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A MECHANISTIC STUDY OF THE OXOVANADIUM(IV)-SALOPHEN CATALYZED OXIDATIVE DECARBOXYLATION OF PHENYLSULFINYLACETIC ACIDS BY HYDROGEN PEROXIDE IN THE PRESENCE OF LIGAND OXIDES -A NON LINEAR HAMMETT CORRELATION

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ABSTRACT

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 ligand oxides like pyridine N-oxide (PyO), picoline N-Oxide (PicNO) and triphenylphosphine oxide (TPPO). Kinetic results reveal that the reaction rate is strongly retarded by all the three ligand oxides. 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

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

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

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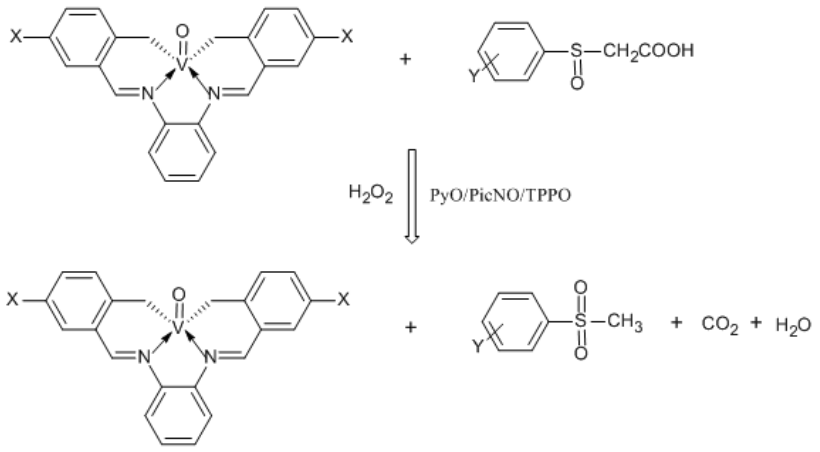
1.INTRODUCTION

Salen complexes, a standard system in coordination chemistry have great potential as catalysts for oxo transfer reactions (Canali & Sherrington, 1999 & Cozzi 2004) and other processes (Cohen et al. 2004 & Groger 2003). They also mimic enzymatic reactions (Doctrow et al. 2002 & Baudry et al. 1993). Heterocyclic *N*-oxides have emerged as potent compounds with anticancer, antibacterial, antihypertensive, antiparasitic, anti-HIV, anti-inflammatory, herbicidal, neuroprotective and procognitive activities. The pyridine *N*-oxide derivatives represent a unique class of antivirals. The pyridine *N*-oxide compounds have previously been demonstrated to be inhibitory against the human immunodeficiency virus (HIV) in cell culture (Stevens et al. 2003 & Balzarini et al. 2005). Several members have previously been found to be active against HIV-1 and/or HIV-2 and human cytomegalovirus (HCMV). The oxide part on the pyridine moiety proved indispensable for anti-coronavirus activity. The potency and virus specificity of the pyridine N-oxide derivatives depend on the nature and specific location of substituents on the different parts of the molecule (Balzarini et al. 2006). Some N-oxide derivatives act as bio reductive drugs (Balzarini et al. 2006). Hence the study of role and action of N-oxides on the activity of metallo-enzymes is important in drug design.

Subramaniam et al. (2016) have explained the effect of ligand oxides (LOs) in the oxidation kinetics of phenylsulfinylacetic acid (PSAA) and phenylmercaptoacetic acid by chromium salen complexes. Donor ligands such as triphenylphosphine oxide (TPPO), pyridine N-oxide (PyO), picoline N-Oxide (PicNO), dimethyl sulfoxiede (DMSO) and water form 1:1 addition complexes with the oxo species (McGarrigle & Gilheany 2005). The ligand oxides (LOs) added is found to coordinate with the metal centre and thus affect the outcome of the reaction (Kavitha & Subramaniam 2023).

Hence, in the present paper investigations were carried out on the redox reaction of PSAA with oxovanadium(IV)-salophen and H_2O_2 in the presence of PyO, PicNO and TPPO. The structure of ligand oxides used in the present study is given in Figure 1. The following scheme summarizes the work described in detail.



Complex: **I** : X = H

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

Scheme 1. Overall reaction scheme for the oxidation of PSAA in the presence of LOs.

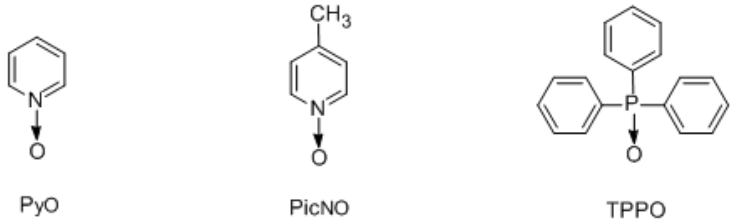


Figure 1. Structure of ligand oxides.

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 ligand oxides like pyridine N-oxide (PyO), picoline N-Oxide (PicNO) and triphenylphosphine oxide (TPPO) 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. 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 et al. 2016).oxovanadium(IV)-salophen complex synthesized was characterized by UV-vis, FT-IR and mass spectral techniques

2.4 Kinetic study

The kinetic study for the oxidation of PSAA and substituted PSAAs with H_2O_2 in the presence of oxovanadium(IV)-salophen complex (**I)** as catalyst in the presence of LOs was carried out in 100 % acetonitrile medium under pseudo first-order conditions. The reactions were initiated by injecting the required amount of H_2O_2 to a thermally equilibrated mixture of PSAA, oxovanadium(IV)-salophen complex and Ligand oxide in acetonitrile. The decay in absorbance of the active

hydroperoxovanadium(V) salophen species with time was followed spectrophotometrically. The addition of ligand oxide to the complex neither shifts the λ_{max} nor increases the optical density.

3.RESULTS

3.1. Active species

Oxovanadium(IV)-salophen (**I**) has an absorption maximum at 396 nm, which arises due to its ligand to metal charge transfer. In the presence of ligand oxide also, addition of H_2O_2 at a higher concentration to the complex shows an increase in intensity at 610 nm as a new broad absorption peak after a time interval, followed by a decrease in intensity during the course of time which depends upon the experimental conditions. This observation demonstrates the formation of hydroperoxovanadium(V) species in the reaction mixture. Further, decrease in the intensity of the weak broad band was observed at 590 nm in the oxovanadium(IV)-salen catalyzed hydrogen peroxide oxidation of phenols (Mathavan et al. 2015) and at 570 nm in the oxovanadium(IV)-salen oxidation of tertiary amines to N-oxides (Mathavan, Ramachandran et al. 2015) at higher concentrations of H_2O_2. In these cases hydroperoxo species were identified as the active species. On this basis, the observed spectral changes are considered as an evidence for the formation of hydroperoxovanadium(V) species in the reaction. The existence of hydroperoxovanadium(V) species in the reactions involving salophen and salen oxovanadium(IV) was confirmed by IR, ^{51}V NMR and theoretical studies by Coletti et al. (2012).

3.2. Dependence of reaction rate on reactants

The pseudo first-order rate constants calculated from the pseudo first-order plots at different concentration of H_2O_2 with LOs are given in Table 1. The effect of $[H_2O_2]$ on reaction rate in the presence of three LOs shows that the rate increases with increase in $[H_2O_2]$ and beyond the optimum range the reaction rate is found to decrease with hydrogen peroxide concentration.

Table 1. Effect of $[H_2O_2]$ in the presence of ligand oxides

10^3 $[H_2O_2]$ (M)	10^3 k_1 (s^{-1})		
	PyO	PicNO	TPPO
	I		
2.0	0.821 ± 0.03	0.523 ± 0.02	0.243 ± 0.02
4.0	1.473 ± 0.05	1.08 ± 0.04	0.610 ± 0.03
7.0	4.03 ± 0.11	3.53 ± 0.07	1.99 ± 0.06
9.0	6.92 ± 0.09	5.88 ± 0.15	2.31 ± 0.08
11.0	5.11 ± 0.06	4.35 ± 0.17	2.00 ± 0.04

[PSAA] = 7.0×10^{-2} M; solvent = 100% CH_3CN; Temp. = 30 °C;
[I] = 5.0×10^{-4} M; [PyO] = [PicNO] = [TPPO] = 5.0×10^{-4} M.

The effect of PSAA on the reaction rate in the presence of three ligand oxides namely PyO, PicNO, TPPO was studied by measuring the rate of the reaction at different [PSAA] in the range from 0.03 M to 0.15 M. The values of pseudo first-order and second-order rate constants calculated are given in Table 2. The pseudo first-order rate constants (k_1) increase with the increase in [PSAA] and the second order rate constant (k_2) calculated using the relation k_1/[PSAA] are found to be constant. The pseudo first-order plots at different [PSAA] are shown in Figure 2. The linear plots between k_1 and [PSAA] passing through the origin (Fig. 3) and the unit slope values observed in the plots of log k_1 *vs.* log [PSAA] with different LOs (Fig. 4) for the oxovanadium(IV)-salophen complex confirm the first order dependence on PSAA.

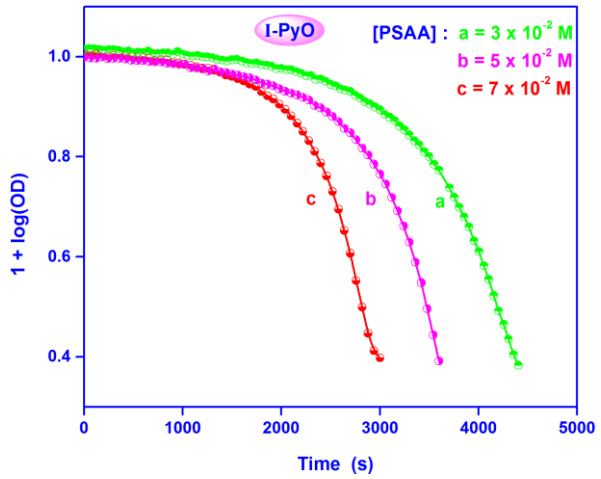


Figure 2. Pseudo first-order plots at different [PSAA].
$[H_2O_2] = 3.0 \times 10^{-3}$M; **[I]** = 5.0×10^{-4} M;
[PyO] = 5.0×10^{-4} M.

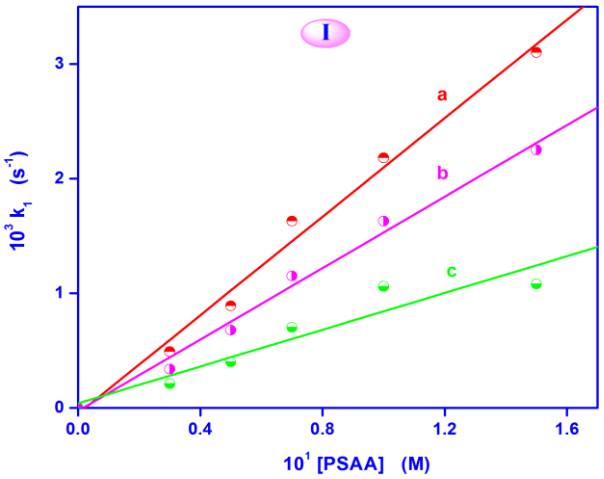


Figure 3. Plots of k_1 *vs.* [PSAA] for the reactions.
a = PyO; b = PicNO; c = TPPO.
General conditions as in Table 5.2

Table 2. Effect of [PSAA] in the presence of ligand oxides for complex **I**.

10^1 [PSAA] (M)	PyO		PicNO		TPPO	
	10^3k_1 (s^{-1})	10^2k_2 ($M^{-1}s^{-1}$)	10^3k_1 (s^{-1})	10^2k_2 ($M^{-1}s^{-1}$)	10^3k_1 (s^{-1})	10^2k_2 ($M^{-1}s^{-1}$)
0.30	0.49 ± 0.01	1.63 ± 2.3	0.338 ± 0.03	1.13 ± 1.0	0.210 ± 0.01	0.70 ± 0.33
0.50	0.89 ± 0.04	1.78 ± 0.8	0.678 ± 0.07	1.36 ± 1.4	0.401 ± 0.03	0.80 ± 0.60
0.70	1.63 ± 0.10	2.30 ± 1.4	1.15 ± 0.02	1.64 ± 0.29	0.702 ± 0.05	1.00 ± 0.71
1.00	2.18 ± 0.06	2.18 ± 0.60	1.63 ± 0.18	1.63 ± 1.1	1.06 ± 0.06	1.06 ± 0.60
1.50	3.10 ± 0.14	2.07 ± 0.93	2.25 ± 0.20	1.50 ± 1.3	1.08 ± 0.10	1.12 ± 0.67

[**I**] = 5.0×10^{-4} M, [PyO] = [PicNO] = [TPPO] = 5.0×10^{-4} M;
Temp = 30 °C; solvent = 100 % CH_3CN; [H_2O_2] = 3.0×10^{-3} M.

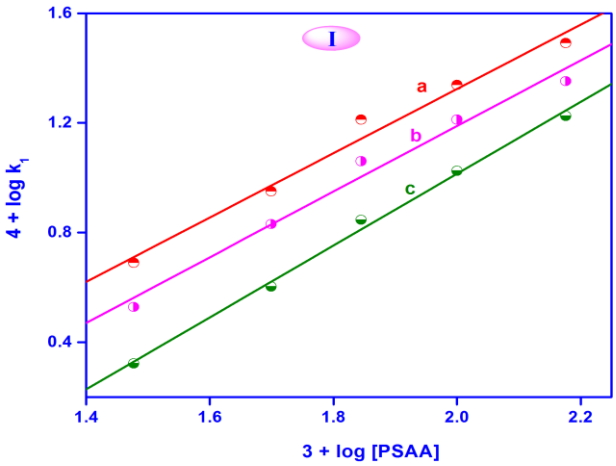


Figure 4. Double logarithmic plots of k_1 and [PSAA].
a = PyO; b = PicNO; c = TPPO. General conditions as in Table 5.2.

The pseudo first-order rate constant increases with increase in concentration of oxovanadium(IV)salophen complex in the presence of LOs which is similar to that observed in the presence of nitrogen bases (Table 3) (Jeevi Esther Rathnakumari et al 2024). However, in the absence of bases and ligand oxides, the rate of the reaction is found to decrease with the increase in concentration of the complex.

Table 3. Effect of [complex] (**I**) in the presence of ligand oxides

10^4 [Complex] (M)	10^3 k_1 (s^{-1})		
	PyO	PicNO	TPPO
	I		
0.1	2.03 ± 0.02	1.74 ± 0.04	0.573 ± 0.02
0.50	2.58 ± 0.08	2.40 ± 0.09	0.920 ± 0.05
1.0	2.91 ± 0.03	2.89 ± 0.13	1.28 ± 0.01
2.5	3.57 ± 0.06	3.22 ± 0.20	1.68 ± 0.08
5.0	4.03 ± 0.11	3.53 ± 0.07	1.99 ± 0.06

[PSAA] = 7.0×10^{-2} M; [H_2O_2] = 7.0×10^{-3} M; Temp = 30 °C; Solvent = 100% CH_3CN;
[PyO] = [PicNO] = [TPPO] = 5.0×10^{-4} M;

3.3. Effect of ligand oxides on the reaction rate

Table 4. Influence of ligand oxides on the reactions of PSAA with H_2O_2 catalysed by **I**

10^3 [LO] (M)	10^3 k_1 (s^{-1})		
	PyO	PicNO	TPPO
	I		
0	3.58 ± 0.11	3.58 ± 0.11	3.58 ± 0.11
0.050	3.50 ± 0.23	3.44 ± 0.30	1.31 ± 0.09
0.075	3.30 ± 0.14	3.18 ± 0.15	1.22 ± 0.07
0.10	3.11 ± 0.09	2.99 ± 0.20	1.10 ± 0.01
0.50	2.58 ± 0.08	2.40 ± 0.09	0.92 ± 0.05

1.0	2.49 ± 0.05	2.33 ± 0.04	0.87 ± 0.02
2.5	2.30 ± 0.07	2.04 ± 0.03	0.79 ± 0.06

[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.

The influence of ligand oxides *viz.* PyO, PicNO and TPPO on the rate of the reaction is studied by measuring the rate constants at different concentrations of LOs ranging from 0.05×10^{-3} M to 2.5×10^{-3} M. The reactions could not be carried out at higher concentrations of LOs as the rate constants were too slow to be measured. The pseudo first-order rate constant values calculated in the absence of ligand oxides and at various ligand oxide concentrations for oxovanadium(IV)-salophen complex are presented in Table 4.

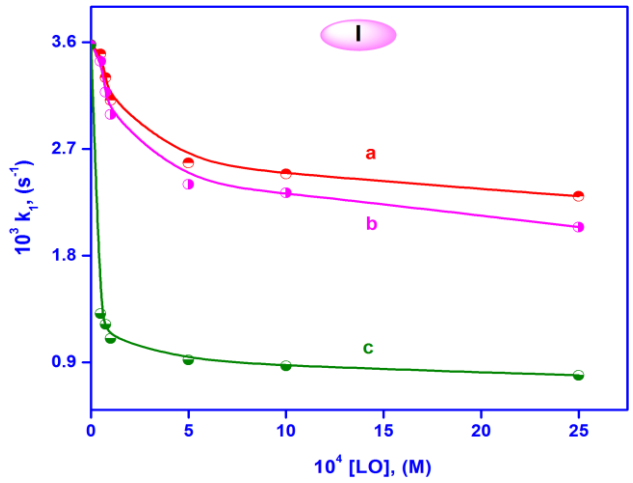


Figure 5. Plots of k_1 *vs.* [LO];
a = PyO; b = PicNO; c = TPPO. General conditions as in Table 4.

The data in Table 4 and Figure 5 clearly show that the extent of rate retardation observed at low concentrations of LO is comparatively more than at higher concentrations. The reaction shows the most retardation and least reactivity with TPPO among the three different LOs and PyO shows least retardation effect and highest reactivity. Thus, the retardation effect shown by the LOs in the oxovanadium(IV)-salophen complex is found to be TPPO > PicNO > PyO. Variations of rate constant with [LO] are graphically represented in Figure 5.

3.4 Substituent effects

In order to understand the influence of substituents in the reaction, the reactivity of PSAA and substituted PSAAs with H_2O_2 in the presence of complex **I** and LOs such as PyO, PicNO and TPPO were studied. The kinetic data in the Table 5 indicate that the reactions in the presence of LOs are sensitive to the nature of the substituents in the aryl moiety of PSAA. Electron withdrawing groups (EWG) in the phenyl ring of PSAA enhance the rate, while Electron donating groups (EDG) in the phenyl ring of PSAA decrease the reaction rate.

In order to confirm the extent of charge separation in the transition state of the reaction, the rate constant values are analysed in terms of Hammett σ values. Since EDG in PSAA retard the reaction rate and EWG in the same accelerate the reaction, a non-linear Hammett plot with downward curvature is seen with all LOs. The Hammett plots are found to have small positive ρ value for EWG (ρ^+ = 0.277 to 0.459) and a fairly high positive ρ value for EDG (ρ^+ = 1.03 to 1.54). The positive ρ values obtained in the present reaction series point out that PSAA acts as an electrophile in the reaction as reported earlier in the presence of bases (Jeevi Esther Rathnakumari et al. 2023). The representative Hammett plots are shown in Figure 6.

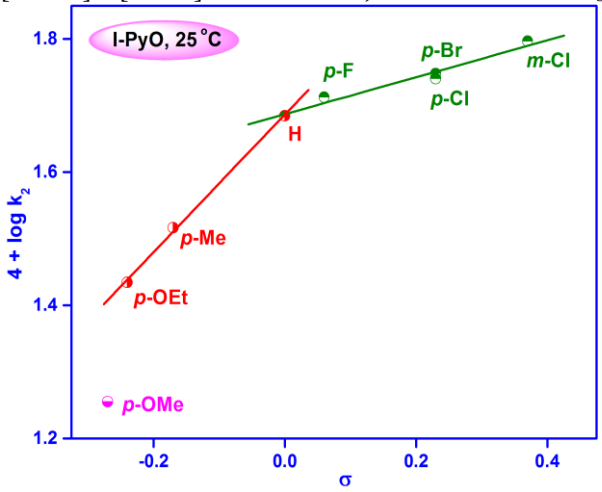
Table 5 Second order rate constants and thermodynamic parameters for the reactions of PSAAs by H_2O_2 in the presence of ligand oxides and complex **I**.

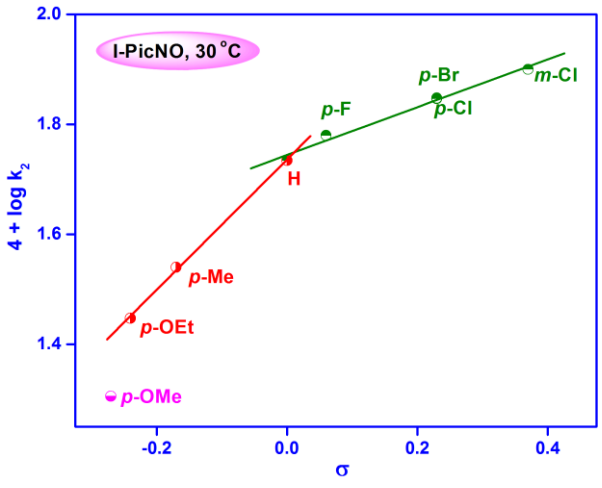
Y	$10^2 k_2$ ($M^{-1} s^{-1}$)			$\Delta^{\ddagger}H$ ($kJmol^{-1}$)	$\Delta^{\ddagger}S$ ($JK^{-1}mol^{-1}$)
	25 °C	30 °C	35 °C		
			PyO		
p-Cl	5.60 ± 0.03	7.88 ± 0.32	9.80 ± 0.15	42.8 ± 2.2	125 ± 6.1
m-Cl	6.26 ± 0.12	8.88 ± 0.31	10.6 ± 0.32	40.4 ± 1.8	132 ± 5.4
p-F	5.16 ± 0.34	6.5 ± 0.08	8.50 ± 0.08	38.1 ± 2.0	142 ± 3.3

[PSAA] 10^{-2} M; = 7.0 × [**I**] = 10^{-4} M; = 5.0 × $[H_2O_2]$ 10^{-3} M; 3.0 × [PyO] =

p-Br	5.50 ± 0.08	7.52 ± 0.15	9.66 ± 0.22	43.1 ± 1.6	125 ± 2.5
H	4.84 ± 0.05	5.96 ± 0.10	8.06 ± 0.10	38.8 ± 2.7	140 ± 9.4
p-Me	3.28 ± 0.03	3.98 ± 0.02	4.80 ± 0.06	29.3 ± 2.1	176 ± 7.2
p-OEt	2.72 ± 0.01	3.00 ± 0.03	3.36 ± 0.04	16.2 ± 1.0	221 ± 4.8
p-OMe	1.80 ± 0.02	2.22 ± 0.05	2.56 ± 0.01	26.9 ± 0.3	188 ± 8.9
ρ_{EWG}	0.277 ± 0.02	0.459 ± 0.01	0.326 ± 0.02		
r	0.982	0.993	0.996		
ρ_{EDG}	1.03 ± 0.04	1.20 ± 0.03	1.54 ± 0.04		
r	0.992	0.991	0.992		
PicNO					
p-Cl	5.38 ± 0.02	7.02 ± 0.04	8.20 ± 0.10	32.2 ± 2.8	161 ± 9.3
m-Cl	5.96 ± 0.05	7.94 ± 0.21	8.86 ± 0.08	30.3 ± 1.9	166 ± 8.8
p-F	4.68 ± 0.08	6.02 ± 0.02	7.14 ± 0.23	32.2 ± 2.2	162 ± 7.4
p-Br	5.30 ± 0.20	7.04 ± 0.10	8.04 ± 0.31	31.9 ± 3.3	162 ± 6.4
H	4.40 ± 0.11	5.42 ± 0.15	6.76 ± 0.17	32.9 ± 4.1	161 ± 10.1
p-Me	2.90 ± 0.03	3.46 ± 0.08	3.76 ± 0.09	19.9 ± 3.2	208 ± 9.4
p-OEt	2.44 ± 0.04	2.80 ± 0.04	3.20 ± 0.06	20.7 ± 2.7	206 ± 3.8
p-OMe	1.66 ± 0.01	2.02 ± 0.06	2.38 ± 0.05	27.4 ± 1.5	187 ± 4.2
ρ_{EWG}	0.351 ± 0.02	0.435 ± 0.03	0.319 ± 0.03		
r	0.998	0.993	0.996		
ρ_{EDG}	1.07 ± 0.05	1.19 ± 0.04	1.38 ± 0.02		
r	0.999	0.999	0.997		
TPPO					
p-Cl	3.50 ± 0.06	4.02 ± 0.05	5.50 ± 0.22	34.3 ±2.1	158 ± 4.5
m-Cl	3.96 ± 0.10	4.50 ± 0.09	6.02 ± 0.31	31.9 ± 3.3	165 ± 3.9
p-F	3.16 ± 0.08	3.56 ± 0.11	4.68 ± 0.16	29.9 ± 2.5	174 ± 8.1
p-Br	3.60 ± 0.13	3.96 ± 0.14	5.40 ± 0.09	30.8 ± 4.2	170 ± 10.5
H	2.92 ± 0.09	3.28 ± 0.14	4.36 ± 0.12	30.5 ± 1.5	173 ± 6.3
p-Me	2.02 ± 0.07	2.26 ± 0.04	2.82 ± 0.07	25.4 ± 1.3	192 ± 7.8
p-OEt	1.58 ± 0.08	1.78 ± 0.07	2.08 ± 0.05	20.7 ± 2.0	210 ± 2.6
p-OMe	1.02 ± 0.05	1.30 ± 0.03	1.58 ± 0.02	33.4 ± 2.8	171 ± 9.4
ρ_{EWG}	0.344 ± 0.04	0.355 ± 0.02	0.379 ± 0.01		
r	0.991	0.993	0.995		
ρ_{EDG}	1.08 ± 0.06	1.08 ± 0.05	1.29 ± 0.05		
r	0.995	0.994	0.992		

[PicNO] = [TPPO] = 5.0 × 10^{-4} M; solvent = 100 % CH_3CN.





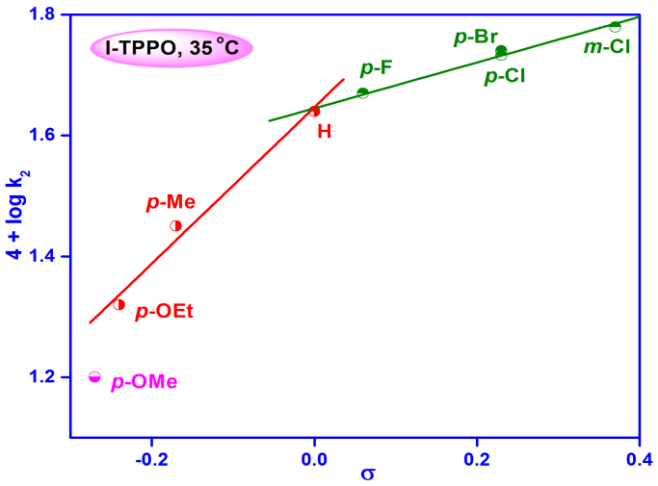


Figure 6. Hammett plots for the substituent variation in PSAA in the presence of ligand oxides: General conditions as in Table 5.

3.5 Thermodynamic parameters

The kinetics of the reaction is followed at three different temperatures 25 ºC, 30 ºC, 35ºC for all PSAAs with complex **I** in the presence of LOs. The second order rate constants and the thermodynamic parameters are calculated using Eyring's plot of $\log(k_2/T)$ against 1/T . The positive $\Delta^{\ddagger}H$ values in Table 5 show the endothermic nature of the reaction and the high negative $\Delta^{\ddagger}S$ values indicate the involvement of structured transition state in the mechanism.

4. DISCUSSION

4.1. Mechanism

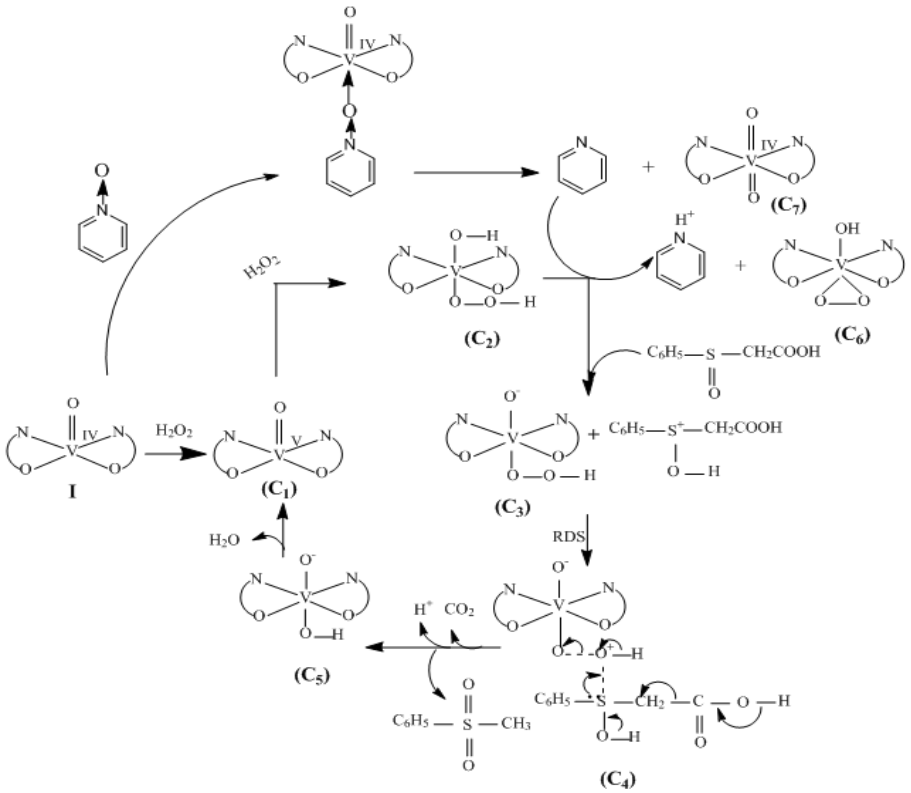
A closer view into the reaction pathway based on the observed experimental results shows, oxovanadium(IV) salophen complex is first oxidized to oxovanadium(V) salophen (**C_1**) by H_2O_2 which further reacts with excess of hydrogen peroxide to form the active species, hydroperoxovanadium(V) salophen (**C_2**). Generation of such species has been proposed as the reactive species in many reactions which involve oxovanadium(IV) Schiff base complex (Grivani et al. 2012) as catalysts.

At this juncture, in the presence of free bases Py or 4-methyl pyridine,that are formed due to N-O cleavage, a possible side reaction which occurs is the abstraction of proton from the hydroperoxo vanadium species. As a result, the active peroxo species is converted into a less active cyclic peroxide which thus causes an obstruction in the catalytic cycle of PSAA oxidation.

The PSAA then abstracts a proton from the acidic hydroxyl group of the active species (**C_2**) and thus (**C_2**) is transformed into intermediate (**C_3**). This proton transfer polarizes the sulfoxide group of PSAA, rendering it electrophilic in nature. The electrophilic nature of PSAA in the present study is confirmed from positive ρ values obtained from the Hammett correlation for both electron donating and electron withdrawing groups of PSAA and the observed substituent effect in the presence of LOs. Based on these observations, an electrophilic attack of sulfur atom of PSAA on the peroxo nucleophilic oxygen leading to the formation of the transition state (**C_4**) in a slow rate determining step is proposed for this reaction. All these changes are schematically represented in Scheme 2.

The RDS proposed in the reaction is found to be in consistence with the observed substitiuent effects. The rate is found to increase with EWG in PSAA and decrease in the case of EDG in PSAA. Finally, a fast internal oxygen atom transfer takes place in the intermediate (**C_4**) leading to the formation of methyl phenyl sulfone with the regeneration of oxovanadium(V) complex.

In the presence of LO, with the increase in concentration of oxovanadium(IV)-salophen complexes the rate of the reaction is found to increase. This may be attributed to the involvement of the complex in the formation of adduct rather than indulging in the decomposition of H_2O_2 which can thus lead to an increase in the rate of reaction. The reaction rate decreases at high concentrations of hydrogenperoxide which is due to the conversion of vanadium complex into inorganic peroxovanadate.



Scheme 2. Mechanistic pathway for the oxidative decarboxylation of PSAA by H_2O_2 in the presence of ligand oxides.

In the present study, the apparent curvature in the Hammett plots has been ascribed to the stabilization of the ground state of PSAA through resonance interaction on changing the substituents from electron withdrawing to electron donating. The resonance structures as a result of interaction between the electron donating substituent and the thionyl functionality are represented in Figure 7.

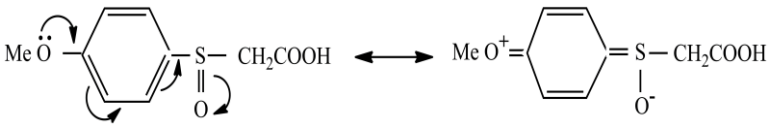


Figure 7. Ground state stabilization of PSAA.

The presence of such resonating structures in electron donating groups stabilizes the GS of the substrate and would cause a decrease in reactivity. This fact is well supported by the observed increase in ρ value from +0.672 for those with EWG to +2.40 for the reaction with EDG. To ascertain the validity of the above argument, the rate data have been treated with the Yukawa-Tsuno equation (Tsuno & Fujio 1996 &1999).

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

The term $(\sigma^+ - \sigma^o)$ is the resonance substituent constant, and 'r' value is a parameter characteristics of a reaction representing the extent of resonance contribution. The observed linear Yukawa-Tsuno plots (Fig. 8) for the reactions under study and the 'r' values obtained reveal the significant importance of resonance interaction in the reaction. The linear Yukawa-Tsuno plots not only prove the ground state stabilization of PSAAs through a resonance interaction but also show a common mechanism for all PSAAs. Um Ik Hwan and coworkers (Lee et al. 2010 & Um et al. 2008) have interpreted the non linear Hammett plots in terms of linear Yukawa-Tsuno plots on the basis of ground state stabilization of the substrate.

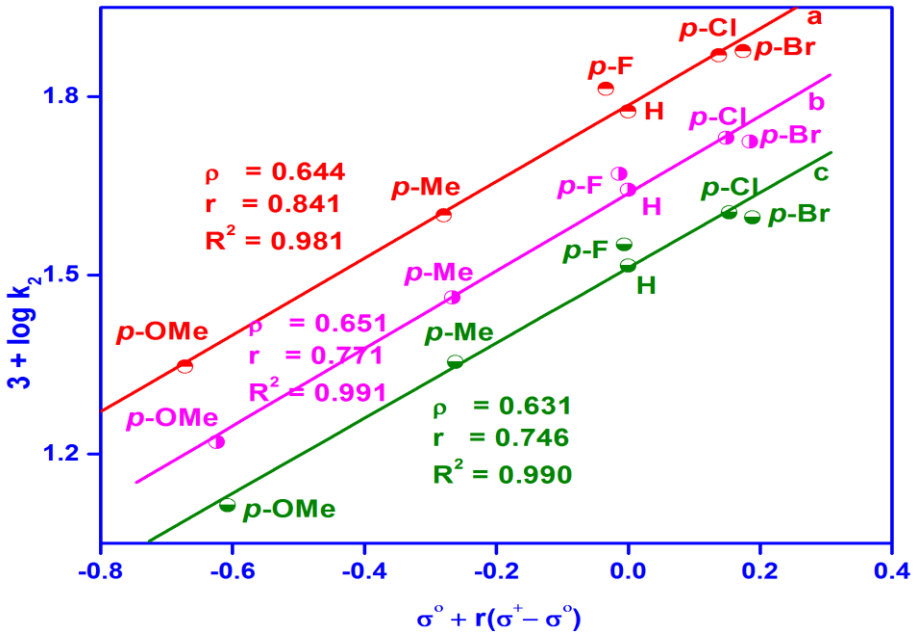


Figure 8. Yukawa-Tsuno plots for the reactions of PSAAs with H_2O_2 and complex **I**.
a = PyO at 30 °C; b = PicNO at 25 °C; c = TPPO at 30 °C.

4.2 Role of Ligand oxides

Usually the coordination of the LO occurs at the axial position to complete the octahedral coordination of the metal atom. In many salen mediated oxidation reactions, the LO-salen adduct formed during the course of the reaction has been proposed as the active oxidizing species and it has been proved that LO-salen adduct is a powerful oxidant than salen complex itself.

In the present study addition of donor LOs viz., PyO, PicNO and TPPO to a mixture of oxovanadium(IV)-salophen, PSAA and H_2O_2 shows no change in the absorption spectrum. From the kinetic data it is found that the added LOs show an impeding effect on the reaction rate which is a rare and unique observation and no such related kinetic study has been yet reported. Thus from the spectral and kinetic evidences it can be ascertained that the catalytic oxidation of PSAA is being interrupted in the presence of LOs.

On the addition of LO, the active oxidizing species concentration necessary for the oxidation of PSAA is found to decrease. This may be attributed by utilization of oxovanadium(IV)-salophen (**C_1**) for adduct formation with LO. The adduct being less stable, undergoes N-O cleavage resulting in the formation of free base and the dioxovanadium complex. This proposal has been supported by the following evidences.

In the oxovanadium(IV)-salen catalysed oxidation of tertiary amines by H_2O_2, Madhavan et al. (2015) have proved that N-oxide formed as the product binds to the oxovanadium(IV) centre which accounts for the low yield of N-oxide formed in the reaction. The vanadium(IV)-N-oxide then undergoes N-O cleavage to form the free base.

Thus on the basis of the above supporting evidences, it is proposed that in the present study, adduct is formed between the oxovanadium(IV)-salophen complex and LO in a parallel reaction with the formation of reactive species (**C_2**). This results in decrease in concentration of active species and accounts for the decrease in rate with increase in concentration of LO. The adduct formed between **I** and PyO and PicNO then undergoes N-O cleavage resulting in the formation of a dioxovanadium complex (**C_7**) and the free bases pyridine and 4-methyl pyridine . No such cleavage has been reported in the adduct formed between the complex and TPPO.

The adduct between the oxovanadium(IV) salophen complex and TPPO is not easily formed and is less stable when compared with other LOs, due to the steric hindrance created by the bulky TPPO during the binding with the vanadium metal centre and also due to decrease in electron density on the oxygen atom of TPPO as a result of the presence of three electron withdrawing phenyl group.

Since the formation of oxovanadium(IV) salophen-TPPO adduct is difficult, the reactivity should have been greater in the presence of TPPO than other LOs. However, the reactivity in the presence of added TPPO is found to be very much less and shows least reactivity among the LOs in this reaction series. Milas et al. (1969) in their patented publication of peroxides and peroxy esters and their preparations in the presence of TPPO, have experimentally shown that TPPO forms triphenylphosphonium peroxide with H_2O_2 Thus concentration of H_2O_2 is decreased which is very essential for the formation of active hydroperoxovanadium species from oxovanadium(IV) salophen complex. This accounts for the higher rate retardation in the PSAA oxidation catalysed by oxovanadium(IV) salophen complex and the oxidant H_2O_2 in the presence of TPPO.

Thus, on the basis of the above arguments, it is concluded that the observed rate retardation with LOs is due to formation of oxovanadium(IV)-salophen-LO adduct and formation of inactive peroxides with LOs which are in competition with catalytic oxidation of PSAA by H_2O_2 and oxovanadium(IV) salophen.

CONCLUSION

The mechanism of the oxovanadium(IV)-salophen catalysed oxidative decarboxylation of several phenylsulfinylacetic acids to methylphenyl sulfone by H_2O_2in the presence of ligand oxides has been investigated. The results show that ligand oxide forms a oxovanadium(IV)-salophen-ligand oxide adduct and inactive peroxides which competes with the formation of active vanadium peroxo species. The active hydroperoxo oxidizing species is also converted to less active cyclic peroxo species in the catalytic cycle and thus an impeding effect is observed in the reaction. 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. As vanadium catalysts offer competitive reactivity to those of metalloenzymes, additional work has to be done towards the understanding of structure−activity relationships.

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