ORIGINAL PAPER

# Epoxidation of alkenes and oxidation of sulfides catalyzed by a new binuclear vanadium *bis*-oxazoline complex

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**Abstract** *Bis*(oxazoline) ligand, [2,2'-(1,3-phenylene)bis(oxazole-4,2-diyl)]-dimethanol, derived from dicyanobenzene was applied as ligand for complexation with vanadium. The catalyst was characterized by FT-IR, UV–Vis, <sup>1</sup>H NMR spectroscopic methods, CHNS, ICP and thermal analyses, and magnetic susceptibility. The catalytic activity of this complex was then studied in the epoxidation of alkenes with TBHP (*tert*-butyl hydroperoxide), in acetonitrile. The effect of reaction parameters such as kind of solvent and oxygen donors was studied in the epoxidation of cyclooctene. The catalytic activity of this catalyst was also investigated in the oxidation of sulfides with  $H_2O_2$  in ethanol and the corresponding sulfoxides and sulfones were produced.

Keywords  $Bis(oxazoline) \cdot Epoxidation \cdot Sulfoxidation \cdot Vanadium complex \cdot TBHP \cdot H_2O_2$ 

## Introduction

The oxidation of organic substrates by transition metal complexes has become an important research area in both organic synthesis and bioinorganic modeling of oxygen transfer metalloenzymes [1–4]. Among these metals vanadium has

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I. Mohammadpoor-Baltork e-mail: imbaltork@sci.ui.ac.ir special interest. Many vanadium complexes have already been synthesized and established oral insulin mimetic activity [5]. Vanadium (V) centers, having low radius/charge ratio, are usually strong Lewis acids, which makes them suitable for the activation of peroxidic reagents [6]. Consequently, vanadium (V) complexes have been established to act as catalyst precursors in numerous oxidation reactions such as epoxidations of alkenes and allylic alcohols, oxidations of sulfides to sulfoxides and sulfones, bromination reactions, oxidations of primary and secondary alcohols to the corresponding aldehydes and ketones, and hydroxylations of alkanes and arenes [7]. *Bis*-oxazoline (= bis[4,5-dihydrooxazole]; box) ligands have established the greatest share of attention in N-containing ligands, for instance salen [8], semicorrins [9], sulfoximines [10], 2,2'-bipyridines [11], diimines [12], amidines [13], and lately, imidates with an exocyclic coordinating N-atom [14]. Box ligands are known as inexpensive, easily available, and pretty much stable [11]. These ligands are very versatile and present several points of range. The selectivity and activity can be modified by changing the starting amino acid, the nature and substituents at the bridge, and the nature of the metal [15]. Consequently, the design, synthesis, and application of  $C_2$ -symmetric box ligands have received a lot of attention [16]. Since their initial report, a lot of research have been devoted toward the synthesis and application of these box ligands. During the last decade, numerous chiral box ligands with different backbones, such as aliphatic chains, aromatic rings, 4.5-dioxolane, dibenzocycloheptene, biphenyl and binaphthyl, and cyclic rings have been reported [17–19]. Interest is also growing in the design of polydentate ligands that could form di- and poly-nuclear complexes [20]. Recent studies indicate that dinuclear and cluster complexes have been used in the catalysis [21, 22], and modeling the catalytic activity of metalloenzymes [23]. Several examples reveal that dinuclear metal complexes can exhibit discrete



Scheme 1 Epoxidation of alkenes and oxidation of sulfides

advantages over mononuclear metal complexes. Such complexes can meditate multielectron transfers [24] and also activate a substrate by simultaneous coordination to two (or more) metal centers [25].

Although the potential of multidentate oxazoline-based ligands is obvious, reports describing their use are still limited. This reason and the successful applications of bisoxazolines, prompted us to explore the prospective of these types of ligands with the combination of exceptional features of vanadium, as catalyst in the epoxidation of alkenes and oxidation of sulfides (Scheme 1).

### **Experimental**

catalyst

All materials and chemicals were of commercial reagent grade and prepared from Merck, Aldrich or Fluka. Alkenes were obtained from Merck or Fluka and were passed through a column containing active alumina and/ or silica to remove peroxide impurities. <sup>1</sup>H NMR spectra were recorded in  $CH_3OH-d_4$  or DMSO-d<sub>6</sub> solvent on a Bruker-Avance 400 MHz spectrometer. FT-IR spectra were obtained as potassium bromide pellets in the range of 400- $4.000 \text{ cm}^{-1}$  and were run on a Jasco 6300D instrument. Gas chromatography experiments (GC) were performed on a Shimadzu GC-16A instrument using a 2 m column packed with silicon DC-200 or Carbowax 20 m. UV-Vis spectra were obtained on a Shimadzu UV 265 spectrometer. The vanadium content of the catalyst was determined by a Jarrell-Ash 1100 ICP spectrophotometer.

The bis-oxazoline ligand was synthesized using our previously reported method [26].

### General procedure for synthesis of vanadium complex

The bis-oxazoline was metallated as follows: A degassed ethanol solution (40 ml) of the corresponding bis-oxazoline (276 mg, 1 mmol) was added to a solution of V(O)



 $(acac)_2$  (1 mmol, 265.16 mg) in absolute ethanol (20 ml) under argon atmosphere. The reaction was stirred under reflux conditions for 24 h. The solution was then cooled, filtered, and evaporated under reduced pressure. This crude product was then dissolved in dichloromethane to remove



Fig. 1 Optimization of catalyst amount in the epoxidation of cyclooctene



Fig. 2 The effect of different oxidants in the oxidation of cyclooctene catalyzed by vanadium complex

Fig. 3 The effect of different solvents in the oxidation of cyclooctene catalyzed by vanadium complex

unreacted V(O)(acac)<sub>2</sub>. This dark green product was then dissolved in methanol, filtered, and the solvent was evaporated under reduced pressure to give the pure product. Yield: (119 mg, 39.3 %, yellow-brownish powder). Elemental Analysis: Anal. found C, 33.35; H, 5.25; N, 4.86. Calc. for  $C_{14}H_{22}N_2O_{12}V_2$  ( $M_W = 512.21$ ) C, 32.83; H, 5.33; N, 4.97.

General procedure for oxidation of alkenes with TBHP catalyzed by vanadium BOX complex

In a round-bottom flask (25 mL) equipped with a condenser, a gas inlet, and a magnetic stirrer, a solution of alkene (1 mmol) in acetonitrile (4 mL) was prepared. The vanadium *bis*-oxazoline complex (0.013 mmol, 0.026 mmol V) and TBHP (2 mmol) were added to this solution and the reaction mixture was stirred under reflux conditions. The reaction progress was monitored by GC. After completion of the reaction, the mixture was directly passed through a short column of silica-gel (1:1, *n*-hexane–ethyl acetate) to remove the catalyst. The elute was evaporated under reduced pressure and the remaining residue was purified by plate thin layer chromatography (eluted with  $CCl_4:Et_2O = 9:1$ ) to afford the corresponding epoxide.

General procedure for oxidation of sulfides with  $H_2O_2$  catalyzed by vanadium BOX complex

In a 25 mL round-bottom flask equipped with a magnetic stirring bar, a solution of sulfide (1 mmol), catalyst (0.01 mmol, 0.02 mmol V) in ethanol (4 mL) was prepared.  $H_2O_2$  (2 mmol) was added to this solution and the reaction mixture was stirred under reflux conditions. The reaction progress was monitored by TLC. After the reaction was completed, the isolation and purification of the products were done as described above.



#### **Results and discussion**

Preparation and characterization of the bis-oxazoline and the vanadium complex

The preparation route for catalyst is shown in Scheme 2. The prepared catalyst was characterized by elemental analysis, magnetic susceptibility, FT-IR, and UV–Vis spectroscopic methods. The FT-IR spectrum of homogeneous  $[V_2(O)_4(H_2O)_4BOX]$  (Fig. S1) shows a band at 1,642 cm<sup>-1</sup> for  $\nu(C = N)$ , and the band at 972 cm<sup>-1</sup> is attributed to the  $\nu(V = O)$  bonds. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>)



Fig. 4 The effect of temperature in the oxidation of cyclooctene catalyzed by vanadium complex

$$\begin{split} &\delta = 8.34 \text{ (t, }{}^{4}J_{\text{H}-\text{H}} = 1.6 \text{ Hz}, 1\text{H}), 7.94 \text{ (dd, }{}^{4}J_{\text{H}-\text{H}} = 1.6 \text{ Hz}, \\ &{}^{3}J_{\text{H}-\text{H}} = 7.6 \text{ Hz}, 2\text{H}), 7.55 \text{ (t, }{}^{3}J_{\text{H}-\text{H}} = 7.6 \text{ Hz}, 1\text{H}), \\ &4.84\text{-}4.80 \text{ (m, 2H, } 2 \times \text{CHN} = \text{C}), 4.45\text{-}4.29 \text{ (m, 4H}, \\ &2 \times \text{CH}_2\text{O}), 3.56\text{-}3.31 \text{ (m, 4H, } 2 \times \underline{\text{CH}_2\text{OH}}) \text{ (Fig. S2)}. \end{split}$$

As seen in Fig. S3, the  $[V_2(O)_4(H_2O)_4BOX]$  shows a peak at  $\lambda_{max} = 214$  nm which is attributed to the  $O(p\pi) \rightarrow V(d\pi)$  charge-transfer transition [27]. TG and DTG data show that this complex decomposes in three steps at about 180, 400, and 600 °C (Fig. S4). This is in accordance with the data obtained from melting point studies.

According to the ICP and CHN analyses, the ratio between V and the ligand was 1.93 that confirms that the catalyst consists of two vanadium metals and is therefore binuclear. The magnetic susceptibility experiments showed that this complex is diamagnetic and therefore it is a V(V) complex with no *d* electron.

Catalytic alkene epoxidation with TBHP in the presence of the vanadium complex as catalyst

Initially, the catalytic activity of the prepared catalyst was tested using cyclooctene as reference alkene. All reactions were continued until no progress was observed. Oxidation was carried out in the presence of catalytic amounts of vanadium *bis*-oxazoline. First, we optimized the catalyst amount in the oxidation of cyclooctene. The results showed that when 0.013 mmol of catalyst was used in the oxidation

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Row	Substrate	Dreadu at <sup>a</sup>	Conversion	Epoxide	Time	TOF
		Product	$(\%)^{b}$	Yield (%)	(h)	(h <sup>-1</sup> )
1		0	96	96	6	6.0
2	$\bigcirc$		100	4	10	3.8
3			91	45	6	5.7
4			99	0	8	4.7
5	$\frown \frown \frown \frown$	$\sim \sim \sim \circ$	96	96	10	3.6
6	$\checkmark \checkmark \checkmark \checkmark \checkmark$	~~~~ <sup>0</sup>	94	94	10	3.5
7	$\checkmark \checkmark \checkmark \checkmark \checkmark \checkmark$	~~~~~ <sup>0</sup>	64	64	10	2.4
8	$\checkmark \checkmark \checkmark \checkmark \land \land$	~~~~~°	25	25	10	0.9

a Reaction conditions: alkene (1 mmol), TBHP (2 mmol), catalyst (0.013 mmol, 0.026 mmol V), acetonitrile (4 mL)

<sup>b</sup> GC yield based on the starting alkene

Entry	Catalyst	Alkene	Oxidant	Conditions (°C)/solvent	$TOF(h^{-1})$	References
1	$[V_2(O)_4(H_2O)_4BOX]$	Styrene	TBHP	Reflux/acetonitrile	5.7	This work
2	Mo <sub>2</sub> O <sub>4</sub> (acac) <sub>2</sub> box	Styrene	TBHP	Reflux/DCE	5.4	[26]
3	[MoI <sub>2</sub> (CO) <sub>3</sub> (pheH)]	Cyclooctene	TBHP	55/DCE	2	[28]
4	[MoO <sub>2</sub> [1,2-diphenylethylenebis(3- oxyethylpyrrole)salicylideneiminate]]	Cyclooctene	TBHP	Reflux/DCE	5	[29]
5	$[(L_1)_2 V = O]^a$	Styrene	TBHP	RT/toluene	0.4	[30]
6	$[(L_1)_2 MoO_2]^a$	Styrene	TBHP	RT/toluene	0	[30]

Table 2 Comparison of the results obtained for epoxidation of alkenes catalyzed by  $[V_2(O)_4(H_2O)_4BOX]$  with some previously reported systems

<sup>a</sup>  $HL_1 = 2-(4,4'-dimethyl-3',4'-dihydroxazol-2'-yl)phenol$ 



Fig. 5 The effect of catalyst amount in the oxidation of diphenyl sulfide with  $H_2O_2$  catalyzed by  $[V_2(O)_4(H_2O)_4BOX]$ 

of cyclooctene with 2 mmol of TBHP, the highest yield was obtained. Whereas trace amounts of products (10 %) were detected when the same reaction was carried out in the absence of catalyst (Fig. 1).

The effect of different oxidants such as  $H_2O_2$ , NaIO<sub>4</sub>, *tert*-BuOOH and  $H_2O_2$ /Urea (UHP) was also investigated in the oxidation of cyclooctene. The results showed that *tert*-BuOOH is the best oxy- gen source (Fig. 2). To further optimize the conditions, different solvents were also used in the oxidation of cyclooctene with *tert*-BuOOH. In general, all results showed that except DMF all solvents gave pretty much good yields after 24 h. Acetonitrile was chosen as the best solvent since it gave higher yields in 6 h (Fig. 3). The temperature of the reaction was also optimized by repeating the reaction in various temperatures. At room temperature (25 °C), the product yields were low and with increasing the reaction temperature to 75 °C (refluxing acetonitrile), the conversion increased significantly (Fig. 4).

Under the optimized reaction conditions, different alkenes including cyclic and linear ones were oxidized by this catalytic system (Table 1). In this catalytic system, cyclooctene was completely converted to its corresponding epoxide with 100 % selectivity. While, in the oxidation of cyclohexene, the major product was cyclohexene-1-one, and only trace amounts of the corresponding epoxide were produced. In the epoxidation of styrene, a 1:1 mixture of epoxide: benzaldehyde was produced while in the epoxidation of a-methylstyrene no epoxide was produced and the product was acetophenone. In the case of linear alkenes such as 1-heptene, 1-octene, 1-decene, and 1-dodecene, the corresponding epoxides were obtained in good to high yields with 100 % selectivity. In these reactions, by increasing the alkene chain, the reactivity reduced. This can be attributed





Fig. 7 The effect of various oxidants in the oxidation of diphenyl sulfide with  $H_2O_2$  catalyzed by  $[V_2(O)_4(H_2O)_4BOX]$ 

to the reducing of the mobility of the alkene by increasing the alkene chain.

Comparison of the obtained results in this work with those of the previously reported similar molybdenum complex [26], showed that in some cases, the product yields are higher using vanadium complex. For example, with 1-octene a TOF of 5.6 was obtained with the vanadium catalyst, whereas, with molybdenum catalyst the corresponding TOF was 2.7 [26]. To further show the efficiency of this catalytic system, some of the results obtained by our method were compared with some of those reported in the literature (Table 2). As can be seen, in all cases the present method is more efficient in the epoxidation of alkenes.



Fig. 8 The effect of the amount of oxidant in the oxidation of diphenyl sulfide in 5 min

Oxidation of sulfides with  $H_2O_2$  catalyzed by  $[V_2(O)_4(H_2O)_4BOX]$ 

The reaction conditions were also optimized in the oxidation of sulfides with  $H_2O_2$  in which diphenyl sulfide was used as a model substrate. In the optimization of catalyst amount, the best results were obtained when 0.01 mmol (0.02 mmol V) of catalyst was applied with 2 mmol of  $H_2O_2$  after 5 min. Under these conditions, the conversion was 100 % and the sulfoxide selectivity was 100 %. No better results were obtained when higher amounts of catalyst were used. When the reaction was continued for 20 min, a 1:1 mixture of sulfoxide: sulfone was produced. This indicates that the producing sulfoxide converts to sulfone. Trace amounts of the products were detected when

Table 3 Sulfide oxidation with  $[V_2(O)_4(H_2O)_4BOX]$  in the presence of ethanol and  $H_2O_2^a$ 

Row	Sulfide	Time (min)	Conversion	Product <sup>a</sup>		TOF
			(%) <sup>b</sup>	Sulfoxide (%)	Sulfone (%)	$(h^{-1})$
1	s-()-	5	100	100	0	615
		30	100	85	15	103
2	HOS_	1	100	100	0	3077
		30	100	95	5	103
3	С С С С С С С С С С С С С С С С С С С	5	100	100	0	615
		20	100	95	5	154
4	S	25	90	90	0	111
		60	100	80	20	51
5	S S S S S S S S S S S S S S S S S S S	5	70	65	5	431
		45	100	90	10	68
6	<i>s</i> √s	1	100	100	0	3077
6		30	100	0	100	103
7	S	1	90	90	10	2769
1			15	100	0	100
8	C) <sup>s</sup> C)	5	95	95	0	585
		20	100	50	50	154
9	SS	1	95	95	0	2923
		20	100	0	100	154

a Reaction conditions: sulfide (1 mmol),  $H_2O_2$  (2 mmol), catalyst (0.01 mmol, 0.02 mmol V), ethanol (4 mL)

<sup>b</sup> GC yield based on the starting sulfide

Entry	Catalyst	Oxidant	Conditions (°C)/solvent	$TOF(h^{-1})$	References
1	[V <sub>2</sub> (O) <sub>4</sub> (H <sub>2</sub> O) <sub>4</sub> BOX]	H <sub>2</sub> O <sub>2</sub>	Reflux/ethanol	2,923	This work
2	Mo <sub>2</sub> O <sub>4</sub> (acac) <sub>2</sub> box	TBHP	Reflux/DCE	750	[26]
3	V(O)(acac)[(2S,4R)-N-benzyl-4 hydroxy- 4- phenyl-2-(1,1 diphenylmethyl)pyrrolidinylmethanol]	H <sub>2</sub> O <sub>2</sub> /TBHP	55/acetonitrile	530/832	[31]
4	MoO2L, L = (2S,4R)-N benzyl- 4-hydroxy-4- phenyl-2-(1,1-diphenylmethyl)pyrrolidinylmethanol	H <sub>2</sub> O <sub>2</sub> /TBHP	55/acetonitrile	447/258	[31]
5	cis-[MoO <sub>2</sub> (phox) <sub>2</sub> ] <sup>a</sup>	UHP	(1:1) mixture of CH <sub>2</sub> Cl <sub>2</sub> /CH <sub>3</sub> OH	114	[32]
6	[Mn(phox) <sub>2</sub> (MeOH) <sub>2</sub> ]ClO <sub>4</sub> <sup>a</sup>	UHP	(1:1) mixture of CH <sub>2</sub> Cl <sub>2</sub> /CH <sub>3</sub> OH	219	[33]
7	Mn(phox) <sup>a</sup> <sub>3</sub>	UHP	(1:1) mixture of CH <sub>2</sub> Cl <sub>2</sub> /CH <sub>3</sub> OH	205	[33]

Table 4 Comparison of the results obtained for sulfoxidation of methylphenyl sulfide catalyzed by  $[V_2(O)_4(H_2O)_4BOX]$  with some previously reported systems

<sup>a</sup> Hphox = 2-(20-hydroxyphenyl)oxazoline

the same reaction was carried out in the absence of catalyst (Fig. 5).

To choose the reaction media, different solvents were also tested and ethanol was chosen as the best solvent because of not only being a green solvent but also the higher amount of sulfoxide produced (Fig. 6).

Different oxidants such as  $H_2O_2$ , NaIO<sub>4</sub>, *tert*-BuOOH, and  $H_2O_2$ /Urea (UHP) were also investigated in the oxidation of diphenyl sulfide. The results showed that  $H_2O_2$  is the best oxygen source (Fig. 7).

Various  $H_2O_2$  molar amounts were also tested. The results showed that when 2 mmol of the oxidant was used, the highest yields of sulfoxide were obtained (Fig. 8).

This catalytic system is extremely green and efficient and catalyzes the oxidation of a wide range of sulfides, and the sulfoxide and sulfone are produced using catalyst, substrate, and oxidant in a molar ratio of 1:100:200, respectively. The results are summarized in Table 3. Most sulfides were completely converted to their corresponding sulfoxides while upon increasing the reaction times, the sulfones were also detected in the reaction mixture. In all cases, two different reaction times are reported. In the case of linear sulfides, by increasing the reaction time, the selectivity completely changed to sulfone production.

The obtained results in this work were compared with those of the previously reported similar molybdenum complex [26]. As shown, the product yields are higher using vanadium complex [26]. To further show the efficiency of this catalytic system, some of the results obtained by our method were compared with some of those reported in the literature for methylphenyl sulfide (Table 2). As can be seen, in all cases the present method is more efficient in the sulfoxidation of sulfides. It is also important to note that the oxidant ( $H_2O_2$ ) and the solvent (ethanol) are both green, which are of practical importance from an environmental point of view (Table 4).

## Conclusion

In summary, we synthesized a new binuclear vanadium complex and demonstrated its high catalytic activity in the oxidation of various alkenes using TBHP and acetonitrile and green oxidation of sulfides using  $H_2O_2$  and ethanol as green solvent and oxidant, respectively, under homogeneous conditions. The excellent chemoselectivity of this complex toward alkenes and the sulfur group, as well as the high yields makes it a good choice for oxidation.

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