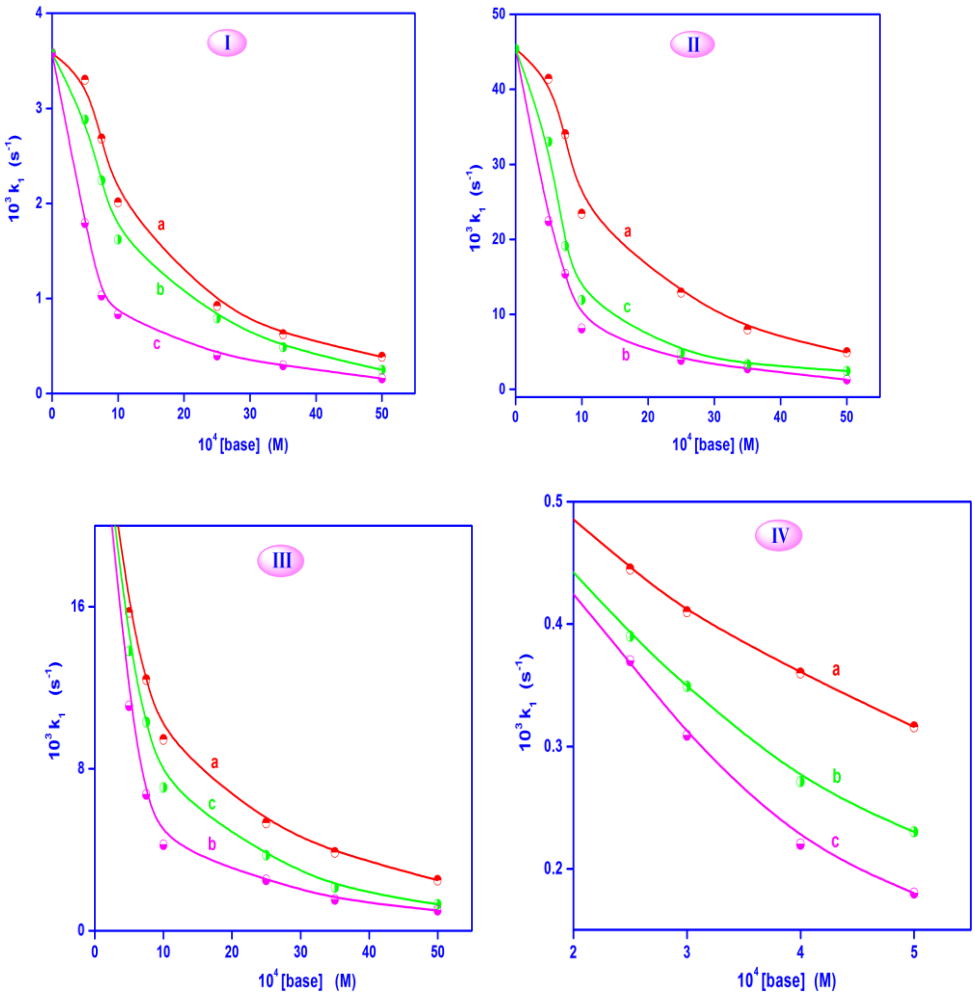


Figure 5 Variation of pseudo first-order rate constant with [N-base].
[PSAA] = 7.0×10^{-2} M; [H_2O_2] = 7.0×10^{-3} M; [**I-IV**] = 5.0×10^{-5} M;
a = Py, b = Im, c = MeIm.

4. DISCUSSION

The observed decrease in reaction rate at high concentrations of hydrogen peroxide in all the four complexes (**I**-**IV**) may be visualized by the conversion of vanadium complex into inorganic peroxovanadate (Jeevi Esther Rathnakumari, et al. 2023). The existence of diperoxovanadates at higher concentration of H_2O_2 is proposed in the reactions of vanadium catalysed oxidation with hydrogen peroxide peroxide (Conte, & Floris, 2010) and proved by ^{51}V NMR studies (Karpyshev, et al. 2000).

The rate of the reaction is found to increase 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 decrease in percentage conversion into inactive diperoxo vanadate with increase in concentration of complex.

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. It is observed that the rate constant decreases with the increase in nitrogen base concentration. 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 phenylmercaptoacetic acids by axial ligands Py, Im and MeIm in oxovanadium(IV)-salen complex reaction (Kavitha, & Subramaniam, 2020) was explained on the basis of 1:1 adduct formation between oxovanadium(IV)-salen complex and N-base. A similar decrease in the rate of sulfoxidation of thiodiglycolic acid by axial ligands Py, Im and MeIm in $[Fe(III)salen]^+$ reaction (Subramaniam, et al. 2014) 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, et al. 2002). The decrease in the yield of epoxide during increase in amount of Im in the epoxidation of olefins by Mn(III)-oxazoline complexes Bagherzadeh, et al. 2006) was explained as a result of increase in concentration of $[Mn(phox)_2(ImH_2)]^+$ which prevents the coordination of H_2O_2 to the central metal atom. In the Mn^{III}(salen) catalysed H_2O_2 oxidation of diphenyl sulphide (Chellamani, & Alhaji, 2009) and methyl phenyl sulfide (Chellamani, et al. 2007). Chellamani *et al.* have shown that nitrogen bases bind irreversibly and strongly at the metal centre of the reactive species which precludes the binding of sulphides to the reactive species, that is an essential condition for the oxidation reaction to proceed. This resulted in retardation of reaction rate.

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 in small amount which competes with the formation of active vanadium peroxo species. As there is a competition between the peroxo species formation and the 1:1 adduct formation in the reaction mixture, nitrogen bases restrict the free coordination site of oxovanadium(V)-salophen that would be required for binding of H_2O_2 and 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.

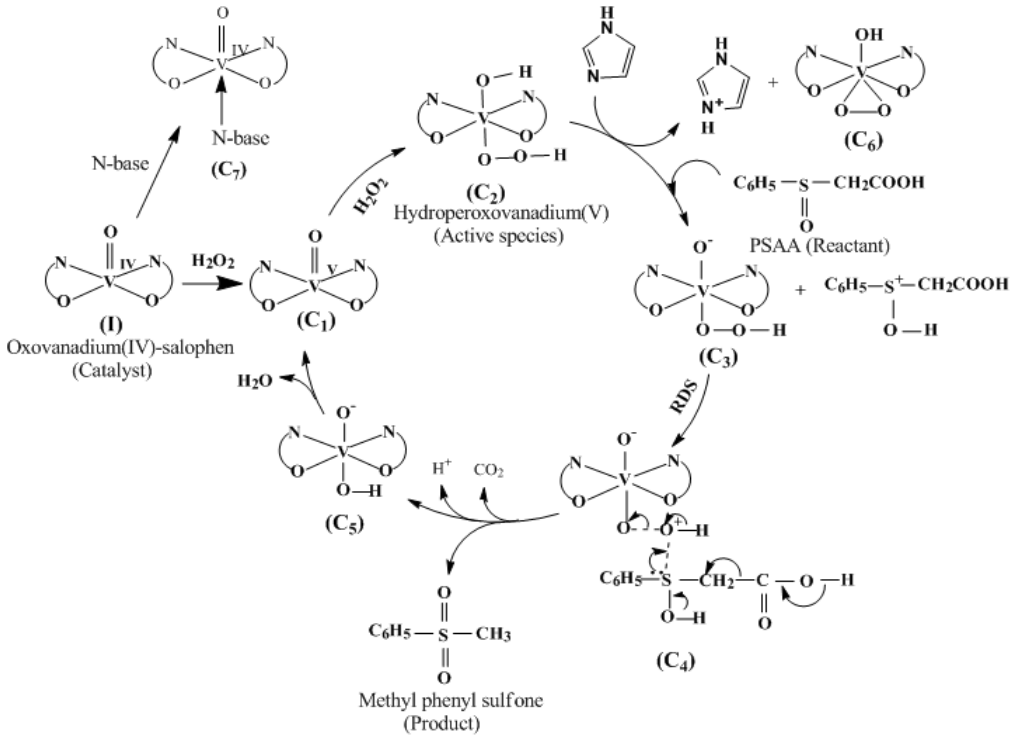
In the present study strong π donating ligands like Im and MeIm have higher retarding effect than less π donating pyridine ligand. This gives a direct evidence that Im and MeIm can form adduct with oxovanadium(IV)-salophen complex more easily than Py, which prevents the formation of active hydroperoxo 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 hydroperoxo vanadium(V) species.

Another possible reason for the rate retardation with nitrogenous bases is the conversion of more active hydroperoxo oxidizing species to less active cyclic peroxo species 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 Coletti *et al.* (2012) using theoretical studies. The less active cyclic peroxo intermediate species hinders the oxidation of PSAA by hydroperoxo vanadium(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 oxidation of hydrocarbons by H_2O_2 catalysed by Mn-porphyrins and imidazole system (Battioni, et al. 1988) catalytic oxidation of sulfides to sulfoxides by UHP using Mn(III)-oxazoline complexes in the presence of imidazole (Bagherzadeh, et al.2008) and in the oxidation of olefins and

sulfides catalysed by Manganese(III)-tridentate Schiff base complex using UHP as oxidant (Bagherzadeh, et al. 2008).

It is interesting to note that among the three nitrogenous bases investigated, MeIm with a strong π-donating ability (Safe, et al. 1994 and Mohajer, et al. 2004) shows the highest retarding effect on rate in parent (**I**) and chloro (**IV**) oxovanadium(IV)-salophen complexes. On the other hand, in the complexes containing electron donating methoxy (**II**) and methyl (**III**) substituents, Im shows the highest rate retarding effect. In all the four complexes Py shows the highest reactivity (Table 4) which has the least π-donating ability The observed order of reactivity among the N-bases is found to be Py > MeIm > Im in complexes **II** and **III** and Py > Im > MeIm in complexes **I** and **IV**. 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 which is responsible for rate retardation.

The higher reactivity in the presence of MeIm than Im in complexes **II** & **III** containing electron releasing substituents can be explained as follows: The methyl group in MeIm considerably prevents the binding of MeIm with the high electron density vanadium centre in complexes **II** and **III**. This preferential binding of Im over MeIm with complexes **II** and **III** prevent the binding of H_2O_2 to form the active species followed by high retardation in rate. On the other hand, as MeIm has higher binding ability with the low electron density vanadium atom of complexes **I** and **IV** than Im, MeIm 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, et al. 1991 & 1992) Py has the least binding ability and shows higher reactivity. Thus the observed order of reactivity in the presence of nitrogen base unambiguously supports the proposed scheme 2 of mechanism as reported in the earlier paper (Jeevi Esther Rathnakumari, et al. 2023).



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

5. CONCLUSION

Owing to the importance of nitrogen bases in biological systems the kinetic study for the reactions of PSAA with H_2O_2 catalysed by oxovanadium(IV)-salophen complexes were carried out in the presence of nitrogen bases like Im, MeIm and Py. Introduction of electron donating group in the salophen moiety enhance the reaction rate while the electron withdrawing group retard the reaction rate when compared to the unsubstituted complex. The observed order of reactivity among the oxovanadium(IV)-salophen

complexes is **II** > **III** > **I** > **IV**. The results reveal that the reaction rate is strongly retarded by all the three nitrogen bases and highly sensitive to the nature of base. The observed order of retardation among different bases is Py < Im < MeIm with complexes **I** and **IV** and Py < MeIm < Im with complexes **II** and **III**.

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