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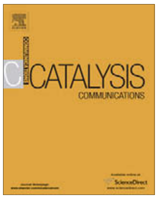

Electronic effects of substituents on the oxidation potentials of vanadyl complexes with tetradentate Schiff base ligands derived from 1,2-propylenediamine

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ABSTRACT

Two tetradentate Schiff base ligands (H_2L^{1-2}) (H_2L^1 = bis(2-hydroxy-3-methoxy-benzaldehyde)-1,2-propandiimine, H_2L^2 = bis(2-hydroxy-4-methoxy-acetophenone)-1,2-propandiimine) were prepared by reaction of 1,2-propylenediamine and *o*-hydroxycarbonyls compounds containing a methoxy group and characterized by elemental analysis, FT-IR, ^1H and ^{13}C NMR. The vanadyl complexes were synthesized and characterized. The catalytic potential of these complexes was tested for the oxidation of cyclooctene and styrene using *tert*-butylhydroperoxide (TBHP) as oxidant. It has been shown that the presence of electron-donating substituents on the aromatic ring as well as the imine bond can effectively improve the catalytic activity and the product selectivity of catalysts.

1. Introduction

The oxidation of hydrocarbons using transition metals Schiff base complexes has attracted both academic and industrial interest [1]. They are efficient catalysts in homogeneous and heterogeneous conditions. The catalytic activity of these complexes depends on the nature of substituents as well as the metal centre [1–4]. The interest in vanadium coordination chemistry promoted by the presence of this element in biological systems [5], and by catalytic [4], inhibitory [6], medicinal [7,8] and structural [9–11] properties of its compounds. The potential catalytic abilities of vanadium compounds have lead to an increasing interest in vanadium coordination chemistry in recent years [2]. Homogeneous catalysts of oxovanadium(IV) complexes have been shown to induce organic reactions such as the oxidation of sulfides to sulfoxides and sulfones [12–14], the epoxidation of alkenes [15–18], the hydroxylation of hydrocarbons [19], and the oxidation of alcohols to aldehydes and ketones [20,21]. These studies are indicative that oxovanadium(IV) complexes are potential catalysts to influence the yield and selectivity in chemical transformation.

In continuation of our efforts to develop new oxovanadium(IV)-based homogeneous oxidation catalysts, we report herein the synthesis of two new oxovanadium(IV) Schiff base complexes with electron donor substituents that exhibited higher potential catalytic activity and product selectivity for the oxidation of cyclooctene and styrene with *tert*-butylhydroperoxide (TBHP).

2. Experimental

2.1. Instruments and reagents

All chemicals were supplied by either Merck or Fluka. Solvents (ethanol and acetonitrile) were dried and distilled by standard methods before use [22]. Chemicals were used as received. Infrared spectra were recorded as KBr pellets using a Unicam Matson 1000 FT-IR. Elemental analyses (C, H, N) were performed using a Heraeus Elemental Analyzer CHN-O-Rapid (Elemental-Analyze system KBr pellets, Gmbh, West Germany). ^1H and ^{13}C NMR spectra were obtained in $CDCl_3$ solution on a Bruker FT-NMR 250 (250 MHz) spectrometer. A varian (AA220) flame atomic absorption spectrometer was used for vanadium determination. A Metrohm 757 VA Computrace was employed to evaluate electrochemical measurements at room temperature (25 °C) under nitrogen with 0.1 M tetrabutylammonium hexafluorophosphate (TBAH) as the supporting electrode. The reaction products of oxidation analyzed by HP Agilent 6890 gas chromatograph equipped with a HP-5 capillary column (phenyl methyl siloxane 30 m × 320 μm × 0.25 μm) and flame-ionization detector.

2.2. Synthesis of ligands

2.2.1. Bis(2-hydroxy-3-methoxy benzaldehyde)-1,2-propandiimine (H_2L^1)

H_2L^1 was prepared according to the described procedure [23]. To a stirred ethanolic solution (20 ml) of 1,2-propylenediamine

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(0.074 g, 1 mmol), 2-hydroxy-3-methoxybenzaldehyde (0.308 g, 2 mmol) was added. The bright yellow solution was stirred and heated to reflux for 1 h. A yellow precipitate was obtained that was filtered off and washed with diethyl ether. Yield (95%), melting point 125 °C. Analysis calculated for $C_{19}H_{22}N_2O_4$ (342.2): C, 68.68; H, 6.42; N, 8.18. Found: C, 68.93; H, 6.01; N, 8.72%. Selected FT-IR data, υ (cm^{-1}): 3423 (O–H), 2923–3015 (C–H), 1630 (C=N), 1561 (C=C), 1031 (C–O). ^{1}H NMR (δ): 1.39, 1.41 (d, 3H, $NCH_2CH(CH_3)N$), 3.58, 3.65 (d, 2H, $NCH_2CH(CH_3)N$), 3.65–3.93 (m, 1H, NCH_2-$CH(CH_3)N$), 4.03, 4.16 (s, 6H, OMe), 6.44–6.90 (m, 6H, Ar*H*), 8.27, 8.31 (s, 2H, *H*C=N), 13.70, 13.78 (s, 2H, OH). $^{13}C\{^1H\}$NMR (δ): 20.4 ($NCH_2CH(CH_3)N$), 55.9 ($NCH_2CH(CH_3)N$), 56.0 (NCH_2CH-$(CH_3)N$), 64.7, 65.5 (OCH_3), 113.9, 151.3 (aromatic C), 164.5, 166.4 (C=N).

2.2.2. Bis(2-hydroxy-4-methoxy acetophenone)-1,2-propandiimine (H_2L^2)

To a stirred ethanolic solution (20 ml) of 1,2-propylenediamine (0.074 g, 1 mmol), 2-hydroxy-4-methoxyacetophenone (0.304 g, 2 mmol) was added. The mixture was stirred and heated to reflux for 1 h. A yellow precipitate was obtained that was filtered off and washed with diethyl ether. Yield (90%), melting point 130 °C. Analysis calculated for $C_{21}H_{26}N_2O_4$ (370.2): C, 68.12; H, 7.02; N, 7.56. Found: C, 68.36; H, 6.82; N, 7.83%. Selected FT-IR data, υ (cm^{-1}): 3400 (O–H), 2916–3000 (C–H), 1623 (C=N), 1560 (C=C), 1160 (C–O). ^{1}H NMR (δ): 1.39, 1.50 (d, 3H, $NCH_2CH(CH_3)N$), 2.50, 2.60 (d, 2H, $NCH_2CH(CH_3)N$), 3.40–3.89 (m, 1H, $NCH_2CH(CH_3)N$), 3.76, 3.81 (s, 6H, O7.02–6.82Me), 6.24–7.70 (m, 6H, Ar*H*), 2.25, 2.35 (s, 6H, $(CH_3)C$=N), 12.75, 12.81 (s, 2H, OH). $^{13}C\{^1H\}$NMR (δ): 14.24, 14.43 ($NCH_2CH(CH_3)N$), 54.6 ($NCH_2CH(CH_3)N$), 53.7 ($NCH_2CH(CH_3)N$), 55.2 (OCH_3), 101.9, 168.8 (aromatic C), 170.5, 172.0 (C=N), 20.0 ($(CH_3)C$=N).

2.3. Preparation of vanadyl complexes (VOL^x (x = 1–2))

The complexes were prepared by a general procedure: the ligand, H_2L^1 (0.34 g, 1 mmol) or H_2L^2 (0.40 g, 1 mmol) was dissolved in 30 ml of ethanol. An ethanolic solution of oxobis(pentane-2,4-dionato)vanadium(IV) (0.265 g, 1 mmol) was added and the reaction mixture was refluxed for 2 h. The colored solution was concentrated to yield colored powders. The products washed with warm ethanol. General structure of oxovanadium(IV) complexes have been shown in Fig. 1. The melting points, yields, and elemental analyses for the complexes are given in Table 1.

2.4. General oxidation procedure

Catalytic experiments were carried out in a 50 ml round bottom flask fitted with a water condenser. In a typical procedure, 0.032 mmol vanadyl complex was dissolved in 10 ml solvent (chloroform, acetonitrile or dichloromethane). Then 10 mmol alkene (cyclooctene or styrene) was added to the reaction mixture and 30 mmol TBHP was added. The reaction mixture was refluxed for 6 h. The oxidation products were identified by comparison with authentic samples (retention times in GC).

3. Results and discussion

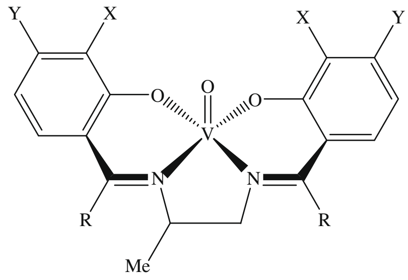
3.1. Characterization of the ligands and oxovanadium(IV) complexes

3.1.1. IR spectral studies

A practical list of IR spectral data is presented in Table 2. Comparison of the spectra of the complexes with the ligands provides evidence for the coordination mode of ligand in catalysts. The Schiff base ligands exhibit a broad band around 2969–3430 cm^{-1} region due to the presence of extensive hydrogen bonding between phenolic hydrogen and azomethine nitrogen atoms. Absence of this band in the spectra of complexes indicates the breaking of hydrogen bonding followed by coordination of phenolic oxygen to the metal ion after deprotonation. A sharp band appearing at 1623–1630 cm^{-1} due to υ(C=N) (azomethine), shifts to lower wave number by 15–16 cm^{-1} and appears at 1607–1623 cm^{-1}. This indicates the involvement of azomethine nitrogen in coordination. IR spectra of VOL^1 shows υ(V=O) at 969 cm^{-1} and for VOL^2 at 984 cm^{-1}. Tetradentate Schiff base oxovanadium(IV) complexes with υ(V=O) around 970 cm^{-1} are in monomeric form. Thus, both of VOL^1 and VOL^2 are assigned to have monomeric structure [24].

3.1.2. Electrochemical studies

The electrochemical properties of the VO–Schiff base complexes (VOL^1 and VOL^2) were investigated in CH_3CN, using TBAH (0.1 M) as the supporting electrolyte by cyclic voltammetry. Fig. 2 shows the cyclic voltammograms of 0.01 mmol of VOL^1 complex in acetonitrile at various scan rates. Both vanadyl complexes exhibit a



Complex	R	X, Y
VOL^1	H	**X**: OMe, **Y**: H
VOL^2	Me	**X**: H, **Y**: OMe

Fig. 1. Oxovanadium(IV) complexes used in this study.

Table 1
Physical and analytical data of the complexes.

	Compound formula	Formula weight	Yield (%)	Color	Found (calculated)			
					%C	%H	%N	%V
VOL^1	$VC_{19}H_{20}N_2O_5$	406.9	90	Green	56.39 (56.08)	4.61 (4.91)	6.93 (6.88)	12.46 (12.51)
VOL^2	$VC_{21}H_{24}N_2O_5$	432.7	85	Green	58.03 (58.34)	5.14 (5.55)	6.79 (6.47)	11.89 (11.77)