

# Synthesis, characterization and study of vanadyl tetradentate Schiff base complexes as catalyst for C-H bond activation of olefins with *tert*-butylhydroperoxide

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## Introduction

Particular attention has recently paid to the synthesis and study of the diimino tetradentate Schiff bases and their complexes. This is due to a variety of reasons, not the least of which is their crucial role in some biological processes such as the biological function of bacteriorhodospin [1]. These complexes are used in some chemical processes as catalyst and also as biological models in understanding the structure of biomolecules and biological processes [2,3].

The biological importance of vanadium compounds in different oxidation states are many faceted. Vanadium compounds are also of major concern because of their adverse effect on the hydroprocessing catalysts used in the refining crude oil [4,5]. In addition, Selective epoxidation of olefins catalyzed by high-valence early transition metal complexes such as Mo(II), V(IV), V(V), and Ti(V) have become of the most important industrial processes due to the recent utilization of the *tert*-butyl alcohol co-product for manufacture of propylene oxide as an octane booster in gasoline (Halcon process)[6]. More recently, vanadium (IV) co-ordination compounds have been shown to catalyze selective oxidation of alkenes by molecular oxygen [7-9].

The present article describes our recent work on the oxidation of cyclohexene and cyclooctene by *tert*-butylhydroperoxide (TBHP) using oxovanadium (IV) tetradentate Schiff base complexes as the catalysts.

## Materials and Methods

1,2-propylenediamine, appropriate aldehyde or ketone and vanadyl acetylacetonate for preparing Schiff base ligands and vanadyl complexes were used as received from commercial suppliers. Solvents were dried and distilled by standard methods before use. Solvents for electrochemical experiments were re-distilled and passed through a column of activated alumina. Schiff base ligands were obtained by condensation of the 1,2-propylene diamine and appropriate aldehyde or ketones in absolute ethanol. Oxovanadium (IV) complexes were prepared from reaction of Schiff base ligands with vanadium(IV) oxide acetylacetonate in ethanol. Catalytic oxidation reactions were performed in stirred flasks. The reaction products were monitored at periodic time intervals using gas chromatography. The oxidation products were identified by comparison with authentic samples (retention times in GC).

## Results and Discussion

The oxovanadium(IV) complexes with tetradentate Schiff base ligands that were used in this study are shown in Figure 1. They are remarkably stable to air, water and heat.

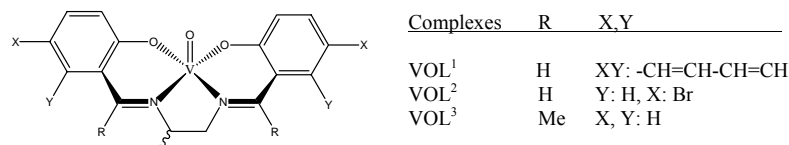


Figure 1. General structure of the studied oxovanadium complexes

The vanadyl complexes were tested as catalyst for oxidation of cyclohexene and cyclooctene. The catalytic activity of homogeneous catalysts is shown in Table 1 and 2.

Table 1. Oxidation of cyclohexene with TBHP catalysed by vanadyl complexes in CH<sub>3</sub>CN

Catalyst	Conversion (%)	TOF (h <sup>-1</sup> )	Selectivity (%)		
			Epoxide <sup>a</sup>	Alcohol <sup>b</sup>	Ketone <sup>c</sup>
VOL <sup>1</sup>	20.8	34	78.1	5.5	16.4
VOL <sup>2</sup>	29.9	48	45.5	9.6	45.3
VOL <sup>3</sup>	37.4	61	61.5	6.1	32.3

Solvent: 10 ml; Catalyst: 1.02×10<sup>-3</sup>mol; duration: 6 h, at reflux; cyclohexene: 1 ml; TBHP: 2 ml  
<sup>a</sup> cyclohexene oxide; <sup>b</sup> 2-cyclohexene-1-ol; <sup>c</sup> 2-cyclohexen-1-one

Table 2. Oxidation of cyclooctene with TBHP catalysed by vanadyl complexes in CH<sub>3</sub>CN

Catalyst	Conversion (%)	TOF (h <sup>-1</sup> )	Selectivity (%)		
			Epoxide <sup>a</sup>	Alcohol <sup>b</sup>	Ketone <sup>c</sup>
VOL <sup>1</sup>	56.2	70	96.4	3.8	-
VOL <sup>2</sup>	46.3	58	88.4	6.6	4.8
VOL <sup>3</sup>	74.9	93	93.2	4.2	2.4

Solvent: 10ml; Catalyst: 1.02×10<sup>-3</sup>mol; duration: 6h, at reflux; cyclooctene: 1ml; TBHP: 2ml  
<sup>a</sup> cyclooctene oxide; <sup>b</sup> 2-cyclooctene-1-ol; <sup>c</sup> 2-cyclooctene-1-one

Reactivity of the catalysts would be modulated by control of ligand substitution. The trend observed in Tables 1 and 2 could be explained by donor ability of ligands (H<sub>2</sub>L<sup>1</sup>> H<sub>2</sub>L<sup>2</sup>> H<sub>2</sub>L<sup>3</sup>) available in the complex catalysts. As Wang et al. [10] have pointed out recently, the key point in the conversion of olefins to products is the reduction of L-M<sup>n+</sup> to L-M<sup>(n-1)+</sup>. This reduction to be facilitated by increasing the number of electron donating groups in the ligands.

The electrochemical behavior of the catalysts was investigated using cyclic voltammetry method (see Table 3). The vanadyl complexes VOL<sup>X</sup> (X=1-3) exhibit a reversible electrochemistry behavior. The peak separation for the cathodic and anodic cyclic voltammetric peak potentials is very close to 60-80 mV, indicating that the number of electron transferred should be 1. The fact that the reduction is completely reversible indicates that the five-coordinate geometry is stable in both oxidation states, at least on the cyclic voltammetry time scale.

Table 3. Formal potential for redox couples vanadium (V/IV)<sup>a</sup>

Complex	E°(V(V)/V(IV) (mV) versus AgCl/Ag (ΔE <sub>p</sub> (mV))
VOL <sup>1</sup>	517 (83)
VOL <sup>2</sup>	589 (84)
VOL <sup>3</sup>	496 (77)

<sup>a</sup> Electrochemical measurements made in anhydrous acetonitrile containing 0.1 M tetrabutylammonium hexafluorophosphate (TBAH)

## Significance

The catalytic system described here is an inexpensive method for oxidation of olefins, with the advantage of high activity, selectivity, re-usability and short reaction time.

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