Oxovanadium (IV) salen catalysed oxidations of organic sulphides with H2O2 and electrochemical behavior of complexes

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Abstract: - Oxovanadium(IV)-salen Schiff base complexes are used as catalysts for the oxidation of organic sulphides with H_2O_2 as oxidant to form sulfoxides. The complexes are able to generate hydroperoxo complexes with H_2O_2 which are used as catalyst.. This hydro peroxovanadium(V) facilitates the nucleophilic attack by the sulfide to form sulfoxide and hence the rate of reaction is increased. The oxidation is selective and sulfoxide is the only product of the reaction and the sulfoxide moiety is formed which is important in the biological activities. The catalytic oxidations of organic compounds with oxidants such as H_2O_2 are less wasteful than the traditional methods. The kinetic study on the H_2O_2 oxidation of organic sulfides catalysed by OVIV salen complexes in dichloromethane was carried out under pseudo first order conditions and this reaction follows the Michaelis-Menten kinetics. In order to account for the spectral and kinetic results we have proposed a possible mechanism involving proton coupled electron transfer in the reaction. The electrochemical methods also provide highly valuable information regarding catalytic process that the oxidation of V(IV) to V(V) and reduction of V(V) to V(IV) is one electron transfer process.

Keywords: Oxovanadium(IV) salen complexes, Sulfides and Michalis-Menten kinetics

INTRODUCTION

Schiff bases are playing an important role in inorganic chemistry, as they easily form stable complexes with most transition metalions. The development of the field of bioinorganic chemistry has increased the interest in Schiff base complexes, since it has been recognized that many of these complexes may serve as models for biologically important species [1-3]. Vanadium chemistry has attracted attention due to its interesting structural features [4] and biological relevance. The biochemical aspects of vanadium complexes have further promoted the coordination chemistry of vanadium [5]. Oxovanadium (IV) Schiff base complexes have much interest as catalysts due to its interesting structural and biological properties [10]. It catalyses many reactions like oxygenation,[11] hydrolysis, electro-reduction and decompositions. Vanadium is a physiologically essential element found in both anionic and cationic forms with oxidation states ranging from -1 to +5. Catalytic oxidations of organic compounds with oxidants such as molecular oxygen and H_2O_2 are less wasteful than the traditional methods and are now important reactions both in the laboratory and an industrial scale. The oxovanadium(IV) complexes are used as the catalysts in the presence of oxidizing agent H_2O_2 which is converted into oxidized form of stable dioxo-V^V complexes. This peroxocomplex was used as a catalyst for many oxidation reactions. Oxovanadium catalyzed sulfoxidation is an important transformation both for the relevance of the product obtained (sulfoxides and sulfones) and for the information that this reaction can give on the nature of the active peroxo species involved into the process can be chemo and stereoselective, yielding mainly sulfoxides with high enantiometric excess. The sulfoxide moiety is involved in important biological activities serves as a ligand for asymmetric synthesis and they may act both as electrophiles and nucleophiles depending on the nature of the oxidant.

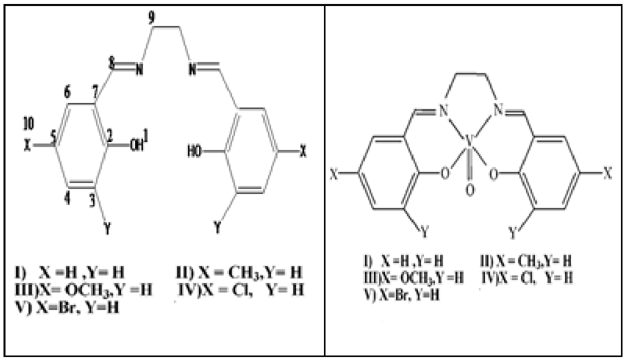
EXPERIMENTAL

Preparation of Schiff base salen ligands (I -V)

The general procedure for the synthesis of salen ligands involves the condensation of salicylaldehyde/ substituted salicylaldehyde and ethylenediamine in a 2:1 ratio in an alcoholic medium. The salen ligands were recrystallised from ethanol as bright yellow crystals. The parent H2salen ligand was prepared by refluxing a mixture of 3.66g (3.1ml, 30mmol) of salicylaldehyde and 0.9g (1.0 ml, 15mmol) of ethylenediamine in 150ml of methanol for 1h. The yellow crystalline solid was collected at pump and washed with cold methanol and dried in air. The melting point of the salen ligand prepared in the present study is 126˚C.

Preparation of [oxovanadium (IV) salen] complexes (I -V)

The Oxovanadium(IV)-salen complexes were prepared by the reaction of stoichiometric amounts of the respective ligands with hydrated vanadyl sulphate [$VOSO_4.3H_2O$] in methanol solution. All the five salen ligands and oxovanadium(IV) salen complexes were characterized by various spectral techniques like UV-vis, IR, NMR,EPR and Cyclic Voltametry (CV).



Kinetic studies and rate measurements

The kinetic studies of oxidation of sulphides with active oxidant H_2O_2 and oxovanadium complex were carried out in dichloromethane (DCM) under pseudo-first order conditions using excess of substrate over the oxidant. The rate of decay of active species generated in the reaction mixture was followed spectrophotometrically from the decrease in absorbance at appropriate wavelengths. A set of duplicate runs was carried out and the rate constants quoted are the average values.

RESULTS AND DISCUSSION

The progress of the reaction is followed by maintaining the concentrations of the substrates atleast 10 times greater than over the complex.The absorbance value of complex I at 380 nm decreases from initial upto 360 seconds and after that the absorbance value increases upto 720 seconds and slightly increases further. These spectral changes are shown in Figure.1. This indicates that there is the formation of peroxo complex which oxidizes the sulphide into sulfoxide and sulfone. After that the absorbance started to increase and attains the steady value and no further changes in the absorbance. The rate of the reaction increases with increase in substrate concentration, but attains saturation at high substrate concentration. The inference from the saturation, extent of binding of substrates to the complex is almost same. Thus the redox reaction proceeds through Michalis-Menten kinectics which is shown in the Figure 1.1.

Fig. 1: UV-vis absorption spectral changes of complex I with addition of H_2O_2

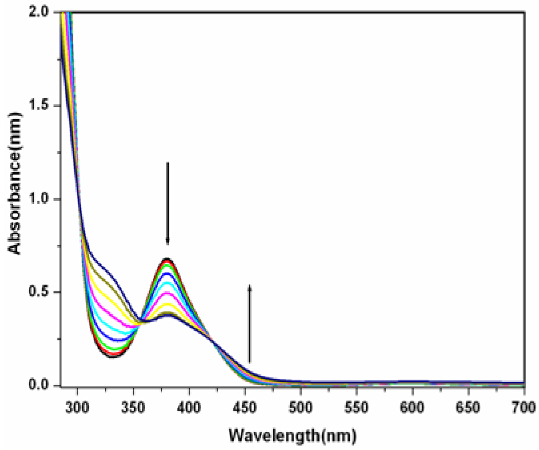
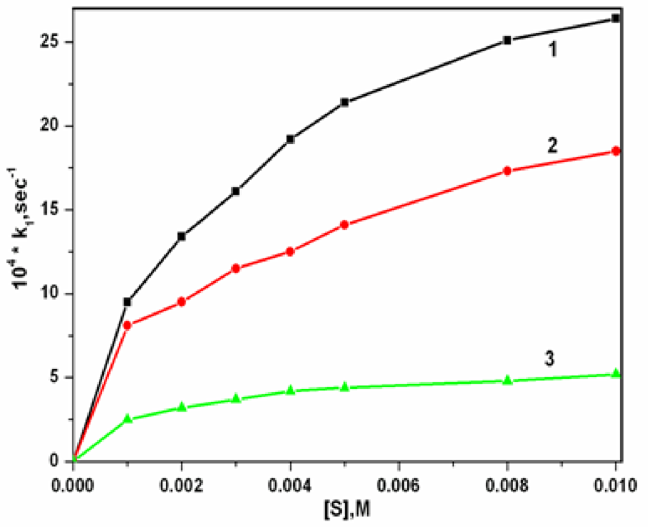


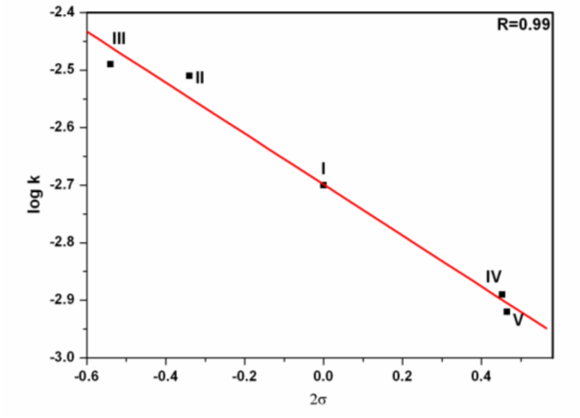
Fig. 1.1: Michalis-Menten Kinetics



Effect of substituent:

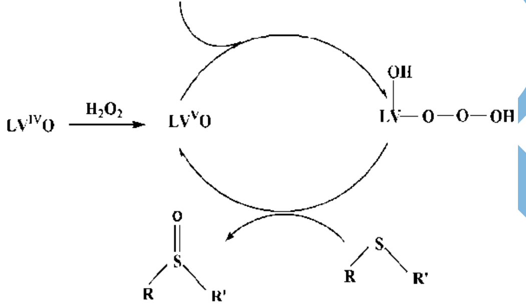
The Hammett plot for oxidation of sulfides using oxovanadium(IV)-salen complexes gives negative ρ values in the range from -0.36 to -0.45. This value indicates that there is a good correlation and the positive charge is developed at the centre in the transition state of the reaction.

Figure 1.2: Hammet plot for oxovanadium (IV) salen Complexes with $C_6H_5SC_2H_5$



Mechanism of the reaction:

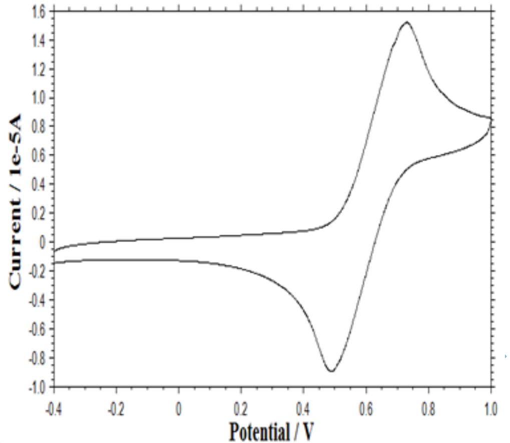
We reported the oxidation of organic sulphides into sulphoxides by using oxovanadium(IV)-salen complexes with H_2O_2 as oxidants. From the spectral changes we concluded the vanadium(IV)-salen complex is converted into hydroperoxovanadium(V) complex with excess of H_2O_2, which is active species used for the oxidation of sulphides to sulfoxides.[12] The proposed mechanism for the oxidation of sulphides by the oxovanadium(IV)-salen complex in the presence of H_2O_2 is shown below.



Electrochemical behavior of Oxovanadium(IV)salen complexes:

The electrochemical methods also provide highly valuable information regarding catalytic process since catalytic conversions are frequently accompanied by the change in the structure of the complex and the oxidation state of the metal. An oxidation peak is observed at nearly 0.5mV and VO(Salen) is oxidized to [VO(salen)]+ in a fully reversible one electron step. The electron is removed from the non bonding orbital and the V(V) complex is formed. Upon reversal of the scan direction the V(V) complex is reduced at lower potential observed at nearly 0.3mV. These results reveal that the redox process for all the vanadyl schiffbase complexes under study is the one electron transfer reaction. The wave is assignable to the V+5/V+4 redox couple.[13,14]

Fig. 2: Cyclic voltammogram of oxovanadium (IV) salen complexes



Effect of scan rate:

By increasing the scan rate from 50 to 200, there is a shift in peak potential. The cathodic peak potential shifted more negatively, and anodic peak potential shifted more positively also with increase in current. Scanrate variation of complex I CH3CN with 0.1M TBAP at 50,100,200 mVs-1 shown in figure 2.1 and the corresponding scanrtae values are shown in Table 2.1.

Figure 2.1: scan rate variation of complex

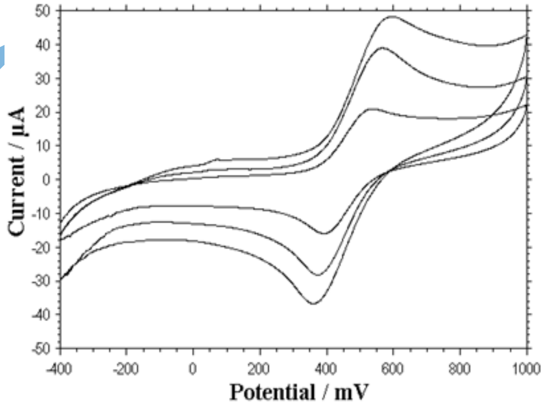


Table 2.1 Scan rate variation of complex

Scan rate (mV s^{-1})	Anodic potential(mV)	Cathodic potential (mV)
50	0.529	0.388
100	0.564	0.372
200	0.584	0.359

Effect of substituent:

The Ep_a values are more positive according to the sequence MeO<Me<H<Br<Cl and the cathodic peak potential (Ep_c)

becomes less negative according to the sequence MeO<Me<H<Br<Cl increasing in both electron withdrawing and π-acceptor qualities of the substituents. Cyclic voltammograms for the complexes(I-V) in DMF is shown in the **Figure2.2** indicates the effect of substituent, and the corresponding Ep_a and Ep_c values are given in the **Table 2.2.**

Fig.2.2: Effect of substituent for complexes (I to V) in DMF

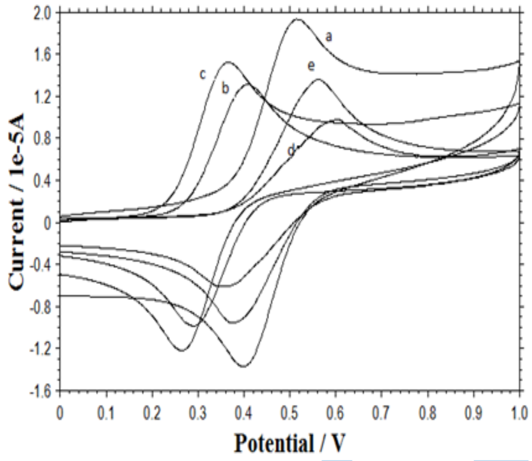


Table 2.2: Effect of substituent in complexes (I to V)

Complex	Ep_a (IV → V)	Ep_c▼ (V → IV)
I	0.5053	0.2971
II	0.3939	0.2895
III	0.3631	0.2705
IV	0.5791	0.3666
V	0.5499	0.3689

Effect of Solvent:
The electrochemical behavior of oxovanadium (IV)salen complexes were studied in CH_3CN, DCM, DMF, DMSO and CH_3OH solvents and TBAP as a supporting electrolyte. The results are presented in the Table **2.3** and the cyclic voltamagram of complex II in various solvents are shown in the Fig. **2.3.**

Figure 2.3 Cyclic voltammogram of II in various solvents

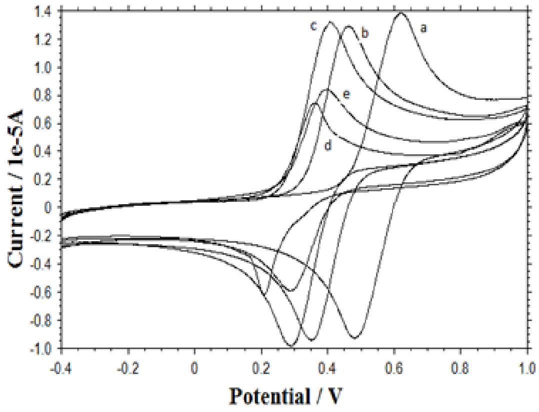


Table 2.3 Effect of solvents with complex

Complex	DCM	CH_3CN	DMF	DMSO	CH_3OH
I	0.7094	0.3958	0.4012	0.4745	0.4016
II	0.6087	0.3397	0.3417	0.3511	0.3491
III	0.6237	0.2979	0.3168	0.3271	0.3375
IV	0.7420	0. 4663	0.4729	0.4951	0.4500
V	0.7094	0.4991	0.4594	0.4798	0.4647

The results show that the cyclic voltammograms of the studied complexes are solvent dependent. Generally, Methanol solvent, with the highest donor number (32.0), should stabilize the product of the oxidation reaction via coordination to the centre of the V(IV) complexes. The less ΔE values for acetonitrile, and the less donor number than the other solvents indicate the acetonitrile will be a good solvent for the complexes.

CONCLUSION

The kinetic studies were performed under pseudo order condition by spectrophotometrically and which follows Michalis-Menton behavior and the rate constants were calculated by the plot of absorbance versus time. The UV-visible absorption spectra of the complexes were changed by the addition of hydrogen peroxide. A catalytically active species peroxo complexes produced by the interaction of oxovanadium (IV)-salen with H_2O_2.

In the absence of catalysts the oxidation of substrates precedes very slow manner. In order to account for the spectral and kinetic results we have proposed a possible mechanism involving proton coupled electron transfer in the reaction. From the redox potential values, we concluded that the oxidation of V(IV) to V(V) and reduction of V(V) to V(IV) by one electron transfer process.

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