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Intermediates of Asymmetric Oxidation Processes Catalyzed by Vanadium(V) Complexes

K. P. Bryliakov and E. P. Talsi

Boriskov Institute of Catalysis, Siberian Division, Russian Academy of Sciences, Novosibirsk, 630090 Russia

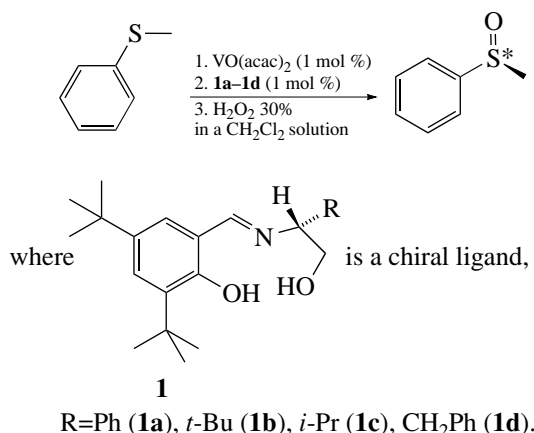
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Abstract—The $[\text{VO}(\text{acac})_2]/\text{Schiff base}$ [*R*-2-(*N*-3,5-di-*tert*-butylsalicylidene)amino-2-phenyl-1-ethanol, *S*-2-(*N*-3,5-di-*tert*-butylsalicylidene)amino-3,3-dimethyl-1-butanol, *S*-2-(*N*-3,5-di-*tert*-butylsalicylidene)amino-3-methyl-1-butanol, or *R*-2-(*N*-3,5-di-*tert*-butylsalicylidene)amino-3-phenyl-1-propanol]/ H_2O_2 catalytic systems for the asymmetric oxidation of sulfides and the $[\text{VO}(\text{acac})_2]/(3bR,4aR)$ -2-(3,4,4-trimethyl-3*b*,4,4*a*,5-tetrahydrocyclopropa[3,4]cyclopenta[1,2-*c*]pyrazol-1-yl)ethanol/*tert*-butyl hydroperoxide/TBHP and $\text{VO}(\text{OAlkyl})_3/[2,2]\text{paracyclophane-4-carboxylic acid } N$ -(1,1-dimethylethyl)-*N*-hydroxamide/TBHP catalytic systems for the asymmetric epoxidation of allylic alcohols were studied using ^{13}C , ^{51}V , and ^{17}O NMR spectroscopy. The key intermediates of these systems (peroxo and alkylperoxo complexes of vanadium(V)) were detected, their structures in solution were studied, and the reactivity was evaluated.

INTRODUCTION

The development of methods for the preparation of optically pure compounds is a priority branch of present-day metal complex catalysis. At the same time, studies of the mechanisms of asymmetric catalytic reactions have received little attention. It is evident that knowledge of the detailed mechanism of operation of a particular system can be of crucial importance in revealing factors responsible for the level of asymmetric induction and the yield of products, as well as in improving the available systems. This article is a brief review of studies that were performed at the Boriskov Institute of Catalysis, Siberian Division, Russian Academy of Sciences, on the active intermediates of the following three catalytic systems based on vanadium complexes with chiral ligands: (1) the $[\text{VO}(\text{acac})_2]/\text{Schiff bases}$ [*R*-2-(*N*-3,5-di-*tert*-butylsalicylidene)amino-2-phenyl-1-ethanol (**1a**), *S*-2-(*N*-3,5-di-*tert*-butylsalicylidene)amino-3,3-dimethyl-1-butanol (**1b**), *S*-2-(*N*-3,5-di-*tert*-butylsalicylidene)amino-3-methyl-1-butanol (**1c**), and *R*-2-(*N*-3,5-di-*tert*-butylsalicylidene)amino-3-phenyl-1-propanol (**1d**)]/ H_2O_2 systems for the asymmetric oxidation of sulfides and the (2) $[\text{VO}(\text{acac})_2]/(3bR,4aR)$ -2-(3,4,4-trimethyl-3*b*,4,4*a*,5-tetrahydrocyclopropa[3,4]cyclopenta[1,2-*c*]pyrazol-1-yl)ethanol (2)/*tert*-butyl hydroperoxide (TBHP) and (3) $\text{VO}(\text{OAlkyl})_3/[2,2]\text{paracyclophane-4-carboxylic acid } N$ -(1,1-dimethylethyl)-*N*-hydroxamide (3)/TBHP systems for the asymmetric epoxidation of allylic alcohols.

The first test system was developed for the enantioselective oxidation of organic sulfides [1] (Scheme 1).



Scheme 1.

Since the publication by Kagan [2] about a modified Sharpless reagent, the titanium tetraethoxide/tartrate ligand/water/alkyl hydroperoxide system, the asymmetric oxidation of sulfides has attracted considerable interest. Chiral sulfoxides are used in the pharmaceutical industry, household chemical goods, and agricultural chemistry. However, the above titanium–tartrate systems are characterized by low catalyst turnover numbers; this is an obstacle to the wide commercialization of these systems. The vanadium system considered in this paper can operate at a catalyst concentration of 0.01 mol % [1]. In this case, it exhibited an enantiomer excess (*ee*) of up to 59% even with a simple substrate, thioanisole (for other substrates, the *ee* was as high as 85%). Thus, this system is attractive in terms of both practical applications and detailed mechanistic studies.

The second and third systems studied in this work were designed for the asymmetric epoxidation of allylic alcohols. The early most outstanding success in this area of oxidation catalysis was associated with the well-known Sharpless system, which was discovered by Katsuki and Sharpless: titanium tetraethoxide/tartrate ligand/alkyl hydroperoxide [3, 4]. This system remains unsurpassed in terms of asymmetric induction level; however, it is characterized by a small turnover number of no higher than 10–20, which stimulates the search for new organometallic catalysts. The second of the above systems was first studied at the Boreskov Institute of Catalysis, Siberian Division, Russian Academy of Sciences; the maximum diastereoisomer excess (*de*) was 56% for linalool [5] (Scheme 2).

The third test system based on vanadium complexes with chiral hydroxamic acids is a return to the system that was also developed previously by Sharpless (vanadyl *tris*(alkoxide)/chiral hydroxamic acid/*tert*-butyl hydroperoxide [6]) on a new level: the ligand (hydroxamic acid **3**) incorporates a *para*-cyclophane fragment, which exhibits planar chirality [7] (Scheme 3).

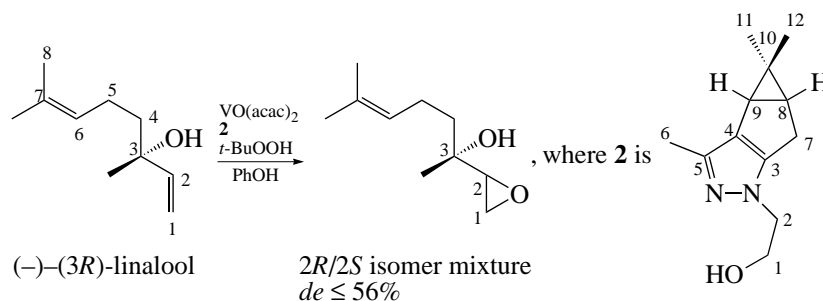
Undoubtedly, a key point in the understanding of reaction mechanisms is knowledge of the nature of intermediates (structure, stability, and reactivity). The intermediates of the above three systems were studied using NMR spectroscopy. The monitoring of vanadium complexes in reaction mixtures was performed by measuring ^{51}V NMR spectra, whereas ^{13}C and ^{17}O NMR spectroscopy was used for determining the structures of intermediates.

$[\text{VO}(\text{acac})_2]/\mathbf{1a}/\text{H}_2\text{O}_2$ Systems

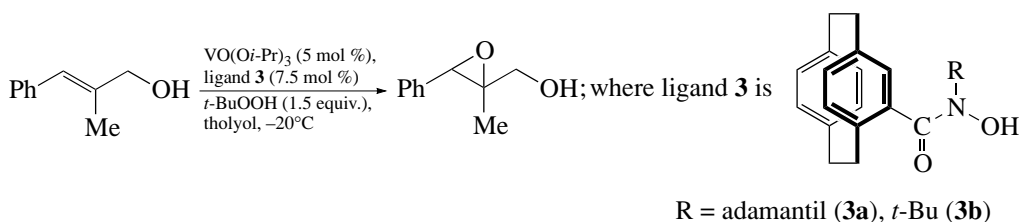
Previously [8a], it was found that, in the $[\text{VO}(\text{acac})_2]/\mathbf{1a}/\text{H}_2\text{O}_2$ catalytic system in a CH_2Cl_2 solution immediately after the addition of H_2O_2 , two signals (at –511 and –645 ppm) were predominant in the ^{51}V NMR spectrum (Fig. 1). Signals **A** and **B** were tentatively attributed to the peroxo complexes of vanadium(V) containing chiral ligand **1**. Signal **C** belongs to the bis(peroxo) complex $[\text{VO}(\text{O}_2)_2(\text{H}_2\text{O})]^-$ [9]. However, with the use of ^1H NMR spectroscopy, it was found that a large quantity of free (uncomplexed) ligands were present in the system. Moreover, parent vanadyl(IV) acetylacetonate is paramagnetic, which impairs resolution in the ^1H and ^{13}C NMR spectra. Therefore, to avoid the undesirable presence of free ligands and paramagnetic vanadium(IV) impurities, we successfully used tris(isopropyl) orthovanadate $[\text{VO}(\text{Oi-Pr})_3]$ as a source of vanadium. Moreover, the system was made homogeneous: 80–90% hydrogen peroxide dissolved in CH_3CN was used as an oxidizing agent.

$[\text{VO}(\text{Oi-Pr})_3]/\text{Chiral Schiff Base } \mathbf{1a}/\text{H}_2\text{O}_2$ System

Figure 2a demonstrates the ^{51}V NMR spectra of vanadium(V) compounds formed in the $[\text{VO}(\text{Oi-Pr})_3]/\mathbf{1a}/\text{H}_2\text{O}_2$ system at -12°C . Two signals of equal integral intensities and equal widths at –514 ($\Delta\nu_{1/2} = 700$ Hz) and –651 ppm ($\Delta\nu_{1/2} = 680$ Hz) were predominant in the spectrum. These signals are identical to



Scheme 2.



Scheme 3.

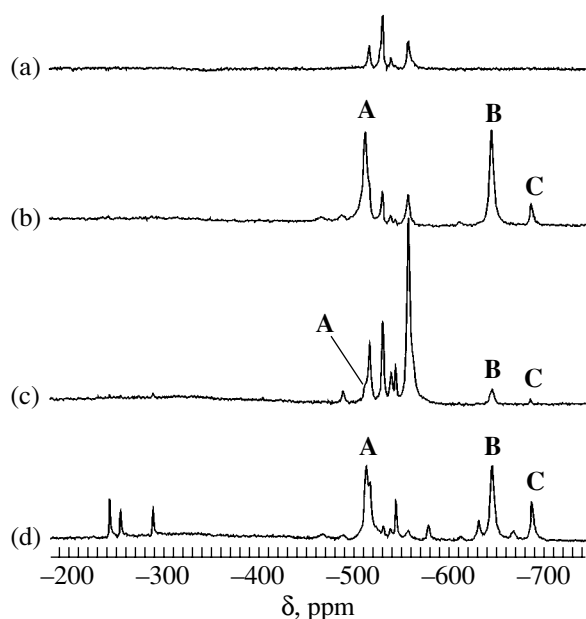


Fig. 1. ^{51}V NMR spectra of a solution of 2.5 mg of $\text{VO}(\text{acac})_2$ and 7 mg of ligand **1a** in 600 μl of CH_2Cl_2 ; the spectra were measured (a) before the onset of reaction and at different points in time after the addition of 3 μl pf 30% H_2O_2 : (b) after 3 min, (c) after 60 min, and (d) 3 min after the addition of another 3 μl of H_2O_2 .

those in the $[\text{VO}(\text{acac})_2]/\mathbf{1a}/\text{H}_2\text{O}_2$ system, and they belong to the two complexes \mathbf{A}_{1a} and \mathbf{B}_{1a} [8b]. The concentration ratio between complexes \mathbf{A}_{1a} and \mathbf{B}_{1a} is close to 1, and the line widths are approximately equal.

At room temperature, complexes \mathbf{A}_{1a} and \mathbf{B}_{1a} symmetrically disappeared with $\tau_{1/2} \approx 20$ min. The concentration of these complexes can be restored by the addition of a new portion of hydrogen peroxide. The addition of thioanisole (to a concentration of 0.5 M) resulted in the rapid disappearance of both complexes within a spectral accumulation time (2 min). Thus, either or both of the complexes (\mathbf{A}_{1a} and \mathbf{B}_{1a}) are active toward sulfide. The ^{51}V chemical shifts of complexes \mathbf{A}_{1a} and \mathbf{B}_{1a} lie within a range typical of the monoperoxo complexes of vanadium(V) with O- and N-donor ligands [9–12]. All the above data suggest that \mathbf{A}_{1a} and \mathbf{B}_{1a} are peroxo complexes of vanadium(V) (see also [13]). Signals at -200 to -400 ppm belong to unidentified degradation products of complexes \mathbf{A}_{1a} and \mathbf{B}_{1a} (marked with asterisks in Fig. 2a). The intensity of these signals increased with time as the intensity of signals due to \mathbf{A}_{1a} and \mathbf{B}_{1a} decreased. A line at -688 ppm belongs to the complex $[\text{VO}(\text{O}_2)_2(\text{H}_2\text{O})]^-$ [9].

It was found that peroxo complexes \mathbf{A}_{1a} and \mathbf{B}_{1a} each contain one chiral ligand per vanadium atom. As judged from the widths of ^{51}V signals, these complexes are mononuclear [8b]. In the spectrum in Fig. 2b, a signal of complex **A** ($\delta(\underline{\text{CH}}_2 = 79.5$ ppm) and a signal of

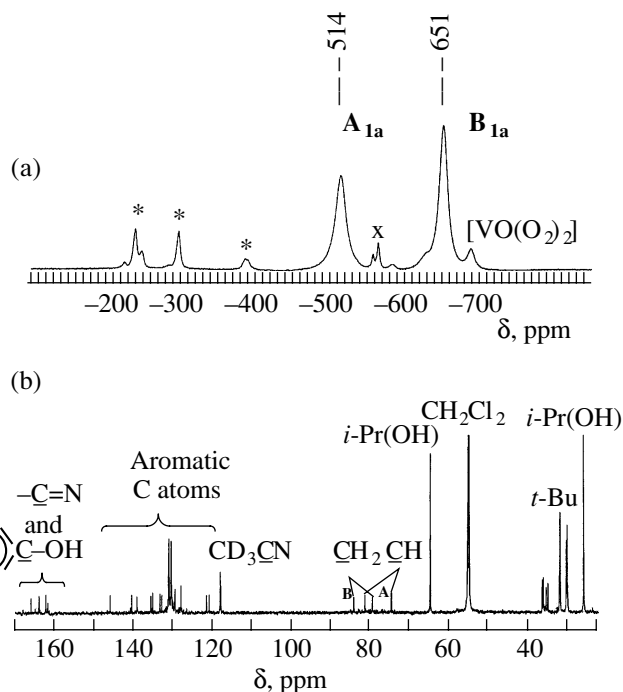


Fig. 2. (a) ^{51}V and (b) $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of the $[\text{VO}(\text{O}i\text{-Pr})_3]/\mathbf{1a}/\text{H}_2\text{O}_2$ system at -12°C . Line x belongs to the residual complex $[\text{VO}(\text{O}i\text{-Pr})\mathbf{1a}]$.

complex **B** ($\delta(\underline{\text{CH}}_2 = 84.1$ ppm) are marked; two other marked signals in this region belong to the $\underline{\text{CH}}$ carbon atoms of complexes \mathbf{A}_{1a} and \mathbf{B}_{1a} . Signals in the region 120–150 ppm are the lines of aromatic carbon atoms of \mathbf{A}_{1a} and \mathbf{B}_{1a} ; lines in the region 160–170 ppm belong to the $\underline{\text{C}}=\text{N}$ and aromatic $\underline{\text{C}}-\text{OH}$ carbon atoms of **A** and **B**.

$[\text{VO}(\text{O}i\text{-Pr})_3]/\mathbf{1b}\text{--}\mathbf{1d}/\text{H}_2\text{O}_2$ Systems: The Nature of Active Intermediates

Two sorts of complex **B** occurred in the $[\text{VO}(\text{O}i\text{-Pr})_3]/\mathbf{1b}/\text{H}_2\text{O}_2$ system; because of this, two ^{51}V NMR signals appeared in the region characteristic of complexes of this type (-633 and -650 ppm), whereas one peak at -395 ppm belonged to complex **A** (Fig. 3).

The existence of two forms of complexes \mathbf{B}_{1b} resulted in additional splitting of ^{13}C NMR signals due to $\underline{\text{CH}}_2$ carbon atoms (peaks at 77.1 and 77.3 ppm) and asymmetric $\underline{\text{CH}}$ carbon atoms (86.0 and 86.1 ppm; Fig. 3b, insert). This allowed us to distinguish the lines of \mathbf{B}_{1b} from the lines of \mathbf{A}_{1b} ($\underline{\text{CH}}_2$ at 65.7 ppm and $\underline{\text{CH}}$ at 74.5 ppm). Note that the chemical shift of the $\underline{\text{CH}}_2$ carbon of \mathbf{A}_{1b} (65.7 ppm) is close to the shift in free **1b** (63.5 ppm), whereas the shifts of the $\underline{\text{CH}}_2$ carbon of \mathbf{B}_{1b} are much greater (77.1 and 77.3 ppm). This fact indicates that the $\underline{\text{CH}}_2$ carbon atom in \mathbf{A}_{1b} is much less dis-

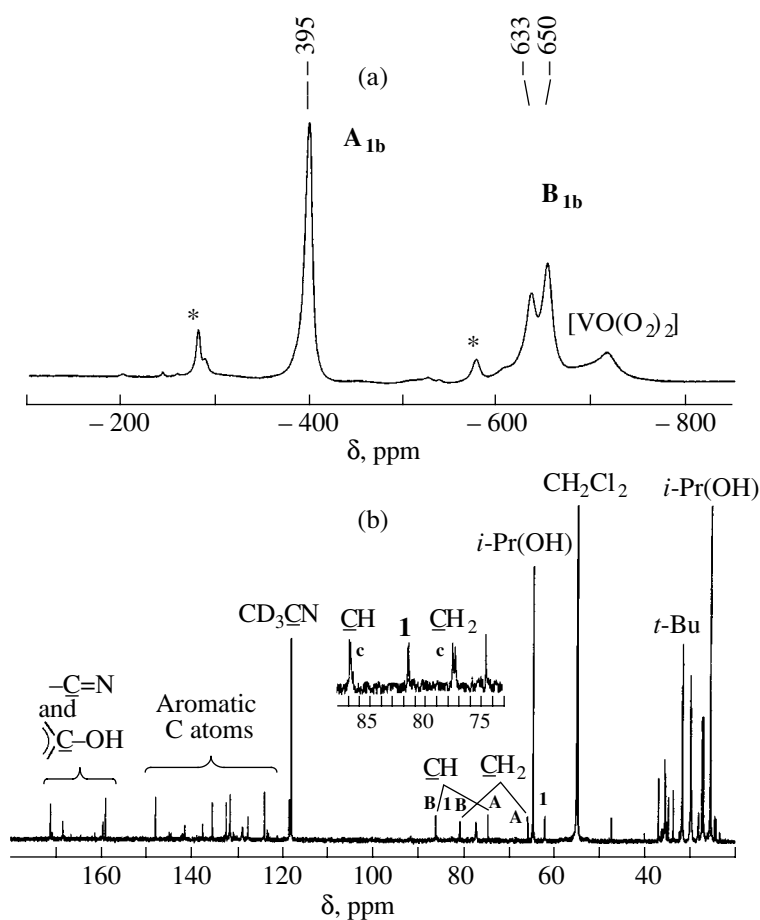
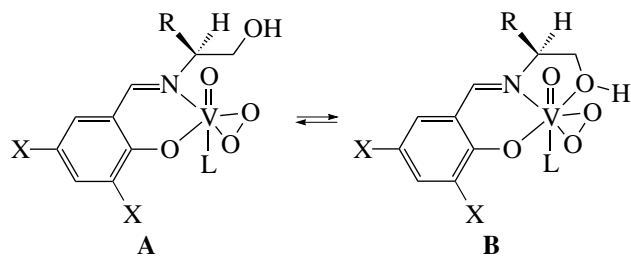


Fig. 3. (a) ^{51}V and (b) $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of the $[\text{VO}(\text{O}i\text{-Pr})_3]/\mathbf{1b}/\text{H}_2\text{O}_2$ system at -12°C . (a) Signals (*) in the region from -200 to -300 and at -580 ppm belong to unidentified products of the degradation of \mathbf{A}_{1b} and \mathbf{B}_{1b} . (b) Signals due to free ligand $\mathbf{1b}$ are marked with **1** ($\delta(\underline{\text{C}}\text{H}_2) = 62.2$ ppm; $\delta(\underline{\text{C}}\text{H}) = 81.0$ ppm).

turbed by ligand coordination to vanadium than that in \mathbf{B}_{1b} . Scheme 4 illustrates the structures proposed for complexes **A** and **B** with consideration for the above special features (ligand $\text{L} = i\text{-PrOH}$ or H_2O). The ligand coordination is bidentate or tridentate in complex **A** or **B**, respectively.



Scheme 4.

The ^{51}V and ^{13}C NMR spectra of vanadium complexes in the $[\text{VO}(\text{O}i\text{-Pr})_3]/(\mathbf{1a}\text{--}\mathbf{1d})/\text{H}_2\text{O}_2$ systems with all ligands $\mathbf{1a}\text{--}\mathbf{1d}$ were recorded. In all cases, the concentration ratio **A/B** was of the order of 1; complexes **A** and **B** with any ligands exhibited approximately equal activities toward thioanisole. The ^{51}V chemical shifts of

complexes \mathbf{B}_{1a} , \mathbf{B}_{1b} , \mathbf{B}_{1c} , and \mathbf{B}_{1d} were very close (Table 1). Thus, it is reasonable to expect that the structure of all complexes **B** is analogous to the structure of complex \mathbf{B}_{1b} (Scheme 4). Based on the same arguments, com-

Table 1. The ^{51}V chemical shifts (ppm) of the peroxo complexes of vanadium(V) (ppm) in the $[\text{VO}(\text{O}i\text{-Pr})_3]/(\mathbf{1a}\text{--}\mathbf{1d})/\text{H}_2\text{O}_2$ catalytic systems at -12°C

Entry	Ligand	Complex A	Complexes B
1	1a	-514	-651
2	1b	-395	-633, -650
3	1c	-396	-636, -654
4	1d *	-386	-633, -650

* At 5°C .

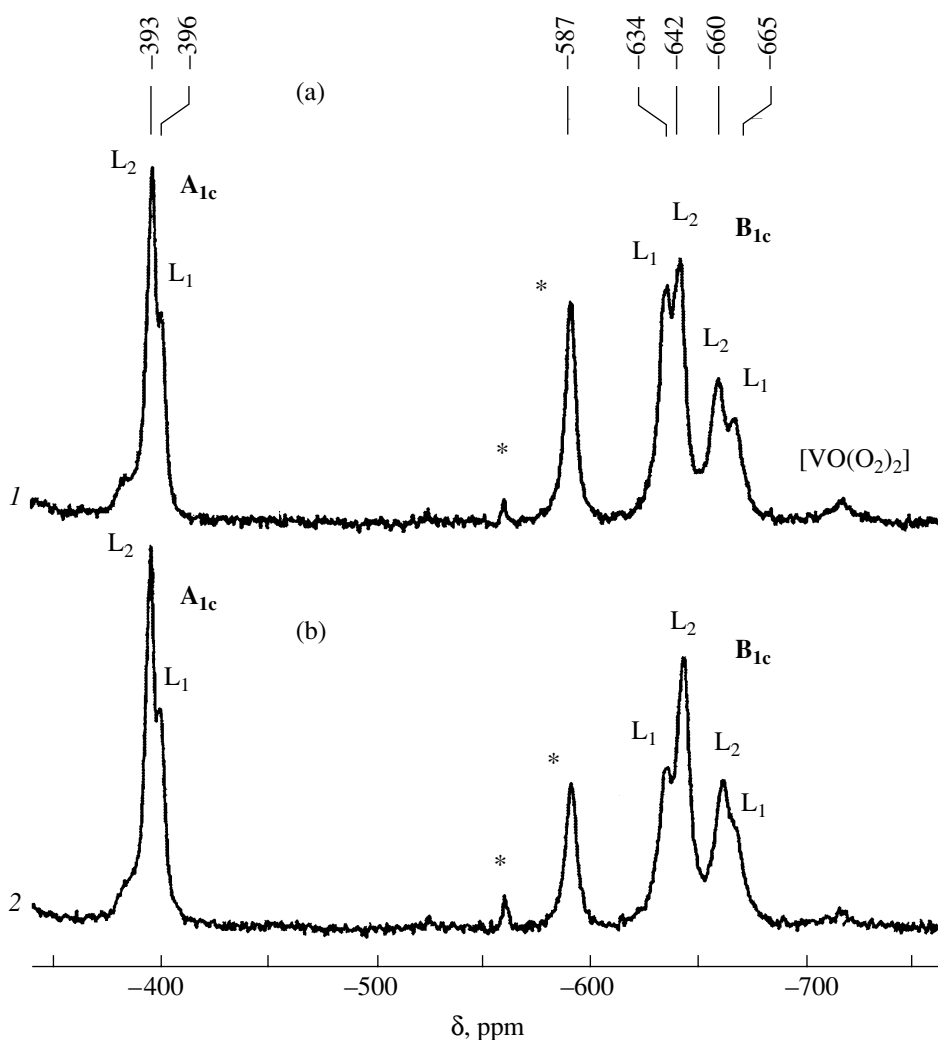
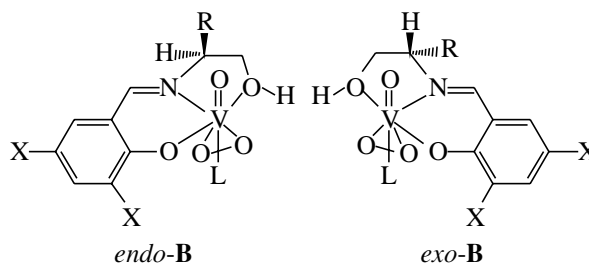


Fig. 4. ^{51}V NMR spectra of vanadium(V) complexes formed in the $[\text{VO}(\text{O}i\text{-Pr})_3]/\mathbf{1c}/\text{H}_2\text{O}_2$ system in a CH_2Cl_2 solution at 5°C : (a) 100 μl of $i\text{-PrOH}$ was added; (b) 300 μl of $i\text{-PrOH}$ was added. Lines marked with L_1 and L_2 belong to complexes \mathbf{A}_{1c} and \mathbf{B}_{1c} with different axial ligands L ($\text{L}_1 = \text{H}_2\text{O}$; $\text{L}_2 = i\text{-PrOH}$). Signals marked with asterisks were unidentified.

plexes \mathbf{A}_{1b} , \mathbf{A}_{1c} , and \mathbf{A}_{1d} (Table 1) should have the same structure—the structure of complex \mathbf{A} (Scheme 4; $\text{L} = \text{H}_2\text{O}$ or $i\text{-PrOH}$).

Let us discuss the reason for the appearance of two ^{51}V NMR signals for complexes \mathbf{B}_{1b} , \mathbf{B}_{1c} , and \mathbf{B}_{1d} (see Table 1) using complex \mathbf{B}_{1c} as an example. By analogy with the results obtained using vanadium(V) complexes with amino acid salicylaldimines and polyhydric alcohols [14] and with data published by Bolm *et al.* [15], we assumed the existence of two diastereomers of complexes \mathbf{B}_{1c} (*endo* and *exo* forms; Scheme 5, where $\text{L} = \text{H}_2\text{O}$ or $i\text{-PrOH}$). The ^{51}V NMR signals at -636 and -654 ppm correspond to these forms. It was found experimentally (5°C) that each diastereomer of \mathbf{B}_{1c} can exhibit two peaks in the ^{51}V NMR spectrum because of H_2O or $i\text{-PrOH}$ coordination to one of the coordination

sites: peaks at -634 and -642 ppm belong to the predominant isomer, whereas the second isomer exhibits signals at -660 and -665 ppm (Fig. 4).



Scheme 5.

Thus, the monoperoxo complexes of vanadium(V), which are intermediates in a catalytic system for the enantioselective oxidation of sulfides, were success-

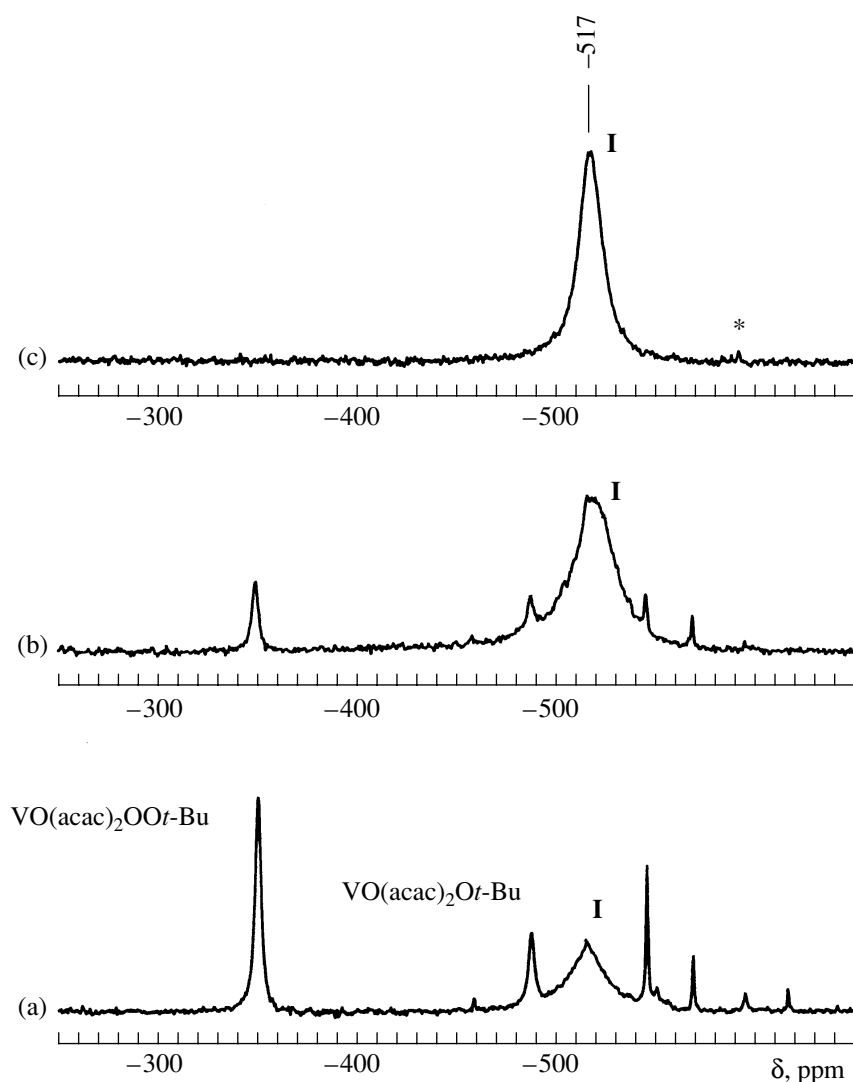


Fig. 5. ^{51}V NMR spectra of vanadium(V) complexes formed in the $[\text{VO}(\text{acac})_2]/\mathbf{2}/t\text{-BuOOH}$ system in a CH_2Cl_2 solution at 20°C : (a) $[\text{VO}(\text{acac})_2] = 0.019\text{ M}$, $[\mathbf{2}] = 0.024\text{ M}$, and $[t\text{-BuOOH}] = 0.083\text{ M}$; (b) $[\text{VO}(\text{acac})_2] = 0.019\text{ M}$, $[\mathbf{2}] = 0.10\text{ M}$, and $[t\text{-BuOOH}] = 0.33\text{ M}$; (c) $[\text{VO}(\text{On-Bu})_3] = 0.01\text{ M}$ and $[\mathbf{2}] = 0.025\text{ M}$. The signal of residual $\text{VO}(\text{On-Bu})_3$ is marked with an asterisk ($\delta = -591\text{ ppm}$).

fully characterized with the use of the NMR spectra of various nuclei.

$[\text{VO}(\text{acac})_2]/\text{Terpene Ligand } \mathbf{2}/\text{tert-Butyl Hydroperoxide System}$

The oxidation of linalool with TBHP in the presence of $[\text{VO}(\text{acac})_2]$ in catalytic amounts was first described in 1973 [16]. In this case, 1,2-monoepoxide was prepared almost quantitatively. In the system that will be considered below, the highest diastereoisomer excess was 56% (toluene; 20°C ; $[\mathbf{2}]/[\text{VO}(\text{acac})_2] = 6 : 1$) at 97% conversion of linalool [5].

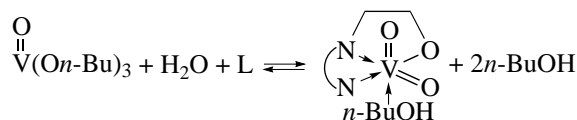
Figure 5 demonstrates the spectra of vanadium compounds occurring in the $[\text{VO}(\text{acac})_2]/\mathbf{2}/\text{TBHP}$ catalytic system. The data of predecessors allowed us to

attribute some of the observed signals: $\delta = -350\text{ ppm}$ ($[\text{VO}(\text{acac})_2\text{OO}t\text{-Bu}]$) and $\delta = -489\text{ ppm}$ ($[\text{VO}(\text{acac})_2\text{O}t\text{-Bu}]$) [17]. A broad signal at -517 ppm ($\Delta\nu_{1/2} = 1.0\text{ kHz}$) belongs to a new complex denoted by **I**. Its chemical shift lies in the region typical of vanadium(V) complexes with O,N-donor ligands [18]. Note that complex **I** can be quantitatively prepared in solution from $[\text{VO}(\text{On-Bu})_3]$ and ligand **2** (Fig. 5c). This fact was used in the subsequent study: $[\text{VO}(\text{On-Bu})_3]$ was taken in place of $[\text{VO}(\text{acac})_2]$ as a source vanadium compound; this allowed us to obtain qualitative ^{13}C NMR spectra. Complex **I** contains one ligand molecule per vanadium atom; ^{13}C NMR data are given in Table 2. A comparison between the chemical shifts in the ligand and complex **I** demonstrates that carbon atoms at the

1-, 3-, and 5-positions are most perturbed by coordination. Thus, it is most likely that the ligand coordination is tridentate (Table 2).

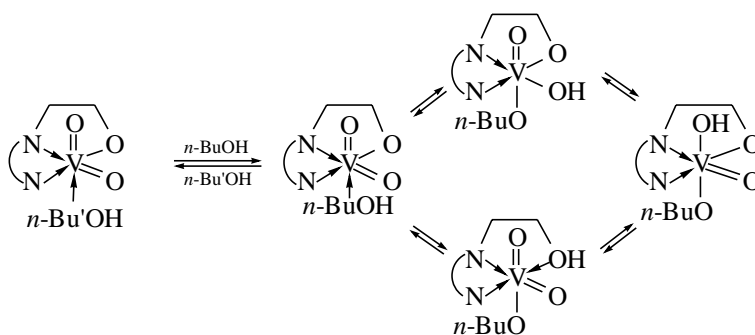
The ^{17}O NMR spectrum of complex **I** exhibited one line at 1175 ppm ($\Delta\nu_{1/2} = 800$ Hz), which is typical of O^{2-} and OH^- in the six-coordinated complexes of vanadium(V) [19]. Bridging oxygen atoms (V–O–V, characteristic signals in the region 500–600 ppm) were not detected. Thus, **I** is a mononuclear vanadium(V) complex containing one chiral ligand and O^{2-} and OH^- ligands.

It was also found that complex **I** was formed only if 1 equiv. of H_2O was added to the system in accordance with Scheme 6 [5].



Scheme 6.

Scheme 7 demonstrates the most probable structure of complex **I** and the exchange processes: proton transfer between oxygen atoms and ligand exchange at the axial position [5].



Scheme 7.

Reaction of Complex **I** with *tert*-Butyl Hydroperoxide

On the addition of various amounts of TBHP to a solution of complex **I**, it was found that the ^{51}V chemical shift depends on the concentration of TBHP. This fact suggests rapid exchange between at least two species that occur in solution (Fig. 6). At the same time, $t\text{-BuOO}^-$ groups coordinated to vanadium were not detected in the ^{13}C NMR spectra at temperatures from -90 to 0°C . These facts are indicative of the formation of the very short-lived complex **I** · TBHP. The concen-

tration of TBHP in the sample remained constant at -5°C ; the addition of linalool resulted in a decrease in the TBHP concentration, and the formation of diastereomeric linalool oxide was observed ($[\mathbf{2}] = [\text{L}] = 0.024$ M; $[\text{TBHP}] = 0.4$ M; $[\text{linalool}] = 0.2$ M; *de* 28%; almost complete conversion for 15 min). This suggests that the complex **I** · TBHP is active toward allylic alcohols and can lead to an asymmetric reaction.

The following should be explained for determining the nature of the complex **I** · TBHP: (1) the short life-

Table 2. The ^{13}C chemical shifts (ppm) of ligand **2** and complexes **I** and **I** · TBHP in a CH_2Cl_2 solution

Sample	Atom number*											
	1	2	3	4	5	6	7	8	9	10	11	12
2	62.8	52.7	143.6	126.3	152.9	13.4	24.6	14.6	35.5	23.5	27.3	27.6
I **	73.7	52.4	148.6	127.9	155.4	14.3	25.2	14.8	35.2	23.9	27.3	27.8
I · TBHP***	73.6	52.3	148.0	127.5	155.1	14.4	24.9	14.7	35.0	23.7	27.4	27.6

* Carbon atoms are numbered in accordance with Scheme 2.

** Complex **I** ($[\text{I}] = 0.010$ M) was prepared from $\text{VO}(\text{On-Bu})_3$ and **2** ($2/\text{V} = 1 : 1$) in 3 ml of CH_2Cl_2 .

*** To sample **I** ($[\text{I}] = 0.024$ M; $2/\text{V} = 1 : 1$; 3 ml of CH_2Cl_2), 60 μl of $t\text{-BuOOH}$ was added at -5°C ; $[t\text{-BuOOH}] = 0.2$ M. The signals of $t\text{-BuOOH}$: 26.5 ($\text{C}(\underline{\text{CH}}_3)_3$) and 81.5 ppm ($\underline{\text{C}}(\text{CH}_3)_3$).

time of the complex, (2) the absence of $t\text{-BuOO}^-$ groups coordinated to vanadium, and (3) why the complex was formed with TBHP but not formed with $t\text{-BuOH}$ (no concentration dependence of the ^{51}V chemical shift). All of these facts were explained in terms of a hypothesis on the formation of an outer-sphere 1 : 1 complex between **I** and TBHP [5, 20]. The experimentally found dependence of the ^{51}V chemical shift of the complex **I** · TBHP at various temperatures is fully consistent with the following theoretical function for an outer-sphere 1 : 1 complex [5]:

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

Here, δ_{obs} is the observed ^{51}V chemical shift of the outer-sphere complex **I** · TBHP, δ_{a} is the shift of complex **I** in the absence of TBHP, $[\text{TBHP}]_0$ is the concentration of the added peroxide, K is the stability constant of the outer-sphere complex, and Δ is a parameter with dimensions of chemical shift.

Equation (1) allowed us to find constants K at various temperatures (Table 3). In turn, the thermodynamic parameters of complexation were calculated from the temperature dependence of K : $\Delta H_{298}^0 = -6.5 \pm 2.0$ kJ/mol and $\Delta S_{298}^0 = -20 \pm 6$ J mol $^{-1}$ K $^{-1}$. These values are typical of outer-sphere complexes [20].

Thus, Bryliakov *et al.* [5] characterized the outer-sphere complex **I** · TBHP in solution using the NMR spectra of various nuclei. This complex is the last observed intermediate in the asymmetric epoxidation of allylic alcohols. It is most likely that the true intermediate responsible for the step of oxygen transfer is formed in the reaction of the outer-sphere complex with a substrate (allyl alcohol).

*[VO(Oi-Pr)₃]/Chiral Hydroxamic
Acid 3/tert-Butyl Hydroperoxide*

This system exhibited the best results in the oxidation of 2-methyl-3-phenyl-1-propanol: *ee* 71% and 85% yield with ligand **3a** [7b] and *ee* 72% at 81% yield with ligand **3b** [7a]. TBHP was used as a stoichiometric oxidizing agent. Note that it is universally recognized that the alkylperoxo complexes of vanadium(V) are active intermediates in catalytic systems based on vanadium complexes and TBHP [21]. However, only one example of the alkylperoxo complexes of vanadium (which were characterized by ^1H and ^{13}C NMR and IR spectroscopy) active toward olefins was published: $\text{VO}(\text{OOR})(\text{R}^1\text{-OPhsal-R}^2)$, where $\text{R}^1\text{-OPhsal-R}^2$ is the tridentate *N*-(2-oxidophenyl)salicylaldiminato ligand [21a, 21b]. In this work, the formation of active alkylperoxo complexes of vanadium (V) in asymmetric catalytic system is studied for the first time.

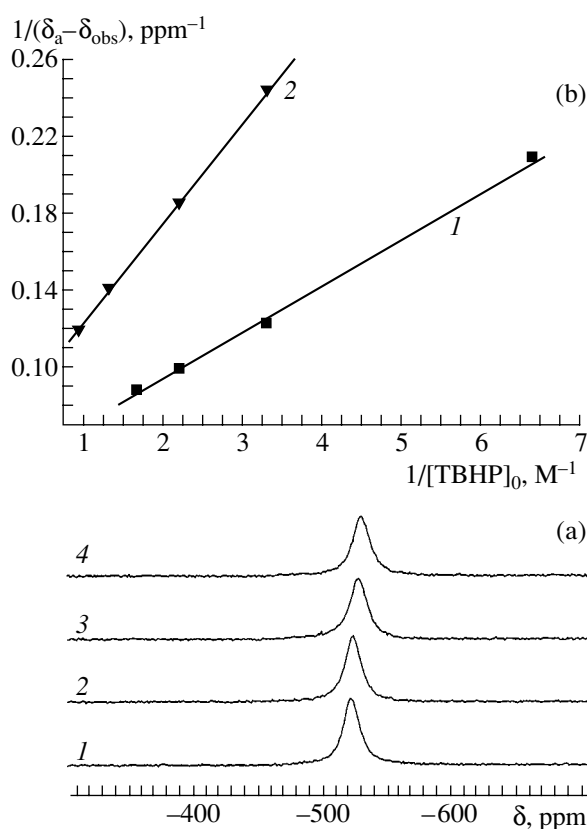


Fig. 6. (a) ^{51}V NMR spectra of vanadium(V) compounds formed by the interaction of complex **I** (0.01 M) and $t\text{-BuOOH}$ in CH_2Cl_2 at 258 K; $[\text{TBHP}] = (1) 0, (2) 0.17, (3) 0.33, \text{ and } (4) 0.50$ M. (b) The plot of $1/(\delta_{\text{a}} - \delta_{\text{obs}})$ against $1/[\text{TBHP}]$, where δ_{obs} is the observed ^{51}V chemical shift of the outer-sphere complex [**I** · TBHP] at (1) 233 or (2) 291 K. Solid lines were drawn using the least-squares technique in accordance with Eq. (1).

*Reaction of Tris(alkyl)orthovanadate
with Chiral Hydroxamic Acid 3*

$[\text{VO}(\text{On-Bu})_3]$ was used as the parent vanadium compound. The monitoring of vanadium(V) compounds in the reaction solution demonstrated that the

Table 3. Stability constant (K) of the outer-sphere complex **I** · TBHP in CH_2Cl_2 at various temperatures

$T, \text{ K}$	$K, \text{ M}^{-1}$
203	2.35 ± 0.50
233	2.00 ± 0.10
258	1.75 ± 0.05
291	1.36 ± 0.11
313	1.04 ± 0.10

Table 4. The ^{13}C , ^{51}V , and ^{17}O NMR chemical shifts (ppm) for ligand **3a** and vanadium(V) complexes **II**–**IV** in CH_2Cl_2 solutions at 20°C

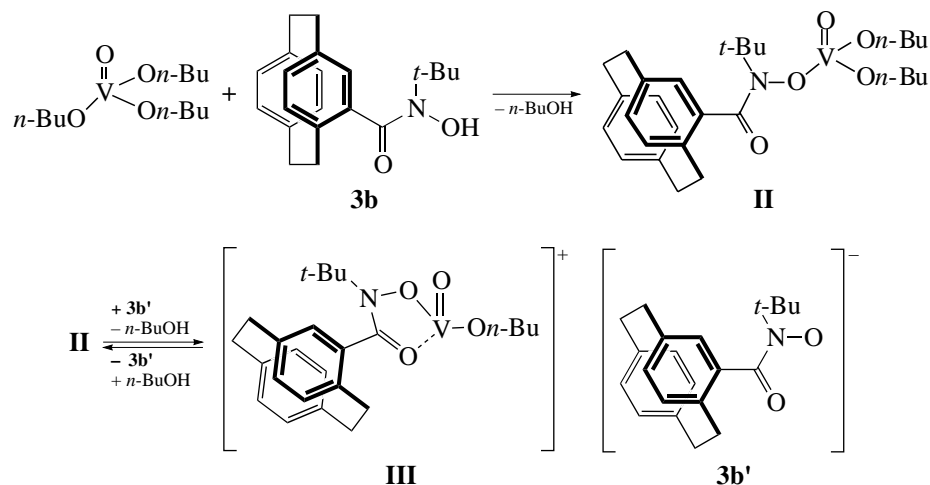
Compound	C=O	N–C(CH ₃) ₃	OCH ₂	OOC(CH ₃) ₃	^{51}V	$\text{V}=^{17}\text{O}$
$\text{VO}(\text{On-Bu})_3$	–	–	84.3 ^a	–	–594	1162 ^a
3b	170.1	62.5	–	–	–	–
II	165.2	66.5	82.2 ^b	–	–508	n. d ^c
III + 1a ^d	165.4	65.3	86.8, 83.5, 83.8 ^e	–	–451, –440	1244
	(163.7)	(65.6)			–446, –437	n. d ^c
IV + 1a ^d	165.6	66.0, 66.2	–	84.9, 85.0 ^f	–355	1265
	(163.7)	(65.6)			–361	
3b ^g	165.6	62.4	–	–	–	–
<i>n</i> -BuOH	–	–	63.7	–	–	–
<i>t</i> -BuOOH	–	–	–	81.6	–	– ^h

^a Data from [19a].^b The ^{13}C shifts of *n*-BuOV: 14.8, 20.0, 36.2, and 63.7 ppm.^c Not detected.^d Complex **III** and compound **3b**' simultaneously appeared in solution; therefore, the ^{13}C NMR spectra of the mixtures of **III** + **3b**' and **IV** + **3b**' were compared.^e The ^{13}C chemical shifts of *n*-BuOV groups: 15.1, 20.8, 37.0, 83.5, 83.8 (narrow lines), and 86.8 ppm (broad line).^f The ^{13}C chemical shift of $\text{VO}(\text{OC}(\text{CH}_3)_3)_3$ is 27.8 ppm.^g Obtained in the following experiment: a solution of ligand **3b** in CH_2Cl_2 was shaken with solid NaOH at -20°C .^h The ^{17}O chemical shifts of oxygen atoms in *t*-BuOOH: 210 and 264 ppm.

addition of 1 equiv. of hydroxamic acid **3b** to $[\text{VO}(\text{On-Bu})_3]$ resulted in the disappearance of the signal of the latter and in the appearance of a new narrow line (-508 ppm, $\Delta\nu_{1/2} = 93$ Hz) due to a new vanadium(V) compound denoted as **II** (Fig. 7, spectra *a*, *b*) [22]. At higher ligand/vanadium ratios, the concentration of **II** decreased, whereas the concentration of four complexes denoted as **III** increased (Fig. 7, spectra *c*, *d*).

The structure and composition of the complexes were studied in detail using ^{13}C , ^{51}V , and ^{17}O NMR spectroscopy (Table 4).

Complex **II** contains one molecule of **3b** and two *n*-butoxide fragments per vanadium atom. Thus, it is most likely that **II** is the complex $\text{VO}(\text{On-Bu})_2(\text{3b}')$, where **3b**' denotes the anionic form of the ligand (Scheme 8).

**Scheme 8.**

It is most likely that complex **III**, which is formed at ratios of ligand/vanadium > 1, occurs as the ion pair **III** · **3b'** in solution (Scheme 8 and Table 4) [22]. It is of interest that four species of complex **III** were simultaneously detected in solution. They cannot differ in axial ligand because the addition of coordinating molecules (H_2O , n -butanol) had no effect on the ratio between them. Consequently, the four complexes **III** are diastereomers (Scheme 9; $\text{L} = n\text{-BuOH}$). These structures can be obtained by varying the relative positions of the *para*-cyclophane fragment and $\text{V}=\text{O}$ and $\text{N}-t\text{-Bu}$ groups with respect to the horizontal plane.

The catalytic system exhibited the best results at a ligand/vanadium ratio of 1.5 : 1 [7]. The results suggest that at this ratio complexes **III** were formed almost quantitatively because of special features of equilibrium in Scheme 8; at the same time, an excess of the ligand did not inhibit substrate coordination.

*Active Intermediates
in the $[\text{VO}(\text{OAlkyl})_3]/\mathbf{3b}/\text{tert-Butyl}$
Hydroperoxide System*

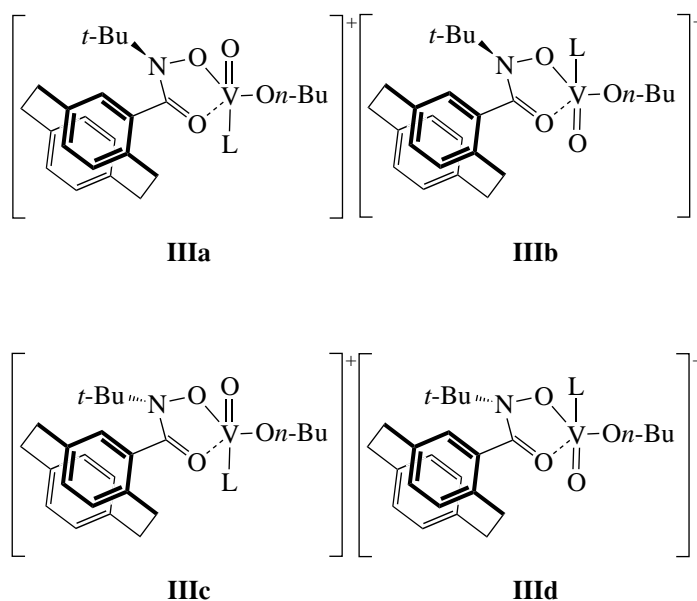
On the addition of a large excess of TBHP to complexes **III**, the formation of new compounds **IV** was detected using the ^{51}V NMR spectra (Fig. 8). The concentration of **IV** was settled in 10–12 h; in this case, two complexes with signals at –335 and –361 ppm in a ratio of about 3 : 1 were predominant. After the addition of a substrate, the concentration of complexes **IV** decreased with time, and the concentration of complexes **III** increased again (Fig. 8, spectra *b*, *c*). According to ^{13}C NMR data, geraniol was completely converted into the

corresponding 2,3-epoxide 24 h after the addition of geraniol. Upon mixing a geraniol solution and TBHP in the absence of a catalyst, epoxide formation was not detected for several days. This fact indicates that complexes **IV** are responsible for the epoxidation of allylic alcohols. Both of the processes (the formation of complexes **IV** and their reactions with a substrate) are slow; this is consistent with published data on reaction times (up to seven days) [7, 21d, 23].

*Nature of Intermediates
in the $[\text{VO}(\text{OAlkyl})_3]/\mathbf{3b}/\text{tert-Butyl}$
Hydroperoxide System*

It was found that active complexes **IV** contain ligand **3b** and a vanadyl fragment (line at 1265 ppm in the ^{17}O NMR spectrum is a superposition of signals due to two complexes **IV**). Moreover, it was found using ^{13}C NMR spectra that complexes **IV** contain one coordinated $t\text{-BuOO}^-$ group: signals at 84.9 and 85.0 ppm (Fig. 9, Table 4). Scheme 10 illustrates the assumed structures of intermediates **IVa** and **IVb**. It is most likely that ^{51}V NMR signals at –349 and –373 ppm (Fig. 9) belong to two other conceivable stereoisomers that differ in the position of their $\text{N}-t\text{-Bu}$ group.

As can be seen in Scheme 10, complexes **IV** contain a labile axial ligand: $n\text{-BuOH}$, allyl alcohol, or ligand **3b** present in an excess (at high ligand **3b**/vanadium ratios). This fact may explain the inhibition of the reaction at ratios between ligand **3b** and vanadium equal to 3 or higher.



Scheme 9.

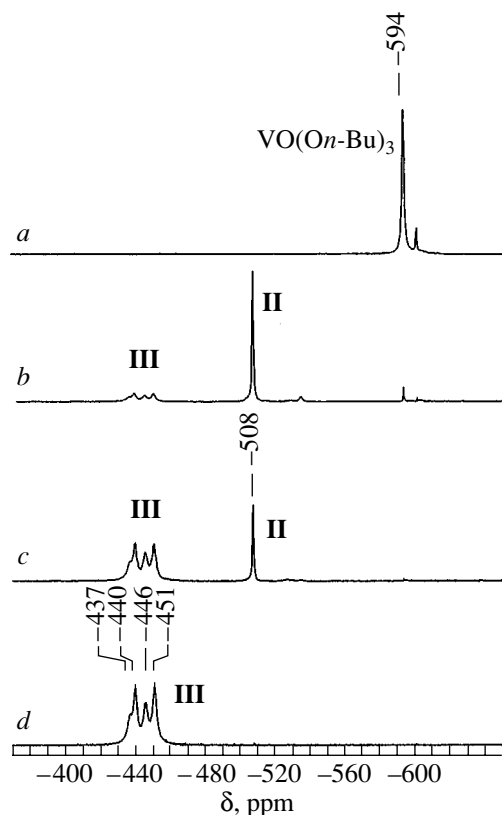
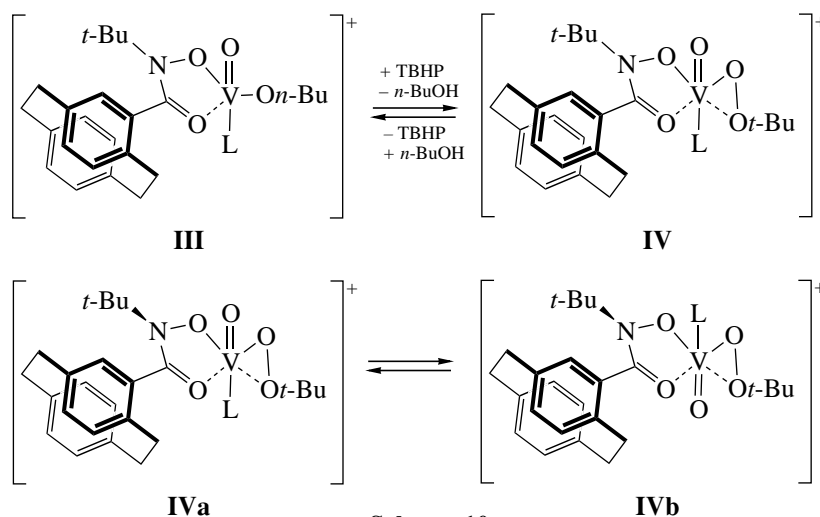


Fig. 7. ^{51}V NMR spectra of vanadium(V) compounds formed in the $[\text{VO}(\text{On-Bu})_3]/\mathbf{3b}$ system in a CH_2Cl_2 solution at 20°C ($[\text{VO}(\text{On-Bu})_3] = 0.05 \text{ M}$): (a) $[\text{VO}(\text{On-Bu})_3]$; (b) $[\text{VO}(\text{On-Bu})_3]$ and ligand $\mathbf{3b}$ ($\mathbf{3b}/\text{V} = 1 : 1$); (c) $[\text{VO}(\text{On-Bu})_3]$ and ligand $\mathbf{3b}$ ($\mathbf{3b}/\text{V} = 1.5 : 1$); and (d) $[\text{VO}(\text{On-Bu})_3]$ and ligand $\mathbf{3b}$ ($\mathbf{3b}/\text{V} = 1.73 : 1$).

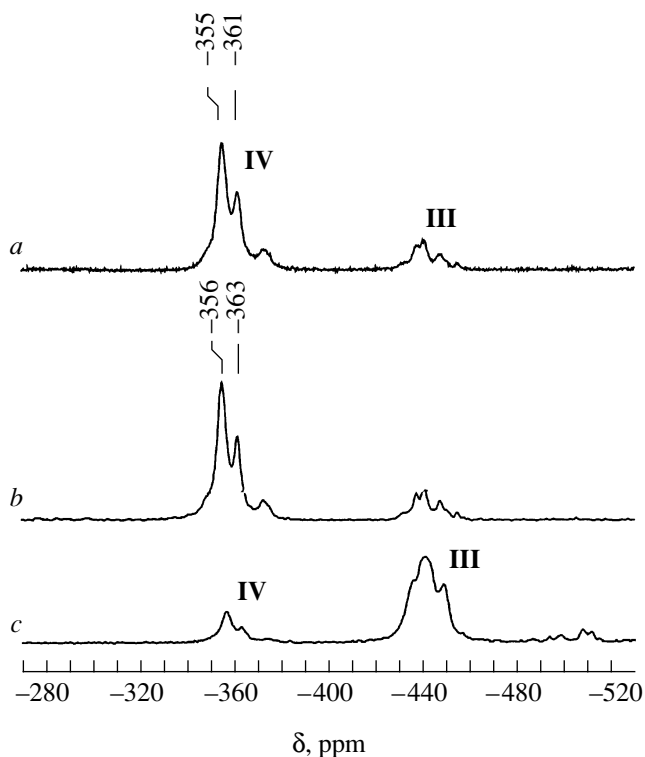
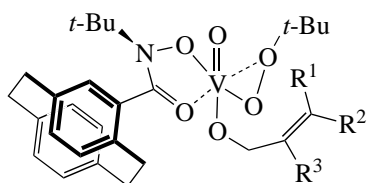


Fig. 8. ^{51}V NMR spectra of vanadium(V) compounds formed in the $[[\text{VO}(\text{On-Bu})_3]/\mathbf{3b}/\text{TBHP}]$ system in a CH_2Cl_2 solution at 20°C : (a) $[\text{VO}(\text{On-Bu})_3] = 0.05 \text{ M}$, ligand $\mathbf{3b}$ ($\mathbf{3b}/\text{V} = 1.73 : 1$), $[\text{TBHP}] = 0.67 \text{ M}$, 12 h after the addition of TBHP; (b) 180 μl of geraniol was added, $[\text{geraniol}] = 0.35 \text{ M}$; (c) 24 h after the addition of geraniol.

Summarizing the data, the structure of the transition state was proposed (Scheme 11). This structure is consistent with published concepts

of intermediates in other systems based on vanadium complexes with hydroxamic acids [6, 21d].



Scheme 11.

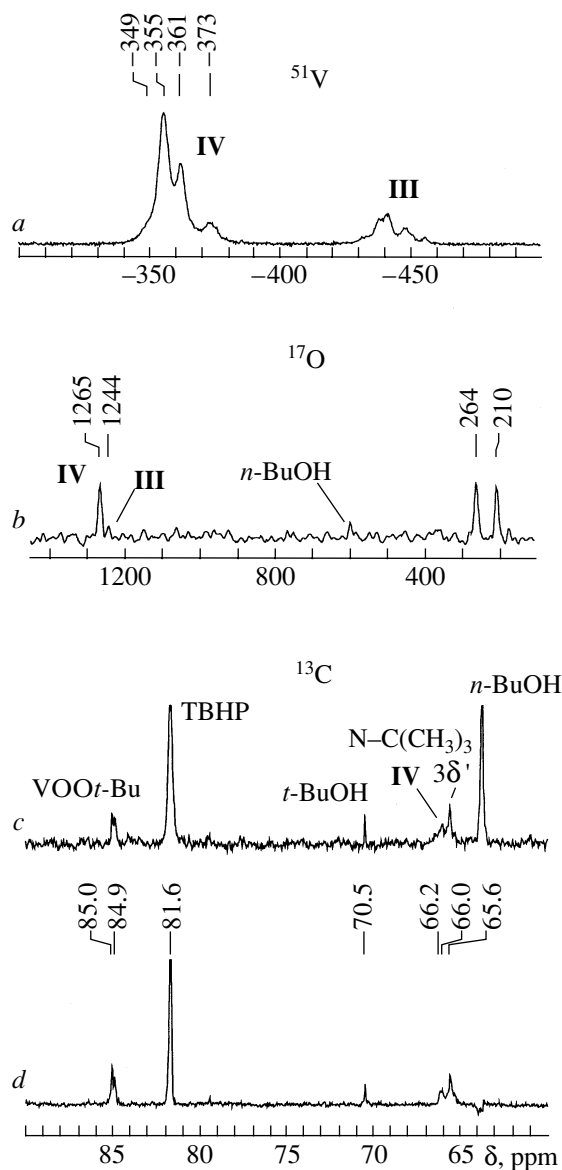


Fig. 9. ^{51}V NMR spectra of vanadium(V) compounds formed in the $[\text{VO}(\text{On-Bu})_3]/\mathbf{3b}/\text{TBHP}$ system in CH_2Cl_2 at 20°C ; $[\text{VO}(\text{On-Bu})_3] = 0.05\text{ M}$; ligand $\mathbf{3b}$ ($\mathbf{3b}/\text{V} = 1.73 : 1$); and $[\text{TBHP}] = 0.67\text{ M}$: (a) ^{51}V NMR spectrum, (b) ^{17}O NMR spectrum, (c) ^{13}C NMR spectrum with broadband proton decoupling, and (d) ^{13}C NMR spectrum of quaternary carbon atoms with broadband proton decoupling.

The question of which diastereomer (**IVa** or **IVb**) is more active in epoxidation reactions is still open. However, it is likely that they exhibit comparable activities; this is one of the main factors responsible for the level of asymmetric induction in this system.

CONCLUSIONS

Catalytic systems for the asymmetric oxidation of sulfides ($[\text{VO}(\text{acac})_2]/\text{Schiff bases } \mathbf{1}/\text{H}_2\text{O}_2$) and for the asymmetric epoxidation of allylic alcohols ($[\text{VO}(\text{acac})_2]/\text{terpene ligand } \mathbf{2}/\text{TBHP}$ and $\text{VO}(\text{Oalkyl})_3/\text{hydroxamic acid } \mathbf{3}/\text{TBHP}$) were studied using ^{13}C , ^{51}V , and ^{17}O NMR spectroscopy. In the first system, the structure and reactivity of the monoperoxo complexes of vanadium(V) with chiral Schiff bases were characterized; these complexes are the intermediates of the catalytic system for the enantioselective oxidation of sulfides. In the second system, the last observable intermediate of the asymmetric epoxidation of allylic alcohols was detected in solution; this intermediate is an outer-sphere complex between a chiral vanadium(V) complex and TBHP. The thermodynamic parameters of its formation were studied, and its structure was discussed. In the third system, the alkylperoxo complexes of vanadium(V) were first detected and characterized using physical techniques; these complexes are active intermediates in the asymmetric epoxidation of allylic alcohols. Two diastereomeric alkylperoxo complexes of vanadium(V) occurred in solution; this may be a factor that limits the level of asymmetric induction. Published data on the structure and reactivity of intermediates are very limited. We hope that our data will be highly valuable for the optimization of catalytic systems based on vanadium complexes.

ACKNOWLEDGMENTS

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