Synthesis and Electrochemistry of Vanadium(IV) Schiff Base Complexes

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The electrochemical properties of vanadyl(IV) derivatives, namely salen Schiff base complexes of the type [VO(Salen)] (5-BrSalen, 5-NO_2Salen, 5-MeOSalen, salpn (bis(salicylaldehyde)-1,3-propanediamine, 5-BrSalpn, 5-NO_2Salpn, 5-MeOSalpn, Me_2Salen, Salophen, 5-BrSalophen, and 5-MeOSalophen) were investigated. The equatorial Schiff base ligands affect the oxidation potentials *via* interaction with the d-orbitals of the vanadyl metal ion. The cathodic peak potential (E_{pc}) becomes less negative according to the sequence MeO- < H- < Br- < NO_2-.

INTRODUCTION

The family of Schiff bases derived from diamines (especially ethylene diamine), phenolic aldehydes and salen has proved to be the source of versatile ligands for many transition metals, including vanadium(IV) [1-4]. Salen complexes of transition metals have been used in solution as biomimetic catalysts for oxygen atom transfer, and as catalysts for enantioselective epoxidation, aziridinations, mediating organic redox reactions and other oxidative processes [5,6]. Vanadium complexes are very interesting as model compounds for the clarification of several biochemical processes [7,8]. We chose salen for this investigation, as its ligand framework is similar to porphyrins. Porphyrin and Schiff base ligands are capable for supporting metals in a variety of oxidation states. However, the metal or the ligand may become oxidized [9].

The electrochemical methods also provide highly valuable information regarding catalytic processes since catalytic conversions are frequently accompanied by the change in the

structure of the complex and the oxidation state of the metal; however, the electrochemical approaches for these purposes have not been fully explored. Knowledge of the electronic and steric effects that control the redox chemistry of these metal complexes may prove to be critical in the design of new catalysts. Our goal in the present study is to investigate these metal-mediated processes by electrochemistry. The present work was undertaken to test and expand upon the earlier conclusions [10,11] by studying the electronic and steric influence of salen derivatives on electrochemical properties of V(IV) Schiff base complexes (Fig. 1).
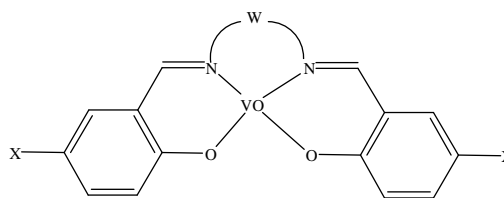
W = -CH_2-CH_2-	X = H, MeO, Br, NO_2
W = -CH_2-CH_2-CH_2-	X = H, MeO, Br, NO_2
W= -C_6H_4-	X = H, MeO, Br

Fig. 1. The structure of [VO(Chel)], complexes.

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EXPERIMENTAL

Materials

Ethylenediamine, propanediamine, 1,2-diaminobenzene, 2-hydroxyacetophenone, salicylaldehyde, 5-nitrosalicyl-aldehyde, 5-methoxysalicylaldehyde, 5-bromosalicylaldehyde, vanadylacetylacetonate, methanol, DMF, THF, acetonitrile, and tetrabutylammonium perchlorate were purchased from Merck, Aldrich and Fluka.

Physical Measurements

Infrared spectra were recorded using a Perkin Elmer 781 IR spectrophotometer. Electronic absorption spectra were recorded on a Jasco V-530 spectrometer. Elemental analyses were performed by using a Heraeus CHN-O-RAPID elemental analyzer.

Cyclic voltammograms (CVs) were obtained using an Autolab modular electrochemical system (Eco Chemie, Ultrecht, The Netherlands) equipped with a PSTA 20 module and driven by GPES (Eco Chemie) in conjunction with a three-electrode system and a personal computer for data storage and processing. An Ag/AgCl (saturated KCl)/3 M KCl reference electrode, a Pt wire (counter electrode) and a glassy carbon working electrode, (Metrohm 0.0314 cm^2) were employed for the electrochemical studies. Voltammetric measurements were performed at room temperature in DMF solution with 0.1 M tetrabutylammonium perchlorate as the supporting electrolyte.

Synthesis of the Complexes

H_2Salen and other Schiff bases used in this research were prepared as previously reported, by condensation of 1,2-diamine with aldehyde (1:2 molar stoichiometric ratio) in methanol or ethanol [10]. The [VO(Chel)] where chel = Salen, 5-BrSalen, 5-NO_2Salen, 5-MeOSalen, Salpn, 5-BrSalpn, 5-NO_2Salpn, 5-MeOSalpn, Me_2Salen, 5-BrSalophen, and 5-MeOSalophen, were prepared by previously described methods [5,6,12-14].

RESULTS AND DISCUSSION

In order to investigate the effects of the Schiff base substitutions on the oxidation potential of [VOL],
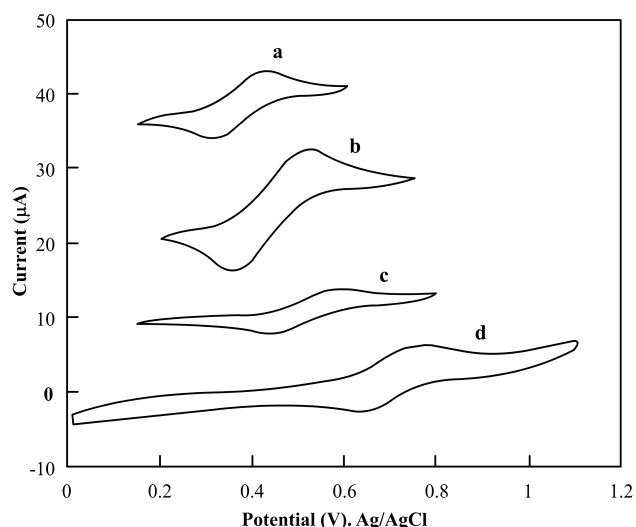
Fig. 2. Cyclic voltamograms of [VO(5-X-Salen)] complexes in 0.1 M, tetrabutylammonium perchlorate DMF solution at room temprature and scan rate of 100 mVs^{-1}: X = MeO (a), X = H (b), X = Br (c), X = NO_2 (d).

voltammetric experiments were carried out in DMF solution at room temperature, taking into consideration the electrochemical behavior of the ligands to obtain more details of the electron transfer processes of these complexes. A typical cyclic voltammogram of the [VO(Salen)] complex in the potential range of 0.0 to 1.0 V (*vs*. Ag/AgCl) is shown in Fig. 2b. An oxidation peak is observed at ca. 0.512 V. VO(Salen) is oxidized to the mono cation [VO(Salen)]$^+$ in a fully-reversible one-electron step. The electron is removed from the nonbonding orbitals and the V(V) complex is formed. Upon reversal of the scan direction, the V(V) complex is reduced to V(IV) at lower potentials. Multiple scans resulted in nearly superposable cyclic voltammograms, thereby showing that the five coordinate geometry is stable in both oxidation states, at least on the cyclic voltammetry time scale. These results reveal that the redox process for all of the vanadyl Schiff base complexes under study is the one-electron transfer reaction. The oxidation potentials for the different complexes are set out in Table 1. The formal potentials ($E_{1/2}$ (IV $\leftrightarrow$ V)) for the V(IV/V) redox couple were calculated as the average of the cathodic (E_{pc}) and anodic (E_{pa}) peak

Table 1. Oxidation Potentials (in V) for [VO(chel)], in DMF (I = 0.1 M, Tetrabutylammonium Perchlorate)

No.	chel	E_{pa} (IV → V)	E_{pc} (V → IV)	$E_{1/2}$ (IV ↔ V)
1	Salen	0.512	0.326	0.419
2	5-MeOSalen	0.465	0.250	0.358
3	5-BrSalen	0.600	0.415	0.508
4	5-NO$_2$Salen	0.770	0.600	0.685
5	Me$_2$Salen	0.455	0.306	0.380
6	Salpn	0.565	0.482	0.524
7	5-MeOSalpn	0.455	0.365	0.410
8	5-BrSapn	0.630	0.510	0.570
9	5-NO$_2$Salpn	0.893	0.678	0.786
10	Salophen	0.600	0.445	0.522
11	5-MeO Salophen	0.525	0.415	0.470
12	5-Br Salophen	0.700	0.486	0.593

Table 2. Oxidation Potentials (in V) for [VO(chel)], in Different Solvents (I = 0.1 M, Tetrabutylammonium Perchlorate)

No.	chel		E_{pa} (IV → V)	E_{pc} (V → IV)	$E_{1/2}$ (IV ↔ V)
1	Salen	DMF	0.512	0.326	0.419
2	″	CH$_3$OH	0.441	0.331	0.386
3	″	CH$_3$CN	0.452	0.340	0.396
4	″	THF	0.538	0.155	0.346
5	Salpn	DMF	0.565	0.482	0.524
6	″	CH$_3$OH	0.566	0.490	0.528
7	″	CH$_3$CN	0.472	0.394	0.433
8	″	THF	0.452	0.245	0.348
9	Salophen	DMF	0.600	0.445	0.522
10	″	CH$_3$OH	0.512	0.415	0.464
11	″	CH$_3$CN	0.552	0.455	0.504
12	″	THF	0.833	0.200	0.516

potentials of this process (see Tables 1 and 2).

The Electronic Effect of Schiff Base Ligands

The influence of different substituents on the electronic structure of a series of the vanadyl Schiff base complexes was determined by cyclic voltammetry (Table 1). The cyclic voltammograms of VO(Salen) derivatives are shown in Fig. 2. The voltammograms of the other VO derivatives have the same trend.

The results show that in each series of ligands (all Schiff bases with aliphatic and aromatic imine bridges), the anodic peak potential (E_{pa}) corresponding to the intramolecular

reductive coupling of the imine groups varies, as would be expected from the electronic effects of the substituents at positions 5,5′. Thus, E_{pa} becomes more positive according to the sequence MeO- < H- < Br- < NO_2-. On the other hand, the cathodic peak potential (E_{pc}) becomes less negative according to the sequence MeO- < H- < Br- < NO_2-, increasing in both electron-withdrawing and π-acceptor qualities of the substituents. Similar results have been reported previously for analogous copper(II), nickel(II), and cobalt(III) systems, and have been interpreted under the assumption that the strong electron-withdrawing effects (with the best π-acceptor quality) stabilize the lower oxidation state while the electron-donating groups (with the least π-acceptor quality) have a reverse effect [10,11,15,16]. However, another possibility would be that, owing to the decrease in donor ability of the ligand groups (mainly the phenoxy groups) the stabilities of both V(IV) and V(V) decrease through the above mentioned sequence but for the V(V), there is some extent [16]. For all series, Hammett-type relationships were found between the E_{pa} values and the appropriate *para*-substituent parameters [17], which reflect the variation of the electrode potential as a function of the electron-withdrawing ability of the substituents at positions 5,5′ (Fig. 3). The results show that the decrease in the basicity of the phenoxy group through the trend of MeO- > H- > Br- > NO_2- would be determinant for the electrochemical sequences observed.

It is clear that both views have the same effect on the oxidation and reduction potentials. While the first (electron-withdrawing and π-acceptor) property decreases the electron density of the metal center by electron-withdrawing groups (good π-acceptors) and increases it *via* the electron-donating groups (weak π-acceptors), the latter (σ-donor) property decreases or increases the electron density on the metal center *via* σ-donation power. Thus, the electron-withdrawing groups are weak σ-donors and the electron-donating groups are good σ-donors. Therefore, the vanadium oxidation reaction intermediates of a complex, such as [VO(5-MeOSalen)]$^+$, are the most stable, while [VO(5-NO_2Salen)]$^+$ is the most reactive. The oxidation of V(IV) increases as follows: 5-MeOSalen < Salen < 5-BrSalen < 5-NO_2Salen.

Complexes with aromatic imine bridges (salophen derivatives) have the same effect on the potentials; however, vanadyl salophen complexes are oxidized at higher potentials.
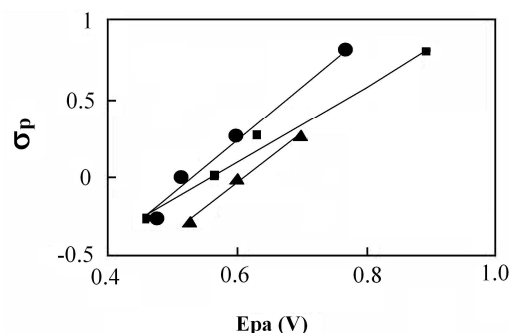
Fig. 3. Correlation between the Epa values for Schiff-bases and the respective σ substituents (*p*-substitution) for salen derivatives (●) (r = 0.990), salpn derivatives (■) (r = 0.994), and salophen derivatives (▲) (r = 0.995).

The extensions of the π-system on salophen Schiff bases make better π-acceptors Schiff base than salen Schiff bases. In the other words, the donation power of salophen is less than that of salen.

Accordingly, the substituents on the Schiff base ligands have a similar effect than those of salen complexes. Also, substituents on the functional groups on the azomethane carbon affected the oxidation of vanadyl complexes. While the oxidation of [VO(Me$_2$Salen)] occurs at 0.455 V, the oxidation potential for salen is 0.510 V. Therefore, the methyl groups stabilize the [VO(Me$_2$Salen)]$^+$ complex through electron release and the oxidation potentials of V(IV) increase according to the following trend: Me$_2$Salen < Salen < Salpn < Salophen.

Since vanadium(IV) and vanadium(V) complexes always gives adducts of the form [V(IV)=O → V(V=O]$^+$ [18], an alternative rationalization for the electrochemical results in an association which occurs upon the oxidation of mononuclear [VOL] to yield the V(IV)/V(V) adducts as soon as the vanadium(V) species is produced. The subsequent oxidation of the vanadium(IV) partner yielding mononuclear [V(IV)=O]$^+$ would require fast association/dissociation on the voltammetric time scale: 2[VOL] = [(VOL)$_2$]$^+$ + e$^-$ = 2[VOL]$^+$ + e$^-$. More detailed electrochemical studies are required in order to define this system more clearly.

The Steric Effect of Schiff base Ligands

To study the steric effect of Schiff bases on the anodic peak potentials, salpn and its derivatives were selected. As the results show in Table 1, V(IV) is oxidized at higher potentials by increasing the steric effects. On the other hand, the range of potentials is varied by changing the steric and electronic parameters. While the potentials for salen derivatives is about 305 mV, that of salpn is about 440 mV. Apparently, by increasing the steric effects of the Schiff base, the planarity of the complex is decreased. The donor power of salpn is less than that of salen and the salpn complexes are therefore oxidized at higher potentials.

The Solvent Effect

The electrochemical behavior of VOL (where L = salen, salpn, or salophen) were studied in acetonitrile (AN), THF, DMF and methanol solvents, with 14.6, 20, 26.5, and 32 donor numbers, respectively. The results are shown in Table 2 and Fig. 4. From the structure and properties of the vanadyl Schiff base complexes, we expect good correlation between the redox potentials and solvent properties. The studied complexes are five-coordinated and have a free site. The donor solvents can therefore, coordinate to this type of complex and stabilize them, especially the V(V) products of electrochemical reactions. The results show that the cyclic voltammograms of the studied complexes are solvent dependent. However, no clear trend between the CVs and the properties of the solvents, such as the donor number of the solvent, has been determined. Generally, methanol solvent, with the highest donor number, should stabilize the product of the oxidation reaction *via* coordination to the center of the V(IV) complexes.

The interesting point about salpn complexes is the effect of solvent on oxidation potentials. While the oxidation potentials of the [VO(salpn)] complex are different in different solvents, the ΔE for different solvents is nearly constant. It seems that upon oxidation, while the product $[V(V)O(Salen)(Sol)]^+$ is formed from $[V(IV)O(Salen)]$, the product $[V(V)O(Salpn)(Sol)]^+$ is formed from salpn $[V(IV)O(Salpn)(Sol)]$. However, salpn vanadium complexes involve the solvent molecule before and after oxidation. In fact, during the electron transfer reaction, the least amount of structure distortion of these VO(salpn) complexes takes place during the time scale of the CV, which correlates well with their catalytic activities [5]. Therefore, the coordination
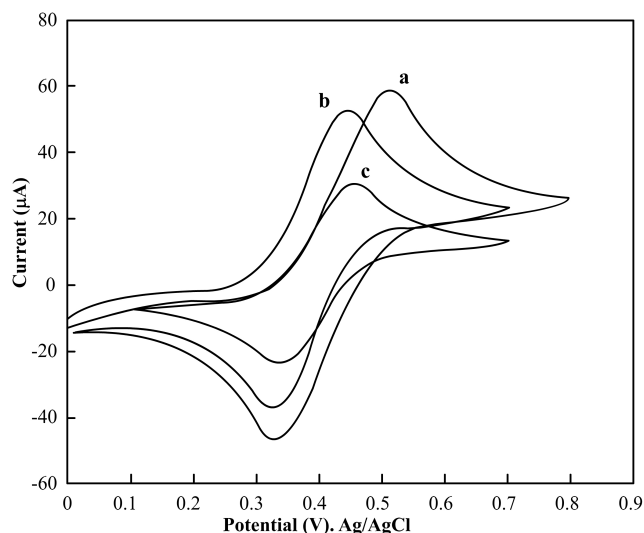
Fig. 4. Cyclic voltamogram of [VO(Salen)] in different solvents containing 0.1 M of tetrabutylammonium perchlorate at room temprature and scan rate of 100 mV s^{-1}: DMF (a), CH$_3$OH (b), AN (c).

number 6 for vanadium(IV) in the VO(salpn) complexes is favored, resulting in the polymeric form of the salpn complexes and their low catalytic activity in solution [5,6].

The phenolic oxygen of the salpn Schiff bases in the solid state could coordinate to five-coordinated vanadium Schiff base complexes and stabilize them. In solution, the donor molecules, like solvents, could coordinate to such complexes and stabilized them. So these complexes have at least one free site for inner sphere reactions with the appropriate substrates.

The ΔE values for methanol and acetonitrile are less than that of DMF. On the other hand, acetonitrile, with a lower donor number than DMF, is a good solvent for catalysis reactions because the displacement of this solvent by the substrates is easier than for those solvents with higher donor numbers.

CONCLUSIONS

The electrochemical behavior of V(IV) Schiff base complexes leads us to conclude that the anodic peak potentials E_{pa} for the reduction process V(IV) $\rightarrow$ V(V) + e$^-$, which depends on the nature of the equatorial Schiff base ligand,

changes according to the following trend: $Me_2Salen <$ Salen $<$ Salpn $<$ Salophen. The anodic peak potentials E_{pa} of different substituents change according to: 5-MeOSalen $<$ Salen $<$ 5-BrSalen $<$ 5-NO_2Salen.

ACKNOWLEDGEMENTS

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