



Linalool to geraniol/nerol isomerization catalyzed by $(\text{RO})_3\text{VO}$ complexes: studies of kinetics and mechanism

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Dedicated to Prof. Renato Ugo on the occasion of his 65th birthday

Abstract

Highly selective catalytic system $\{(\text{RO})_3\text{VO} + [(\text{Bu})_4\text{N}^+]\text{OH}\}$ for the process of linalool to geraniol + nerol isomerization within the temperature range of 413–513 K is reported. Using the ^{51}V NMR spectroscopy, composition and reactivity of vanadium complexes formed in the catalytic system were investigated. Mononuclear vanadium complexes $(\text{RO})_{3-n}(\text{R}'\text{O})_n\text{VO}$, where RO-linalyl and R'O-geranyl/neryl ligands, $n = 0, 1$ and 2 , are active in the isomerization reaction. The reaction of the ligand $\{\text{linalool}/(\text{geraniol} + \text{nerol})\}$ exchange is very fast and reversible, the equilibrium constant of this reaction was estimated. The rate determining step of the isomerization process is the rearrangement of the coordinated to vanadium linalyl- to geranyl/neryl ligands which, probably, proceeds via reduction–oxidation mechanism. The isomerization of linalool is a reversible reaction and two isomers (geraniol and nerol) are formed by the parallel routs. The equilibrium constant of the linalool/(geraniol + nerol) as well as geraniol/nerol isomerization slightly depends on temperature. The reaction rate is of the first-order on linalool, geraniol and nerol concentrations. The kinetic scheme and mechanism of linalool to geraniol + nerol isomerization are suggested.

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Keywords: Linalool; Geraniol; Nerol; Isomerization; Vanadium complexes; Kinetics; Mechanism; ^{51}V NMR

1. Introduction

Geraniol and nerol (*cis*- and *trans*-isomers of 3,7-dimethyl-2,6-octadiene-1-ol) are valuable fragrant compounds having the delicate aroma of the rose [1]. Besides of the perfume industry these alcohols are used for synthesis of Vitamins A and E [2]. One of the promising methods of these alcohols synthesis is the isomerization of linalool in the presence of V, Mo and W catalysts [3–6]. The allyl rearrangement

process is complicated by the tertiary alcohol dehydration, oxidation of primary alcohol to aldehyde and the catalyst deactivation. The most selective catalysts for this reaction are alkyl orthovanadates [3,6]. The scanty patents [3–5] and publications [6] concerning the allyl rearrangement, reveal some data on the products distribution and geraniol (nerol) yield but give not much information about the kinetics and mechanism of this reaction.

We have discovered that a catalytic system consisting of alkyl orthovanadates and tetrabutyl ammonium hydroxide $[(\text{Bu})_4\text{N}^+]\text{OH}^-$ is extremely stable and selective towards the linalool isomerization reaction within the temperature range of 413–513 K. The

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aim of this work was studying the kinetic peculiarities of the linalool to geraniol/nerol isomerization and clarifying the mechanism of this reaction.

2. Experimental

2.1. Materials

Linalool 3,7-dimethyl-2,6-octadiene-3-ol of 98% purity was isolated from coriander oil ("EFCO", Belgorod, Russia) by rectification and borate ester purification followed by vacuum distillation over Na_2CO_3 before experiments. Commercial reagents *n*-butanol (98%), NH_4VO_3 (98%) and $[(\text{Bu})_4\text{N}^+]\text{OH}^-$ (30% solution in water) (Aldrich) were used as received.

2.2. General method of the catalytic system preparation

Experiments on preparation of catalytic system were performed under vacuum using glass-wall technique. NH_4VO_3 (0.5 mmol) and $[(\text{Bu})_4\text{N}^+]\text{OH}^-$ (0.5 mmol) were dissolved in H_2O (5 g) at 100°C and the resulting colorless water solution was mixed with *n*-butanol (40 g). Water and partly BuOH were distilled off and a pale yellow solution of $(\text{BuO})_3\text{VO}$ (0.5 mmol) + $[(\text{Bu})_4\text{N}^+]\text{OH}^-$ (0.5 mmol) in BuOH (20 g) was obtained. Two grams of this solution (vanadium content 0.05 mmol) and linalool (30 mmol) were loaded in to glass ampoules. Then butanol and linalool (5 mmol) were distilled off under vacuum and the obtained linalool solution of linalyl orthovanadate and $[(\text{Bu})_4\text{N}^+]\text{OH}^-$ (0.2 mol%) was distributed among 10 ampoules which were then sealed off.

2.3. General procedure of the linalool to geraniol/nerol isomerization

A set of ampoules (8–10) charged with the catalytic system were placed in to a thermostat heated at the required temperature $T = (413\text{--}513) \pm 2\text{ K}$ and supplied with a vibration adjustment for mixing the reaction solution inside the ampoules. At definite time ampoules were taken out of the thermostat and the reaction mixture was analyzed by the GLC and ^{51}V NMR methods.

2.4. Product analysis

The reaction products were identified by VG-7070 GC/MS using a $25\text{ m} \times 0.2\text{ mm}$ quartz capillary column (Silicone SE-30). Product contents in the reaction mixture were analyzed by ZVET-500 GLC using a $30\text{ m} \times 0.2\text{ mm}$ quartz capillary column (Silicone SE-30).

2.5. UV and NMR measurements

The UV spectra of vanadium solutions (5–20 μm thickness between the quartz disks) were recorded using UVIKON 923 in the wavelength range of 200–400 nm.

The ^{51}V NMR spectra were measured on an MSL-400 NMR Bruker spectrometer at an operating frequency of 105.24 MHz with a 50 kHz sweep width, 10 μs pulse width and 0.1 s interpulse delay, using VOCl_3 as an external reference. Chemical shifts upfield from the reference are reported as negative. The typical number of scans was about 1000.

3. Results and discussion

3.1. Formation of catalytic system (Linalool + $\text{VO}(\text{OAlk})_3$ + $[(\text{Bu})_4\text{N}^+]\text{OH}^-$)

The general scheme of the catalytic system preparation includes three steps:

- (i) preparation of the $\text{NH}_4^+\text{VO}_3^-$ water solution,
- (ii) preparation of the $(n\text{-BuO})_3\text{VO}$ solution in *n*-BuOH,
- (iii) replacement of *n*-BuOH for linalool.

Preliminary experiments have shown that V(5+) species can be transferred quantitatively from water phase to *n*-BuOH solution using $[(\text{Bu})_4\text{N}^+]\text{OH}^-$ as a phase transfer catalyst. The V(5+) species formed at each step of the preparation were characterized by the UV and ^{51}V NMR methods.

In the UV spectra of NH_4VO_3 solution two absorption bands at 230 and 275 nm belonging to the $(\text{VO}_3^-)_3$ species [7] were observed (Fig. 1a). This complex dominates in water solutions at pH 5.5–8.3 and vanadium concentration $>10^{-3}\text{ mol/l}$. Addition of the equimolar amount of $[(\text{Bu})_4\text{N}^+]\text{OH}^-$ to the

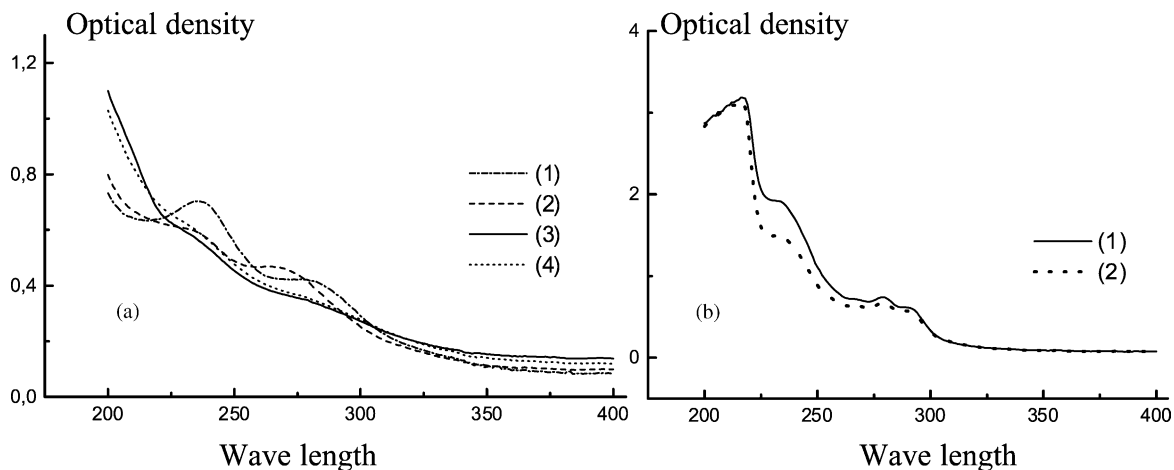


Fig. 1. The UV spectra of the V(5+) complexes at different steps of the catalytic system preparation. (a) (1) NH_4VO_3 (2.5×10^{-2} mol/l) in H_2O ; (2) NH_4VO_3 (2.5×10^{-2} mol/l) + $[(\text{Bu})_4\text{N}^+]\text{OH}^-$ (2.5×10^{-2} mol/l) in H_2O ; (3) $(n\text{-BuO})_3\text{VO}$ (10^{-2} mol/l) + $[(\text{Bu})_4\text{N}^+]\text{OH}^-$ (10^{-2} mol/l) in wet $n\text{-BuOH}$; (4) $(n\text{-BuO})_3\text{VO}$ (2×10^{-2} mol/l) + $[(\text{Bu})_4\text{N}^+]\text{OH}^-$ (2×10^{-2} mol/l) in dry $n\text{-BuOH}$. (b) (1) $(\text{Linalyl})_3\text{VO}$ (10^{-2} mol/l) + $[(\text{Bu})_4\text{N}^+]\text{OH}^-$ (10^{-2} mol/l) in linalool before isomerization reaction; (2) $(\text{linalyl})_3\text{VO}$ (10^{-2} mol/l) + $[(\text{Bu})_4\text{N}^+]\text{OH}^-$ (10^{-2} mol/l) in linalool after isomerization reaction (433 K, linalool conversion 32%).

NH_4VO_3 solution increases its pH up to 10.5 and modifies the UV spectra (Fig. 1a). The intensity of the absorption band at 230 nm decreases and a new band at 262 nm characteristic of HVO_4^{2-} [7] appears. Mixing the ($[(\text{Bu})_4\text{N}^+]\text{OH}^- + \text{NH}_4\text{VO}_3$) water solution with $n\text{-BuOH}$ gives at first yellow solution which quickly becomes colorless. The UV spectra of the vanadium complexes in the wet $n\text{-BuOH}$ solution contains slightly visible absorption bands at 230 and 273 nm. No changes in the UV spectra were observed after dewatering of this solution. The UV spectra of the catalytic system as prepared contain absorption bands at 230, 266, 277 and 289 nm. The same spectrum was observed for the catalytic system after the linalool isomerization (Fig. 1b). Thus, these spectra can be attributed to the catalytically active vanadium complexes.

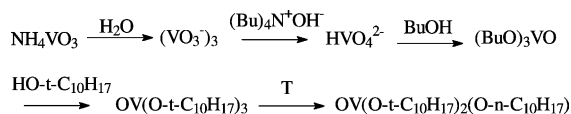
Fig. 2 (0, 1 and 5) demonstrates the ^{51}V NMR spectra of the catalytic system at different steps of its preparation. The intensive signal at -551 ppm observed in the spectra of ($[(\text{Bu})_4\text{N}^+]\text{OH}^- + \text{NH}_4\text{VO}_3$) in $n\text{-BuOH}$ belongs to complex $(n\text{-BuO})_3\text{VO}$ [8]. When $n\text{-BuOH}$ was replaced for linalool (tertiary alcohol) the signal at -551 ppm disappeared and a new signal at -686 ppm was observed which can be attributed to $(\text{linalyl})_3\text{VO}$ complex. Signals at -686 , -645 , -612 and -581 ppm were observed

in ^{51}V NMR spectra of the catalytic system after the reaction of linalool isomerization. This signals can be assigned to $\text{OV}(\text{O-}t\text{-R})_3$, $\text{OV}(\text{O-}n\text{-R})(\text{O-}t\text{-R})_2$, $\text{OV}(\text{O-}n\text{-R})_2(\text{O-}t\text{-R})$ and $\text{OV}(\text{O-}n\text{-R})_3$ complexes, where $\text{O-}t\text{-R}$ is linalyl and $\text{O-}n\text{-R}$ is geranyl/neryl ligands, respectively. Such an assignment was confirmed by the corresponding signal intensities variation when linalool or (geraniol/nerol) were added to the reaction mixture (Table 1).

The results obtained allow one to suggest the following scheme of the formation of the catalytic system under study (Scheme 1).

3.2. ^{51}V NMR monitoring of V(5+) complexes formed in the course of linalool to geraniol/nerol isomerization

The ^{51}V NMR measurements (Fig. 2) and GLC analysis of the reaction mixture were performed for the catalytic system at different degrees of the linalool



Scheme 1.

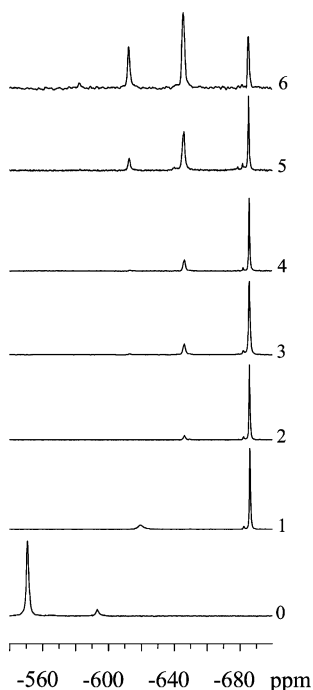


Fig. 2. The ^{51}V NMR spectra of the $\text{V}(5+)$ complexes at different steps of catalytic system preparation: (0) $(n\text{-BuO})_3\text{VO}$ (2×10^{-2} mol/l) + $[(\text{Bu})_4\text{N}^+]\text{OH}^-$ (2×10^{-2} mol/l) in dry $n\text{-BuOH}$; (1) $(\text{linalyl})_3\text{VO}$ (10^{-2} mol/l) + $[(\text{Bu})_4\text{N}^+]\text{OH}^-$ (10^{-2} mol/l) in linalool before isomerization; (5) $(\text{linalyl})_3\text{VO}$ (10^{-2} mol/l) + $[(\text{Bu})_4\text{N}^+]\text{OH}^-$ (10^{-2} mol/l) in linalool after isomerization (433 K, linalool conversion 35.3%) at different concentration of linalool and (geraniol + nerol): the spectra number corresponds to sample number in Table 1.

conversion (Table 1). Initially only linalyl orthovanadate complexes $\text{OV}(\text{O}-t\text{-R})_3$ were found in catalytic system. As the linalool conversion increases, mono geranyl/neryl species $\text{OV}(\text{O}-n\text{-R})_1(\text{O}-t\text{-R})_2$ appear in the solution and these two complexes were dominant among the other vanadium species up to the linalool conversion of 35%. Two and three substituted complexes $\text{OV}(\text{O}-n\text{-R})_2$ and $(\text{O}-t\text{-R})_1 \text{OV}(\text{O}-n\text{-R})_3$, respec-

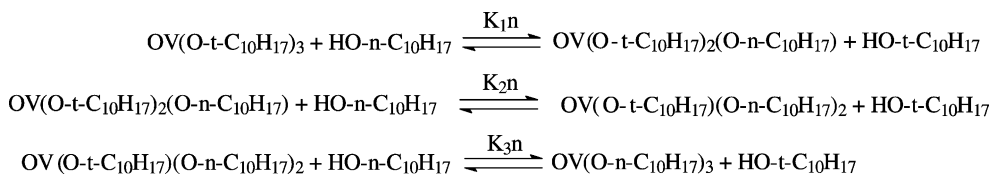
tively, were observed when the excess of the geraniol/nerol mixture was added to catalytic system or small amount of linalool was added to the $\text{OV}(\text{O}-n\text{-R})_3$ solution in the geraniol/nerol mixture. Note, that the ^{51}V NMR spectra were registered in 5 min after addition of the geraniol/nerol mixture or linalool to the solution of the vanadium complexes and the signal relative intensities remain practically constant in the next 30 min. It indicates that the ligand exchange proceeds very fast even at room temperature and in the course of the linalool isomerization process equilibria are achieved (Scheme 2).

Equilibrium constant $K_{1n} = 1.9 \pm 0.1$, $K_{2n} = 0.5 \pm 0.1$ and $K_{3n} = 0.35 \pm 0.05$ of the ligand exchange were estimated from the data presented in Table 1.

3.3. Kinetic peculiarities of linalool to geraniol/nerol isomerization

3.3.1. Effect of $[(\text{Bu})_4\text{N}^+]\text{OH}^-/\text{VO}(\text{OAlk})_3$ ratio

A set of the catalytic systems where the $[(\text{Bu})_4\text{N}^+]\text{OH}^-/[\text{V}]$ ratio was varied within 0.25–4.0 have been prepared and tested in the linalool isomerization. In all the experiments only traces of hydrocarbons (products of the linalool dehydration) were observed, whereas in system ($\text{V}_2\text{O}_5 + \text{linalool}$) the intensive linalool dehydration occurred. The variation of the $[(\text{Bu})_4\text{N}^+]\text{OH}^-/[\text{V}]$ ratio does not change the initial reaction rate of the linalool isomerization. Therefore, the presence of $[(\text{Bu})_4\text{N}^+]\text{OH}^-$ in the catalytic system does not influence the active vanadium complex composition and its catalytic activity in the isomerization reaction, but completely suppresses the side reaction of the alcohol dehydration. Hydrolysis and following oligomerization of $\text{VO}(\text{OAlk})_3$ can produce polyvanadates having the acidic properties which can act as an acid–base catalyst of the tertiary alcohol dehydration. The strong base $[(\text{Bu})_4\text{N}^+]\text{OH}^-$ neutralises the polyvanadates in the catalytic system and thus increases the linalool isomerization selectivity.



Scheme 2.

Table 1
The reaction mixture analysis by the ^{51}V NMR and GLC methods

Sample no.	Composition of reaction mixture, mole fraction				Complexes of vanadium ^b $\text{OV}(\text{O}-n\text{-R})_n (\text{O}-t\text{-R})_{3-n}$			
	Reagent and products ^a				$n = 0$ (–686)	$n = 1$ (–646)	$n = 2$ (–613)	$n = 3$ (–581)
	Linalool	Geraniol	Nerol	Geraniol + nerol				
1	1.0	0.0	0.0	0.0	1.00	0.00	0.00	0.00
2	0.942	0.036	0.022	0.058	0.90	0.10	0.00	0.00
3	0.891	0.042	0.067	0.109	0.80	0.19	0.01	0.00
4	0.852	0.091	0.057	0.148	0.73	0.25	0.02	0.00
5	0.647	0.215	0.138	0.353	0.43	0.47	0.10	0.00
6 ^c	0.506	0.302	0.192	0.494	0.22	0.52	0.26	0.00
7 ^d	0.503	0.302	0.195	0.497	0.21	0.46	0.29	0.11
8 ^e	0.180	0.490	0.330	0.820	0.01	0.14	0.36	0.49

^a GLC data.

^b ^{51}V NMR data (chemical shift, ppm).

^c Geraniol/nerol mixture 0.916 g (3/2) was added to 0.986 g of linalyl orthovanadate complex (0.2 mol% solution in linalool).

^d Linalool 0.51 g was added to 0.50 g of geranyl/neryl orthovanadate complex (0.2 mol% in geraniol/nerol mixture (3/2)).

^e Linalool 0.341 g was added to 1.58 g of geranyl/neryl orthovanadate complex (0.2 mol% in geraniol/nerol mixture (3/2)).

3.3.2. General regularities

The linalool isomerization gives two products: geraniol and nerol (Fig. 3a). Accumulation of hydrocarbons (products of the linalool dehydration) in the course of the experiment does not exceed 2 mol%.

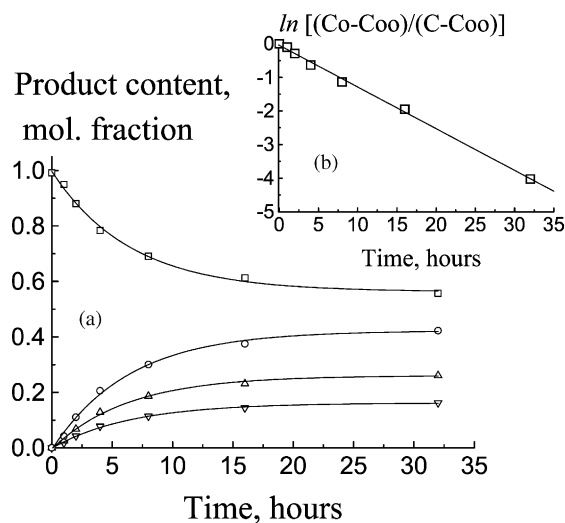


Fig. 3. The kinetic curves of the linalool to geraniol and nerol isomerization: (a) composition of the reaction mixture: (□) linalool, (○) (geraniol + nerol), (△) geraniol, (▽) nerol; (b) the linalool content in semi-logarithmic coordinates: C_0 , C and C_{00} are the initial, current and equilibrium concentration of linalool, respectively. Reaction conditions: $T = 443\text{ K}$, $[\text{linalool}]_0 = 5.5\text{ mol/l}$, $[\text{V}] = 0.1\text{ mol\%}$, $[(\text{Bu})_4\text{N}^+]\text{OH}^- = 0.1\text{ mol\%}$.

The products concentration (geraniol + nerol) grows up asymptotically reaching the limiting value 42.2%. This value agrees with the maximum (geraniol+nerol) yield reported [2–6] and, obviously, corresponds to the thermodynamic equilibrium composition. The kinetic curves of linalool isomerization are well described by the logarithmic function (Fig. 3b):

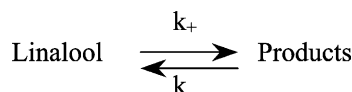
$$\ln \left[\frac{C_0 - C}{C - C_{00}} \right] = (k_+ + k_-) t$$

where C_0 , C and C_{00} are the initial, current and equilibrium concentrations of linalool, k_+ and k_- are the reaction rate constants of the direct and reverse reactions, respectively.

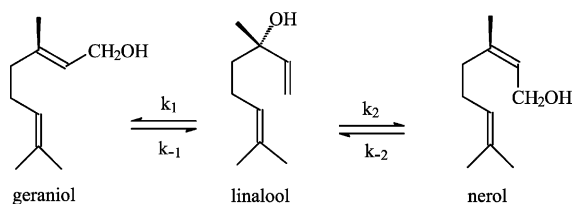
It indicates that the linalool isomerization (Scheme 3) is the reversible process and the reaction rate has the first-order on the reagent and products concentrations. Thus, the kinetics of the linalool conversion can be described by the equation:

$$\frac{-dC}{dt} = k_+ C - k_-(C_0 - C)$$

The sum of the constants ($k_+ + k_-$) can be evaluated as angle tangent of the $\ln[(C_0 - C)/(C -$



Scheme 3.



Scheme 4.

C_{00}] versus time dependence (Fig. 3b). The ratio (k_+/k_-) is equal to the equilibrium constant K_{eq} , which can be calculated from the reaction mixture composition:

$$\frac{k_+}{k_-} = K_{eq} = \frac{C_0 - C_{00}}{C_{00}}$$

Thus, for each experiment the reaction rate constants k_+ and k_- can be evaluated. In particular, for the reaction conditions (Fig. 3) it was found: $k_+ = 0.053 \text{ h}^{-1}$, $k_- = 0.071 \text{ h}^{-1}$.

The ratio of the current concentration [geraniol]/[nerol] = 1.65 ± 0.05 does not depend on the degree of the linalool conversion and catalyst concentration. Hence, geraniol and nerol are formed by the kinetic Scheme 4, including two parallel routes.

According to this scheme the kinetic equation of the linalool isomerization can be expressed as:

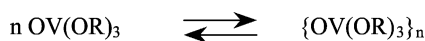
$$\frac{d[L]}{dt} = -(k_1 + k_2) \times [L] + k_{-1} \times [G] + k_{-2} \times [N]$$

where [L], [G] and [N] are the current concentrations of linalool, geraniol and nerol, respectively.

In general, kinetics of three component equilibrium system was examined in [9]. In a special case, when the ratio $[G]/[N] = A$ (A is a constant), determination of the rate constants becomes simpler. Obviously, that $k_1 + k_2 = k_+$ and the $[G]/[N]$ ratio can be expressed as:

$$A = \frac{[G]}{[N]} = \frac{d[G]}{d[N]} = \frac{k_1 \times [L] - k_{-1} \times [G]}{k_2 \times [L] - k_{-2} \times [N]} = \frac{k_1}{k_2} \frac{k_1 k_2 \times [L] - k_{-1} k_2 \times [G]}{(k_1 k_2 \times [L] - k_{-2} k_1 \times [N]) A}$$

There is the only definite set of the rate constants which satisfy to this equation at any value of [L], [G] and [N] ($[G]/[N] = A$). It is evident that this



Scheme 5.

equation is independent of the reagent and products current concentrations when

$$k_{-1} k_2 \times [G] = k_{-2} k_1 \times [N]$$

From this it follows that $A = [G]/[N] = k_1/k_2$. Thus, $k_{-1} = k_{-2} = k_-$ and $k_1 + k_2 = k_+$.

In particular, for the reaction conditions (Fig. 3) the following values of the rate constants were calculated: $k_{-1} = k_{-2} = k_- = 0.071 \text{ h}^{-1}$, $k_1/k_2 = 1.61$, $k_1 = 0.033 \text{ h}^{-1}$, $k_2 = 0.020 \text{ h}^{-1}$.

3.3.3. Effect of the catalyst loading

The curve of the dependence of the initial reaction rate of the linalool isomerization versus the catalyst loading has two parts (Fig. 4). The reaction rate increases monotonously with the catalyst concentration growth up to 0.3 mol% and then remains constant at high catalyst loading 0.3–1.0 mol%. Note, that at the reaction temperature the precipitation of polyvanadates was observed when the catalyst loading exceeds 0.3 mol%. According to the ^{51}V NMR study [8] the equilibrium (Scheme 5) between mononuclear vanadyl esters OV(OR)_3 and its oligomers is settled rapidly in the organic medium.

In the catalytic system with low vanadium concentration ($[V] = 0.1\text{--}0.2 \text{ mol}\%$) mononuclear tetrahedral vanadium complexes were mainly observed by ^{51}V NMR method (Fig. 2). One can conclude that the mononuclear vanadium complexes are active in the linalool isomerization. Thus, the increase in the catalyst loading results in the reaction rate growth (Fig. 4). At high catalyst loading the solid phase of polyvanadates is formed and the concentration of OV(OR)_3 in solution is determined by the solubility of polyvanadates in the reaction medium. The catalytic activity of solid polyvanadates is obviously much lower than that of the vanadium complexes in solution. Thus, the catalytic activity a_i (mol/(mol V h)) of the vanadium complexes in the direct and reverse reaction presented on the kinetic scheme (reagent concentration is assigned 1 mol/l) can be calculated as the ratio of the corresponding rate constants k_i to the vanadium concentration.

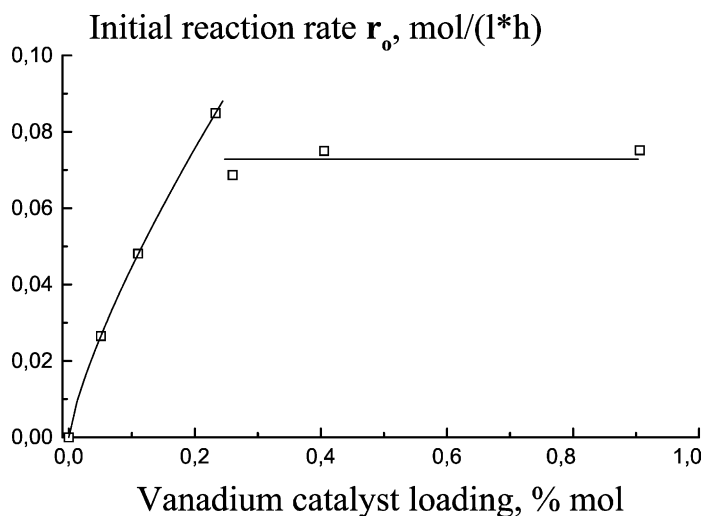


Fig. 4. Dependence of the initial linalool isomerization rate on the vanadium catalyst loading. Reaction conditions: $T = 433$ K, $[\text{linalool}]_0 = 5.5$ mol/l, $[\text{V}] = [(\text{Bu})_4\text{N}^+]\text{OH}^-$.

In particular, for the reaction conditions (Fig. 3) the catalytic activity of $\text{OV}(\text{OR})_3$ was found to be: $a_{-1} = a_{-2} = a_- = 71$ mol/(mol V h), $a_1 = 33$ mol/(mol V h), $a_2 = 20$ mol/(mol V h).

3.3.4. Effect of temperature

The noticeable rate of the linalool isomerization was observed at temperature higher than

413 K (Fig. 5a). The selectivity of the aimed product formation (geraniol + nerol) remains approximately constant (95–99%) with the temperature increase. In comparison with the pure $\text{OV}(\text{OR})_3$ catalyst ($T = 423$ – 443 K) [3–5], the catalytic system $\text{OV}(\text{OR})_3 + [(\text{Bu})_4\text{N}^+]\text{OH}^-$ is very effective at high temperature and reproducible results have been obtained up to 513 K. The initial rate of the

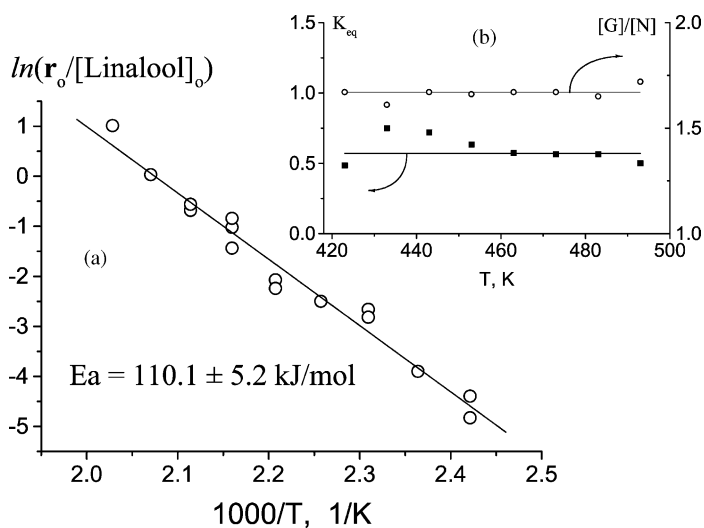


Fig. 5. Effect of temperature on (a) the initial reaction rate of the linalool isomerization r_0 , (b) geraniol/nerol ratio ($[G]/[N]$) and the equilibrium constant of the linalool isomerization K_{eq} . Reaction conditions: $[\text{linalool}]_0 = 5.5$ mol/l, $[\text{V}] = [(\text{Bu})_4\text{N}^+]\text{OH}^- = 0.2$ mol%.

linalool isomerization increases with the temperature increase and in the Arrhenius plot this dependence is linear (Fig. 5a). The activation energy ($E_a = 110.1 \pm 5.2$ kJ/mol) calculated from the Arrhenius plot of the *initial* rate of the linalool isomerization (Fig. 5a) corresponds to the direct reaction. The geraniol/nerol ratio (1.65 ± 0.05) as well as equilibrium constant K_{eq} do not depend on temperature and remain constant within range of 413–493 K (Fig. 5b). Note, that

$$\frac{[G]}{[N]} = \frac{k_1}{k_2} = \frac{k_{10} \exp(-E_{a1}/RT)}{k_{20} \exp(-E_{a2}/RT)}$$

$$K_{eq} = \frac{k_+}{k_-} = \frac{k_1 + k_2}{k_{-1}} = \frac{k_{10} \exp(-E_{a1}/RT) + k_{20} \exp(-E_{a2}/RT)}{k_{-10} \exp(-E_{a-1}/RT)}$$

E_a index corresponds to that for reaction rate constant.

These results indicate that for the direct and reverse reactions of the linalool isomerization process (see kinetic scheme) E_a values are approximately equal to each other (≈ 110.1 kJ/mol).

3.4. Mechanism of the linalool to geraniol/nerol isomerization

3.4.1. Reagent activation

The first step of the isomerization process is the ligand exchange proceeding evidently via five-coordinated vanadium complex (Scheme 6).

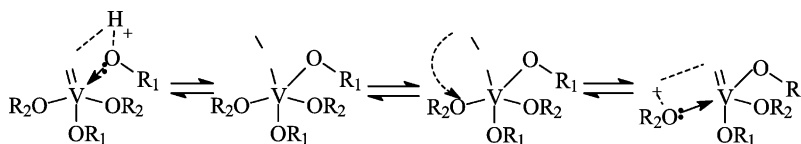
According to the ^{51}V NMR data, the linalool/geraniol/nerol exchange is rather fast even at room temperature. Competition of tertiary and primary alcohols in this reaction is determined by their electron and steric properties. Steric repulsion of the O-*t*-R groups favors the substitution of the first linalyl ligand for the geranyl ligand in the linalyl orthovanadate com-

plexes $\text{OV}(\text{O-}t\text{-R})_3$ ($K_{1n} = 1.9 \pm 0.1$). Higher electronegativity of the O-*t*-R in compared with the O-*n*-R ligand hinders the substitution of the second and the third O-*t*-R ligands ($K_{2n} = 0.5 \pm 0.1$ and $K_{3n} = 0.35 \pm 0.05$). Possibly, the electron donation of the O-*t*-R ligands stabilize V(5+) ion against intermolecular reduction, and the vanadium complexes bearing at least one O-*t*-R ligand, are more stable under reaction conditions. At heating the $\text{OV}(\text{O-}n\text{-R})_3$ complex up to 473 K, reduction of V(5+) species occurred which was evident from the dark blue precipitate formation and the decrease of the ^{51}V NMR spectrum intensity.

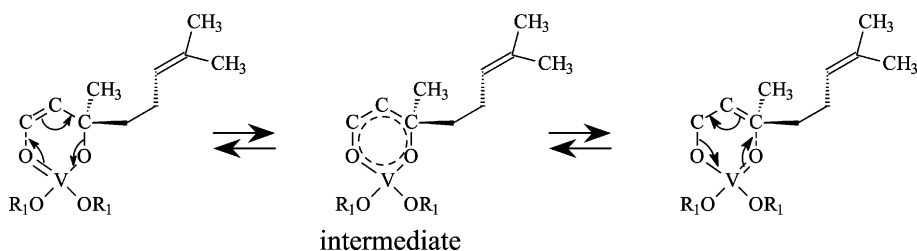
3.4.2. Active intermediate

Both the direct and reverse reactions of the linalool isomerization proceed via the same intermediate (Scheme 7).

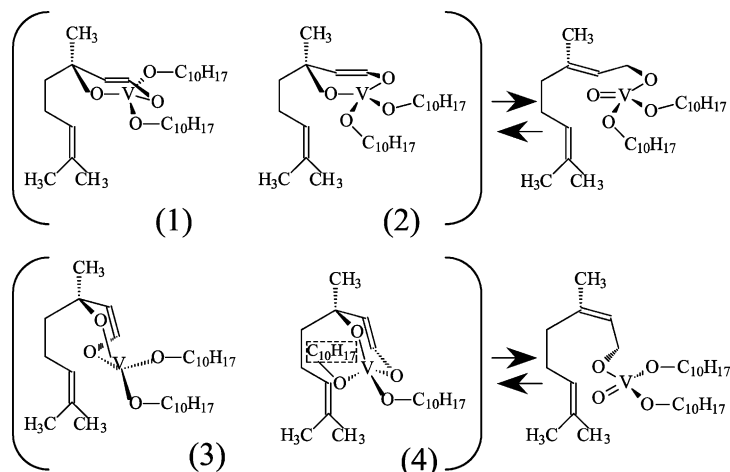
Due to the linalyl ligand C=C double bond polarization and the increased electron density on the vanadyl oxygen atom, the intermolecular interaction between them gives six-membered intermediate. Redistribution of the electron density inside the cycle results in the cleavage of the C–O bond in the linalyl moiety and the formation of a new C–O bond between the terminal C atom and O atom of the vanadyl group. In the result of the shift of C=C position from 1 to 2 and the O atom displacement from position 3 to 1, allyl rearrangement occurs and linalyl transforms to geranyl/neryl. In this process vanadium (5+) provides the electron transfer between carbon atoms in positions of 1 and 3 and acts as a reduction–oxidation catalyst. This process is reversible and the isomerization of geranyl/neryl vanadate complex proceeds via the same intermediate. Taking into consideration the high rate of the ligand exchange one can conclude that the ligand rearrangement inside the vanadium coordination sphere is a rate determining step of the process and the reaction rate constants obtained relate to transformation of the corresponding complexes.



Scheme 6.



Scheme 7.



Scheme 8.

3.4.3. *Cis–trans*-isomers formation

The six-membered intermediate can exist in four isomeric forms which easily transforms into each other (Scheme 8).

Structures (1) and (2) are the precursors of *cis*-isomer (geraniol) formation whereas *trans*-isomer (nerol) form structures (3) and (4). The ratio of reaction rates of the geraniol and nerol formation should be determined by the quantitative relationship between structures (1), (2) and (3), (4). Note, structure (4) has the most hindered space orientation of $C_{10}H_{17}$ groups and the probability of its realization is expected to be rather low. The reverse process should not depend on *cis–trans*-orientation of $-CH_2-O-V(O)(OC_{10}H_{17})_2$ group, so that geranyl/neryl ligands should have the similar reactivity in the process of the intermediate formation. This argumentation is in agreement with the reaction rate constant obtained ($k_{-1} = k_{-2}$; $k_1/k_2 = 1.61$).

4. Conclusions

Formation of the highly selective catalytic system $\{(RO)_3VO + [(Bu)_4N^+][OH]\}$ for the process of the linalool to geraniol + nerol isomerization was studied and it was found that mononuclear vanadium complexes $(RO)_{3-n}(R'O)_nVO$, where RO-linalyl and R'O-geranyl/neryl ligands, $n = 0, 1$ and 2 are active in this reaction. The ligand exchange constant as well as the reactivity of $(RO)_{3-n}(R'O)_nVO$ in the linalool isomerization were estimated. The kinetic peculiarities of this reaction were studied. The kinetic scheme and mechanism of the reversible process of the linalool to geraniol + nerol isomerization were suggested.

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