

# Stereoselective oxidation of linalool with *tert*-butyl hydroperoxide, catalyzed by a vanadium(V) complex with a chiral terpenoid ligand

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## Abstract

Stereoselective epoxidation of (–)-(*R*)-linalool by *tert*-butylhydroperoxide (TBHP) catalyzed by a vanadium(V) complex formed by interaction of [VO(acac)<sub>2</sub>] or [VO(*On*-Bu)<sub>3</sub>] with a new chiral terpenoid ligand (L) is reported. Moderate diastereomeric excess (de 56%) was attained in toluene at 20 °C. <sup>51</sup>V, <sup>13</sup>C and <sup>17</sup>O NMR spectroscopic monitoring of the studied catalytic system showed that a new complex **1** forms quantitatively upon interaction of [VO(*On*-Bu)<sub>3</sub>] with L in CH<sub>2</sub>Cl<sub>2</sub>. Compound **1** is a mononuclear complex of vanadium(V), which incorporates the tridentate chiral ligand L, as well as V=O moieties. It has been shown that TBHP binds to **1** giving a **1**·TBHP adduct with the association constant  $K = 1.36 \pm 0.11 \text{ l mol}^{-1}$  at room temperature and enthalpy  $\Delta_r H_{298}^0 = -6.5 \pm 2.0 \text{ kJ mol}^{-1}$  and entropy  $\Delta_r S_{298}^0 = -20 \pm 6 \text{ J mol}^{-1} \text{ K}^{-1}$ . These thermodynamic parameters are typical for outer sphere complexes (OSCs). Adduct **1**·TBHP is suggested to be a precursor of the active intermediate of the stereoselective epoxidation process.

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**Keywords:** Stereoselective epoxidation; Linalool; Terpenoid ligand; TBHP; NMR; Intermediates; Outer sphere complex

## 1. Introduction

Efforts to perform stereoselective epoxidation of olefins commenced in 1965 with the report by Henbest that a low level of enantiomeric excess (10%) could be achieved using percamphoric acid [1]. A useful level of enantioselectivity remained an elusive goal for 15 years and was reported by Katsuki and Sharpless to be achieved for epoxidation of allylic alcohols using titanium–tartrate complex/TBHP catalytic sys-

tem [2]. Since that time, a variety of transition metal based catalytic systems for stereoselective epoxidation appeared. A great number of Katsuki–Sharpless type systems are still dominating over others ([3,4]). However, the main disadvantage of these systems, a low turnover number, stimulates the search for new efficient catalysts.

Vanadium-based epoxidation of allylic alcohols with TBHP is well-known [5–7]. A number of asymmetric epoxidations based on the use of vanadium chiral complexes and TBHP have been reported [8–13]. Vanadium(V) alkylperoxo complexes were widely accepted as intermediates in the [VO(acac)<sub>2</sub>]/TBHP [5,14–16] and [VO(acac)<sub>2</sub>]/ligand/TBHP [12,17,18] catalytic systems. The X-ray structure of the alkylper-

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105.191 and 54.245 MHz, respectively, using 5 mm or 10 mm cylindrical tubes. For  $^{17}\text{O}$  NMR spectra, high-power probehead was used to increase the sensitivity. Chemical shifts were measured with respect to residual  $\text{CH}_2\text{Cl}_2$  carbons ( $\delta$ : 55.0 ppm) for  $^{13}\text{C}$ , external reference  $\text{VOCl}_3$  for  $^{51}\text{V}$  spectra, and external reference  $\text{H}_2\text{O}$  for  $^{17}\text{O}$  spectra, with positive values in the low-field direction. Typical operation conditions for  $^{51}\text{V}$  measurements were as follows: sweep widths 125,000 Hz, spectrum accumulation frequency 20 Hz, number of scans 4096, 10  $\mu\text{s}$  radio-frequency pulse, 2 K data points. Typical operation conditions for  $^{17}\text{O}$  measurements were the following: sweep widths 125,000 Hz, spectrum accumulation frequency 40 Hz, number of scans 4096, 45° pulse at 10  $\mu\text{s}$ , 2 K data points.  $^1\text{H}$ -decoupled  $^{13}\text{C}$  NMR measurements: sweep widths 30,000 Hz, spectrum accumulation frequency 0.2 Hz, number of scans 1000, 10  $\mu\text{s}$  radio-frequency pulse.  $^{13}\text{C}$  NMR data were collected with 32 K points and zero filled to 64 K.

Samples for NMR measurements were prepared as follows: an appropriate amount (60–600  $\mu\text{mol}$ ) of the vanadium catalyst precursor (either  $[\text{VO}(\text{O}n\text{-Bu})_3]$  or  $[\text{VO}(\text{acac})_2]$ ) was dissolved in 3 ml of  $\text{CH}_2\text{Cl}_2$  in a 10 mm glass NMR tube. Then the ligand, L, was added as a solid to obtain the desired L/V ratio (1:1 to 6:1). If necessary, *tert*-BuOOH, linalool, etc. were added. Samples were kept at an appropriate temperature in the probehead, and  $^{51}\text{V}$  and  $^{13}\text{C}$  spectra were run with the parameters stated above. To record  $^{17}\text{O}$  NMR, 0.003 ml of  $\text{H}_2^{17}\text{O}$  (4.6% in  $^{17}\text{O}$ ) was added to the sample containing the solution of  $[\text{VO}(\text{O}n\text{-Bu})_3]$  and L in 2 ml of  $\text{CH}_2\text{Cl}_2$ .

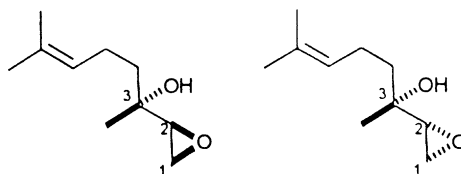
### 3. Results and discussion

#### 3.1. Stereoselective epoxidation of (–)-*R*-linalool in $[\text{VO}(\text{acac})_2]/\text{L}/\text{TBHP}$ catalytic system

The oxidation of linalool with TBHP in the presence of catalytic amounts of  $[\text{VO}(\text{acac})_2]$  was first described by Sharpless and Michaelson in 1973 [5]. The reaction was found to give nearly quantitatively the previously unknown 1,2-monoepoxide. The epoxide diastereomeric ratios were not reported in [5].

The results on the  $[\text{VO}(\text{acac})_2]$ -catalyzed oxidation of (–)-*R*-linalool with TBHP both in the

absence and in the presence of the chiral ligand L are given in Table 1. We have found that the oxidation of (–)-*R*-linalool with TBHP in the presence of  $[\text{VO}(\text{acac})_2]$  in toluene resulted in the formation of two diastereomeric monoepoxides, (2*S*,3*R*) and (2*R*,3*R*), with a poor diastereomeric excess (de 4%, Run 1).



The reaction proceeded slowly at room temperature (55% conversion in 49 h). At the same time, the addition of the chiral ligand L considerably enhanced the reaction rate, while the diastereoselectivity increased (Table 1). The use of  $\text{CH}_2\text{Cl}_2$  and  $\text{CCl}_4$  instead of toluene resulted in the de decrease, while in the presence of MeCN as a solvent, the reaction did not proceed. The stereoselectivity increased with increasing concentration of L up to L/ $[\text{VO}(\text{acac})_2]$  molar ratio equal to 6/1 and then remained constant (Table 1). A similar optimum ligand/ $[\text{VO}(\text{acac})_2]$  molar ratio (5/1) has been previously found for the chiral hydroxamic acid ligands [8]. At a constant L/ $[\text{VO}(\text{acac})_2]$  ratio, both the reaction rate and stereoselectivity raised with decreasing vanadium precursor concentration down to  $[\text{VO}(\text{acac})_2] = 0.002 \text{ M}$  (compare Runs 5, 12 and 13). This is a quite unusual phenomenon because ordinarily the lower the chiral catalyst turnover number, the higher the asymmetric induction level [3]. The reason for this is unclear yet and further investigation is needed to explain this phenomenon. We may tentatively suppose that low association constants between the vanadium(V) chiral complex (see later) and the reactants (TBHP, linalool) might be responsible for this. The maximal de values were observed at 20 °C in toluene and attained 56% in optimal reaction conditions.

The oxidation of racemic linalool has revealed that a kinetic resolution of the allylic alcohol takes place: at 70% conversion the yield of the (2*R*, 3*S*) + (2*S*, 3*S*) diastereomers was 5-fold higher than the yield of the (2*S*, 3*R*) + (2*R*, 3*R*) diastereomeric pair. Thus, we may conclude that (+)-*S*-linalool oxidation rate is higher as compared to (–)-*R*-linalool. All these facts

Table 1

Stereoselective epoxidation of (–)-(R)-linalool with TBHP in the presence of the chiral catalyst generated in situ from VO(acac)<sub>2</sub> and L<sup>a</sup>

Run	[VO(acac) <sub>2</sub> ] × 10 <sup>3</sup> (M)	[L] × 10 <sup>3</sup> (M)	Solvent	T (°C)	Time (h)	de (%) <sup>b</sup>	(–)-(R)-Linalool conversion (%)
1	2	–	CH <sub>3</sub> C <sub>6</sub> H <sub>5</sub>	20	49	4	55
2	2	12.5	CH <sub>3</sub> CN	20	120	3	4
3	2	12.5	CCl <sub>4</sub>	20	24	18	90
4	2	12.5	CH <sub>2</sub> Cl <sub>2</sub>	20	24	26	92
5	2	12.5	CH <sub>3</sub> C <sub>6</sub> H <sub>5</sub>	20	24	56	97
6	2	12.5	CH <sub>3</sub> C <sub>6</sub> H <sub>5</sub>	40	8	40	97
7	2	12.5	CH <sub>3</sub> C <sub>6</sub> H <sub>5</sub>	0	72	42	95
8	2	12.5	CH <sub>3</sub> C <sub>6</sub> H <sub>5</sub>	–18	120	39	95
9	2	5	CH <sub>3</sub> C <sub>6</sub> H <sub>5</sub>	20	24	36	96
10	2	18	CH <sub>3</sub> C <sub>6</sub> H <sub>5</sub>	20	24	55	97
11	2	25	CH <sub>3</sub> C <sub>6</sub> H <sub>5</sub>	20	24	56	97
12	5	31	CH <sub>3</sub> C <sub>6</sub> H <sub>5</sub>	20	51	41	95
13	20	125	CH <sub>3</sub> C <sub>6</sub> H <sub>5</sub>	20	120	8	48
14	50	125	CH <sub>3</sub> C <sub>6</sub> H <sub>5</sub>	20	120	3	37

<sup>a</sup> Reaction conditions: 0.004–0.1 mmol of [VO(acac)<sub>2</sub>], 0.2 mmol of (–)-(R)-linalool, 0.025–0.1 mmol of L and 2 ml of a solvent was cooled down to –18 °C and then 0.3 mmol of TBHP (2.6 M toluene solution) was added. Then the reaction was carried out at –18, 0, 20 or 40 °C during 8–120 h.

<sup>b</sup> de = |(2S, 3R) – (2R, 3R)| / (2S, 3R) + (2R, 3R).

collectively show that an asymmetric induction does arise in the L/[VO(acac)<sub>2</sub>]/TBHP/linalool system.

### 3.2. <sup>51</sup>V, <sup>13</sup>C and <sup>17</sup>O NMR spectroscopic monitoring of vanadium(V) species formed in the catalytic systems studied

Fig. 1 demonstrates the <sup>51</sup>V NMR spectra of the major vanadium species present in the catalytic system [VO(acac)<sub>2</sub>] + L + TBHP. When an excess of TBHP (5 μl, 50 μmol) was added to the sample containing 11.4 μmol of [VO(acac)<sub>2</sub>] and 14.4 μmol of L in 600 μl CH<sub>2</sub>Cl<sub>2</sub>, various vanadium(V) signals appeared (Fig. 1a). An earlier study has shown that vanadium(IV) present completely oxidized to vanadium(V) upon the interaction of TBHP with [VO(acac)<sub>2</sub>] [25]. In the <sup>51</sup>V NMR spectra (Fig. 1a and b), two of the peaks observed belong to the well-characterized VO(acac)<sub>2</sub>O*tert*-Bu (δ = –350 ppm) and VO(acac)<sub>2</sub>O*tert*-Bu (δ = –489 ppm) complexes [25]. VO(acac)<sub>2</sub>O*tert*-Bu and VO(acac)<sub>2</sub>O*tert*-Bu species were shown to form in toluene and C<sub>6</sub>D<sub>6</sub> as solvents, too. The broad signal at –517 ppm (Δν<sub>1/2</sub> = 1.0 kHz) can be assigned to a new complex **1** incorporating the chiral ligand L. Its chemical shift is in the field typical for vanadium(V) complexes with O,N-donor ligands [26]. The

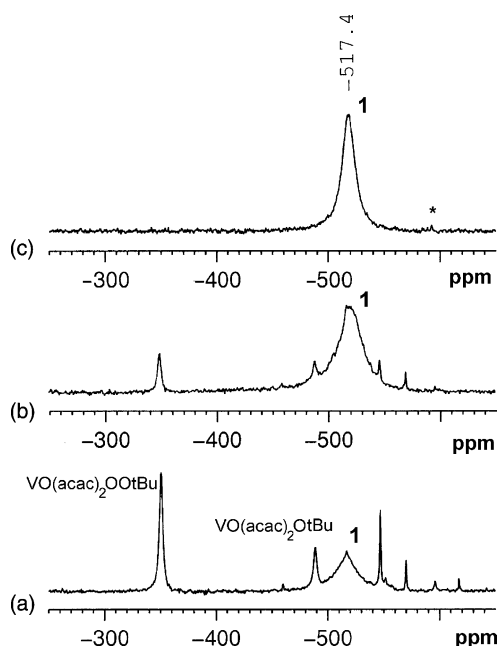


Fig. 1. <sup>51</sup>V NMR spectra of the vanadium(V) complexes formed in the system studied in CH<sub>2</sub>Cl<sub>2</sub> at 20 °C: (a) [VO(acac)<sub>2</sub>] = 0.019 M, [L] = 0.024 M, [*tert*-BuOOH] = 0.083 M; (b) [VO(acac)<sub>2</sub>] = 0.019 M, [L] = 0.10 M, [*tert*-BuOOH] = 0.33 M; (c) [VO(On-Bu)<sub>3</sub>] = 0.01 M, [L] = 0.025 M. The asterisk is to mark signals of the residual VO(On-Bu)<sub>3</sub> (δ = –591 ppm). For notation **1** see text.

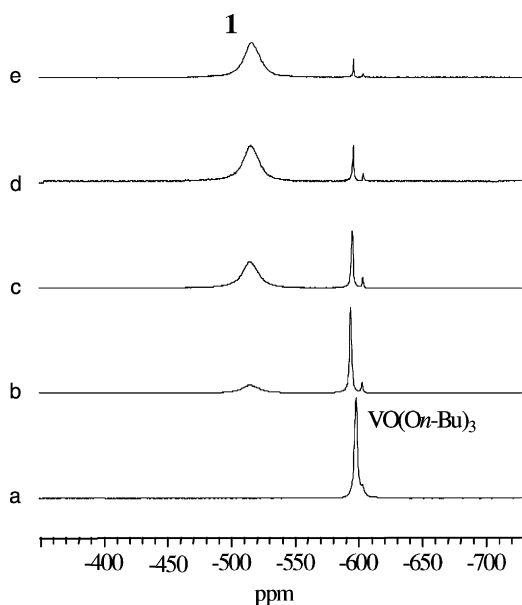


Fig. 2.  $^{51}\text{V}$  NMR spectra of the vanadium species ( $[\text{VO}(\text{On-Bu})_3] = 0.18\text{ M}$ ) in dry, degassed toluene (a); the same sample after the addition of L ( $C_L = 0.27\text{ M}$ ) and  $\text{H}_2\text{O}$  ( $C_{\text{H}_2\text{O}} = 0.063\text{ M}$ ) (b);  $C_{\text{H}_2\text{O}} = 0.10\text{ M}$  (c);  $C_{\text{H}_2\text{O}} = 0.15\text{ M}$  (d);  $C_{\text{H}_2\text{O}} = 0.18\text{ M}$  (e). When  $[\text{VO}(\text{On-Bu})_3] = C_{\text{H}_2\text{O}} = 0.18\text{ M}$ , 96% of the vanadium present in the form of **1**. Special injecting of water is only needed when dried solvent and ligand are used and the samples are handled under argon. When no moisture protection is practised, complex **1** forms without addition of water.

nature of other signals is unclear yet (Fig. 1a). With the increase of the concentration of L ( $48.5\ \mu\text{mol}$ ,  $L/V = 4$ ), complex **1** becomes the predominant species in the solution (Fig. 1b).

Complex **1** can be obtained quantitatively using  $[\text{VO}(\text{O}t\text{ert-Bu})_3]$  or  $[\text{VO}(\text{On-Bu})_3]$  as catalyst precursors (Fig. 1c). This approach allows to record

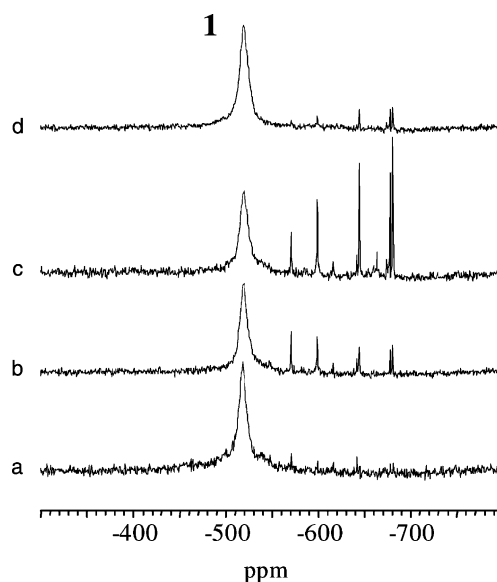


Fig. 3.  $^{51}\text{V}$  NMR spectra of the vanadium species formed in  $600\ \mu\text{l}$  of  $\text{CH}_2\text{Cl}_2$  solution of  $\text{VO}(\text{On-Bu})_3$  ( $0.016\text{ M}$ ) and L ( $0.016\text{ M}$ ): complex **1** (a);  $10\ \mu\text{l}$  of linalool added (b);  $30\ \mu\text{l}$  of linalool added (c); additional amount of L added to make  $[\text{L}] = 0.052\text{ M}$  (d).

high-resolution  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra of **1**. It has been found that to convert  $[\text{VO}(\text{Oalk})_3]$  into **1** quantitatively,  $L/V$  ratio equal or higher than 1:1 is required (Figs. 1–3). This means that complex **1** incorporates one ligand L per vanadium atom. Possible reason why higher than 1:1  $L/V$  ratio is needed to form **1** when one starts from  $[\text{VO}(\text{acac})_2]$ , is that acetylacetonate is a bidentate ligand and high excess of L is required to substitute two acetylacetonate ligands.

$^{13}\text{C}$  NMR chemical shifts of complex **1** along with those of the free ligand L in  $\text{CH}_2\text{Cl}_2$  are presented in Table 2. One can see that chemical shifts of the first,

Table 2  
The  $^{13}\text{C}$  NMR chemical shifts in ppm for ligand L and vanadium(V) complexes **1** and **1**·TBHP in  $\text{CH}_2\text{Cl}_2$

Carbon species <sup>a</sup>	1	2	3	4	5	6	7	8	9	10	11	12
L	62.8	52.7	143.6	126.3	152.9	13.4	24.6	14.6	35.5	23.5	27.3	27.6
<b>1</b> <sup>b</sup>	73.7	52.4	148.6	127.9	155.4	14.3	25.2	14.8	35.2	23.9	27.3	27.8
<b>1</b> ·TBHP <sup>c</sup>	73.6	52.3	148.0	127.5	155.1	14.4	24.9	14.7	35.0	23.7	27.4	27.6

<sup>a</sup> For carbons numbering in L see Section 2.

<sup>b</sup> Complex **1** ( $[\text{I}] = 0.010\text{ M}$ ) was generated by interaction of  $\text{VO}(\text{On-Bu})_3$  with L ( $L/V = 1 : 1$ ) in 3 ml of  $\text{CH}_2\text{Cl}_2$ .

<sup>c</sup> Complex **1** ( $[\text{I}] = 0.024\text{ M}$ ) was generated by interaction of  $\text{VO}(\text{On-Bu})_3$  with L ( $L/V = 1 : 1$ ) in 3 ml of  $\text{CH}_2\text{Cl}_2$ , and  $60\ \mu\text{l}$  of TBHP was added at  $-5^\circ\text{C}$   $[\text{TBHP}] = 0.2\text{ M}$ . Spectra were recorded at this temperature. Signals of TBHP were found at 26.5 ppm ( $\text{C}(\text{CH}_3)_3$ ) and 81.5 ppm ( $\text{C}(\text{CH}_3)_3$ ).

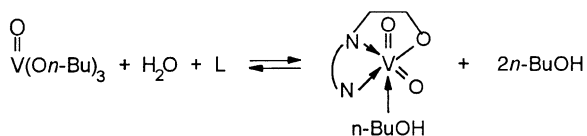
third and fifth carbons of L in complex **1** are most of all perturbed by coordination to vanadium. This tendency could be interpreted in favor of tridentate coordination of L so that those carbon atoms that are distant by two bonds from the metal should be most perturbed by coordination to vanadium. The similar approach was previously used to determine the solution structure of various vanadium(V) complexes [27,28].

It should be particularly emphasized that there were no  $^{13}\text{C}$  NMR signals other than those of coordinated L and free *n*-BuOH observed in L/[VO(*On*-Bu) $_3$ ] (1:1) system. Thus, remaining coordination sites of **1** can be occupied by some inorganic ligands or *n*-BuOH (on assumption of fast exchange between coordinated and free *n*-BuOH).

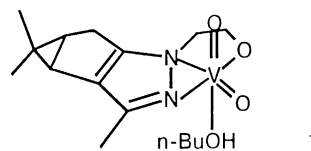
The  $^{17}\text{O}$  NMR spectrum of **1** exhibits a single peak at 1175 ppm ( $\Delta\nu_{1/2} = 800$  Hz). It is characteristic of  $\text{O}^{2-}$  and  $\text{OH}^-$  groups in six-coordinated vanadium(V) complex [29–32]. According to the literature,  $^{17}\text{O}$  NMR peaks of  $\text{O}^{2-}$  and  $\text{OH}^-$  groups are not observed separately because of rapid proton exchange between oxygen atoms [31]. The typical range of chemical shifts for V–O–V bridging oxygen atoms is 500–600 ppm [31]. There were no peaks observed in this region, so dinuclear structure of **1** seems improbable. Thus, based on  $^{17}\text{O}$  NMR data, **1** may be a mononuclear vanadium(V) complex with one tridentate chiral ligand L and V=O and V–OH moieties.

It was found that to form **1** starting from the ligand L and [VO(OAlk) $_3$ ], some water is needed (Fig. 2). Experiments carried out in dry solvents ( $\text{CH}_2\text{Cl}_2$ , toluene) with addition of appropriate amounts of water showed that 1 equivalent of water was consumed

by [VO(*On*-Bu) $_3$ ] to give **1** upon binding L. Most probably, formation of **1** follows the equation:

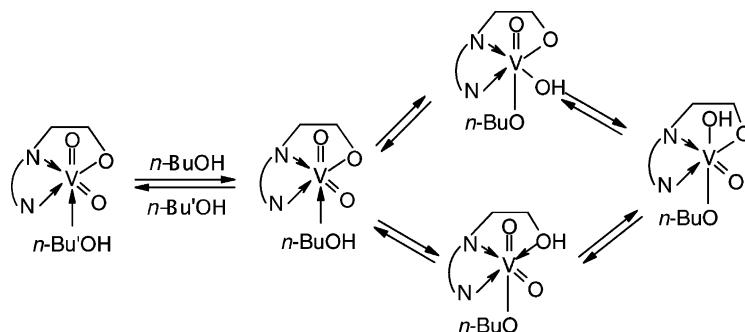


Possible structure of complex **1** is shown below:



The facts that there is a single  $^{17}\text{O}$  resonance for terminal oxygens of **1** as well as a single  $^{13}\text{C}$  resonance for *n*-BuOH can be explained by fast exchange processes: (1) proton transfer between V–O moieties and (2) exchange of the axial (*n*-BuOH) ligand (Scheme 1).

After the addition of linalool to the sample containing **1**, a set of new sharp resonances appears in the range of –570 to –690 ppm in the  $^{51}\text{V}$  spectrum at the expense of the intensity of the resonance at –517 ppm (Fig. 3a–c). Probably, these sharp peaks belong to vanadium species of the type VO(OR) $_n$ (OR $_1$ ) $_{3-n}$ , where  $n = 1\text{--}3$ , R: *On*-Bu, HOR $_1$ : linalool. By adding extra amount of L, the formation of vanadium species with sharp resonances can be suppressed, and the original concentration of **1** can be restored (Fig. 3d). Thus, we may conclude that when added in high excess, linalool can reversibly replace L in the first



Scheme 1. The structures proposed for vanadium(V) complexes existing in solution. The facts that there is a single  $^{17}\text{O}$  resonance for terminal oxygens of **1** and a single  $^{13}\text{C}$  resonance for *n*-BuOH can be explained by fast exchange processes: (1) proton transfer between V–OH and V=O moieties and (2) exchange of the axial ligand (*n*-BuOH).

coordination sphere of vanadium. Note that binding of allylic alcohols to vanadium is well precedented and is believed to be responsible for high regioselectivity in the vanadium-catalyzed oxidation of these compounds with alkylhydroperoxides [5,25]. Based on these data, simultaneous coordination of allylic alcohol and ligand L to vanadium is expected to provide the observed stereoselectivity. One can expect that linalool could substitute *n*-BuOH as the axial ligand. However, we obtained no direct spectral evidences in favor of the formation of such complexes yet.

### 3.3. $^{51}\text{V}$ and $^{13}\text{C}$ NMR study of the interaction of **1** with TBHP

The  $^{51}\text{V}$  chemical shift of **1** in  $\text{CH}_2\text{Cl}_2$  was found to be affected by the presence of TBHP, indicating fast exchange between at least two forms existing in solution. Actually, when the concentration of TBHP increased, the  $^{51}\text{V}$  signal shifted upfield monotonically (Fig. 4). This effect was not observed when equal amounts of *tert*-BuOH instead of TBHP were added. On the contrary, the addition of *tert*-BuOH caused changes in the  $^{51}\text{V}$  spectrum analogous to those observed in **1**/linalool system: L was ejected from the first vanadium coordination sphere, concentration of **1** decreased, and the signal assigned to  $[\text{VO}(\text{O}tert\text{-Bu})_3]$  species ( $\delta = -670$  ppm) grew up at the expense of that of **1**. The identity of  $[\text{VO}(\text{O}tert\text{-Bu})_3]$  was confirmed by synthesizing it independently [20]. As we mentioned already, the ejection of L from the vanadium coordination sphere is reversible, and the formation of  $[\text{VO}(\text{O}tert\text{-Bu})_3]$  can be suppressed by adding extra amounts of L.

It was found that the  $^{13}\text{C}$  NMR spectrum of **1** was virtually unaffected by TBHP coordination (Table 2). No  $^{13}\text{C}$  NMR signals of *tert*-BuOO $^-$  groups coordinated to vanadium were observed in the temperature range of  $-90$  to  $0^\circ\text{C}$ . This might indicate a very short lifetime of **1**·TBHP complex even at low temperature or (/and) a small coordination induced shift. Thus, in contrast to  $[\text{VO}(\text{acac})_2] + \text{TBHP}$  and  $[\text{VO}(\text{On-Bu})_3] + \text{TBHP}$  catalytic systems and the  $[\text{VO}(\text{OO}tert\text{-Bu})(\text{dipic})(\text{H}_2\text{O})]$  complex where the formation of alkylperoxo complexes with  $\text{VO}tert\text{-Bu}$  moieties is well documented [19,25,29], unexpectedly weak complex and labile **1**·TBHP was observed in the **1** + TBHP system.

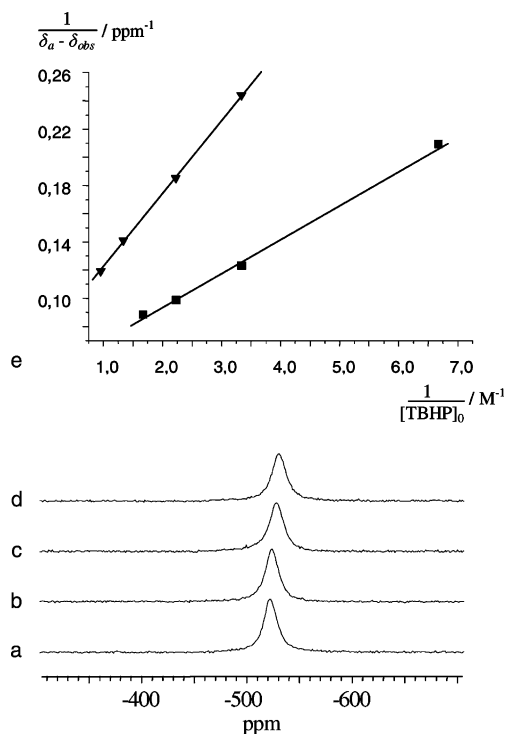


Fig. 4.  $^{51}\text{V}$  NMR spectra of the vanadium species formed in  $600\ \mu\text{l}$  of  $\text{CH}_2\text{Cl}_2$  solution of  $\text{VO}(\text{On-Bu})_3$  (0.01 M) and L (0.02 M) at 258 K (a);  $10\ \mu\text{l}$  of TBHP added (b);  $20\ \mu\text{l}$  of TBHP added (c);  $30\ \mu\text{l}$  of TBHP added (d). Plot of  $1/(\delta_a - \delta_{\text{obs}})$  vs.  $1/[\text{TBHP}]_0$ , where  $\delta_{\text{obs}}$  is the  $^{51}\text{V}$  chemical shift of the  $[\text{1}\cdot\text{TBHP}]$  OSC in  $\text{CH}_2\text{Cl}_2$  solution, at different temperatures: at 233 K (■), at 291 K (▼). Solid lines represent least-square fit to the data (e).

According to the  $^{13}\text{C}$  NMR spectra, TBHP concentration in the sample containing **1** and TBHP was constant at  $-5^\circ\text{C}$  in the absence of organic substrates. Addition of allylic alcohol (linalool) to the solution of **1** and TBHP resulted in a rapid conversion of the former into the corresponding monoepoxides and decrease of TBHP concentration, while concentration of *tert*-BuOH increased. At  $[\text{I}] = [\text{L}] = 0.024$  M,  $[\text{TBHP}] = 0.4$  M and  $[\text{linalool}] = 0.2$  M, complete alkene transformation occurred within 10–15 min. When linalool (0.05 M) was added into the sample containing **1**·TBHP (0.010 M solution in  $\text{CH}_2\text{Cl}_2$ ) generated from  $[\text{VO}(\text{On-Bu})_3]$ , L and  $\text{H}_2\text{O}$  (1:1) and 0.27 M of TBHP, the corresponding monoepoxide formed with de 28%. This demonstrates the reactivity of the observed vanadium(V) species, **1**·TBHP,

towards allylic alcohols and its ability to induce diastereoselectivity.

### 3.4. The stability constant for **1**·TBHP and its temperature dependence: $^{51}\text{V}$ NMR spectroscopic measurement

To explain (1) the short lifetime of the **1**·TBHP complex so that the condition of fast (on NMR timescale) exchange between **1** and **1**·TBHP is always fulfilled, (2) the absence of the  $^{13}\text{C}$  NMR signals of *tert*-BuOO<sup>−</sup> groups coordinated to vanadium and (3) the fact that the addition of *tert*-BuOH results in the formation of  $[\text{VO}(\text{O}i\text{tert-Bu})_3]$  rather than **1**·*tert*-BuOH, we supposed that formation of the **1**·TBHP outer sphere complex (OSC) is the case. Monotonic dependence of the **1**·TBHP  $^{51}\text{V}$  chemical shift on the TBHP concentration is in favor of the formation of a 1:1 OSC [33,34]. This dependence can be used to estimate the association constant for **1**·TBHP formation. The observed  $^{51}\text{V}$  chemical shift of **1**·TBHP involved in a two-position rapid exchange between **1** and **1**·TBHP can be expressed by

$$\delta_{\text{obs}} = (1 - p)\delta_{\text{a}} + p\delta_{\text{b}} \quad (1)$$

where  $\delta_{\text{a}}$  is the  $^{51}\text{V}$  NMR shift of **1** in the absence of TBHP,  $\delta_{\text{b}}$  the  $^{51}\text{V}$  NMR shift of the individual complex **1**·TBHP that could be observed if concentration of TBHP,  $[\text{TBHP}]$ , tended to infinity,  $p$  the probability of **1** being in the coordinated state [33]. In our case, **1**·TBHP forms via reaction:



where  $K$  is the stability constant for **1**·TBHP. The probability  $p$  can be obtained as

$$p = \frac{[\mathbf{1} \cdot \text{TBHP}]}{[\mathbf{1} \cdot \text{TBHP}] + [\mathbf{1}]} \quad (3)$$

Applying the relationship  $[\mathbf{1}] \cdot K = [\mathbf{1} \cdot \text{TBHP}] / [\text{TBHP}]$  one obtains  $p$  as

$$p = \frac{1}{1 + 1/K[\text{TBHP}]} \quad (4)$$

Substituting expression (4) for  $p$  in Eq. (1), we obtain  $\delta_{\text{obs}}$ :

$$\delta_{\text{obs}} = \delta_{\text{a}} + \frac{\Delta}{1 + 1/K[\text{TBHP}]} \quad (5)$$

Table 3

The association constant  $K$  values for the **1**·TBHP OSC at differing temperatures in  $\text{CH}_2\text{Cl}_2$

Complex	$T$ (K)	$K$ ( $\text{mol}^{-1}$ )
<b>1</b> ·TBHP	203	$2.35 \pm 0.50^{\text{a}}$
	233	$2.00 \pm 0.10$
	258	$1.75 \pm 0.05$
	291	$1.36 \pm 0.11$
	313	$1.04 \pm 0.10$

<sup>a</sup> At 203 K, accuracy of the measurement of  $^{51}\text{V}$  chemical shifts is low because of high linewidth of **1**·TBHP resonance.

where  $\Delta = \delta_{\text{b}} - \delta_{\text{a}}$ . Taking into account that  $[\text{TBHP}] \gg [\mathbf{1}]$ , we can apply  $[\text{TBHP}] \approx [\text{TBHP}]_0$ . So, our equation for  $\delta_{\text{obs}}$  should be linear in the following form:

$$\frac{1}{\delta_{\text{obs}} - \delta_{\text{a}}} = \frac{1}{\Delta} + \frac{1}{K\Delta} \frac{1}{[\text{TBHP}]_0} \quad (6)$$

Fig. 4e represents the dependence of  $1/(\delta_{\text{a}} - \delta_{\text{obs}})$  versus  $1/[\text{TBHP}]$  which appeared to be linear. This linearity is in favor of our hypothesis that TBHP interaction with **1** leads to the formation of the 1:1 complex. Measurements of  $K$  at different temperatures gave the values collected in Table 3. All of them fall in the interval  $0.1\text{--}10 \text{ mol}^{-1}$  that is typical for outer sphere complexes formation processes [34].

One can obtain  $\Delta_{\text{r}}H^0$  for **1**·TBHP formation using van't Hoff's equation [35]:

$$\frac{d \ln K}{dT} = \frac{\Delta_{\text{r}}H^0}{RT^2} \quad (7)$$

Assuming that the enthalpy temperature dependence is

$$\Delta_{\text{r}}H_T^0 = \Delta_{\text{r}}H_{298}^0 + \Delta_{\text{r}}C_p^0(T - 298) \quad (8)$$

(i.e.  $\Delta_{\text{r}}C_p$  is regarded as temperature-independent, cf. [35]), substitution of (8) in (7) and subsequent integration gives

$$\ln K = -\frac{A}{T} + B \ln T + C \quad (9)$$

where  $A = (\Delta_{\text{r}}H_{298}^0 - 298\Delta_{\text{r}}C_p^0)/R$ ,  $B = \Delta_{\text{r}}C_p^0/R$ ,  $C$  is an integration constant. In Fig. 5, experimental points  $\ln K$  versus  $1/T$  together with their theoretical simulation according to (9) are presented.  $\Delta_{\text{r}}H_{298}^0$  obtained is  $-6.5 \pm 2.0 \text{ kJ mol}^{-1}$  and  $\Delta_{\text{r}}S_{298}^0$  is estimated



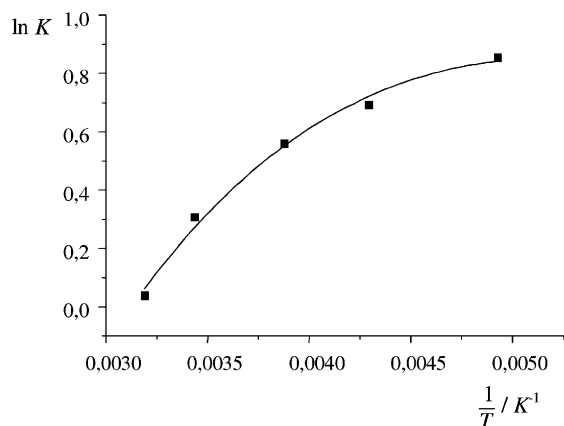


Fig. 5. Plot of  $\ln K$  vs.  $1/T$  (■). Solid line represents the least-square fit to the data according to Eq. (9).

as  $-20 \pm 6 \text{ J mol}^{-1} \text{ K}^{-1}$  that is close to the values typically observed for binding one outer sphere ligand ( $-8$  to  $-20 \text{ kJ mol}^{-1}$  and  $-20$  to  $-60 \text{ J mol}^{-1} \text{ K}^{-1}$ , respectively) [33,34].

Thus, the association constants and the thermodynamic parameters for the formation of complex **1**·TBHP are close to those accepted for outer sphere complexes that confirms our hypothesis. **1**·TBHP OSC is the last observable intermediate in **1** + TBHP catalytic system and is probably the precursor of the actual reactive intermediate in the vanadium catalyzed diastereoselective epoxidation of allylic alcohols in the presence of L.

#### 4. Conclusions

The oxidation of (–)-(R)-linalool by TBHP in the presence of the vanadium(V) complex formed by interaction of  $[\text{VO}(\text{acac})_2]$  or  $[\text{VO}(\text{On-Bu})_3]$  with the new chiral pyrazolyethanol ligand L, affords (2S,3R) and (2R,3R) monoepoxides with moderate diastereomeric excess.  $^{51}\text{V}$  and  $^{13}\text{C}\{^1\text{H}\}$  spectra provided insight into solution structure, stability and reactivity of the vanadium(V) species that operates in the catalytic system studied. It has been shown that the mononuclear vanadium(V) complex **1** is the predominant species in the reaction mixture. It incorporates the tridentate terpenoid ligand L and  $\text{O}^{2-}$  moieties. TBHP binds to **1** to give an outer sphere complex **1**·TBHP with as-

sociation constant  $K = 1.36 \pm 0.11 \text{ l mol}^{-1}$  at room temperature, enthalpy  $\Delta_r H_{298}^0 = -6.5 \pm 2.0 \text{ kJ mol}^{-1}$  and entropy  $\Delta_r S_{298}^0 = -20 \pm 6 \text{ J mol}^{-1} \text{ K}^{-1}$ . The outer sphere complex **1**·TBHP is reactive towards linalool and is believed to be a precursor of the true reactive intermediate in the vanadium catalyzed diastereoselective epoxidation of allylic alcohols. The true intermediate is expected to be formed upon interaction of **1**·TBHP with the substrate.

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