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# Synthesis, crystal structures of oxovanadium(V) complexes with hydrazone ligands and their catalytic performance for the styrene oxidation

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Abstract: Four new oxovanadium(V) complexes,  $[VO(aha)L^1]$  (1),  $[VO(aha)L^{2}]$  (2),  $[VO(aha)L^{3}]$  (3), and  $[VO(aha)L^{4}]$ ·EtOH (4) (Haha =  $H_2L^1$ acetohydroxamic acid, 4-nitrophenyl 2- $H_2L^2 \\$ (2-hydroxybenzylidene)hydrazinecarboxylate, N'-(2-hydroxylbenzylidene)-4-methoxybenzohydrazide,  $H_2L^3$ N'-(2-hydroxylbenzylidene)-4-methylbenzohydrazide,  $HL^4$ N'-(5-bromo-2-hydroxybenzylidene)-3- methyl benzohydrazide), have been prepared and structurally characterized by physico-chemical methods and X-ray diffraction. The V atoms in the complexes are in octahedral coordination, with the three donor atoms of the hydrazone ligand and the deprotonated hydroxyl O atom of the aha ligand defining the equatorial plane, and with the carbonyl O atom of the aha ligand and one oxo O atom occupying the axial positions. Crystal structures of the complexes are stabilized by hydrogen bonds. In addition, the catalytic performances for the peroxidative oxidation (with hydrogen peroxide) of

complexes 1-4 and their starting materials  $VO(acac)_2$  were studied by the reaction of styrene (St) to benzaldehyde (BzA) (the maximum total turnover number is 667) under the mild conditions.

#### Introduction

Benzaldehyde is a valuable chemical that is usually applied in perfumery, dyestuff, pharmaceuticals, resin additives and organic synthesis. One effective method to produce benzaldehyde is the oxidation of styrene (St), which is an important reaction as it represents a significant role for the synthesis of fine chemicals and pharmaceuticals, like styrene oxide, 1-phenylethane-1,2-diol, benzoicacid and phenylacetaldehyde.[1] Therefore, the exploration on the mild reaction conditions and suitable catalysts for styrene oxidation has been paid more and more attention [2-7].

Most of the St oxidation reactions are carried out with heterogeneous catalysts, such as zeolite-Y encapsulated V [8-10]<sup>•</sup> polymer anchored Cu and Mn complexes [11], La, V, Cr, Mn and Ti modified molecular sieves [12-14] etc. However, the advantage of homogeneous catalysts is clearly seen that the reaction can be carried out in the mild condition with high activity, such as Schiff bases porphyrin complexes [15, 16]. This may be attributed to easier spread of catalysts, which lead to more possibilities to emerge more active sites [17].

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Among those active metals for St oxidation reactions, vanadium achieved increasing attention due to its potential catalytic ability [18, 19], especially as an abundant element existing in various life bodies [20-23]. A plenty of oxovanadium complexes show high catalytic activity towards various oxidation reaction, such as sulfides [24, 25], alcohols [26, 27] and alkenes [28-32] oxidations, which happened by the easily changing of vanadium oxidation states at the presence of oxygen, the various possibilities of coordination numbers of oxovanadium complexes and Lewis acid character of the vanadium centers.

Research results show that the complexes with different organic ligands exhibited different catalytic activity. In general, the organic ligands used in catalysts can be divided into five different types: (i) the schiff based ligands; (ii) the tripodal scorpionate ligands; (iii) the pincer chelate ligands; (iv) the triangular amine ligands and (v) the carboxylate ligands [33]. Hydrazone ligands belongs to the first type (schiff based ligands), which is easier to form stable complex with vanadium and makes the structure of the complexes more diversified [34-38]. However, the reports focusing on the catalytic performance of vanadium complexes with hydrazone ligands as homogeneous catalysts in St oxidation are still limited, though stable oxovanadium complexes with N-donor ligands have been proved to be potential catalysts in St oxidation [39].

In this paper, four new oxovanadium(V) complexes, [VO(aha)L1] (1),

[VO(aha)L2] (2), [VO(aha)L3] (3), and [VO(aha)L4]  $\cdot$ EtOH (4) (Haha = acetohydroxamic acid, H2L1 = 4-nitrophenyl 2-(2-hydroxybenzylidene) hydrazinecaroxylate, H2L2 = N'-(2-hydroxybenzylidene)-4-methoxybenzohydrazide, H2L3 = N'-(2-hydroxybenzylidene)-4-methylbenzohydrazide, HL4 = N'-(5-bromo-2- hydroxybenzylidene) -3-methyl benzohydrazide; (Scheme 1) were synthesized and structurally characterized. Furthermore, these complexes were also used as catalysts in St oxidation, using 30 % H<sub>2</sub>O<sub>2</sub> solution as the oxidant.



Scheme 1 The structure schemes of the  $H_2L$ 

**Experimental** 

#### Materials and methods

All Reagents and solvents were purchased from commercial suppliers and used without further purification. The hydrazones were prepared according to the literature method [40]. Elemental analyses were performed on a Perkin-Elmer 240C elemental analyzer. IR spectra were

recorded on a Jasco FT/IR-4000 spectrometer as KBr pellets in the 4000–400 cm<sup>-1</sup> region. UV-Vis spectra were recorded on a Lambda 900 instrument. X-ray diffraction was carried out on a Bruker SMART 1000 CCD area diffractometer. <sup>1</sup>H NMR data were recorded on a Bruker 300 MHz instrument with  $d^6$ -DMSO as solvent.

#### Synthesis of complexes

The complexes were prepared according to the same method. An ethanolic solution (20 mL) of the hydrazone (1.0 mmol) was added with stirring to an ethanolic solution (20 mL) of VO(acac)2 (1.0 mmol, 0.267 g) and acetohydroxamic acid (1.0 mmol, 0.075 g). The mixture was stirred at room temperature for 30 min to give solution with color from light yellow to deep brown. X-ray quality single crystals were formed by slow evaporation of the solutions in air after a few days.

#### Synthesis of [VO(aha)L1] (1)

Deep brown single crystals. Yield: 45%. Anal. calcd. for  $C_{17}H_{15}N_4O_8V$ : C, 45.0; H, 3.3; N, 12.3%. Found: C, 44.8; H, 3.4; N, 12.4%. IR data: 3126 (w), 1605 (s), 1512 (s), 1436 (w), 1338 (s), 1262 (m), 1217 (w), 1179 (w), 1113 (w), 1011 (w), 973 (m), 902 (w), 849 (w), 754 (m), 673 (w), 631 (w), 579 (m), 491 (w), 456 (w). UV-Vis spectra data in acetonitrile [nm ( $\varepsilon$ , M<sup>-1</sup> cm<sup>-1</sup>)]: 218 (2.65 × 10<sup>4</sup>), 267 (1.95 × 10<sup>4</sup>),

307 (1.89 × 10<sup>4</sup>), 420 (5.49 × 10<sup>3</sup>). <sup>1</sup>H NMR (300 MHz, DMSO) δ 13.91 (s, 1H, N*H*), 9.02 (s, 1H, C*H*=N), 8.23 (d, 2H, Ar*H*), 7.73 (d, 1H, Ar*H*), 7.55 (t, 1H, Ar*H*), 7.18 (d, 2H, Ar*H*), 7.00 (t, 1H, Ar*H*), 6.85 (d, 1H, Ar*H*), 5.05 (t, 2H, C*H*<sub>2</sub>), 2.00 (s, 3H, C*H*<sub>3</sub>).

#### Synthesis of [VO(aha)L2] (2)

Deep brown single crystals. Yield: 53%. Anal. calcd. for  $C_{17}H_{16}N_3O_6V$ : C, 49.9; H, 3.9; N, 10.3%. Found: C, 49.8; H, 4.1; N, 10.1%. IR data: 3232 (w), 1606 (s), 1547 (w), 1498 (s), 1449 (w), 1420 (w), 1377 (w), 1333 (m), 1260 (m), 1219 (w), 1163 (m), 1033 (w), 955 (m), 900 (w), 827 (w), 751 (m), 673 (w), 638 (w), 588 (m), 555 (w), 475 (w). UV-Vis spectra data in acetonitrile [nm ( $\varepsilon$ , M<sup>-1</sup> cm<sup>-1</sup>)]: 218 (1.94 × 10<sup>4</sup>), 294 (1.72 × 10<sup>4</sup>), 333 (1.33 × 10<sup>4</sup>), 425 (6.33 × 10<sup>3</sup>). <sup>1</sup>H NMR (300 MHz, DMSO)  $\delta$  13.94 (s, 1H, NH), 9.07 (s, 1H, CH=N), 7.85 (d, 2H, ArH), 7.75 (d, 1H, ArH), 7.55 (t, 1H, ArH), 7.04–6.88 (m, 3H, ArH), 6.87 (d, 1H, ArH), 3.81 (s, 3H, OCH<sub>3</sub>), 2.09 (s, 3H, CH<sub>3</sub>).

#### Synthesis of [VO(aha)L3] (3)

Deep brown single crystals. Yield: 37%. Anal. calcd. for  $C_{17}H_{16}N_3O_5V$ : C, 51.9; H, 4.1; N, 10.7%. Found: C, 52.0; H, 4.1; N, 10.5%. IR data: 3145 (w), 1607 (s), 1540 (m), 1521 (m), 1472 (w), 1438 (m), 1391 (m), 1333 (m), 1277 (m), 1215 (w), 1175 (w), 1121 (m), 997

(w), 966 (m), 901 (w), 824 (w), 759 (w), 669 (w), 631 (w), 588 (m), 551 (w), 480 (w). UV-Vis spectra data in acetonitrile [nm ( $\epsilon$ , M<sup>-1</sup> cm<sup>-1</sup>)]: 218 (2.59 × 10<sup>4</sup>), 280 (2.56 × 10<sup>4</sup>), 333 (1.46 × 10<sup>4</sup>), 431 (7.71 × 10<sup>3</sup>). <sup>1</sup>H NMR (300 MHz, DMSO)  $\delta$  13.96 (s, 1H, NH), 9.10 (s, 1H, CH=N), 7.82–7.75 (m, 3H, ArH), 7.54 (t, 1H, ArH), 7.30 (d, 2H, ArH), 7.00 (t, 1H, ArH), 6.88 (d, 1H, ArH), 2.37 (s, 3H, PhCH<sub>3</sub>), 2.10 (s, 3H, CH<sub>3</sub>).

#### Synthesis of [[VO(aha)L4]·EtOH (4)

Deep brown single crystals. Yield: 61%. Anal. calcd. for C19H21BrN3O6V: C, 44.0; H, 4.1; N, 8.1%. Found: C, 44.2; H, 4.0; N, 8.2%. IR data: 3389 (w), 3177 (w), 1611 (s), 1512 (s), 1460 (w), 1408 (s), 1377 (s), 1344 (w), 1280 (s), 1219 (w), 1198 (w), 1124 (m), 1089 (w), 1039 (m), 1002 (m), 971 (m), 912 (w), 875 (w), 827 (m), 723 (w), 654 (w), 598 (s), 574 (w), 560 (w), 491 (w), 463 (w), 445 (w). UV-Vis spectra data in acetonitrile [nm (ɛ, M-1 cm-1)]: 223 (2.32 × 104), 273 (2.34 × 104), 335 (1.27  $\times$  104), 436 (7.32  $\times$  103). 1H NMR (300 MHz, DMSO)  $\delta$ 14.08 (s, 1H, NH), 9.10 (s, 1H, CH=N), 8.00 (s, 1H, ArH), 7.72–7.64 (m, **3H**, ArH), 7.38 (d, 2H, ArH), 6.86 (d, 1H, ArH), 2.37 (s, 3H, PhCH3), 2.11 (s, 3H, CH3).

#### X-ray Crystallographic Determination

Diffraction intensities for the complexes were collected at 298(2) K

using a Bruker SMART 1000 CCD area diffractometer with MoK $\alpha$ radiation ( $\lambda = 0.71073$  Å). The collected data were reduced using the SAINT program [41], and multi-scan absorption correction was performed using the SADABS program [42]. The structures were solved by direct method and refined against  $F^2$  by full-matrix least-squares method using the SHELXTL package [43]. All non-hydrogen atoms were refined anisotropically. The amino H atoms in the complexes were located from difference Fourier maps and refined isotropically, with N–H distances restrained to 0.90(1) Å, and with  $U_{iso}(H)$  set to 0.08 Å<sup>2</sup>. The remaining H atoms in the complexes were placed in calculated positions and constrained to ride on their parent atoms. The crystallographic data for the complexes are summarized in **Table S1**. Selected bond lengths and angles are listed in **Table 1**.

	Com	plex 1		
V1-O1	1.841(2)	V1-O2	1.993(2)	
V1-O6	2.188(2)	V1-07	1.8673(19)	
V1-08	1.585(2)	V1-N1	2.069(2)	
O8-V1-O1	99.85(12)	O7-V1-N1	163.30(10)	
O1-V1-O7	107.42(9)	O8-V1-O6	169.03(10)	
O1-V1-O2	150.84(10)	O2-V1-O6	80.36(8)	
08-V1-N1	96.96(11)	N1-V1-O6	93.95(9)	
	Com	plex 2		
V1-O1	1.836(2)	V1-O2	1.962(2)	
V1-O4	2.195(2)	V1-O5	1.858(2)	
V1-O6	1.571(2)	V1-N1	2.076(3)	
O6-V1-O1	99.51(14)	O6-V1-O5	95.95(12)	

Table 1 Selected bond lengths (Å) and angles (°) for the complexes

O5-V1-N1159.94(10)O5-V1-O294.96(9)O1-V1-O2156.69(11)O1-V1-N184.78(10)							
O1-V1-O2 156.69(11) O1-V1-N1 84.78(10)							
	)						
06-V1-O4 171.13(12) 01-V1-O4 85.08(11)	)						
Complex 3							
V1-O1 1.843(4) V1-O2 1.959(3)							
V1-O3 2.219(4) V1-O4 1.871(4)							
V1-O5 1.582(4) V1-N1 2.072(4)							
O4-V1-O2 90.94(15) O5-V1-O4 97.3(2)							
O1-V1-N1 84.29(17) O4-V1-N1 156.40(19	))						
O1-V1-O2 155.23(16) O5-V1-O3 171.79(19	))						
O1-V1-O3 85.86(17) N1-V1-O3 83.12(16)	)						
Complex 4							
V1-O1 1.8608(18) V1-O2 1.9379(17	')						
V1-O3 2.2231(18) V1-O4 1.8524(17	')						
V1-O5 1.579(2) V1-N1 2.0853(19	))						
O4-V1-O3 75.58(7) O5-V1-O1 99.64(10)	)						
O4-V1-O1 104.53(8) O1-V1-O2 154.56(8)	)						
O1-V1-N1 84.85(7) O4-V1-N1 159.68(8)	)						
O5-V1-O3 171.90(9) O2-V1-O3 82.34(7)							

#### Catalytic oxidation reaction

The oxidation catalytic reactions were carried out under atmospheric pressure in the glass flasks with condenser pipes in a water bath with magnetic stirring. In a typical experiment, fixed amount of the catalysts (complex 1 to 4) was dissolved in 3.00 mL of desired solvent. Then a certain amount of styrene was added according to this order. At last, the required amounts of  $H_2O_2$  (30 %  $H_2O_2$  solution) was added into the solution. The formation of the main product is outlined in **Scheme 2**.



Scheme 2. Main product observed during the catalytic oxidation of styrene

For the products analysis, 0.03 g of methylbenzene (internal standard) and 1.5 mL of diethyl ether (to extract the substrate and the organic products from the reaction mixture) were added. The obtained mixtures were stirred for 10 min and then a sample (0.2  $\mu$ L) was taken from the organic phase and analyzed by a GC equipped with a capillary column and a flame ionization detector by the internal standard method. The catalytic performance was evaluated in terms of the conversion of St selectivity to the BzA and the turn over number (TON), according to the following equations:

% St Conversion = 
$$\frac{St_{in} - St_{out}}{St_{in}} \times 100$$
 (1)  
% Selectivity to BzA =  $\frac{mols of BzA \text{ produced}}{mols of reacted St} \times 100$  (2)  
TON of BzA =  $\frac{mols of BzA \text{ produced}}{mols of catalyst}$  (3)

#### **Results and Discussion**

#### **Synthesis**

The hydrazones were synthesized by the reaction of equimolar

quantities of aldehydes with hydrazines in methanol. The complexes were synthesized by reaction of ethanolic solution of the hydrazones with VO(acac)<sub>2</sub> and acetohydroxamic acid. The complexes were characterized by elemental analysis, IR, UV-vis and <sup>1</sup>H NMR spectra. Structures of the complexes were further confirmed by X-ray crystallography.

#### **Structural description of complexes 1-4**

The molecular structures of the complexes 1-4 are shown in Figures 1-4, respectively. And molecular packing diagrams are shown in **Figures** S1-S4. X-ray crystallography reveals that the complexes are similar oxovanadium(V) compounds. It should be pointed out that the vanadium in the starting materials is in V(IV) oxidation state, but it appears to be V(V) in compounds 1-4, indicating that it was oxidized by air since no other oxidants existed during the reaction procedures. The difference among the complexes is the variety of the hydrazone ligands. The coordination sphere around the vanadium atoms is a distorted octahedral configuration with a six-coordinated structure as a  $[V^VO(ONO)(OO)]$ type. The V atoms in the complexes are in octahedral coordination, with the phenolate oxygen O1, imino nitrogen N1 and enolate oxygen O2 of the hydrazone ligands, and the deprotonated hydroxyl oxygen (O7 for 1, O5 for 2, O4 for 3 and 4) of the aha ligand defining the equatorial plane, and with the carbonyl oxygen (O8 for 1, O4 for 2, O3 for 3 and 4) of the

aha ligand and one oxo oxygen (O8 for 1, O6 for 2, O5 for 3 and 4) occupying the axial positions. The form of the hydrazone ligands is consistent with the observed O2 - C8 and N2 - C8 bond lengths of 1.309(3) Å and 1.286(4) Å, respectively in 1, 1.316(3) Å and 1.295(4) Å in 2, 1.319(6) Å and 1.298(7) Å in 3 and 1.298(3)Å and 1.304(3) Å in 4. This is in agreement with the reported complexes containing the enolate form of hydrazone ligands [44-46], whereas the O2 - C8 bond is considerably short for reported complexes with the coordinated keto form of the hydrazone system. The acetohydroxamic serves as the bidentate co-ligand to present the hydroxamate form. It is confirmed by the bond lengths of C17-N4 is 1.324(4) Å for 1 and C17-N3 are 1.318(4) Å, 1.311(7) Å, 1.313(3) Å for 2, 3 and 4, while the bond lengths of C17–O6 is 1.251(3) Å for 1, C17–O4 is 1.239(4) Å for 2, C17–O3 are1.244(6) Å, 1.244(3) Å for 3 and 4 respectively, which are consistent with the reported values of analogous complexes [1, 47]. The distances between V atoms and the oxo oxygen are in the range of 1.57-1.59 Å, indicating they are typical V=O bonds. The displacement of the V atoms from the equatorial planes toward the axial oxo oxygen are 0.255(1) Å for 1, 0.272(1) Å for 2, 0.310(1) Å for 3, and 0.282(1) Å for 4. The coordinate bond lengths in the complexes are comparable to each other, and also comparable to those observed in other similar oxovanadium complexes [48]. The distortion of the octahedral coordination can be observed by the

coordinate bond angles, ranging from 74.05(9) to 107.42(9)° (1), 74.78(9) to 102.11(13)° (2), 74.66(16) to 104.15(17)° (3), and 74.52(7) to 104.53(8)° (4), for the perpendicular angles, and from 150.84(10) to 169.03(10)° (1), 156.69(11) to 171.13(12)° (2), 155.23(16) to 171.79(19)° (3), and 154.56(8) to 171.90(9)° (4), for the diagonal angles. The ethanol molecule of complex **4** is linked to the vanadium complex molecule through an O–H…N hydrogen bond [O6–H6 = 0.82 Å, H6…N2 = 2.06 Å, O6…N2 = 2.875(3) Å, O6–H6…N2 = 177.4°; symmetry code for i: 1/2 + x, 3/2 - y, -1/2 + z].



**Figure 1** A perspective view of the molecular structure of **1** with the atom labeling scheme. The thermal ellipsoids are drawn at the 30% probability level.



Figure 2 A perspective view of the molecular structure of 2 with the atom labeling scheme. The thermal ellipsoids are drawn at the 30% probability level.



Figure 3 A perspective view of the molecular structure of 3 with the atom labeling scheme. The thermal ellipsoids are drawn at the 30% probability level.



**Figure 4** A perspective view of the molecular structure of **4** with the atom labeling scheme. The thermal ellipsoids are drawn at the 30% probability level. Hydrogen bond is show as a dashed line.

#### **IR** spectral studies

The IR spectra of the complexes are presented in the Fig. S5–S8 exhibiting weak and sharp bands in the region 3100–3250 cm<sup>-1</sup>, which are assigned to the v(N-H) vibrations. The broad and weak absorption band centered at 3389 cm<sup>-1</sup> in complex **4** is assigned to the v(O-H) vibration. The v(C=O) stretches are absent in the complexes, which is consistent with the enolisation of the amide functionalities and subsequent proton replacement by the vanadium atoms. The bands appearing in the region 1260–1280 cm<sup>-1</sup> are assigned to the  $v(C-O_{enolic})$  vibrations. The strong absorption bands at 1605 cm<sup>-1</sup> in **1**, 1606 cm<sup>-1</sup> in **2**, 1607 cm<sup>-1</sup> in **3**, and 1611 cm<sup>-1</sup> in **4**, are attributed to the v(C=N) vibration

[49]. The bands observed at 973 cm<sup>-1</sup> in **1**, 955 cm<sup>-1</sup> in **2**, 966 cm<sup>-1</sup> in **3**, and 971 cm<sup>-1</sup> in **4**, are assigned to the v(V=O) stretches [50].

#### **UV-Vis spectral studies**

The UV-vis absorption spectra of complexes 1–4 in acetonitrile solution are presented in the Fig. S5–S8. The spectral features of 1-4 are quite similar. The lowest energytransition broad band is observed in visible region at 420–425 and 431–436 nm for complexes 1–4, which is attributed to the LMCT transition [51] as a charge transfer from a p-orbital on the lone-pair of ligands oxygen atoms to the empty d-orbital of the vanadium atom. The other strong band at 307 nm for 1, 333 nm for 2 and 3, 335 nm for 4 corresponds to the intraligand  $n\rightarrow\pi^*$  absorption peak. The high energy absorptions at 218 nm, 223 nm and 267-294nm are most likely due to a  $\pi\rightarrow\pi^*$  transition of conjugated system in ligands. [46] Whereas the absence of the *d-d* transition band is indicative of the +5 oxidation state of V.

#### <sup>1</sup>H-NMR spectral studies

The <sup>1</sup>H-NMR spectra in d<sup>6</sup>-DMSO at 300MHz of complexes are shown in **Fig. S5–S8**. The singlet at  $\delta = 13.91$ , 13.94, 13.96 and 14.08 ppm assignable to –NH and  $\delta = 9.02$ , 9.07 and 9.10 ppm due to –CH=N–, respectively. In addition, the methyl group at C-17 in aha ligand appears

as a singlet at  $\delta = 2.00, 2.09, 2.10$  and 2.11ppm (3H) and the singlets at  $\delta = 8.23$ -6.85 ppm assignable to ArH. A singlet at  $\delta = 5.05$  ppm(2H) for 1, a singlet at  $\delta = 3.81$  ppm (3H) for 2 and a singlet at  $\delta = 2.37$  (3H) for 3 and 4 ,are ascribed to the –CH<sub>2</sub>, terminal –OCH3 and PhCH<sub>3</sub>, respectively. The absence of a singlet from –OH confirms enolization prior to complexation followed by deprotonation during complexation. This is also evident from the X-ray crystal structure studies.

#### Catalytic activity

The effects of solvents on the St oxidation over complex **3** as catalyst are investigated and results are shown in **Figure 5**. As we all known, the solvent plays an important and sometimes decisive role in the catalytic behavior of a catalyst. Thus, the effect of solvents, such as acetonitrile (MeCN), ethanol (EtOH), methanol (MeOH), petroleum ether (PE), N, N-dimethylformamide (DMF) and distilled water (H<sub>2</sub>O) on reactivity was studied in current catalytic St oxidation system catalyzed by complex **3** in the presence of H<sub>2</sub>O<sub>2</sub>. Blank experiment has showed that nearly no product was detected without solvent. It was found that the vanadium complex showed the highest reactivity only when the reaction was performed in EtOH media (TON=534), which may be attributed to the polarity of solvent, that can make different phases uniform to promote mass transfer. This suggesting can be proved by using distilled water as

the solvent, in which, the react mixture is remained two phases and the TON value was only 7. Although the conversion of St in MeOH is similar to EtOH (about 40 %), the TON value is about half (284) of EtOH, which means that more by-products were produced when the media was MeOH. The reactivity was lower in the order of MeCN, DMF and PE with the TON values of 124, 42 and 16, respectively. Among them, DMF has the power of capturing free radicals, which may be the reason why lower catalytic activity was shown in it, considering that the St oxidation is a radical reaction.





We explored the effect of the St to  $H_2O_2$  molar ratio over complex 3 by keeping the amounts of St (0.7200 g, 9.170 mmol) and catalyst (0.0006 g) in ethanol (3 mL) at 60 °C for 4 h fixed. As shown in Fig. 6, the amount of  $H_2O_2$  has an interesting effect on the catalytic activity. The

TON and conversion increased with the St to  $H_2O_2$  molar ratio to a maximum value as 534 and 53 % at 1:1 and 2:1, respectively. After then, they all decreased, which may be caused by the further oxidation of BzA by  $H_2O_2$ , and the dilution of the reaction mixture by the presence of larger amount of water molecules in excess  $H_2O_2$  aqueous.



**Figure 6** Effect of the styrene to  $H_2O_2$  molar ratio on the St oxidation. Reaction conditions: St (0.520 g, 5 mmol), catalyst (0.0006 g), time (4 h), temperature (60 °C) and ethanol (3 mL).



**Figure** 7 Effect of the temperature on the St oxidation. Reaction conditions: St (0.520 g, 5 mmol),  $H_2O_2$  (0.57 g, 5 mmol), catalyst (0.0006 g), ethanol (3 mL).

The effect of reaction temperatures on the conversion and selectivity for the St oxidation catalyzed by complex **3** was studied and the results are shown in **Fig. 7**. As can be seen, with the temperature increased from 40 to 78 °C, the St conversion increased from 13 to 70%, but the selectivity to BzA decreased from 66 to 14%. It is consistent with the fact that the vinyl C-H bonds of St molecules are very active at a high temperature. But more by-products produced when the reaction reacted at the high temperature.

The effect of different catalysts on the St oxidation reactions were carried out in 3 mL of ethanol for 4 h at 60 °C with 1:1 molar ratio of St to  $H_2O_2$  and 0.0015 mmol catalysts. In the absence of any catalyst (**Table** 2),  $H_2O_2$  alone was unable to oxidize St to a significant extent, indicating that the reaction can occur only when a catalyst promoted it. Comparison was made between complexes 1-4 (Table 2, entries 1-4), which represented that the order of the catalytic activities was 3 > 2 > 1 > 4, which meant that complex 3 was the best catalyst for styrene oxidation among the 1, 2, 4 and the starting material  $VO(acac)_2$ . The reason why different complexes exhibited different catalytic abilities is that the ligands have caused the changes of the electronic states of center metal which can provide active sites in the St oxidation. The high catalytic ability of complex 3 may be attributed to the weak electron withdrawing effect of the terminal group in hydrazone ligand which only containing the benzyl group so that it is easier to provide active site of center metal during the reaction. It is also the reason why complex 2 performed better activity than 1. Complex 4 showed the lowest activity because of the dissociative ethanol having an impeditive effect when the reaction reacted

in ethanol. We confirmed it by changing acetonitrile as the solvent.

**Table 2** Effect of catalyst on the styrene oxidation. Reaction conditions: styrene (0.520 g, 5 mmol),  $H_2O_2$  (0.57 g, 5 mmol), catalyst (0.0006 g), time (4 h), temperature (60 °C) and ethanol (3 mL).

Entry	Catalyst	Conv./%	Sel./%	TON
1	VO(aha)L <sup>1</sup>	53	25	424
2	$VO(aha)L^2$	48	31	497
3	$VO(aha)L^3$	42	39	534
4	VO(aha)L <sup>4</sup> ·EtOH	43	27	381
5	$VO(acac)_2$	50	25	401
6	-	26	2	-

#### Conclusions

In this work, four new complexes have been successfully synthesized by the reaction of VO(acac)<sub>2</sub> with the hydrazone and acetohydroxamic acid in ethanol for the first time. The single-crystal X-ray diffraction analyses reveal that the vanadium atoms are six-coordinate in the complexes and in an octahedral environment. In the catalytic study of the vanadium complex using H<sub>2</sub>O<sub>2</sub> as oxidant for styrene oxidation, we found that our four new oxovanadium (V) complexes can be considered as potential catalysts, and the order of the catalytic activities is 3 > 2 > 1 > 4, which can be contributed to the difference of electronegativity of the group in ligands. Parameters such as solvent, temperature and oxidant concentration were changed and showed the different catalytic effects on both activity and selectivity of the oxidative process. Under normal conditions, St oxidation was carried out with excellent activity catalyzed by the complexes **3** (TON of 667).

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#### Declaration

It is not under consideration for publication elsewhere. Its publication is approved by all authors and explicitly by the responsible authorities where the work was carried out.

#### Appendix A. Supplementary data

CCDC 1472971 (1), 1472972 (2), 1472973 (3) and 1472974 (4) contains the supplementary crystallographic data for complexes 1- 4. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts /retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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