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Linear Free energy relationship and Temperature dependance studies in the oxovanadium (IV) salophen catalysed oxidation of phenylsulfinylacetic acids by hydrogen peroxide in the presence of nitrogen bases

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Abstract

Nitrogen donors have long been used as axial ligands to mimic the function of axial cysteine thiolate or histidine imidazole in natural metallo proteins. Nitrogen bases like imidazole (Im), pyridine (Py) and their derivatives exhibit various types of biological activities. Realizing the importance of nitrogen bases in biological systems the substituent effect and temperature dependance studies for the reactions of PSAA and substituted PSAA with H_2O_2 catalysed by oxovanadium(IV) salophen was carried out in the presence of nitrogen bases like Im, MeIm and Py. The study of substituent effect shows EWG in PSAA accelerate the rate of the reaction while the EDG retard the reaction rate. The analysis of kinetic data using Hammett equation shows a nonlinear curve. However, in the present study, linear Yukawa-Tsuno plots are observed which 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 plots. The thermodynamic parameters, $\Delta^{\ddagger}H$ and $\Delta^{\ddagger}S$ are evaluated from the slope and intercept of the linear Eyring's plots.

Keywords: Coordination Chemistry, Hammett Equation , Yukawa–Tsuno Equation ,Eyring Equation ,Oxidation Catalysis

1.Introduction

Coordination of vanadium(V) complexes with oxygen/nitrogen compounds forms bioinorganic catalysts. Salophen ligand readily combines with vanadium salts and forms oxovanadium complexes which show binding properties with proteins [1,2]. The cation, $[O=V(IV)]^{+}$ can potentially interact with amine, amide, hydroxyl, imidazole, thiolate and carboxylate functionalities of proteins [3].Nitrogen donors have long been used as axial ligands to mimic the function of axial cysteine thiolate or histidine imidazole in natural metallo proteins [4,5]. Nitrogen bases like imidazole (Im), pyridine (Py) and their derivatives exhibit various types of biological activities *viz.*, antimicrobial, analgesics, anticancer, antidiabetic etc., [6,7]. The reactivity of complexes derived from metal-salen derivatives can be tuned [8,9] by adding donor ligands in the reaction mixture. Addition of imidazole (Im), 1-methylimidazole (MeIm) or pyridine (Py) to metal-salen related complexes significantly lowers the oxidation potential by coordination with the metal ion and results in altering the electrochemical properties and their reactivity [10-12].

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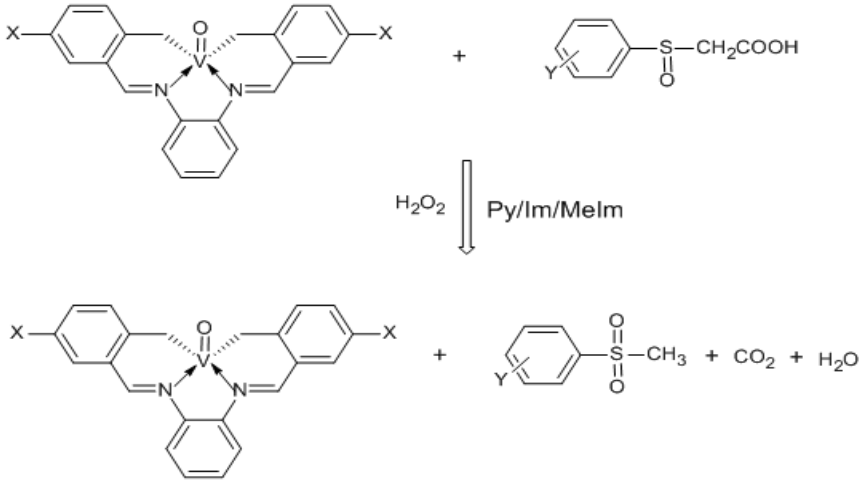

Complex : X = H (**I**); -OCH_3 (**II**); -CH_3 (**III**); -Cl (**IV**).

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

Scheme 1. Overall scheme of the reaction.

This paper reveals the effect of substituents and temperature dependance on the oxidative decarboxylation of different substituted PSAAs by H_2O_2 catalyzed by oxovanadium(IV) salophen complexes (**I-IV**) in the presence of nitrogen bases like Im, MeIm and Py. The overall reaction scheme is represented in Scheme 1.

2. Kinetic studies

The kinetic study for the reaction of PSAA and substituted PSAAs with H_2O_2 and oxovanadium(IV) salophen complexes in the presence of nitrogen bases is 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 complex at an appropriate wavelength. A double beam BL 222 Elico UV-vis spectrophotometer with an inbuilt thermostat was employed to follow the kinetics of the reaction. The reactions were started quickly by injecting H_2O_2 into the reaction mixture

containing PSAA, oxovanadium(IV) salophen complex and the nitrogen base at zero time, in a quartz cuvette.

3. Absorption 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 is added to the complex, no substantial shift in the absorption maxima or increase in the absorbance of the oxovanadium(IV) salophen complex is observed. However, it is interesting to note 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 some time interval followed by decrease in absorbance during the course of time as observed in the absence of nitrogen bases. This observation clearly indicates that 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. The existence and involvement of hydroperoxovanadium(V) as the reactive species in the reactions involving salophen and salen oxovanadium(IV) complexes is confirmed by Coletti et al. [13] using IR, ^{51}V NMR and theoretical studies.

Another interesting observation noted in the kinetic studies with complexes (**I-IV**) 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 the hydrogen peroxide (Figure 1). Similar induction period observed in

the oxygenation reactions of sulfides [14] and cyclohexane [15] catalyzed by Co(II)salen complexes is explained by time taken for the generation of the active oxidizing species, Co(III) hydroperoxide adduct, [Co(III)-salenOOH] in these reactions.

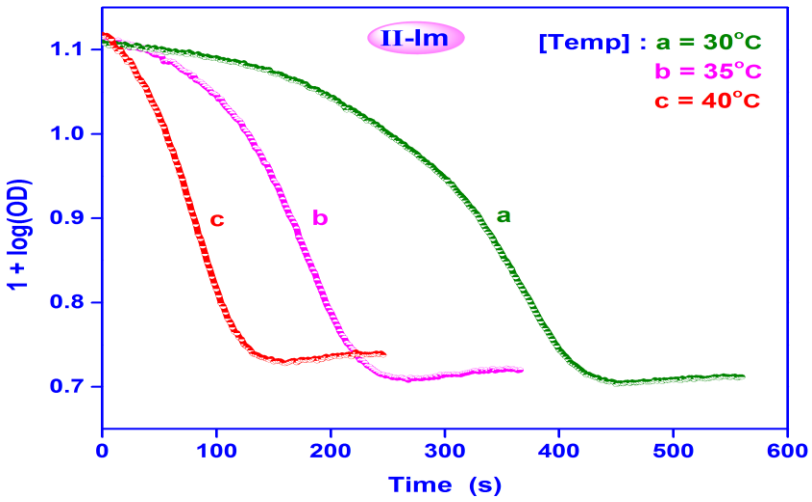

Figure 1. Pseudo first-order plots at three different temperatures.
[PSAA] = 7.0×10^{-2} M; [H_2O_2] = 7.0×10^{-3} M; [**II**] = 5.0×10^{-5} M; [Im] = 5.0×10^{-4} M.

Hence, it is concluded from the observed induction period and the increase in the absorbance at 610 nm, the active oxidizing species, hydroperoxovanadium(V) salophen is formed from vanadium(V) complex and hydrogen peroxide and its generation is a slow process which requires certain time. The decrease in induction period observed with temperature in the reaction may be due to the easy formation of hydroperoxo species at high temperature.

4. Results and Discussion

4.1 Effect of substituents and linear free energy relationship

In order to understand the nature of the transition state and the extent of charge transfer, several *para*- and *meta*- substituted PSAAs are utilized to carry out the reaction

with H_2O_2 in the presence of three oxovanadium(IV) salophen complexes (**I**, **II** and **IV**) and the bases like Py, Im and MeIm (Table 1 and 2). The substituent effect is also studied at three different temperatures 25 °C, 30 °C and 35 °C with complex **I**. The observed kinetic data show that the reaction is sensitive to the change of substituents in the phenyl ring of PSAA and the salophen moiety of the complex. It is interesting to note that EWG in PSAA accelerate the rate of the reaction while the EDG retard the reaction rate. The kinetic data are analysed using Hammett equation. The plots of log k_2 *vs*. Hammett′s substituent constants (σ) show a nonlinear downward curvature with two distinct lines for groups comprising of electron withdrawing and electron donating substituents converging at the parent compound. The Hammett plots which show the effect of substituents on the reaction rate are graphically demonstrated in Figure 2. Another significant feature observed in the Hammett correlation is the anomalous behavior of methoxy substituent which shows a positive deviation from the rest of the substituents.

Table 1. 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 three oxovanadium(IV) salophen complexes with three nitrogen bases are given in Table 2. The positive ρ value indicates the electrophilic behavior of the PSAA towards the oxidant in the reaction. The ρ values observed in the presence of N-bases are little higher compared to the ρ values observed in the absence of N-bases . From these ρ values, it is presumed that the transition state in the absence of N-bases is more reactant like and in the presence of N-bases it is more product like. Thus, it is concluded that the added N-bases affect the position of transition state of the reaction.

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Table 2. Second-order rate constants for the oxidative decarboxylation of PSAAs by **II** & **IV** in the presence of nitrogen bases.

X	$10^2 k_2$ ($M^{-1}s^{-1}$)					
	II			**IV**		
	Py	Im	MeIm	Py	Im	MeIm
p-Cl	87.5 ± 0.81	63.5 ± 1.1	61.2 ± 0.4	0.199 ± 0.03	0.197 ± 0.02	0.195 ± 0.01
m-Cl	98.2 ± 1.5	68.4 ± 0.08	69.8 ± 0.21	0.224 ± 0.02	0.214 ± 0.01	0.208 ± 0.02
p-F	82.4 ± 2.2	49.0 ± 0.04	53.1 ± 0.06	0.182 ± 0.02	0.173 ± 0.01	0.167 ± 0.01
p-Br	89.1 ± 1.9	61.7 ± 0.05	61.7 ± 0.03	0.209 ± 0.01	0.200 ± 0.02	0.194 ± 0.02
H	74.8 ± 2.3	44.2 ± 0.03	45.6 ± 0.04	0.171 ± 0.01	0.164 ± 0.01	0.161 ± 0.02
p-Me	57.7 ± 1.1	26.2 ± 0.42	28.8 ± 0.21	0.103 ± 0.02	0.090 ± 0.01	0.081 ± 0.01
p-OEt	50.4 ± 0.93	19.1 ± 0.31	22.1 ± 0.19	0.076 ± 0.01	0.060 ± 0.02	0.054 ± 0.02
p-OMe	32.6 ± 0.84	14.4 ± 0.26	16.3 ± 0.10	0.058 ± 0.01	0.048 ± 0.53	0.045 ± 0.02
ρ_{EWG}	0.287 ± 0.02	0.525 ± 0.04	0.465 ± 0.03	0.275 ± 0.01	0.311 ± 0.01	0.312 ± 0.02
r	0.974	0.980	0.980	0.995	0.997	0.991
ρ_{EDG}	0.705 ± 0.11	1.49 ± 0.20	1.28 ± 0.09	1.43 ± 0.02	1.76 ± 0.04	1.93 ± 0.03
r	0.998	0.995	0.996	0.997	0.992	0.997

[PSAA] = 5.0×10^{-2} M; [H_2O_2] = 5×10^{-3} M; [Py] = [Im] = [MeIm] = 5×10^{-4} M; [**II**] = 3×10^{-4} M; [**IV**] = 1×10^{-4} M; Temp. = 30 °C;
solvent = 100 % CH_3CN.

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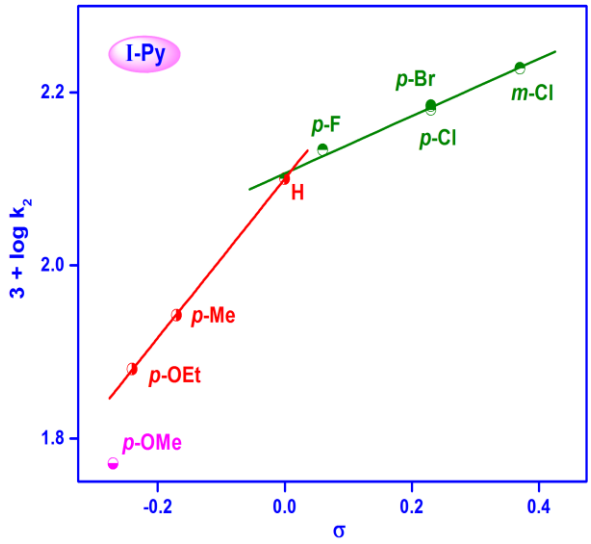

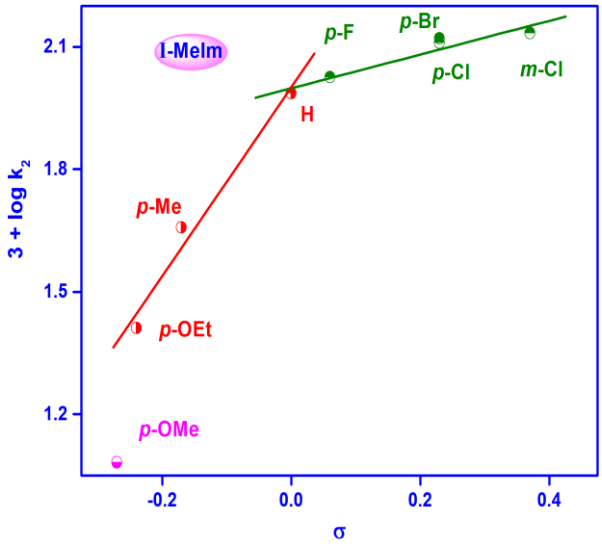

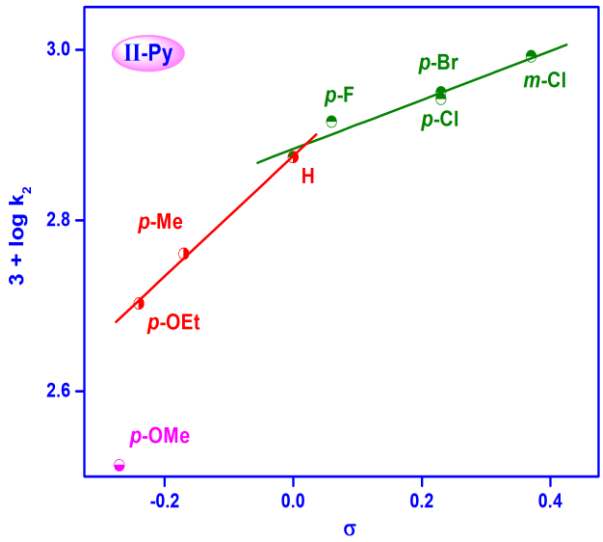

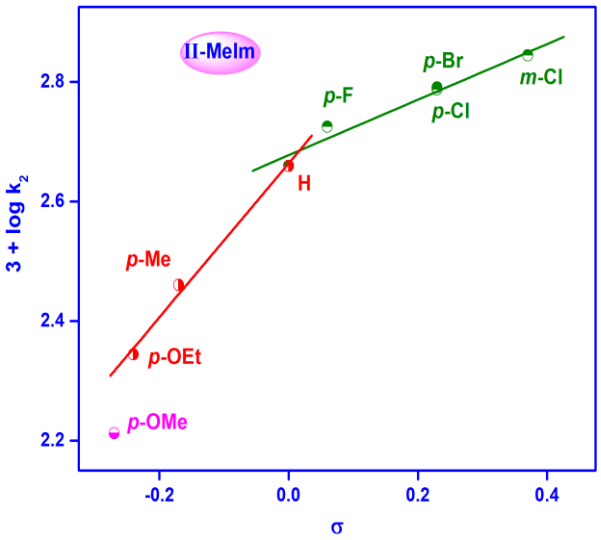

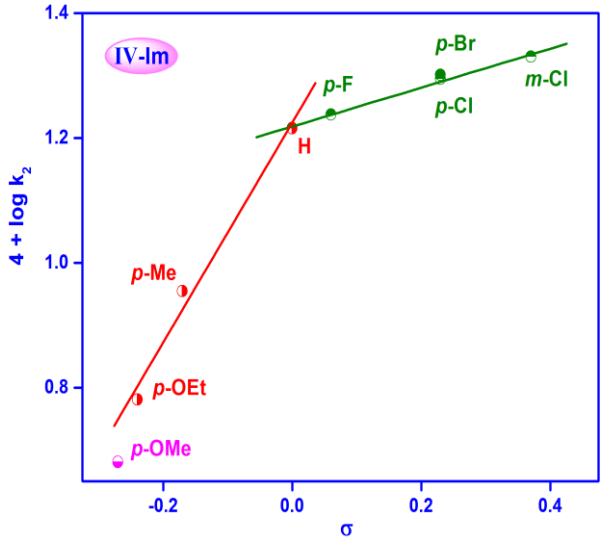

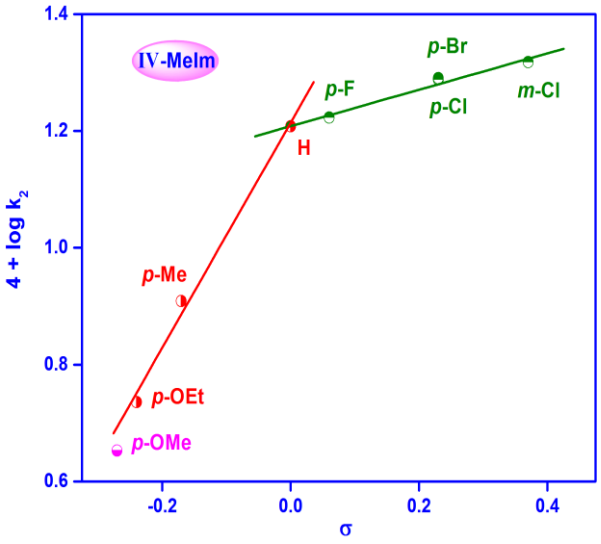

Figure 2. Hammett plots for the reaction between PSAAs and H_2O_2 with complexes. [PSAA] = 5.0×10^{-2} M; [H_2O_2] = 5.0×10^{-3} M; [**I**] = [**II**] = 3.0×10^{-4} M; [**IV**] = 1.0×10^{-4} M; [N-base] = 5.0×10^{-4} M; solvent = 100 % CH_3CN; T = 30 °C.

Such nonlinear plots with two different ρ^+ values have been reported earlier in reactions involving hydrolysis of *o*-arylthionobenzoates [16], pyridinolysis of substituted 2,4-dinitrophenyl benzoates [17] and in the reactions of nucleophiles with aryl benzoates [18]. In all these cases, the Hammett parameter changed from a large positive ρ value to a small one as the substituent changes from an EDG to a strong EWG and the observed nonlinearity was explained on the basis of ground state stabilization of the substrates possessing EDG.

The effect of substituents in the oxovanadium(IV) salophen reveals that the reaction rate is enhanced by the electron donating methoxy group and strongly retarded when electron withdrawing chloro group is introduced in the 5,5′-positions of the salophen moiety. The Hammett plots obtained by plotting log k_2 *vs*. 2σ with different substituted PSAAs show two straight lines for electron donating and electron withdrawing substituents each with negative ρ values. The behavior of the substituent in 5,5′-positions in the salophen ligand of vanadium(IV) complexes is found to be different from that of other salen complexes of Fe(III), Cr(III), Mn(III) and Co(II) [19-24] where EDGs retard the rate while EWGs accelerate the rate.

4.2. Influence of temperature and thermodynamic parameters

The kinetic data for the reactions of PSAAs and H_2O_2 at 25 °C, 30 °C and 35 °C with complex **I** in the presence of N-bases (Table 1) show a linear increase in the rate of oxidation with temperature. The kinetic study is also extended to PSAA with complexes (**II-IV**) at three different temperatures, 30 °C, 35 °C and 40 °C in the presence of three

N-bases (Table 3). The thermodynamic parameters, $\Delta^{\ddagger}H$ and $\Delta^{\ddagger}S$ evaluated from the slope and intercept of the linear Eyring′s plots (Figure 3) are also shown in Table 1 and 3. The entropy of activation is found to be negative and the enthalpy of activation is relatively small in all the four complexes. The almost constant activation parameters observed with all the four individual complexes in the presence of three different nitrogen bases confirm that the reaction between PSAA and H_2O_2 follows the same mechanism in all cases. The positive $\Delta^{\ddagger}H$ values suggest that the reaction is endothermic in nature.

Table 3. Second-order rate constants (k_2) at different temperatures and thermodynamic parameters.

Nitrogen base	10^2k_2 (M^{-1} s^{-1})			$\Delta^{\ddagger}H$ (kJ mol^{-1})	$\Delta^{\ddagger}S$ (JK^{-1} mol^{-1})
	30 °C	35 °C	40 °C		
			II		
Py	59.1 ± 0.51	75.8 ± 2.6	101.4 ± 3.2	40.1 ± 2.6	-117.2 ± 9.2
Im	32.0 ± 1.1	54.6 ± 0.93	66.6 ± 1.3	55.5 ± 3.2	-70.9 ± 4.3
MeIm	47.2 ± 0.62	58.4 ± 0.25	78.6 ± 2.5	37.9 ± 4.5	-126 ± 5.1
			III		
Py	22.4 ± 1.1	28.0 ± 1.0	37.1 ± 0.92	39.3 ± 2.1	-128 ± 10.1
Im	19.7 ± 0.26	26.3 ± 0.81	35.4 ± 1.1	44.4 ± 2.7	-112 ± 9.5
MeIm	15.9 ± 0.36	19.9 ± 0.95	26.6 ± 1.3	40.2 ± 3.6	-128 ± 7.7
			IV[a]		
Py	0.871 ± 0.03	1.57 ± 0.03	2.49 ± 0.11	84.5 ± 5.3	-6.11 ± 1.1
Im	0.594 ± 0.06	0.974 ± 0.01	1.61 ± 0.02	79.8 ± 4.2	-24.3 ± 2.8
MeIm	0.554 ± 0.04	0.868 ± 0.04	1.30 ± 0.07	78.2 ± 3.8	-30.6 ± 3.5

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

[N-base] = 5.0×10^{-4} M; [a][N-base] = 2.5×10^{-4} M; solvent = 100 % CH_3CN.

The correlation between $\Delta^{\ddagger}H$ and $\Delta^{\ddagger}S$ for all substituted PSAAs are found to be linear. 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 Figure 4. The linear isokinetic relation between $\Delta^{\ddagger}H$ and $\Delta^{\ddagger}S$ reveals that all PSAAs follow the same mechanism.

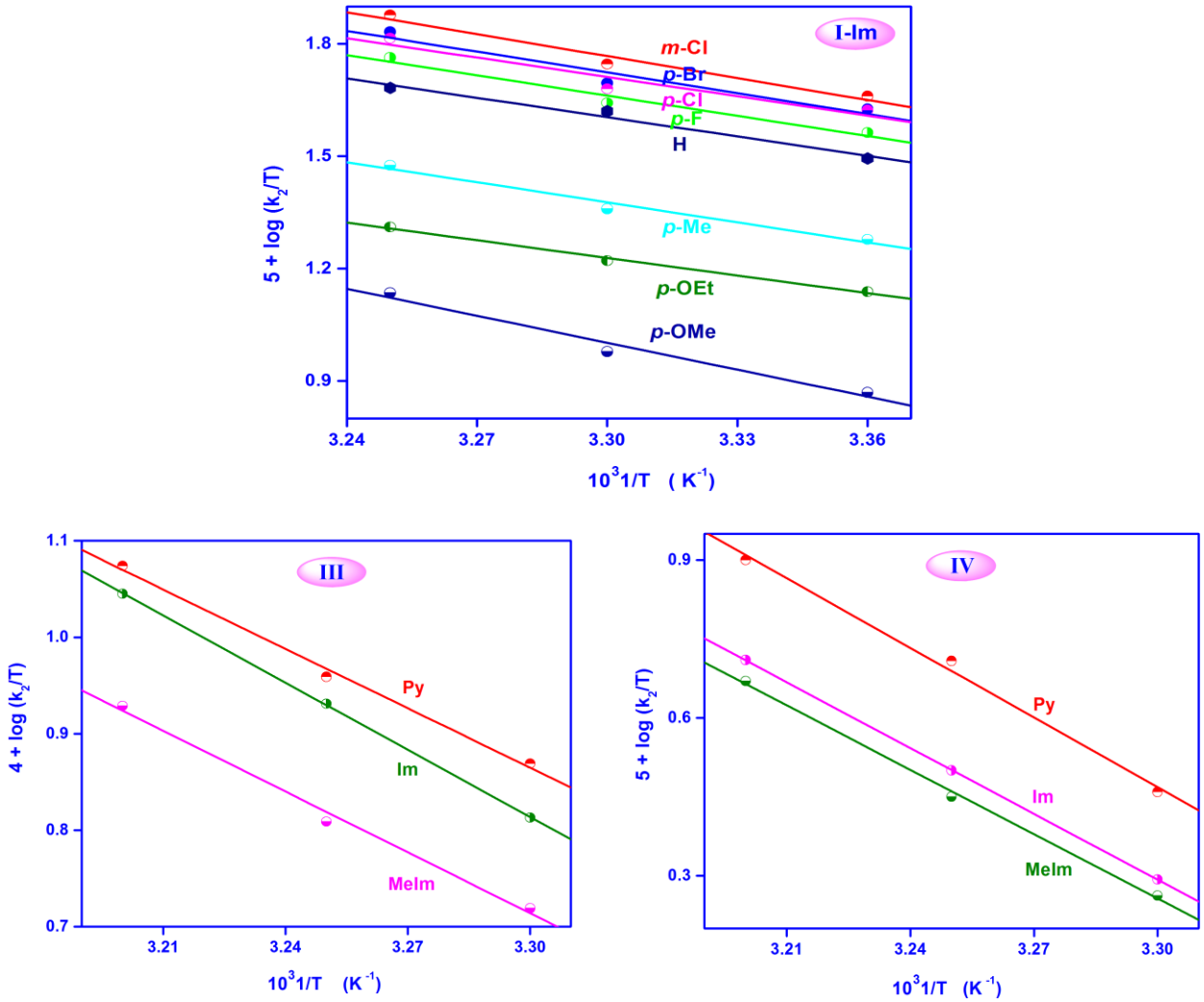

Figure 3 Eyring′s plots for the reactions of PSAAs and H_2O_2 in the presence of complex and N-base; General conditions as in Table 4.5.

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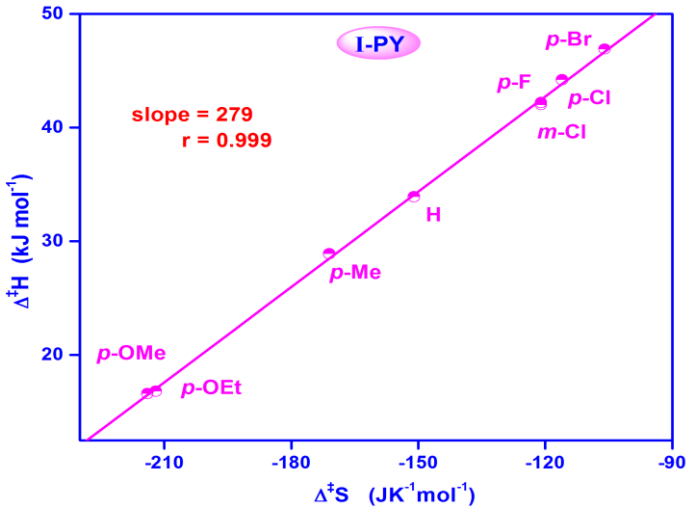

Figure 4. Plot of $\Delta^{\ddagger}H$ *vs*. $\Delta^{\ddagger}S$ for the reactions of PSAAs and H_2O_2 with **I** in the presence of pyridine.

4.3 Nonlinear Hammett plot and linear Yukawa-Tsuno plot

A nonlinear Hammett plot with two intersecting linear portions has been traditionally explained on the basis of a change in the reaction mechanism or a change in RDS within a proposed mechanism [25]. However, in the aminolysis reactions of substituted phenyl-2-methoxybenzoates [26], 4-pyridyl substituted benzoates [27] and 2-pyridyl substituted benzoates [28] the observed nonlinear Hammett plots have been interpreted by ground state stabilization of the substrates. Neuvonen et al. [29] have explained the enhanced reactivity of esters containing EWG by decrease in the resonance stabilization of the ground state (GS) of esters. 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. The resonance interaction between the electron donating substituent and the thionyl functionality is represented in Figure 5

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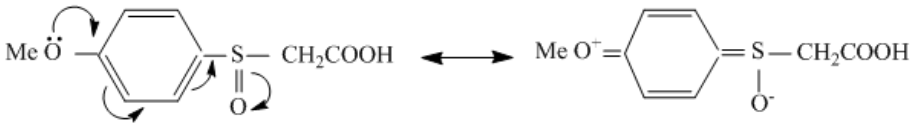

Figure 5 Ground state stabilization of PSAA.

The presence of such resonance structures in electron releasing groups, stabilizes the GS of the substrate and would cause a decrease in reactivity. The above argument is supported by the significant positive deviation observed in the Hammett plot as the substituent becomes a stronger EDG (Figure 2). 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 for the reactions 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 [30].

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

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 (Figure 6) for the reactions under study and almost unit value of '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 plots. Um and coworkers [18,28] also interpreted the non linear Hammett plot and linear Yukawa-Tsuno plots in terms of ground state stabilization of the substrate.

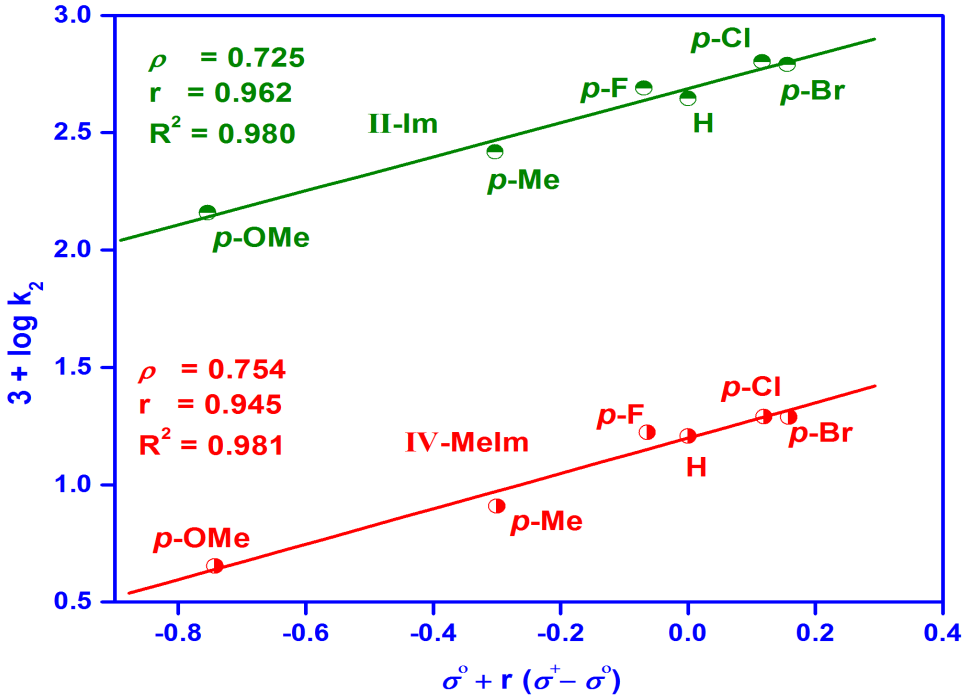

Figure 6. Yukawa-Tsuno plots for the reactions of PSAAs with H_2O_2 and complex **II** and **IV** at 30 °C in the presence of N-bases.

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