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Importance of ground state stabilization in the oxovanadium(IV)-salophen mediated reactions of phenylsulfinylacetic acids by hydrogen peroxide – Non-linear Hammett correlation

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ABSTRACT

A systematic study on the oxidative decarboxylation of a series of phenylsulfinylacetic acids (PSAA) by hydrogen peroxide with four oxovanadium(IV)-salophen catalysts in 100% acetonitrile medium is presented. The hydroperoxovanadium(V)-salophen generated from the reaction mixture is identified as the bonafide active oxidizing species. Introduction of electron donating groups (EDG) in the oxovanadium(IV)-salophen catalyst and electron withdrawing groups (EWG) in PSAA enhances the reactivity, whereas EWG in the catalyst and EDG in PSAA have a retarding effect on the reaction. A Hammett correlation displays a non-linear downward curvature, which consists of two intersecting straight lines and the ρ value shifts from small positive to moderately high as the substituents change from EWG to EDG. The importance of the ground state stabilization of PSAA is inferred from a linear Yukawa–Tsuno plot. Based on the observed substituent effects and the spectral changes, a mechanism involving electrophilic attack of PSAA on the nucleophilic peroxo oxygen atom of the vanadium complex in the rate determining step followed by oxygen atom transfer is proposed.

1. Introduction

The coordination chemistry of vanadium is of current interest because of its existence in abiotic as well as biotic systems. The presence of vanadium in biological systems, its insulin enhancing action [1] and anticancer activity [2] has driven a considerable amount of research. Several Schiff base vanadium complexes have been used as insulin enhancing agents, oral insulin substitutes for the treatment of diabetes and for the treatment of obesity and hypertension [3]. Schiff base complexes formed between oxovanadium(IV)/dioxovanadium(V) and chelating ligands with hetero atoms are found to be involved in a variety of biochemical and medicinal processes, such as haloperoxidation [4], phosphorylation [5], nitrogen fixation [6], tumor growth inhibition and prophylaxis against carcinogenesis [7]. Metal complexes of salen and salophen ligands have been used in medicinal studies as models for superoxide dismutase [8,9]. While manganese-salophen/salen derivatives display cyto-protective features in fibroblast cultures via hydrogen peroxide scavenging [10], oxovanadium(IV)-salophen complexes inhibit the growth of AGS gastric cell lines [11]. Certain metal-salophen complexes have been designed for their application as functional materials [12].

Recent advances have shown vanadium complexes to be effective catalysts for the activation of peroxides by virtue of vanadium in terms of stereoselectivity, reactivity and specificity [13,14]. The capability of these complexes to form metalloperoxo species, which in turn effectively transfer an oxygen atom to reductants with a high degree of selectivity, made them synthetically useful for obtaining valuable molecules. Oxovanadium-Schiff base complexes have been reported as effective catalysts in the oxidation of sulfides [15,16], alcohols [13], phenols [17], tertiary amines to N-oxides [18], epoxidation of olefins [19] and hydroxylation of phenols [20,21]. Salophen, a tetradentate Schiff base derived from 1,2-phenylenediamine and salicylaldehyde, and its derivatives are able to stabilize different metal ions in various oxidation states and control a variety of catalytic transformations [22].

Oxidative decarboxylation plays an important role in biological systems, organic synthesis and drug metabolism. In humans,

Abbreviations: PSAA, phenylsulfinylacetic acid; EWG, electron withdrawing group; EDG, electron donating group; GS, ground state; OD, optical density; *r*, correlation coefficient.

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oxidative decarboxylation continually produces carbon dioxide in all live tissues during metabolism. Oxidative decarboxylation, in conjunction with electron transport and oxidative phosphorylation, takes place in the mitochondrial membrane and provides the basis of human cell respiration [23]. Anti-inflammatory drugs such as indomethacin and ibuprofen are decarboxylated during drug metabolism by cytochrome p-450 in vivo and the carbon dioxide released was found to reduce pain [24,25]. Enantiopure sulfoxides constitute a class of versatile chiral controllers and useful synthons in asymmetric synthesis and the pharmaceutical industry [26]. Further, sulfur substituted amino acids, vitamins, drugs and other xenobiotics are often involved in metabolism/-catabolism [27]. The chemistry of sulfones has been explored due to their therapeutic activities like antimicrobial [28], anticancer [29], anti-HIV [30], antimalarial [31] and anti-inflammatory [32]. Additionally, several drug molecules used for the treatment of leprosy, dermatitis herpetiformis [33] and tuberculosis [34] are found to contain the sulfone moiety. Hence the oxidation of organic sulfur compounds has been the subject of extensive studies in recent years. Phenylsulfinylacetic acid (PSAA), a sulfoxide containing acid group, is an ambidentate ligand and with its three donor atoms acts as a good chelating agent.

Recently, systematic attempts have been made with PSAA in this laboratory to study the mechanism and substituent effects during co-oxidation with oxalic acid by Cr(VI) [35], oxidative decarboxylation by Cr(VI) [36] and its reaction in the presence of cetyltrimethylammonium bromide [37] and picolinic acid [38], electron transfer reactions with iron(III)-polypyridyl complexes [39] and the catalytic effect of nitrogen bases [40] and ligand oxides [41] in the reactions with oxo(salen)chromium(V) complexes. Although vanadium(IV)-salen systems have been used as efficient catalysts in the asymmetric oxidation of organic sulfides by Fujita et al. [42] and Sun et al. [43], no detailed kinetic study has been reported so far in the literature on organic sulfur compounds by oxovanadium(IV)-salophen complexes. Nevertheless, Coletti et al. [44] used several salophen oxovanadium complexes as catalysts during the selective oxidation of sulfides to sulfoxides. Recently Sankareswari et al. [11] have synthesized eight salophen ligands and their oxovanadium(IV) complexes having different substituents and characterized these complexes by UV–Vis, FT-IR, EPR, ESI-MS, ^{1}H and ^{13}C spectral methods. They also reported their interaction with bovine serum albumin and cytotoxicity against cancer. The synthesis and X-ray structural characterization of such complexes were reported even earlier by Weberski Jr. et al. [45]. All these facts paved the way to explore the catalytic activity of oxovanadium(IV)-salophen complexes in the reactions of PSAAs with H_2O_2 and the results obtained on the mechanistic and substituent effects are discussed in this paper. The overall scheme of the reaction is as shown below.

2. Experimental

2.1. Synthesis of the oxovanadium(IV)-salophen complexes

The synthesis of the oxovanadium(IV)-salophen complexes was accomplished by a procedure slightly different from that reported in the literature [46]. To a hot methanolic solution (50 cc) of vanadyl sulfate ($VOSO_4{\cdot}5H_2O$; 0.25 g, 1 mM), the appropriate salophen ligand (1 mM) was added with stirring. The mixture was refluxed for one hour and cooled to room temperature. The green crystals separated were filtered, washed with diethyl ether and dried. Recrystallization was carried out from pure hot methanol. The absorption spectral data for the complexes (**I** to **IV**) are consistent with the literature data [11,44]. Their absorption maxima are 396 (**I**), 440 (**II**), 416 (**III**) and 410 nm (**IV**). The salophen ligands were prepared by a procedure similar to that reported in the literature [44]. Two equivalents of salicylaldehyde were dissolved in a minimum volume of boiling methanol (20 ml) and it was added dropwise to one equivalent of 1,2-benzenediamine in 5 ml methanol. The solution was refluxed for one hour and then cooled to room temperature. The yellow solid thus obtained was filtered, washed with methanol, diethyl ether and dried. All the compounds gave UV–Vis spectra consistent with their structures and literature data [47].

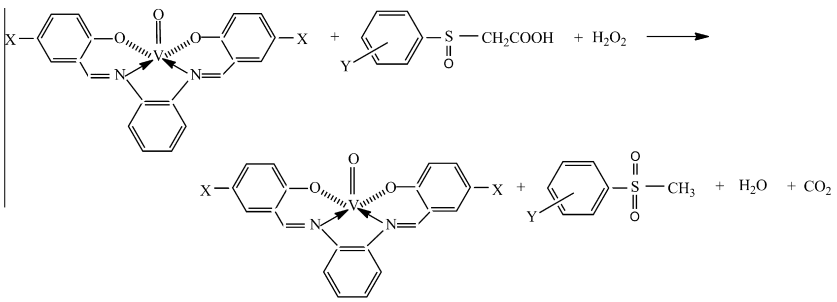
2.2. Preparation of phenylsulfinylacetic acids

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 [35]. PSAA and the *p*-chloro, *m*-chloro, *p*-bromo, *p*-fluro, *p*-methoxy and *p*-ethoxy PSAAs were purified by recrystallization from 1:1 benzene and ethyl acetate solvent mixture, whereas *p*-methyl PSAA was recrystallized with chloroform and PET ether. The purity of the PSAAs was checked by melting point [35] and LC–MS. The recrystallized PSAAs were kept inside a vacuum desiccator in order to prevent their decomposition with moisture in the atmosphere. The phenylmercaptoacetic acids were prepared by the condensation of the corresponding thiophenols with chloroacetic acid in alkaline medium [35].

Salicylaldehyde, 5-methyl, 5-methoxy and 5-chloro salicylaldehydes (Alfa Aeser), $VOSO_4{\cdot}5H_2O$ (Sigma–Aldrich), thiophenol (SD fine) and the substituted thiophenols (Sigma–Aldrich) were purchased and used as such. H_2O_2 (GR, Merck) and acetonitrile (HPLC grade, Merck) were used as received.

2.3. Kinetic studies

A double beam BL 222 Elico UV–Vis bio spectrophotometer with an inbuilt thermostat was employed to record the absorption



(**I**) X = H; (**II**) X = OCH_3; (**III**) X = CH_3; (**IV**) X = Cl

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

spectra, measure the absorbance and to follow the kinetics of the reactions. The kinetic study for the oxidative decarboxylation of PSAA and substituted PSAAs by H_2O_2 in the presence of oxovanadium(IV)-salophen complexes was carried out in 100% acetonitrile medium under pseudo first order conditions with an excess PSAA concentration over the H_2O_2 and complex concentrations. The reactions were started by quickly injecting H_2O_2 into the reaction mixture containing PSAA and the oxovanadium(IV)-salophen complex at zero time, in a quartz cuvette. The rate of the reaction was measured by following the decay of the absorbance of the hydroperoxovanadium(V)-salophen complex with time at the appropriate wavelength. Neither the oxovanadium(IV)-salophen complex nor hydrogen peroxide efficiently oxidizes the PSAA alone, they do so only in combination in acetonitrile medium.

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 the substrate. The error in the rate constants was calculated according to 95% of the student's *t*-test. The thermodynamic parameters, the enthalpy of activation ($\Delta^{\ddagger}H$) and entropy of activation ($\Delta^{\ddagger}S$), were evaluated from a linear Eyring's plot of log (k_2/T) versus $1/T$ by the least square method.

2.4. Product analysis

A solution containing 3 mM of PSAA, 0.3 mM of oxovanadium (IV)-salophen complex and 3 mM of H_2O_2 in 10 ml CH_3CN was stirred at room temperature until the completion of the reaction. The reaction mixture was then evaporated to dryness and the solid obtained was extracted with chloroform to recover the organic product. The chloroform extract was dried over sodium sulfate and the solvent was removed by evaporation. The product obtained was analyzed using IR and mass spectral techniques. Strong bands at 1148 and 1290 cm^{-1}, characteristic of symmetric and asymmetric stretching vibrations respectively of the $>SO_2$ group, were observed in the IR spectrum (Supporting information Fig. S1). The peak eluted in the LC–MS at a retention time of 1.829 min, ionizing in the APCI (+) mode at a mass of 157 (Supporting information Fig. S2) and the parent peak at M/Z = 156 in the GC–MS (Supporting information Fig. S3) clearly show that methyl phenyl sulfone is the only product of the reaction.

3. Results

The kinetics of the reaction were measured out at different initial concentrations of the reactants, oxovanadium(IV)-salophen, PSAA and H_2O_2, keeping the other reaction conditions as constant. The pseudo first order rate constants, evaluated from the linear portions of decrease in OD at different [PSAA], show a linear increase with concentration. However, the second order rate constants remain the same for all concentrations. The calculated values of the pseudo first order and second order rate constants as a function of concentration of PSAA are presented in Table 1. The unit slope values obtained from the plots of log k_1 versus log [PSAA], the observed linear plots between k_1 and [PSAA] and the constant second order rate constants at different [PSAA] for all the four oxovanadium(IV)-salophen complexes under pseudo first order conditions confirm the first order dependence of the reaction on PSAA.

Although the reaction is found to exhibit first order dependence on all the four oxovanadium(IV)-salophen complexes, as evidenced from excellent linear log OD versus time plots, the pseudo first order rate constants are found to decrease with the increase in concentration of complexes **I** to **IV**. In contradiction, it is observed that at lower concentrations of H_2O_2 there is a significant increase in the pseudo first order rate constants, while at higher H_2O_2 concentrations, beyond a particular concentration the reaction rate begins to decrease for all the complexes **I** to **IV**. The variation of the rate constant with the concentrations of vanadium complex and H_2O_2 is shown in Table 2. Among the four oxovanadium(IV)-salophen complexes, the methoxy (**II**) and methyl (**III**) oxovanadium(IV)-salophen complexes are found to be more reactive than the parent complex (**I**) and the chlorooxovanadium(IV)-salophen complex (**IV**) shows the least reactivity.

3.1. Activation parameters and linear free energy relationship

The substituent effect and linear free energy relationship were studied using several para- and meta-substituted PSAAs with H_2O_2 in the presence of complexes **I**, **II** and **IV** at 30 °C and also at three different temperatures with complex **I** to understand the nature of the transition state, rate determining step and the extent of charge transfer. It has been noted that the temperature has a positive effect on rate only in a limited range of temperatures. The reaction rate is too slow to be measured at low temperatures, while at high temperatures the rate decreases. The observed decrease in rate at higher temperatures beyond a particular temperature may be due to the decomposition of H_2O_2. The thermodynamic parameters $\Delta^{\ddagger}H$ and $\Delta^{\ddagger}S$, evaluated from the slope and intercept of the linear Eyring's plots, are shown in Table 3. The entropies of activation are found to be highly negative, while the enthalpies of activation have relatively small positive values. The positive $\Delta^{\ddagger}H$ values suggest that the reaction is endothermic in nature. The correlation between $\Delta^{\ddagger}H$ and $\Delta^{\ddagger}S$ for the various substituted PSAAs is found to be linear (Supporting Information Fig. S4). The isokinetic temperature calculated from the linear $\Delta^{\ddagger}H$ versus $\Delta^{\ddagger}S$ plot is found to be 326 K, which is above the experimental temperature and indicates that the application of the Hammett equation to the title reaction is valid. The linear isokinetic relation between $\Delta^{\ddagger}H$ and $\Delta^{\ddagger}S$ reveals that all PSAAs follow the same mechanism.

The observed kinetic data in Table 3 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 observed that electron donating groups (EDG) in PSAA retard the rate of reaction while electron withdrawing groups (EWG) accelerate the rate. The analysis of the kinetic data and the plot of log k_2 versus the

Table 1
Dependence of the pseudo first order and second order rate constants on [PSAA].

10^2 [PSAA] (M)	**I**		**II**		**III**		**IV**	
	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})	10^3 k_1 (s^{-1})	10^2 k_2 (M^{-1} s^{-1})
3.0	0.550 ± 0.02	1.83 ± 0.67	6.76 ± 0.05	22.5 ± 1.7	4.15 ± 0.03	13.8 ± 1.0	0.119 ± 0.01	0.397 ± 0.33
5.0	0.841 ± 0.01	1.68 ± 0.20	12.3 ± 0.08	24.6 ± 1.6	7.62 ± 0.02	15.2 ± 0.40	0.152 ± 0.01	0.304 ± 0.20
7.0	1.39 ± 0.03	1.98 ± 0.43	18.6 ± 0.02	30.7 ± 0.29	10.6 ± 0.04	15.1 ± 0.57	0.210 ± 0.01	0.300 ± 0.14
9.0	1.84 ± 0.02	2.04 ± 0.22	23.3 ± 0.01	25.9 ± 0.11	13.1 ± 0.06	14.6 ± 0.67	0.291 ± 0.02	0.322 ± 0.22
11.0	2.30 ± 0.05	2.09 ± 0.45	29.8 ± 0.11	27.1 ± 1.0	16.3 ± 0.01	14.8 ± 0.09	0.341 ± 0.02	0.310 ± 0.18

Complex = 1.5×10^{-4} M; [H_2O_2] = 3.0×10^{-3} M; T = 30 °C; solvent = 100% CH_3CN.

Table 2
Dependence of the pseudo first order rate constant on oxovanadium(IV)-salophen [**I**–**IV**][a] and $[H_2O_2]$.[b]

10^4 [complex] (M)	10^3 $[H_2O_2]$ (M)	10^3 k_1 (s^{-1})			
		I	**II**	**III**	**IV**
0.25	3.0	1.58 ± 0.04	20.9 ± 0.12	13.9 ± 0.80	0.310 ± 0.02
0.50	3.0	1.24 ± 0.02	16.6 ± 0.02	11.1 ± 0.21	0.235 ± 0.03
0.75	3.0	1.00 ± 0.01	12.1 ± 0.06	8.18 ± 0.04	0.154 ± 0.01
1.0	3.0	0.83 ± 0.09	9.61 ± 0.15	6.02 ± 0.13	0.138 ± 0.03
1.5	3.0	0.55 ± 0.02	6.76 ± 0.05	4.15 ± 0.03	0.119 ± 0.02
3.0	3.0	0.17 ± 0.03	3.81 ± 0.02	1.49 ± 0.01	–
1.5	1.0	1.01 ± 0.01	14.1 ± 0.06	7.59 ± 0.07	0.203 ± 0.01
1.5	3.0	1.84 ± 0.08	23.3 ± 0.01	13.1 ± 0.06	0.291 ± 0.04
1.5	4.0	2.83 ± 0.06	29.8 ± 0.53	20.9 ± 0.51	0.510 ± 0.02
1.5	5.0	5.58 ± 0.09	40.9 ± 0.21	28.5 ± 0.15	0.809 ± 0.06
1.5	7.0	8.69 ± 0.15	52.3 ± 0.09	24.4 ± 0.09	1.09 ± 0.01
1.5	9.0	13.0 ± 0.10	61.8 ± 0.32	45.2 ± 0.61	1.18 ± 0.07
1.5	11.0	11.5 ± 0.20	59.3 ± 0.11	40.1 ± 0.08	1.11 ± 0.05
1.5	13.0	8.10 ± 0.17	48.1 ± 0.20	32.3 ± 0.12	1.02 ± 0.03

[a] [PSAA] = 3.0×10^{-2} M.
[b] [PSAA] = 9.0×10^{-2} M, T = 30 °C, Solvent = 100% CH_3CN.

Table 3
Second order rate constants (k_2), thermodynamic and Hammett parameters for the reactions of PSAAs with H_2O_2 catalyzed by oxovanadium(IV)-salophen complexes.

Y	**I** 10^2 k_2 (M^{-1} s^{-1})			$\Delta^{\ddagger}H$ (kJ mol^{-1})	$-\Delta^{\ddagger}S$ (JK^{-1} mol^{-1})	**II** 10^2 k_2 (M^{-1} s^{-1})	**IV**	ρ	r
	25 °C	30 °C	35 °C			30 °C	30 °C		
p-Cl	7.98 ± 0.15	10.6 ± 0.23	12.9 ± 0.29	33.7 ± 3.1	153 ± 6.8	91.2 ± 0.31	1.79 ± 0.08	−1.74 ± 0.09	0.999
m-Cl	8.98 ± 0.48	12.6 ± 0.31	15.8 ± 0.47	40.9 ± 2.8	128 ± 8.1	99.9 ± 0.50	1.89 ± 0.12	−1.72 ± 0.14	0.999
p-F	7.46 ± 0.39	8.91 ± 0.35	11.5 ± 0.25	29.7 ± 1.5	167 ± 7.3	87.1 ± 0.44	1.71 ± 0.03	−1.76 ± 0.10	0.998
p-Br	8.20 ± 0.18	11.3 ± 0.41	13.4 ± 0.34	35.0 ± 1.2	148 ± 5.3	95.5 ± 0.40	1.81 ± 0.07	−1.72 ± 0.11	0.999
H	7.28 ± 0.19	8.70 ± 0.16	10.6 ± 0.12	25.8 ± 1.7	180 ± 12	79.4 ± 0.10	1.60 ± 0.09	−1.70 ± 0.10	0.999
p-Me	4.79 ± 0.11	5.05 ± 0.09	7.50 ± 0.22	30.6 ± 2.8	168 ± 9.2	50.1 ± 0.21	1.12 ± 0.03	−1.66 ± 0.12	0.997
p-OMe	1.40 ± 0.06	2.82 ± 0.02	3.55 ± 0.11	68.4 ± 2.1	50.2 ± 8.5	20.0 ± 0.35	0.591 ± 0.06	−1.53 ± 0.08	0.999
p-OEt	3.89 ± 0.09	4.29 ± 0.10	6.64 ± 0.24	37.2 ± 3.0	148 ± 7.8	35.5 ± 1.3	0.901 ± 0.09	−1.60 ± 0.06	0.999
ρ^{+}_{EWG}	0.239 ± 0.03	0.451 ± 0.11	0.446 ± 0.03			0.247 ± 0.03	0.180 ± 0.02		
r	0.982	0.987	0.986			0.970	0.985		
ρ^{+}_{EDG}	1.12 ± 0.07	1.30 ± 0.04	0.853 ± 0.07			1.40 ± 0.05	1.01 ± 0.04		
r	0.998	0.998	0.999			0.988	0.995		

[**I** = **II** = **IV**] = 1.0×10^{-4} M, [PSAA] = 5.0×10^{-2} M, $[H_2O_2] = 5.0 \times 10^{-3}$ M, solvent = 100% CH_3CN.

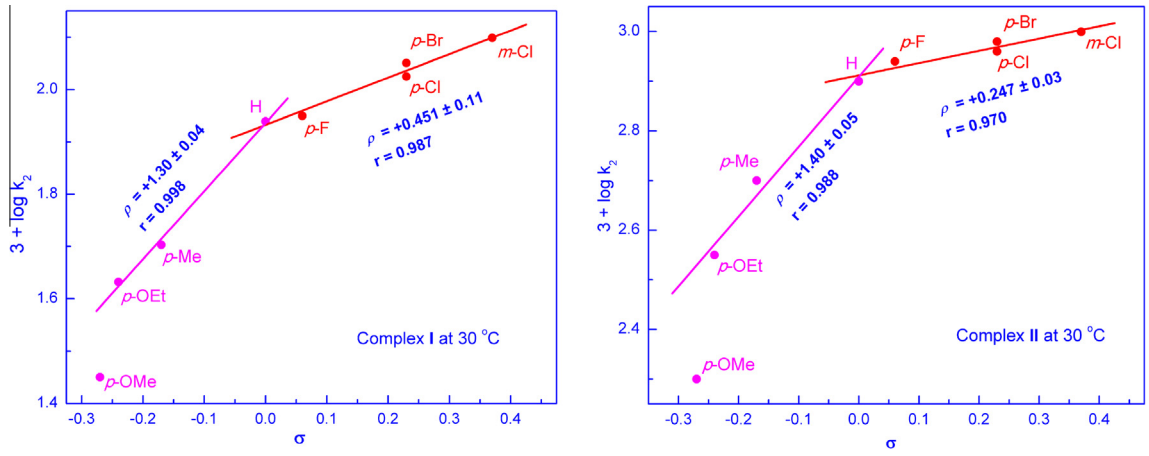


Fig. 1. Hammett plot for the reactions between the PSAAs and H_2O_2 in the presence of **I** and **II**. [I] = [II] = 1.0×10^{-4} M, [PSAA] = 5.0×10^{-2} M, $[H_2O_2] = 5.0 \times 10^{-3}$ M, solvent = 100% CH_3CN, T = 30 °C.

Hammett's σ substituent constants show non-linear behavior. The Hammett plots (Fig. 1) exhibit distinct curvature with two intersecting linear portions. The data in Table 3 and Fig. 1 reveal that the reaction is fairly susceptible to electron releasing substituents with positive ρ values (0.853–1.40) and less susceptible to electron withdrawing substituents, which are indicated by rather small positive ρ values (0.180–0.451). A similar trend of the substituent effect has already been reported in the alkaline hydrolysis of *o*-arylthionobenzoates [48], pyridinolysis of substituted 2,4-dinitrophenyl benzoates [49] and in the reactions of nucleophiles

with aryl benzoates [50]. In all these cases the Hammett parameter changes from a large positive ρ value to a small one as the substituent changes from an EDG to a strong EWG, and the observed non-linearity is explained on the basis of ground state stabilization of the substrates possessing an EDG. Another interesting observation noted in the Hammett correlation is the anomalous behavior of the methoxy substituent which shows a significant positive deviation from the rest of the substituents.

The effect of the substituents in the salophen ligand of the oxovanadium(IV)-salophen complex reveals that the reaction rate is very much enhanced by the electron releasing methoxy group and strongly retarded when the electron withdrawing chloro group is introduced. The Hammett plots obtained by plotting log k_2 versus 2σ of substituted complexes with different PSAAs show a single straight line for both electron releasing and electron withdrawing substituents, with high negative ρ values ranging between −1.53 and −1.76. From Table 3 it has been observed that the values of the reaction constant (ρ) are almost constant for all PSAAs, implying that the extent of transmission of the electronic effect is the same in every case.

4. Discussion

4.1. Active species

Oxovanadium(IV)-salophen (**I**) has an absorption maximum at 396 nm, which arises due to its ligand to metal charge transfer. This peak is slightly affected by the addition of H_2O_2 after a certain period of time and shows a blue shift, with an absorption maximum of 393 nm, which indicates a change in the species. Coletti et al. [44] have prepared the oxovanadium(V)-salophen complex and reported the absorption maximum of the complex as 393 nm. This clearly indicates that in the present study the oxovanadium(IV)-salophen complex is oxidized to the oxovanadium (V)-salophen complex with H_2O_2. In addition, it is interesting to note that addition of H_2O_2 at a higher concentration to the complex shows an increase in intensity of a new broad absorption peak around 610 nm after a time interval, followed by a decrease during the course of time, which depends upon the experimental conditions (Fig. 2). This observation demonstrates the formation of a new intermediate vanadium species in the reaction mixture.

A similar observation, noted around 560 nm in the asymmetric oxidation of sulfides to sulfoxides by Schiff base-oxovanadium(IV) and (V) complexes with organic hydro peroxides [46] was explained on the basis of the formation of hydroperoxovanadium (V) species. Further, a 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 [17] and at 570 nm in the oxovanadium(IV)-salen oxidation of tertiary amines to N-oxides [18] 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 evidence for the formation of hydroperoxovanadium(V) species in the reaction. The formation and involvement of peroxovanadium(V) species as an active intermediate was also confirmed in the peroxidative oxidation of benzene and mesitylene by vanadium(IV) and (V) complexes with a nitrogen and oxygen containing ligand catalyst [51], sulfides and benzoin by polystyrene bound oxidovanadium(IV) and dioxidovanadium(V) [52], sulfides and styrene by an oxovanadium(IV) complex catalyzed by N,S donor ligands [53] and oxovanadium(IV)-salen catalyzed H_2O_2 oxidation of phenols to catechol [17] and tertiary amines to N-oxides [18]. The existence of hydroperoxovanadium(V) species in the reactions involving salophen and salen oxovanadium(IV) complexes was confirmed by IR, ^{51}V NMR and theoretical studies by Coletti et al. [44].

Another prominent observation noted in the pseudo first order plots during the kinetic runs with complex **I** was an initial well defined induction period for a definite period of time, followed by gradual decrease in absorbance. The induction period and initial time taken for the decrease in OD were found to decrease with increase in temperature and concentrations of the complex and hydrogen peroxide (Fig. 3). It is suggested that the induction period is due to slow generation of the active oxidizing species, hydroperoxovanadium(V), during the course of the reaction. The observed decrease in the induction period with temperature may be due to the easy formation of hydroperoxo species at high temperatures. However, when substituents are introduced into complex **I**, they do not show any appreciable induction period which indicates the instantaneous generation of peroxo species during the reactions with **II**–**IV**. A similar induction period observed during the oxygenation reactions of cyclohexane [54] and sulfides [55], catalyzed by cobalt(III)-salen ion, was explained on the basis of a delay in the generation of the active species [Co(III)-salen-OOH].

4.2. Mechanism

The existence of an induction period and an increase in the absorbance at 610 nm in the present study are rationalized by

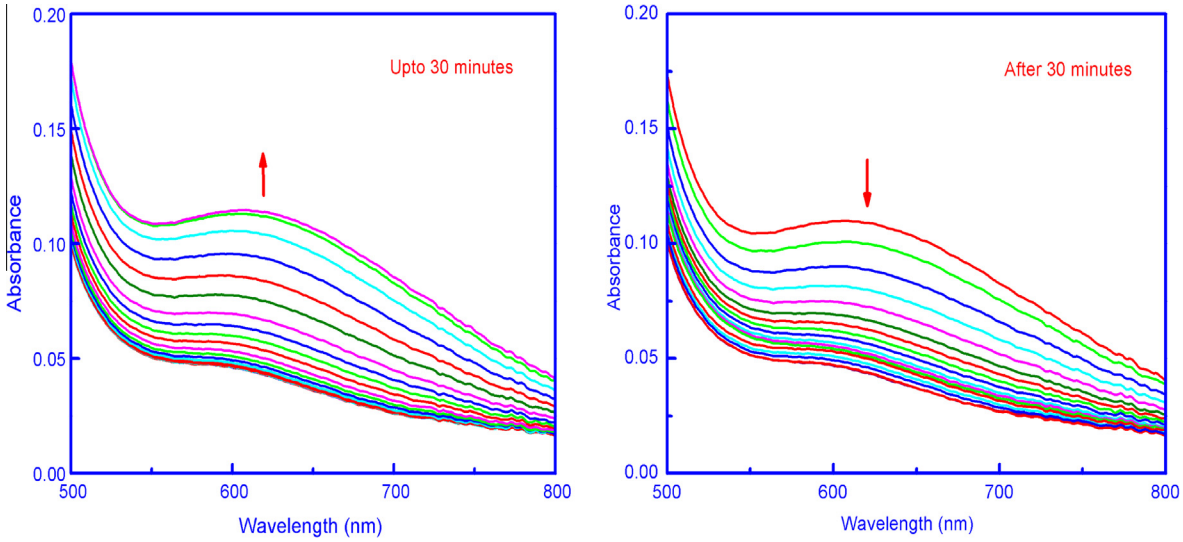


Fig. 2. Absorption spectral changes of complex **I** with time on addition of H_2O_2. [**I**] = 5.0×10^{-4} M, [H_2O_2] = 5.0×10^{-3} M.

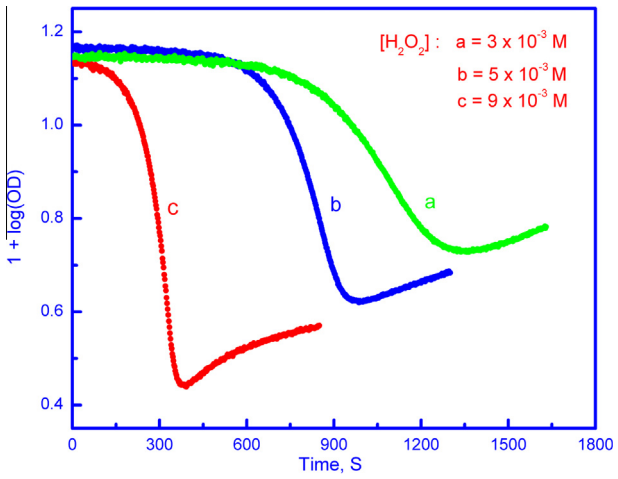
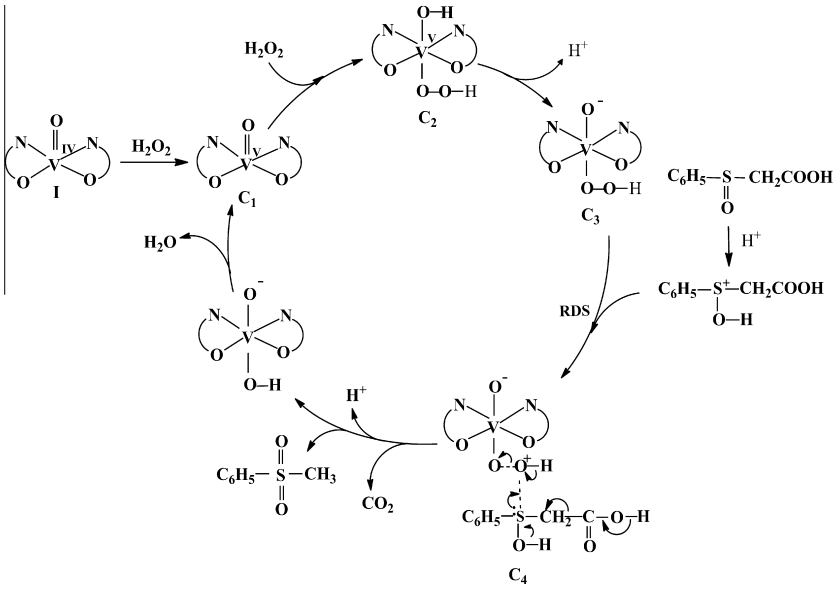


Fig. 3. Pseudo first order plots for the reactions of PSAA with complex **I** at different $[H_2O_2]$. [I] 1.5×10^{-4} M, [PSAA] = 9.0×10^{-2} M.

the slow generation of the active oxidizing species, hydroperoxovanadium(V)-salophen, from the vanadium(IV) complex and H_2O_2. It is proposed that the oxovanadium(IV)-salophen complex is first oxidized to oxovanadium(V)-salophen (**C_1**) which further reacts with excess of hydrogen peroxide to form the active species, hydroperoxovanadium(V)-salophen (**C_2**). The formation of the hydroperoxo species in the reaction is ascertained by the occurrence of the reaction only in the presence of H_2O_2 and the salophen complex together. An analogous scheme for the generation of active species has been proposed in the epoxidation of cyclooctene by an oxovanadium(IV)-Schiff base complex [56]. In the hydroxylation reactions of aromatic compounds by H_2O_2 using a vanadium (IV) based catalyst [57], it has been shown that the vanadium(IV) complex first interacts with H_2O_2 and rapidly transforms into a stable vanadium(V) species, which further reacts with H_2O_2 to yield a peroxovanadium(V) intermediate species. As the hydroperoxo species is acidic in nature, it is transformed into the intermediate (**C_3**) by the release of a proton. The acid behavior of the hydroxyl group coordinated to the vanadium center is confirmed by Coletti et al. [44] from its pK_a value. The proton released from **C_2** polarizes the sulfoxide group of PSAA, rendering the sulfur as electrophilic in nature. The biphilic nature of the organic sulfoxides, electrophilic or nucleophilic, is well established and it depends on the nature of the oxidant involved in the reaction [58,59].

The behavior of sulfoxide in a reaction is ascertained from a study of substituent effects. Negative ρ values for nucleophilic sulfoxides [60,61] and positive ρ values for electrophilic sulfoxides [58,62] have been reported in reactions with different substituents. From the observed positive ρ values for both electron releasing and electron withdrawing groups of PSAA in the Hammett correlation of the substituent effect, it is concluded that PSAA behaves as electrophile. The behavior of sulfoxide as an electrophile is well established in the oxidation reactions of sulfoxides with fluorenone carbonyl oxide [62] and permanganate [58] where nucleophilic attack of the oxidant on the sulfoxide in the rate determining step has been proposed. On this basis, an electrophilic attack of the sulfur atom of PSAA on the peroxo nucleophilic oxygen atom leading to the formation of the transition state (**C_4**) in a slow rate determining step (RDS) is proposed for the reaction. Based on the above discussions, the following mechanism (Scheme 1) involving the catalytic cycle of oxovanadium(V)-salophen is proposed for the oxidative decarboxylation of PSAA by H_2O_2.

The proposed RDS is consistent with the observed substituent effects, i.e. the increase in rate with EDG in the complex and EWG in PSAA and also the decrease in rate by EWG in the complex and EDG in PSAA. The increase in rate with EDG in the complex is due to the increase in nucleophilicity of the complex. A similar rate acceleration was observed by Mathavan et al. [18] in the oxovanadium(IV)-salen catalyzed oxidation of tertiary amines by H_2O_2. EWG in the phenyl ring of PSAA makes the sulfur atom more electropositive, thereby facilitating the electrophilic approach of PSAA towards the nucleophilic peroxo oxygen atom. On the other hand, EDG in the phenyl ring of PSAA makes the sulfur atom less electropositive and thus slows down the electrophilic attack of PSAA on the nucleophilic oxygen atom. The intermediate (**C_4**) then undergoes fast internal oxygen atom transfer, leading to the formation of a methyl phenyl sulfone with the regeneration of the oxovanadium(V) complex. The observed increase in OD in the pseudo first order plots after a certain period of time (Fig. 3) is interpreted by the regeneration of the oxovanadium(V)-salophen



Scheme 1. Catalytic cycle of the oxovanadium(V)-salophen complex during the oxidative decarboxylation of PSAA.

complex. In the epoxidation reaction of alkenes catalyzed by oxovanadium(IV)-Schiff base complexes with organic peroxides, it has been shown that the final form of the complex is oxovanadium(V) [63]. A similar nucleophilic oxygen transfer from the active hydroperoxide to electropositive sulfur atom has been proposed in the vanadium-Schiff base catalyzed sulfoxidation [64]. The formation of the methyl phenyl sulfone in the absence of any other oxygen sources clearly demonstrates that the oxygen atom incorporated in PSAA is derived from the hydroperoxovanadium(V)-salophen species.

In the reactions of H_2O_2 catalyzed by oxovanadium salophen and salen complexes it has been shown that the oxidation of the substrate and decomposition of H_2O_2 take place simultaneously [44,65]. Thus the observed decrease in reaction rate with the increase in concentration of the oxovanadium(IV)-salophen complexes (Table 2) can be interpreted by the fast decomposition of hydrogen peroxide. The observed decrease in the reaction rate at high concentrations of hydrogen peroxide in all four complexes (Table 2) may be visualized by the conversion of the vanadium complex into the inorganic peroxovanadate (Fig. 4). The existence of diperoxo vanadates at high concentrations of H_2O_2 has been shown in the reactions of vanadium(IV) base catalyzed oxidations [66,67] and proven by ^{51}V NMR studies [68].

4.3. Interpretation of the non-linear Hammett plot

The existence of distinct curvature with two intersecting linear portions in a non-linear Hammett plot has been traditionally interpreted as a change in the reaction mechanism or a change in the RDS within a given mechanism [69,70]. However in the present study the apparent downward curvature in the Hammett plots has been ascribed to stabilization of the ground state of PSAA through a resonance interaction on changing the substituents from electron withdrawing to electron releasing. This argument is supported by the significant negative deviation observed in the Hammett plot as the substituent becomes a stronger EDG. The resonance structures as a result of the interaction between the electron donating substituent and the thionyl functionality are represented in Fig. 5.

The presence of such resonance structures in substances with electron releasing groups stabilizes the GS and causes a decrease in reactivity. Accordingly, one can expect a large ρ value for EDG compared with EWG. In fact the ρ value decreases considerably from 1.30 for the reactions with EDG to 0.451 for those with EWG. Thus the deviation from the Hammett correlation is taken as evidence for ground state stabilization by EDG. The observed non-linear Hammett plots in the aminolysis reactions of substituted phenyl-2-methoxy benzoates [71], 4-pyridyl substituted benzoates [72] and 2-pyridyl substituted benzoates [73] have been interpreted by ground state stabilization of the substrates. Neuvonen et al. [74] have explained the enhanced reactivity of esters

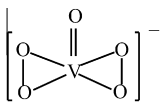


Fig. 4. Structure of peroxovanadate.

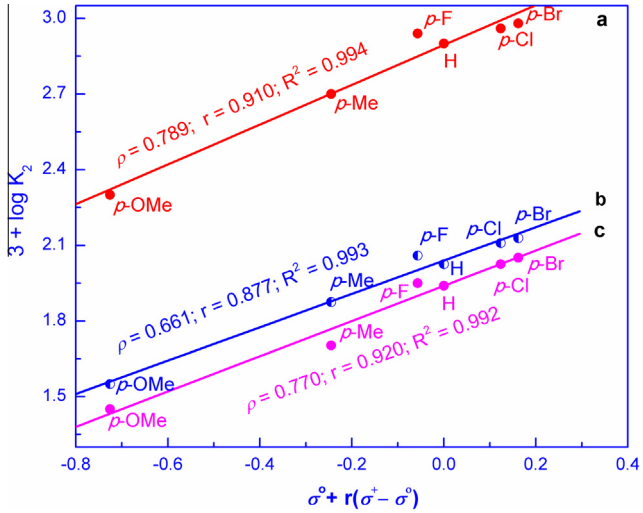


Fig. 6. Yukawa–Tsuno plots for the reactions of PSAAs with H_2O_2 and the complexes. a = **II** at 30 °C, b = **I** at 35 °C, c = **I** at 30 °C.

containing EWG by the decrease in the resonance stabilization of the GS of the esters.

To examine and ascertain the validity of the above argument, the rate data have been treated with the Yukawa–Tsuno equation [75–77].

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

The term $(\sigma^+ - \sigma^o)$ is the resonance substituent constant, while the '*r*' value is a parameter characteristic of a reaction representing the extent of the resonance contribution. Interestingly the Yukawa–Tsuno plots (Fig. 6) exhibit a good linearity for the reactions under study and the '*r*' values obtained (0.877–0.920) suggest that the resonance interaction is relatively significant. The observed linear Yukawa–Tsuno plots not only confirm a common mechanism for all PSAAs but also prove that the ground state stabilization of the PSAAs through a resonance interaction is the cause for the non-linearity in the Hammett plots. Um Ik-Hwan and coworkers [73,78] have reported such type of linear Yukawa–Tsuno plots for non-linear Hammett plots and explained this on the basis of ground state stabilization of the substrate.

5. Conclusion

In the oxidative decarboxylation of phenylsulfinylacetic acids to methyl phenyl sulfones by H_2O_2 and catalyzed by oxovanadium (IV)-salophen complexes, hydroperoxovanadium(V)-salophen has been identified as the active species. The observed order of reactivity, OMe > Me > H > Cl, among substituted oxovanadium(IV)-salophen complexes has been explained on the basis of electronic effects. A mechanism involving electrophilic attack of PSAA on the peroxo nucleophilic oxygen atom of the active species formed between the oxidant and catalyst, followed by fast oxygen atom transfer to PSAA has been proposed for the reaction. The Hammett correlation of the kinetic data of the substituted PSAAs gave a downward curvature with small positive ρ values for EWG and moderately high positive ρ values for EDG, while better linearity

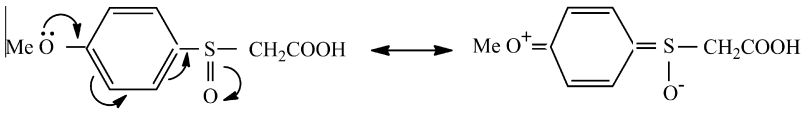


Fig. 5. Ground state stabilization of PSAA.

is observed when the kinetic data were treated with the Yukawa–Tsuno equation. The non-linear Hammet plot and the observed linear Yukawa–Tsuno plot have been explained on the basis of ground state stabilization of PSAA through a resonance interaction between the electron donating substituent and the sulfinyl group.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.poly.2016.06.038.

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