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^{51}V and ^{13}C NMR spectroscopic study of the peroxovanadium intermediates in vanadium catalyzed enantioselective oxidation of sulfides

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Abstract

Using ^{13}C and $^{13}C\{^1H\}$ NMR spectroscopy, structure and reactivity of vanadium peroxo complexes formed in the catalytic system [VO(O*i*-Pr)$_3$]/Schiff base ligand/H_2O_2 for enantioselective oxidation of sulfides were concerned. It was shown, that two types of monoperoxo vanadium(V) species bearing one Schiff base ligand per vanadium atom predominated in this catalytic system at low temperature. These complexes are unstable at room temperature and decompose with half-life time of 20 min. The rate of this decomposition markedly increases in the presence of methyl phenyl sulfide. Addition of a fresh portion of H_2O_2 restores partially the peroxo vanadium intermediates. These data suggest that the peroxo vanadium species observed could be the active intermediates in enantioselective oxidation of sulfides. Two types of peroxo complexes found, probably, differ in the mode of Schiff base ligand coordination.

Keywords: Asymmetric oxidations; Sulfoxides; Chiral Schiff bases; Peroxo complexes of vanadium; NMR; Intermediates

1. Introduction

Chiral sulfoxides are an important class of compounds that are finding increasing use as chiral auxiliaries in asymmetric synthesis [1]. The most attractive method for their preparation is the enantioselective oxidation of the easily available prochiral sulfides. Modified Katsuki–Sharpless oxidizing reagent affording sulfoxides with ee up to 95% is the most frequently used so far for this important transformation [2]. Currently, there is much interest in the development of new simple oxidizing systems. In 1995, the very promising method for the asymmetric oxidation of sulfides had been reported [3,4]. It employed a catalyst formed in situ at room temperature from [VO(acac)$_2$] and chiral Schiff bases of type **1**, where R = *t*-Bu, and 30% aqueous H_2O_2 as the oxidizing agent. The catalytic system was extremely efficient and afforded chiral sulfoxides (ee_{max} = 85%) in concentrations of 0.01 mol% of the catalyst. However, the structure of the oxygen transferring species within the catalytic cycle remained unknown [5]. Earlier attempts to investigate the system containing [VO(acac)$_2$], a ligand, and H_2O_2, by ^{51}V NMR spectroscopy showed that several species of vanadium with higher oxidation states were formed [3,4,6]. We report here the first ^{51}V and $^{13}C\{^1H\}$ NMR in situ

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characterization of the active intermediates of this catalytic system.

2. Experimental

$^{13}C\{^1H\}$ and ^{51}V NMR spectra were recorded on a Bruker DPX-250 spectrometer at 62.87 and 65.73 MHz, respectively, using 5 mm cylindrical tubes. Chemical shifts were measured with respect to internal reference TMS for ^{13}C, and external $VOCl_3$ for ^{51}V spectra, with positive values in the low-field direction. Typical operation conditions for ^{51}V measurements were the following: sweep widths, 250 000 Hz; spectrum accumulation frequency, 10 Hz; number of scans, 4000; 3 μs radio-frequency pulse; 16K data points. ^1H-decoupled ^{13}C NMR measurements: sweep widths, 25 000 Hz; spectrum accumulation frequency, 0.2 Hz; number of scans, 1000; 90° radio-frequency pulse; duration, 6.2 μs. For ^{13}C *J*-modulated spectra, 140 Hz J_{C-H} value was used. Data were collected with 32K points and zero filled to 64K. Optical rotations were measured with a JASCO model DIP-360 polarimeter. Enantiomeric excesses (ee) were calculated using known optical rotation values of enantiomerically pure sulfoxides [7,8]. (*R*)- and (*S*)-2-aminoalcohols were obtained from the corresponding commercially available amino acids as described [9].

2.1. Sample preparation

40 mg of the ligand **1** was dissolved in 600 μl of CH_2Cl_2, then [VO(O*i*-Pr)$_3$] (20 μl, ca. 1 eq.) was added at room temperature. According to ^{13}C and ^{51}V NMR, VO(O*i*-Pr)$_3$ rapidly and quantitatively converted into the complex [VO(O*i*-Pr)**1a**] via this procedure. Then the sample was cooled down to −12°C, and 30–40 μl (ca. 1 eq. in H_2O_2) of H_2O_2 solution (H_2O_2 (90%):CD_3CN = 1:10) was added, and $^{13}C\{^1H\}$ and ^{51}V NMR spectra were recorded at this temperature. CH_2Cl_2 was obtained commercially (Aldrich Chem. Co.), stored under molecular sieves and used without further purification.

2.2. Synthesis of Schiff bases

Equivalent amounts of 2-aminoalcohol and 3,5-di-*tert*-butylsalicylic aldehyde were dissolved in an appropriate volume of $CHC1_3$ and kept over anhydrous Na_2SO_4 until the complete disappearance of aminoalcohol was evidenced by TLC (approximately 1 day). Short column purification and drying in vacuo gave the pure products as yellow amorphous solids or syrups.

2.2.1. (R)-2-(N-3,5-di-tert-butylsalicylidene)amino-2-phenyl-1-propanol (**1a**)

NMR spectra, δ_H (250.13 MHz; CH_2Cl_2, Me_4Si) 1.30 (9H, s, $C(CH_3)_3$), 1.44 (9H, s, $C(CH_3)_3$), 3.90 (2H, m, CH_2OH), 4.47 (1H, m, N–CH), 7.18–7.47 (7H, m, Ph), 8.54 (1H, s, CH=N), 13.7 (1H, s, Ph–OH); δ_C (62.87 MHz; CH_2Cl_2, Me_4Si) 30.4 (3C, $\underline{C}(CH_3)_3$), 32.4 (3C, $C(\underline{C}H_3)_3$), 35.2 (1C, $\underline{C}(CH_3)_3$), 36.13 (1C, $\underline{C}(CH_3)_3$), 68.8 ($\underline{C}H_2OH$), 78.0 ($\underline{C}H$–N), 119.1, 127.7, 128.4, 128.5, 128.9, 129.9, 137.7, 141.1, 141.7, 159.1 ($\underline{C}$–OH), 168.7 ($\underline{C}H$=N). Yield 70%.

2.2.2. (S)-2-(N-3,5-di-tert-butylsalicylidene)amino-3,3-dimethyl-1-butanol (**1b**)

NMR spectra, δ_H (250.13 MHz; CH_2Cl_2, Me_4Si) 0.97 (9H, s, $CHC(CH_3)_3$), 1.32 (9H, s, $CHC(CH_3)_3$), 1.44 (9H, s, $C(CH_3)_3$), 2.91 (1H, dd, NCH), 3.72 (2H, dd, CH_3O), 3.90 (2H, dd, CH_3O), 7.14 (1H, d, Ph), 7.42 (1H, d, Ph), 8.38 (1H, s, CH=N), 13.9 (1H, s, Ph–OH); δ_C (62.87 MHz; CH_2Cl_2, Me_4Si) 28.0 (3C, $C(\underline{C}H_3)_3$), 30.4 (3C, $C(\underline{C}H_3)_3$), 32.4 (3C, $C(\underline{C}H_3)_3$), 34.2 (1C, $\underline{C}(CH_3)_3$), 35.2 (1C, $\underline{C}(CH_3)_3$), 36.1 (1C, $\underline{C}(CH_3)_3$), 63.5 ($\underline{C}H_2O$), 82.5 (N$\underline{C}$H), 119.0, 127.4, 128.1, 137.6, 141.4, 159.3 ($\underline{C}$OH), 168.2 ($\underline{C}$=N). Yield 67%.

2.2.3. (S)-2-(N-3,5-di-tert-butylsalicylidene)amino-3-methyl-1-butanol (**1c**)

NMR spectra, δ_H (250.13 MHz; CH_2Cl_2, Me_4Si) 0.94 d and 0.98 (6H, d, $(\underline{C}H_3)_2CH$], 1.34 (9H, s, $C(CH_3)_3$), 1.46 (9H, s, $C(CH_3)_3$), 1.97 (1H, m, $(CH_3)_3C\underline{H}$), 3.04 (1H, m, CH–N), 3.80 (2H, m, $C\underline{H}_2OH$), 7.19 (1H, d, Ph), 7.42 (1H, d, Ph), 8.41 (1H, s, CH=N), 13.7 (1H, s, Ph–OH); δ_C (62.87 MHz; CH_2Cl_2, Me_4Si) 19.8 (1C, $(\underline{C}H_3)_3CH$), 21.2 (1C, $(\underline{C}H_3)_3CH$), 30.9 (3C, $C(CH_3)_3$), 31.6 (1C, $(CH_3)_3\underline{C}H$), 32.5 (3C, $C(\underline{C}H_3)_3$), 35.7 (1C, $C(\underline{C}H_3)_3$), 36.4 (1C, $\underline{C}(CH_3)_3$), 66.1 ($\underline{C}H_2OH$), 79.3 ($\underline{C}H$–N), 119.3, 127.7, 128.3, 138.0, 141.8, 159.7 ($\underline{C}$–OH), 168.3 ($\underline{C}H$=N). Yield 81%.

*2.2.4. (R)-2-(N-3,5-di-tert-butylsalicylidene)amino-3-phenyl-1-propanol (**1d**)*

NMR spectra, δ_H (250.13 MHz; CH_2Cl_2; Me_4Si) 1.39 (9H, s, $C(CH_3)_3$), 1.57 (9H, s, $C(CH_3)_3$), 3.00 (2H, m, CH_2Ph), 3.57 (1H, m, N–CH), 3.82 (2H, m, CH_2OH), 7.13–7.51 (7H, m, Ph), 8.26 (1H, s, CH=N), 13.8 (1H, s, Ph–OH); δ_C (62.87 MHz; CH_2Cl_2, Me_4Si) 30.5 (3C, $C(\underline{C}H_3)_3$), 32.51 (3C, $C(\underline{C}H_3)_3$), 35.3 ($\underline{C}H_2Ph$), 36.2 (1C, $\underline{C}(CH_3)_3$), 40.3 (1C, $\underline{C}(CH_3)_3$), 66.9 ($\underline{C}H_2OH$), 74.4 ($\underline{C}H$–N), 119.0, 127.4, 127.5, 128.3, 129.6, 130.7, 137.7, 139.6, 141.4, 159.3 ($\underline{C}$–OH), 168.2 ($\underline{C}H$=N). Yield 78%.

2.3. Oxidation of sulfides

Methyl phenyl sulfide (**2**) (4.26 mmol) was added to a magnetically stirred (120 rpm) solution of vanadyl acetylacetonate (11 mg, 0.042 mmol) and Shiff base (**1a**–**1c**) (0.064 mmol) in 10 ml of CH_2Cl_2. Resulting solution was thermostated at 1°C, and 4.7 mmol of 30% hydrogen peroxide were added drop-wise. Temperature was elevated to 20°C within 1 h, and stirring was continued for another 12 h. Resulting sulfoxides **2** were purified as described in [3,4].

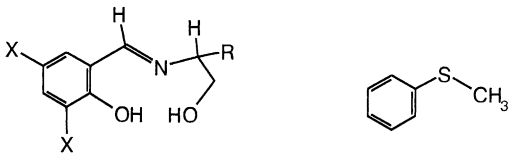
3. Results and discussion

The data summarized in Table 1 correlates the asymmetry level induced in the resulting sulfoxide with the R substituent in **1** (Fig. 1). As reported [2], the chirality transfer generates the same configuration at the sulphur atom as in the catalyst, i.e. (*R*)-sulfoxide was obtained using the ligand derived from D-amino alcohol.

Table 1
Catalytic enantioselective oxidation of sulfide **2**

No.	Ligand	Yield (%)	ee (%)	Configuration[a]
1	**1a**	70	26	*R*
2	**1b**	73	56	*S*
3	**1c**	50	29	*S*
4	**1d**	60	27	*R*

[a] Absolute configuration and ee values were determined by isolating the sulfoxide and comparison of its optical rotation values with literature data. All reactions were performed as described in Section 2.3.



1 2

a: X= *t*-Bu , R= Ph (R)
b: X= *t*-Bu , R= *t*-Bu (S)
c: X= *t*-Bu , R= *i*-Pr (S)
d: X= *t*-Bu , R= CH_2Ph (R)

sulfide

Fig. 1. Ligands (**1a**, **1b**, **1c**) and sulfide **2** used in the asymmetric catalytic oxidation reactions.

Earlier, ^{51}V NMR monitoring of the catalytic system [$VO(acac)_2$]/**1a**/30% H_2O_2 in CH_2Cl_2 at −12°C showed that the two peaks (at −514 and −651 ppm) predominate in the spectrum at the initial stage of reaction [10]. They were assigned to vanadium(V) peroxo complexes. However, the ^1H NMR spectrum showed a considerable quantity of uncomplexed ligand. In order to avoid the undesired presence of free ligand and of paramagnetic vanadium(IV) impurities as well, [$VO(O\textit{i}\text{-}Pr)_3$] was used as a catalyst precursor. To improve the resolution in the ^{13}C NMR spectra, the system was made homogeneous by using CH_3CN solution of 90% H_2O_2 as the oxidant.

3.1. ^{51}V and ^{13}C NMR study of [$VO(Oi\text{-}Pr)_3$]/**1a**/H_2O_2 system in CH_2Cl_2

Fig. 2 shows ^{51}V and $^{13}C\{^1H\}$ NMR spectra of the vanadium(V) species formed in the catalytic system [$VO(O\textit{i}\text{-}Pr)_3$]/**1a**/$H_2O_2$ in CH_2Cl_2. Two predominant ^{51}V resonances of equal integral intensities and of similar line-widths at −514 ($\Delta\nu_{1/2}$ = 700 Hz) and −651 ppm ($\Delta\nu_{1/2}$ = 680 Hz) at −12°C (Fig. 2a) are the same as for [$VO(acac)_2$]/**1a**/H_2O_2 system and belong to two complexes $\mathbf{A_{1a}}$ and $\mathbf{B_{1a}}$. Several ^{51}V NMR spectra have been recorded at different temperatures. At −20°C, ^{51}V signals are very wide ($\Delta\nu_{1/2}$ = 1500 Hz), their relative intensities being equal. In the range of 0 to +20°C, the ratio of $\mathbf{A_{1a}}$ and $\mathbf{B_{1a}}$ is virtually unchanged versus that at −12°C (ca. 1:1). Line-widths of $\mathbf{A_{1a}}$ and $\mathbf{B_{1a}}$ signals also remain nearly equal.

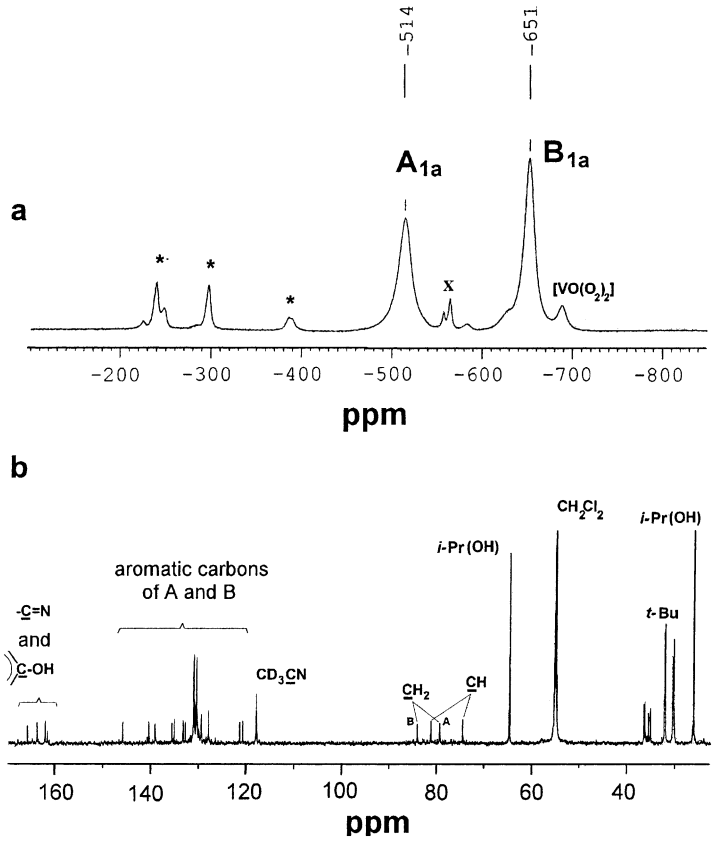


Fig. 2. ^{51}V (a) and ^{13}C{^{1}H} NMR (b) spectra of sample prepared as described with ligand **1a** at −12°C. In (a), minor species at −200 to −400 ppm are still to be identified. Signal **X** belongs to the residual [VO(O*i*-Pr)**1a**]. In (b), one signal of complex **A** ($\delta(CH_2) = 79.5$ ppm) as well as that of complex **B** ($\delta(CH_2) = 84.1$ ppm) is assigned. The remaining two signals are assigned to CH carbons of complexes **A** and **B**. Resonances at 120–150 ppm are those of aromatic carbons. Signals at 160–170 ppm belong to C=N and aromatic C–OH carbons of **A** and **B**.

At room temperature, complexes $\mathbf{A_{1a}}$ and $\mathbf{B_{1a}}$ decompose in a strictly parallel manner with half-life time of about 20 min. Addition of a fresh portion of H_2O_2 restores partially concentrations of these intermediates. The addition of sulfide **2** (to a concentration of 0.5 M) to the sample of Fig. 2 at room temperature results in rapid disappearance of $\mathbf{A_{1a}}$ and $\mathbf{B_{1a}}$ within a time of data accumulation (2 min). Thus, at least one of the complexes ($\mathbf{A_{1a}}$ or $\mathbf{B_{1a}}$) or both are active towards sulfide. ^{51}V NMR chemical shifts of $\mathbf{A_{1a}}$ and $\mathbf{B_{1a}}$ are within the range expected for monoperoxo complexes of vanadium(V) with O- or N-donor ligands [11–17]. All presented data suggest that complexes $\mathbf{A_{1a}}$ and $\mathbf{B_{1a}}$ are peroxo vanadium(V) species (see also reviews [18,19]). Peaks at −200 to −400 ppm (Fig. 2a) belong to still unidentified products of complexes $\mathbf{A_{1a}}$ and $\mathbf{B_{1a}}$ degradation. The intensity of these peaks grows with the decrease of complexes $\mathbf{A_{1a}}$ and $\mathbf{B_{1a}}$ concentration. The signal at −688 ppm belongs to the well-known bis(peroxo) vanadium(V) complex $[VO(O_2)_2(H_2O)]$ [11].

To make definitive conclusions on the solution structure of complexes $\mathbf{A_{1a}}$ and $\mathbf{B_{1a}}$, it is necessary to obtain informative ^{13}C{^{1}H} and ^{51}V NMR spectra of one and the same sample. Fig. 2b shows ^{13}C{^{1}H} NMR spectrum of the sample of Fig. 2a. The resonances of uncoordinated **1a** and initial [VO(O*i*-Pr)$_3$] are not observed in this spectrum. Thus, [VO(O*i*-Pr)$_3$] almost quantitatively converts into complexes $\mathbf{A_{1a}}$ and $\mathbf{B_{1a}}$. The existence of two types of complexes

results in appearance of two sets of the ^{13}C NMR signals for coordinated **1a**. This effect is most clearly observed for the signals of CH_2 and asymmetric CH carbon atoms of coordinated **1a** (Fig. 2b). $^{13}C\{^1H\}$ *J*-modulated spectra allowed to distinguish CH_2 and CH carbon atoms. The relative intensities of the observed couple of signals are 1:1 in agreement with 1:1 ratio of complexes $\mathbf{A_{1a}}$ and $\mathbf{B_{1a}}$ (Fig. 2b). Thus, peroxo complexes $\mathbf{A_{1a}}$ and $\mathbf{B_{1a}}$ both contain one Schiff base ligand per vanadium atom. This important conclusion can be made although we cannot assign ^{13}C NMR peaks of complexes $\mathbf{A_{1a}}$ and $\mathbf{B_{1a}}$ to a particular complex.

The width of a ^{51}V NMR resonance in solution is proportional to the correlation time τ_c and increases with the increase of the size of a molecule [20]. $\mathbf{A_{1a}}$ and $\mathbf{B_{1a}}$ have the similar ^{51}V NMR line-widths ($\Delta\nu_{1/2} \approx 700$ Hz) and therefore both are expected to be mononuclear.

Thus, the data obtained strongly suggest that two types of mononuclear monoperoxo vanadium complexes $\mathbf{A_{1a}}$ and $\mathbf{B_{1a}}$ incorporating one Schiff base ligand could be the active intermediates of the catalytic systems $[VO(acac)_2]$/**1a**/H_2O_2 and $[VO(Oi\text{-}Pr)_3]$/**1a**/H_2O_2. Possible distinctions in the structures of complexes $\mathbf{A_{1a}}$ and $\mathbf{B_{1a}}$ are discussed below.

*3.2. ^{51}V and ^{13}C NMR study of $[VO(Oi\text{-}Pr)_3]$/**1b**/H_2O_2 system in CH_2Cl_2*

The ^{51}V NMR spectrum of the catalytic system $[VO(Oi\text{-}Pr)_3]$/**1b**/H_2O_2 shows that in this case complex $\mathbf{B_{1b}}$ exists in solution in two forms (peaks at −633 and −650 ppm), complex $\mathbf{A_{1b}}$ exhibiting single resonance at −395 ppm (Fig. 3a). The ratio of concentrations of $\mathbf{A_{1b}}$ and $\mathbf{B_{1b}}$ determined from integration of ^{51}V peaks is 1:1. Complexes $\mathbf{A_{1b}}$ and $\mathbf{B_{1b}}$ rapidly disappear upon the addition of sulfide **2** to the reaction solution.

The occurrence of two forms of $\mathbf{B_{1b}}$ results in additional doubling of the ^{13}C resonances of CH_2 (peaks at 77.1, 77.3 ppm) and asymmetric CH carbon atom of $\mathbf{B_{1b}}$ (peaks at 86.0, 86.1 ppm in Fig. 3b, insert). This allows to distinguish these signals from those of $\mathbf{A_{1b}}$ (CH_2 at 65.7 and CH at 74.5 ppm, respectively). Noteworthy, the chemical shift of CH_2 carbon atom of $\mathbf{A_{1b}}$ (at 65.7 ppm) is close to that of free **1b** (at 63.5 ppm), while those of $\mathbf{B_{1b}}$ (at 77.1, 77.3 ppm) being markedly larger. This fact implies that CH_2 carbon atom in $\mathbf{A_{1b}}$ is far less perturbed by coordination to vanadium atom than that in $\mathbf{B_{1b}}$. Proposed structures of **A** and **B** that fit this requirement are shown in Scheme 1 (ligand **1** shown has (*R*)-absolute configuration; L may be *i*-PrOH or H_2O molecule). Bidentate coordination of **1** takes place for **A** and tridentate one for **B**. One could expect that the same difference in the mode of Schiff base ligand coordination took place for previously discussed complexes $\mathbf{A_{1a}}$ and $\mathbf{B_{1a}}$ (Fig. 2).

*3.3. The nature of monoperoxo vanadium(V) complexes formed in $[VO(Oi\text{-}Pr)_3]$/**1a–1d**/H_2O_2 systems in CH_2Cl_2*

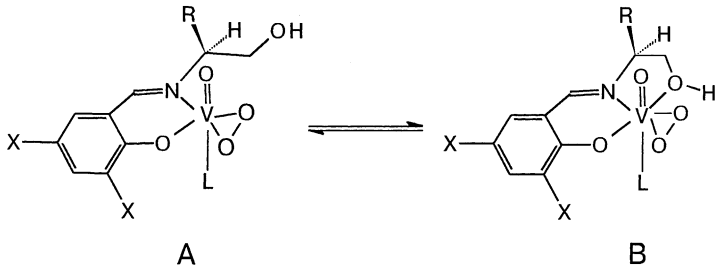
Chemical shifts of the ^{51}V resonances of $\mathbf{B_{1a}}$, $\mathbf{B_{1b}}$, $\mathbf{B_{1c}}$ and $\mathbf{B_{1d}}$ are rather close (Table 2). Thus, the structure of these complexes is analogous to that of complex $\mathbf{B_{1b}}$ (Scheme 1). Based on the same arguments, we believe that complexes $\mathbf{A_{1b}}$, $\mathbf{A_{1c}}$ and $\mathbf{A_{1d}}$ (Table 2) have a common structure of complex **A** (Scheme 1, L = H_2O or *i*-PrOH). The unexpectedly low value of the ^{51}V NMR shift of $\mathbf{A_{1a}}$ (cf. −514 ppm for R = Ph ($\mathbf{A_{1a}}$) and −386 ppm for R = CH_2Ph ($\mathbf{A_{1d}}$)) is still unclear. Note that in all cases where we can distinguish ^{13}C NMR resonances of complexes **A** and **B** (ligands **1b**, **1c** and **1d**), chemical shifts of $\underline{C}H_2$ and asymmetric $\underline{C}H$ carbon atoms of **A** are less perturbed by coordination to vanadium atom than those of **B**.

Let us discuss the origin of two ^{51}V peaks observed for complexes $\mathbf{B_{1b}}$, $\mathbf{B_{1c}}$ and $\mathbf{B_{1d}}$ (Fig. 3a, Table 2). ^{51}V NMR monitoring of the resonances of the complexes $\mathbf{A_{1b}}$, $\mathbf{A_{1c}}$ and $\mathbf{A_{1d}}$ at room temperature shows that they are also a superposition of two very close peaks ($\Delta\delta \leq 3$ ppm) indistinguishable

Table 2
^{51}V NMR chemical shifts of peroxo vanadium complexes observed in $[VO(Oi\text{-}Pr)_3]$/**1a–1d**/H_2O_2 systems at −12°C

No.	Ligand	Complex **A**	Complex **B**
1	**1a**	−514	−651
2	**1b**	−395	−633, −650
3	**1c**	−396	−636, −654
4	**1d**[a]	−386	−633, −650

[a] At +5°C. All samples were prepared as described in Section 2.1.



Scheme 1.

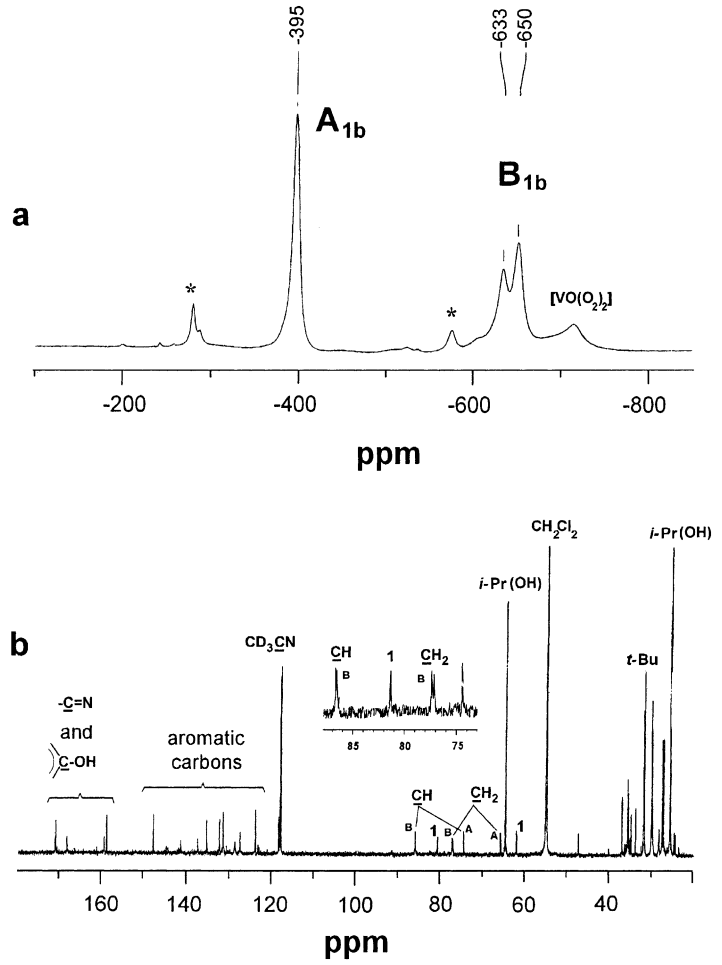


Fig. 3. ^{51}V (a) and $^{13}C\{^1H\}$ NMR (b) spectra of sample prepared as described with ligand **1b** at −12°C. In (a), minor species at −200 to −300 ppm and −580 ppm marked with asterisks are still to be identified. In (b), resonances of complex **A** ($\delta(CH_2) = 65.7$, $\delta(CH) = 74.5$ ppm) and those of complex **B** ($\delta(CH_2) = 77.1$, 77.3 ppm, $\delta(CH) = 86.0$, 86.1 ppm). Resonances at 120–150 ppm are those of aromatic carbons of **A** and **B**. Signals at 157–172 ppm belong to C=N and aromatic C–OH carbons of **A** and **B**. "**1**" stands for peaks of free ligand **1b** ($\delta(CH_2) = 62.2$, $\delta(CH) = 81.0$ ppm).

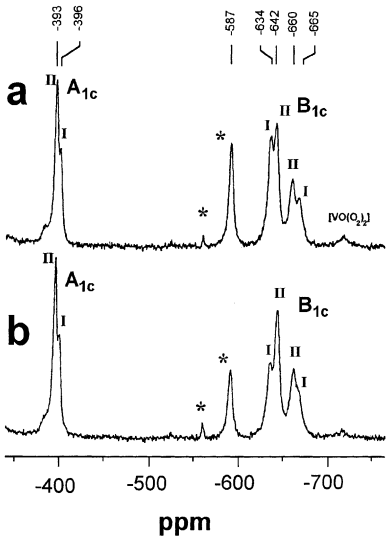
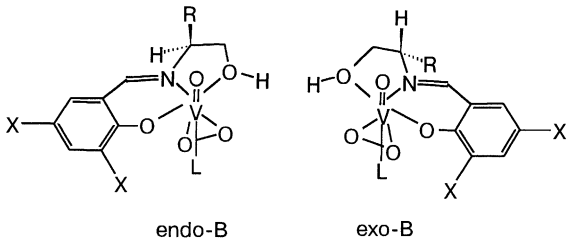


Fig. 4. ^{51}V NMR spectra of sample prepared as described with ligand **1c** at +5°C. In (a), 100 μl of *i*-PrOH added; in (b), 300 μl of *i*-PrOH added. Signals denoted as **I** and **II** are assigned to complexes $\mathbf{A_{1c}}$ and $\mathbf{B_{1c}}$ with different ligands L (**I**: L = H_2O, **II**: L = *i*-PrOH). Peaks marked with asterisks belong to still unidentified vanadium(V) species.

at low temperature because of large line widths. Two forms of complexes **A** and **B** differ by the ligation of various molecules L to one of coordination sites (Scheme 1, L = H_2O or *i*-PrOH). The most detailed experiments confirming this statement were made for the catalytic system [VO(O*i*-Pr)$_3$]/**1c**/H_2O_2 at 5°C. With the increase of *i*-PrOH concentration in solution, the relative intensity of one of the two peaks of $\mathbf{A_{1c}}$ and $\mathbf{B_{1c}}$ gradually increased (compare Fig. 4a and b). It is worth noting that the spectra of Fig. 4 display additional ^{51}V peaks (at −660 and −665 ppm) in the range typical for complex **B**. The total intensity of signals at −660 and −665 ppm is about one-half of that of signals at −634 (L = H_2O) and −642 ppm (L = *i*-PrOH). By analogy with the results reported for vanadium complexes with salicylaldimines of amino acids and chelating alcohols [21] and Bolm's results as well [22], we believe that the existence of two diastereomeric forms of complex $\mathbf{B_{1c}}$ is the case (endo and exo forms, see Scheme 2, where L = H_2O or *i*-PrOH), with the major form displaying ^{51}V resonances at −633 and −642 ppm and the minor one at −660 and −665 ppm. Both



Scheme 2.

isomers exhibit two ^{51}V peaks owing to coordination of H_2O or *i*-PrOH to one of the coordination sites. As described in [21], in the case of vanadium(V) complexes with salicylaldimines of amino acids and chelating alcohols, K_{eq} = [endo]/[exo] depends on the nature of the R substituent at the carbon chiral center (in the order Me < CH_2Ph < $CHMe_2$) and ranges from 2.5 to 31.4 and from 6.1 to 40.5 for 1,2-ethanediol and glycerol, respectively. We believe that picture is the same for our complexes, i.e. exo and endo forms exist for all the ligands used. The ratio between two diasteroisomers in our case is also supposed to depend on the nature of R.

In conclusion, ^{51}V and ^{13}C{^{1}H} spectra provide rather detailed insight into solution structure, stability and reactivity of peroxo vanadium species that operate in a practically promising catalytic system for enantioselective oxidation of sulfides. Such data are very restricted in the literature and are of great importance for optimization of enantioselectivity in catalytic systems based on chiral vanadium complexes and hydrogen peroxide.

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