Effect of heterogeneous and homogeneous pathways on selectivity of pinane-2-ol to linalool isomerization

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Abstract

The regularities of pinane-2-ol isomerization over block catalyst under reagent pressure of 2–45 Torr and within a temperature range of 450–620 °C were studied. A scheme of key product—linalool, as well as side products—hydrocarbons and 5-membered cyclic alcohols formation was suggested. Light hydrocarbons C_1–C_6 are formed by gas phase free radical pathway of pinane-2-ol destruction, hydrocarbons C_{10} by linalool dehydration over catalyst surface acid centers, 5-membered cyclic alcohols by linalool intermolecular cyclization.

The reaction rate constants of *cis/trans*-pinane-2-ol conversion to linalool and its following cyclization to 5-membered alcohols were evaluated. The linalool formation mechanism including the intermolecular interaction of OH group proton resulting in pinane ring opening was suggested. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Linalool; Pinane-2-ol; Isomerization; Kinetics; Mechanism

1. Introduction

The ring opening reaction of cyclic monoterpenes is a promising way to synthesis of fragrance compounds and vitamins [1–3]. In particular, linalool can be prepared by thermal isomerization of pinane-2-ol,
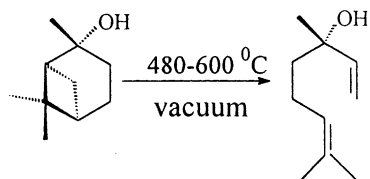
but a small variation of reaction conditions such as reagent pressure, reactor geometry, etc., results in drastic changes in the reaction rate and linalool selectivity [4]. Hydrocarbons of different molecular weights and a set of cyclic alcohols were observed as side products [2]. Unfortunately, there are no publications concerning kinetic study of this process under vacuum for a very short contact time. It may be partly due to the experimental complexity of the reaction mixture, very fast but uniform warming, keeping of the mixture at reaction temperature for very short time (~0.01 s). To perform the experiments an original reactor was designed [4]. The electroconductive unit-type catalyst, capable to get warm by electric current uniformly, was located inside the reactor.

The aim of this work is to clarify the factors determining the selectivity of linalool formation in the process of pinane-2-ol isomerization over the unit-type catalyst and the kinetic peculiarities of this process.

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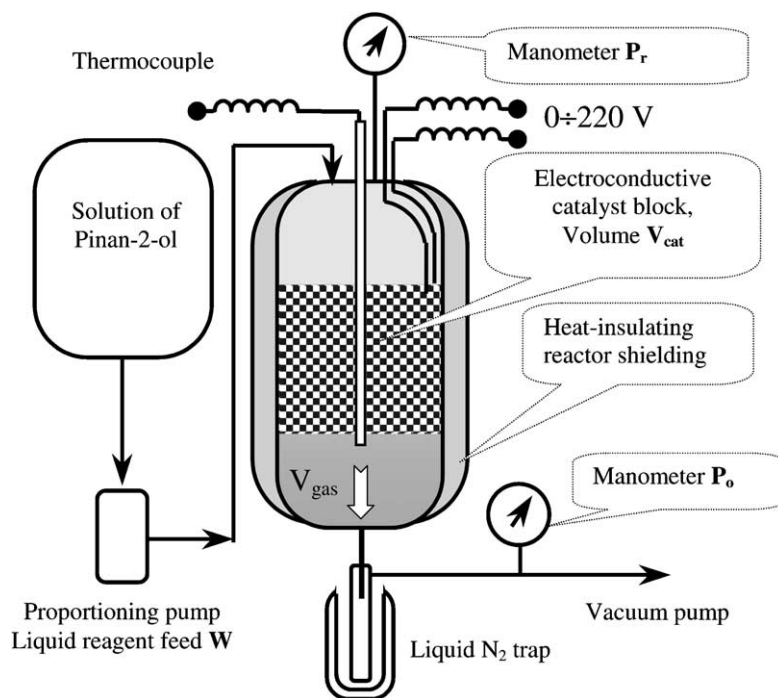*E-mail address:* semkoln@catalysis.nsk.su (V.A. Semikolenov).

Fig. 1. Schematic view of flow reactor for pinane-2-ol thermal isomerization.

2. Experimental

Pinane-2-ol (*cis/trans*-isomer mixture $= 3$) was obtained by α-pinane air oxidation followed by pinane hydroperoxide hydrogenation over Pd/C and vacuum rectification [3].

Pinane-2-ol isomerization tests were performed in a special heat-insulated flow reactor (diameter $d = 30$ mm, height $h = 300$ mm) having no external heater (Fig. 1). The electroconductive unit-type catalyst ($d = 30$ mm, $h = 50$ mm, average channel diameter 2 mm), supplied with a thermocouple and capable uniformly to get warm by electric current, was located inside the reactor. The unit-type catalyst was manufactured from stainless steel capillary 1.5 mm in diameter and 10 m in length. A nickel–chromium wire covered with refractory insulation was inserted inside the capillary. Thus, the capillary can be warmed by the passing of electric current through the nickel–chromium wire. This electric heater was wound around the stainless steel tube (5 mm outside diameter) soldered from one side (this tube was used as the thermowell). The winding consists of five layers separated by stainless steel network with the mesh size $= 4$ mm. Each layer consists of 20 loops with the inter-loop distance 1.0 mm. So the spiral channels with the average diameter 2 mm were formed between the loops of neighbor layers. The external surface of unit-type catalyst was covered with pyrolytic carbon by passing the butadiene flow through the unit-type catalyst at $600\,^\circ$C during 30 min. Due to the high heat conductivity of metal framework the temperature profile along the thermowell was uniform in central part (40 mm) of unit-type catalyst ($\Delta T \leq 5\,^\circ$C at $T = 500$–$600\,^\circ$C). To measure the reagent pressure P_r inside the reactor and outlet pressure P_o, two manometers were used. The pinane-2-ol in BuOH solution was injected into the reactor by a proportional pump, and reaction products were condensed in a trap cooled by liquid nitrogen. The reproducible data were obtained throughout reactor operation (more than 500 h).

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 reaction mixture were determined chromatographically using a $7\,\text{m} \times 3\,\text{mm}$ column, Silicone SE 30/Chromaton N-AW.

Reaction rate constants and activation energies were calculated by using all experimental data. Method of least squares (Origin 5.0, Microsoft Office) was used for statistical data manipulation.

3. Results and discussion

3.1. Pathways of pinane-2-ol transformation

Unreacted pinane-2-ol, the aimed product linalool and three groups of side products—hydrocarbons $C_{10}H_{16}$, a set of hydrocarbons C_1–C_6 and unsaturated 5-membered cyclic alcohols—were detected in the reaction mixture collected in a trap. The relative content of these products in the reaction mixture depends strongly on isomerization process parameters.

3.1.1. Dehydration
The terpene alcohols in the presence of acid catalysts readily undergo dehydration yielding hydrocarbons $C_{10}H_{16}$ [5]. Addition of a small amount of pyridine to pinane-2-ol solution (1.5–2.0 mol%) decreases the yield of hydrocarbons $C_{10}H_{16}$ from 25–30 to 2–5% and increases the linalool yield from 10–15 to 40–50% but does not change the pinane-2-ol conversion [3]. This indicates that hydrocarbons $C_{10}H_{16}$ result from dehydration of linalool rather than pinane-2-ol.
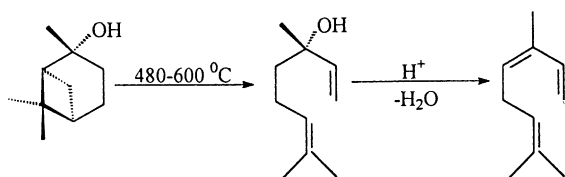
Note that the unit-type catalyst is covered with pyrolytic carbon and surface-COOH groups may act as acid centers. Pyridine or products of its pyrolysis have basic properties and can neutralize the acid centers and thus can inhibit the pathway of linalool dehydration. The pyridine was added to the reaction mixture in all subsequent tests.

3.1.2. Pyrolysis
Pyrolysis of cyclic hydrocarbons proceeds by the branched free radical mechanism and results in low-molecular hydrocarbons [6–9]. The chain initiation as well as free radical death can occur as a result of molecule/free radical collision at the warmed surface. The pyrolysis rate is equal to the product of the free radical initiation rate and the chain length, and the latter is equal to the ratio of the chain propagation and radical death rates. The quantitative kinetic description for a multicomponent chain process is a very complicated problem, but some qualitative analysis of the effect of reagent pressure on pyrolysis rate can be made. If the molecule free path in gas phase is longer than the distance between the neighboring walls L (channel size of catalyst block), the free radical initiation rate should be equal to the rate of free radical death and the chain propagation rate should be equal to zero, because no bimolecular collision in gas phase takes place. Thus, the pyrolysis rate should be equal to zero. On the contrary, if the molecule free path is much shorter than the distance between the walls, the chain will be long enough because of the multiple of bimolecular collision. So, a sharp increase in pyrolysis rate with growth in reagent pressure should be observed.

Setting the effective diameter of pinane-2-ol molecule $\sigma = 0.7$ nm and the reaction temperature $T = 825$ K, the average free path (λ) at the effective pressure inside the reactor P_r can be estimated as:

$$\lambda = \frac{kT}{(2^{1/2}\pi\sigma^2 P_r)},$$

where k is the Boltzmann constant.

The calculations show that at $P_r \approx 20$ Torr, the λ value is equal to 2 μm (the mean size of unit-type catalyst channels $L \approx 2$ mm).

In the process of pinane-2-ol isomerization the yield of low-molecular hydrocarbons C_1–C_6 is negligible and permanent within $P_r = 5$–20 Torr but considerably increases at $P_r > 20$ Torr (Fig. 2). This indicates that the side products—C_1–C_6 hydrocarbons are formed in gas phase by free radical pathway. The ratio λ/L is the key parameter determining contribution of side free radical pathway to the total process of pinane-2-ol conversion. That is why the high-vacuum unusually designed reactors (quartz tube filled with crushed quartz [10], stainless capillary containing a stainless steel rod as a core [2], two disks containing narrow slit-like channels in the form of a spiral between them [11]) and are used to suppress this side pathway.

3.2. Kinetic peculiarities of pinane-2-ol isomerization

3.2.1. Effect of reagent pressure inside the reactor

In the flow reactor process, P_r is a sum of the outlet pressure P_o and pressure drop ΔP due to hydrodynamic resistance of unit-type catalyst:

$$P_r = P_o + \Delta P.$$

If the process is realized in vacuum ($P_o \cong 0$) the value of P_r is determined mainly by pressure drop ΔP, which is related to the flow of gaseous reagents, N (mol/s), through the catalyst block:

$$N = D \, \Delta P,$$

where D is the hydrodynamic resistance.

So, P_r will depend on the feed of pinane-2-ol solution (w) as

$$P_r = P_o + \frac{N}{D} = P_o + \alpha \frac{w}{D},$$

where α is the total content of all components in feeding liquid solution (mol/ml). Indeed, dependence P_r vs. w (Fig. 2a) can be described by the linear function

$$P_r = 0.268 + 13.76w.$$

Thus, the effect of P_r on pinane-2-ol isomerization can be elucidated by varying of the feed pinane-2-ol solution (Fig. 2a and b). In general, the contact time (τ) is defined as the ratio of catalyst block volume (V_{cat}) and gaseous reagent flow V (l/s) at the process temperature (T). Taking into consideration that

$$V = \frac{NRT}{P_r},$$

one can derive

$$\tau = V_{cat} \frac{(P_o + \alpha w/D)}{(\alpha wRT)}.$$

This equation shows that τ decreases with growth in w in the region of high P_o ($P_o \gg \alpha w/D$) and tends to a constant value in the region of low pressure ($P_o \ll \alpha w/D$). Within the range of pinane-2-ol feed studied ($0.268 \ll 13.76w$) (Fig. 2) the contact time remains constant. So, the peculiarities of pinane-2-ol isomerization can be attributed to the reagent pressure but not to the τ variation.

In the region of low P_o (3–15 Torr), the relative concentrations of reagents and products remain constant independently of w. Note that the current reagent
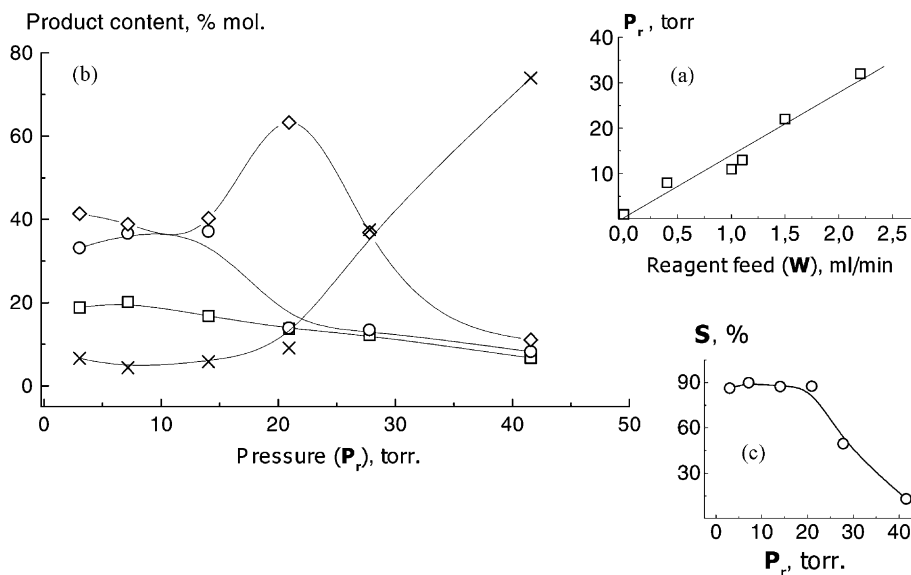

Fig. 2. Dependencies of: (a) reagent pressure inside the reactor (P_r) on reagent feed rate (w); (b) reagent mixture contents; (c) linalool selectivity on reagent pressure inside the reactor (P_r). (–□–) trans-pinane-2-ol, (–○–) cis-pinane-2-ol, (–◇–) linalool, (–×–) hydrocarbons C_1–C_6. Reaction conditions: $T = 560\,°C$; mixture composition: pinane-2-ol (8 mol%), butanol (90.5 mol%), pyridine (1.5 mol%); contact time (τ) = 0.055 s.

partial pressure (P_t) for the first-order reaction is expressed as a function of time (t):

$$P_t = P\,e^{-kt}.$$

This means that the relative concentration of reagents or products should be constant ($P_t/P =$ constant) if $t =$ constant. Thus, one can conclude that the rate of isomerization is of the first order by pinane-2-ol pressure. The number of collision of pinane-2-ol molecules with the catalyst surface per unit time is also proportional to the pinane-2-ol pressure. This indicates that pinane-2-ol activation occurs during the collisions with the surface.

A significant decrease in pinane-2-ol content (mainly due to *cis*-isomer consumption) and an increase in linalool content with P_r rise up to 20 Torr were observed. Further P_r rise results in progressive decrease in pinane-2-ol content and a sharp increase in C_1–C_6 hydrocarbon content.

Linalool selectivity remains constant (90%) in the interval of $P_r = 3$–25 Torr and noticeably diminishes (to 10%) under higher P_r (Fig. 2c).

The kinetics and mechanism of cyclic aliphatic hydrocarbons pyrolysis were studied in [6–8]. Ring opening reaction for 3-, 4-, and 5-membered cycles occurs by monomolecular mechanism at temperature below 600 °C and reduced pressure [6]. Cyclohexane ring opening proceeds by free radical mechanism at

$T > 700$ °C and total pressure of 30–760 Torr [7]. However, molecular reactions can also take place under these conditions.

Pinane-2-ol isomerization seems to proceed mainly by molecular mechanism on the catalyst surface in the interval of $P_r = 3$–15 Torr (Fig. 2). This pathway provides high linalool selectivity. The contribution of free radical chain reaction, both ring opening of 4- and 6-membered cycles of pinane-2-ol and molecule deep destruction yielding hydrocarbons C_1–C_6 is enhanced under $P_r > 20$ Torr.

3.2.2. Effect of contact time

To obtain a dependence of the product composition on contact time, the following series of experiments were performed (Fig. 3). The doze of reaction mixture was passed with a constant feed rate through the reactor heated to a fixed temperature. The reaction products were collected in a trap cooled by liquid N_2. Then the products were analyzed and again passed through reactor under the same conditions and contact time. The difference in mixture composition before and after passing through the reactor is related to the degree of conversion during the contact time (τ). The product composition after multiple (n times) recycling corresponds to conversion at contact time $n\tau$.

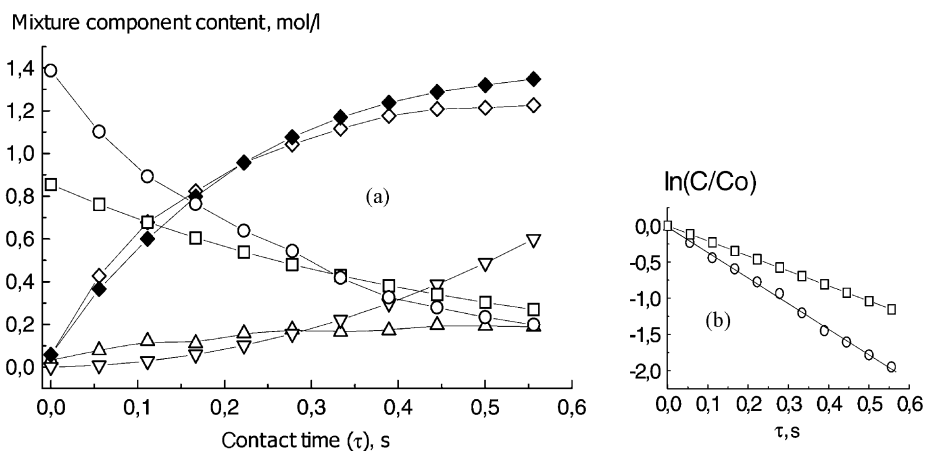*cis*-Pinane-2-ol and *trans*-pinane-2-ol concentrations monotonically decrease with increasing contact

Fig. 3. Effect of contact time (τ) on contents of pinane-2-ol pyrolysis products: (a) in coordinates: reagent concentration–contact time; (b) in semi-logarithmic coordinates. (–□–) *trans*-pinane-2-ol, (–○–) *cis*-pinane-2-ol, (–◇–) linalool, (–◆–) calculated curve of linalool contents, (–△–) hydrocarbons $C_{10}H_{16}$, (–▽–) 5-membered cyclic alcohols. Reaction conditions: $T = 560$ °C; reagent pressure inside the reactor (P_r) = 10–15 Torr; mixture composition: pinane-2-ol (20.0 mol%), butanol (78.0 mol%), pyridine (2.0 mol%).

Table 1
Effect of contact time (τ) on *cis/trans*-pinane-2-ol conversion, linalool yield and selectivity[a]

Contact time τ (s)	Conversion (%)		Linalool	
	cis-Pinane-2-ol	*trans*-Pinane-2-ol	Yield (%)	Selectivity (%)
0.055	20.6	10.9	19.0	83.2
0.11	35.7	20.6	30.3	82.0
0.17	44.9	29.2	36.7	82.9
0.22	54.0	37.0	42.7	78.7
0.28	60.8	43.8	46.5	75.9
0.33	69.9	50.0	49.8	74.3
0.39	76.5	55.4	52.4	71.4
0.44	79.9	60.2	53.9	67.5
0.50	83.1	64.6	54.1	64.1
0.56	85.8	68.5	54.7	60.1

[a] Reaction conditions: $T = 540\,^{\circ}\text{C}$; reagent pressure in the reactor (P_r) = 10–15 Torr; initial reaction mixture composition: linalool (20.0 mol%), butanol (78.0 mol%), pyridine (2.0 mol%). The contact time was varied by recycling of reaction mixture trapped after the passing through the reactor.

time (Fig. 3a, Table 1). Relative concentration dependencies vs. τ in semi-logarithmic coordinates are linear (Fig. 3b). This indicates that the reaction rate is of the first order by both *cis*- and *trans*-pinane-2-ol isomers and the reaction rate constants can be calculated as a tangent of inclination angel of the linear dependencies (Fig. 3b). Note that this conclusion is in agreement with the results obtained earlier at various P_r. The calculated rate constants of conversion of *cis*-pinane-2-ol and *trans*-pinane-2-ol are $k_{cis} = 3.56\ (\pm0.06)\,\text{s}^{-1}$ and $k_{trans} = 2.06\ (\pm0.01)\,\text{s}^{-1}$, respectively.
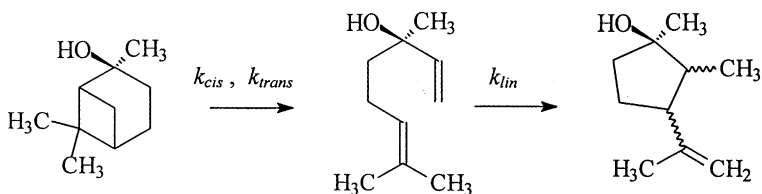

The content of linalool initially increases (Table 1), reaching a maximum at $\tau = 0.5$–$0.6\,\text{s}$, and then gradually decreases. The content of side products of 5-membered hydroxyolefines monotonically grows with τ (Fig. 3a). Obviously, the kinetic scheme of thermal isomerization of pinane-2-ol

includes conversion of linalool to 5-membered hydroxyolefines.

The reaction of linalool cyclization to 5-membered hydroxyolefines is supposed [2,12] to proceed via intramolecular migration of hydrogen according to the scheme:
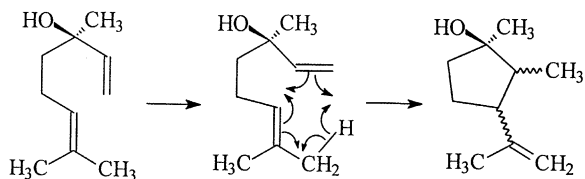
We have studied the kinetic regularities of linalool conversion under the conditions of thermal isomerization of pinane-2-ol (Fig. 4a). With increasing contact time, the content of linalool in the reaction mixture monotonically decreases, and 5-membered hydroxyolefines accumulate in stoichiometric amounts. The absence of pinane-2-ol in the reaction products indicates that thermal isomerization of pinane-2-ol into linalool is an irreversible process. In semi-logarithmic coordinates, the relative concentration of linalool shows a linear dependence on time, which evidences that the rate of cyclization of linalool is of the first order by its concentration (Fig. 4b). Most likely, activation of linalool, like that of pinane-2-ol, proceeds by a heterogeneous mechanism through impacts with the catalyst surface. The calculated constant of the linalool cyclization rate is $k_{\text{lin}} = 0.69\ (\pm0.04)\,\text{s}^{-1}$. Thus, thermal isomerization of pinane-2-ol into linalool and 5-membered hydroxyolefines seems to occur at the catalyst surface according to the kinetic scheme:
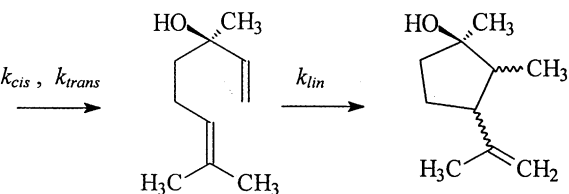
In this case, the kinetics of isomerization of the mixture of *cis*- and *trans*-pinane-2-ol can be described by a system of equations:

$$\frac{\mathrm{d}C_{cis}}{\mathrm{d}\tau} = -k_{cis}C_{cis},$$

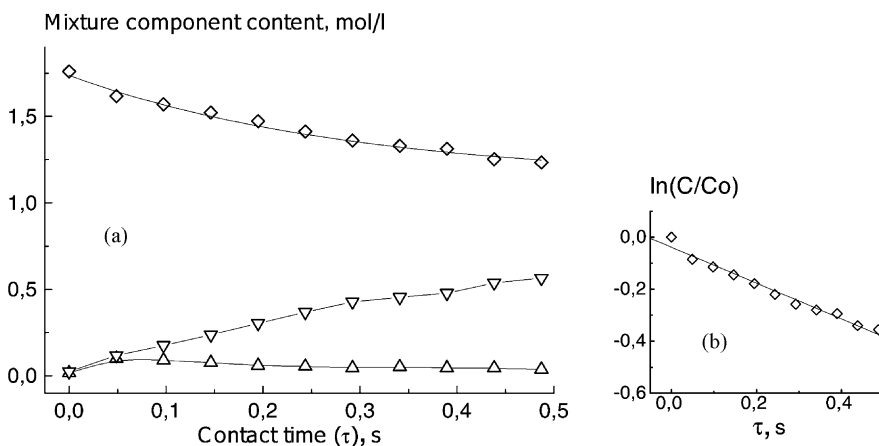$$\frac{\mathrm{d}C_{trans}}{\mathrm{d}\tau} = -k_{trans}C_{trans}$$

Fig. 4. Effect of contact time (τ) on contents of linalool pyrolysis products: (a) in coordinates: reagent concentration–contact time; (b) in semi-logarithmic coordinates. (–◇–) linalool, (–△–) hydrocarbons $C_{10}H_{16}$, (–▽–) 5-membered cyclic alcohols. Reaction conditions: $T = 540\,°C$; reagent pressure in the reactor (P_r) = 10–15 Torr; mixture composition: linalool (20.0 mol%), butanol (78.0 mol%), pyridine (2.0 mol%).

$$\frac{dC_{\lin}}{d\tau} = k_{cis}C_{cis} + k_{trans}C_{trans} - k_{\lin}C_{\lin},$$

$$\frac{dC_{\hol}}{d\tau} = k_{\lin}C_{\lin},$$

where C_{cis}, C_{trans}, $C_{\lin}$ and $C_{\hol}$ are the current concentrations of *cis*-pinane-2-ol, *trans*-pinane-2-ol, linalool and 5-membered hydroxyolefines, respectively.

Ignoring the paths of formation of light (C_1–C_6) hydrocarbons and dehydration products, whose total yield under these conditions does not exceed 10%, we can write the equation of material balance:

$$C_{0cis} + C_{0trans} = C_{cis} + C_{trans} + C_{\lin} + C_{\hol},$$

where C_{0cis} and C_{0trans} are the initial concentrations of *cis*- and *trans*-pinane-2-ol, respectively.

Solution of this system of equations gives an expression for the current concentration of linalool:

$$
\begin{aligned}
C_{\lin} = {} & \frac{k_{cis}C_{0cis}\exp(-k_{cis}\tau)}{k_{\lin} - k_{cis}} \\
& + \frac{k_{trans}C_{0trans}\exp(-k_{trans}\tau)}{k_{\lin} - k_{trans}} \\
& + \left(C_{0\lin} - \frac{k_{cis}C_{0cis}}{k_{\lin} - k_{cis}} - \frac{k_{trans}C_{0trans}}{k_{\lin} - k_{trans}} \right) \\
& \times \exp(-k_{\lin}\tau)
\end{aligned}
$$

or, with regard to the initial concentrations and obtained $k_{\lin}$, k_{cis} and k_{trans} values:

$$
\begin{aligned}
C_{\lin} = {} & -1.72\exp(-3.56\tau) - 1.28\exp(-2.06\tau) \\
& + 3.06\exp(-0.69\tau).
\end{aligned}
$$

This expression shows that the maximum content of linalool in the reaction products can reach 59.05% at $\tau = 0.63\,s$ (Fig. 3a). This is in agreement with the experimental data (54% at $\tau = 0.56\,s$).

3.2.3. Temperature effect

Formation of linalool proceeds at a high rate starting with $T = 480\,°C$. Products of partial opening of the pinanyl cycle, e.g. terpineol, have not been detected. With increasing temperature, the content of pinane-2-ol in the reaction products decreases and that of linalool increases (Fig. 5a, Table 2) with the selectivity of linalool formation falling from 83% (maximum) at $560\,°C$ to 69% at $620\,°C$ (Fig. 5b). In the Arrhenius coordinates, the observed rate constants of *cis*- and *trans*-pinane-2-ol isomerization show linear dependencies on temperature (Fig. 6a). The calculated activation energies for *cis*- and *trans*-pinane-2-ol differ insignificantly: $E_{a(cis)} = 215.1(\pm12.2)\,kJ/mol$ and $E_{a(trans)} = 190.3(\pm2.2)\,kJ/mol$. Most likely, the configuration of pinane-2-ol molecule has a minor effect on the energy of its transition into the
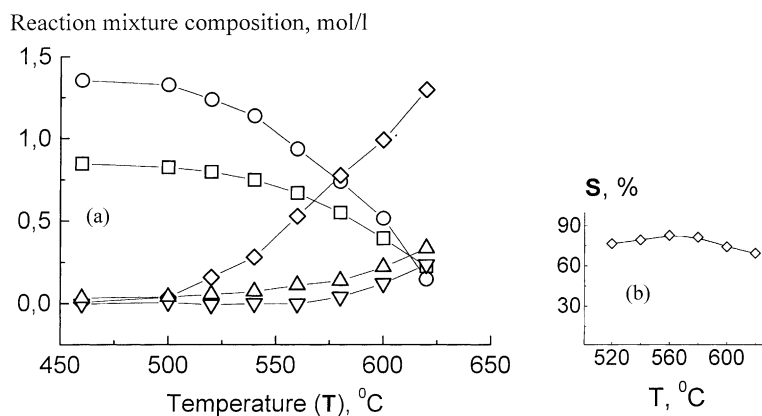
Reaction mixture composition, mol/l

Fig. 5. Temperature effect on: (a) reaction mixture composition; (b) linalool selectivity. (–□–) *trans*-pinane-2-ol, (–○–) *cis*-pinane-2-ol, (–◇–) linalool, (–△–) hydrocarbons C_1–C_6, (–∇–) 5-membered cyclic alcohols. Reaction conditions: reagent pressure inside the reactor $(P_r) = 10$–15 Torr; mixture composition: pinane-2-ol (20.0 mol%), butanol (78.0 mol%), pyridine (2.0 mol%); contact time $(\tau) = 0.055$ s.

activated state. The obtained $E_{a(cis)}$ and $E_{a(trans)}$ values are much lower than the activation energy of the reaction of cyclohexane pyrolysis at $T = 725$–850 °C (357.4–385.8 kJ/mol), which proceeds by a radical-chain mechanism [7]. This difference in activation energies is obviously related to different mechanisms of the reaction. Isomerization of pinane-2-ol into linalool seems to proceed by a molecular mechanism, which does not require great energy expenses for homolytical breaking of chemical bonds resulting in free radicals.

Table 2
Effect of temperature on *cis/trans*-pinane-2-ol conversion, linalool yield and selectivity[a]

Temperature (°C)	Conversion (%)		Linalool	
	Cis-pinane-2-ol	*Trans*-pinane-2-ol	Yield (%)	Selectivity (%)
460	1.7	1.6	0.6	72.0
500	3.8	4.2	1.8	62.5
520	10.4	7.4	7.1	76.6
540	17.6	13.1	12.6	79.3
560	32.2	22.4	23.6	82.9
580	46.5	36.3	34.6	81.4
600	62.65	54.3	44.2	74.3
620	89.2	73.8	57.8	69.4

[a] Reaction conditions: reagent pressure in the reactor $(P_r) = 10$–15 Torr; mixture composition: pinane-2-ol (20.0 mol%), butanol (78.0 mol%), pyridine (2.0 mol%); contact time $(\tau) = 0.055$ s.

The rate constant of linalool cyclization to 5-membered hydroxyolefines shows a linear dependence on temperature on Arrhenius plot, and activation energy is $E_{a(lin)} = 86.2(\pm 4.0)$ kJ/mol (Fig. 6a). This low $E_{a(lin)}$ value is in agreement with the proposed synchronous mechanism of linalool cyclization [2,12], which includes C=C bond polarization and proton migration.

Comparison of $E_{a(cis)}$, $E_{a(trans)}$, and $E_{a(lin)}$ values evidences that rise in temperature should result in an increase in linalool selectivity. The observed decrease in selectivity at $T = 620$ °C is due to an increase in the contribution of free radical processes yielding hydrocarbons C_1–C_6 (Fig. 5b).

For isomerization of the mixture of *cis*- and *trans*-pinane-2-ol the contact time and other experimental conditions were the same for both components in each individual test. Taking into account that the reaction rate is of the first order by reagent concentration, the ratio of the constants of the observed reaction rates for *cis*- and *trans*-pinane-2-ol isomerization (k_{cis} and k_{trans}) can be expressed by the initial C_{0cis} and C_{0trans} and current C_{cis} and C_{trans} values:

$$\frac{k_{cis}}{k_{trans}} = \frac{\ln(C_{cis}/C_{0cis})}{\ln(C_{trans}/C_{0trans})}$$

The ratio k_{cis}/k_{trans} determined from this expression remains constant with increasing temperature (Fig. 6b).
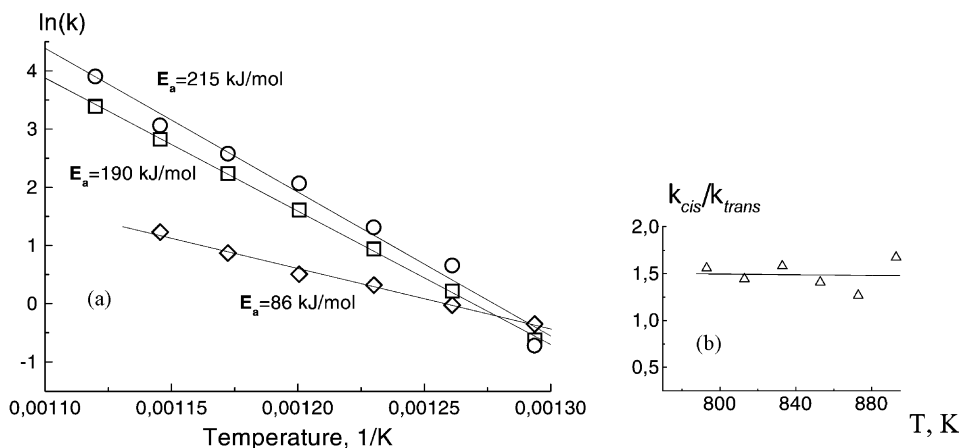
Fig. 6. Temperature effect on: (a) observed reaction rate constants (k) in Arrhenius coordinates; (b) ratio of observed reaction rate constants for pinane-2-ol isomers (k_{cis}/k_{trans}). (–□–) trans-pinane-2-ol, (–○–) cis-pinane-2-ol, (–◇–) linalool. Reaction conditions: reagent pressure in the reactor (P_r) = 10–15 Torr; mixture composition: pinane-2-ol (20.0 mol%), butanol (78.0 mol%), pyridine (2.0 mol%); contact time (τ) = 0.055 s.

The mean value k_{cis}/k_{trans} is 1.49 (±0.06) which is in agreement with k_{cis}/k_{trans} = 1.73 (±0.04) obtained in experiments with different contact times at T = 560 °C.

3.2.4. Reactivity of cis- and trans-isomers of pinane-2-ol

Close values $E_{a(cis)}$ and $E_{a(trans)}$ indicate that activation of both cis- and trans-pinane-2-ol requires approximately the same energy. The higher value of k_{cis} in comparison with k_{trans} is due to the higher pre-exponential factor, which characterizes the probability of transition of activated molecule into reaction product. The most probable cause of this difference is the steric effect of –CH$_3$ group of trans-isomer.

This group hinders favorable orientation of proton of –OH group relative tertiary carbon atom of pinanyl ring.
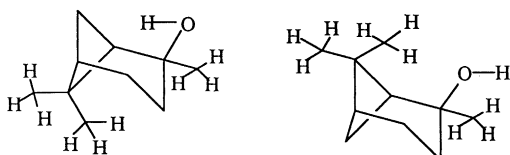
Cis-pinane-2-ol   Trans-pinane-2-ol

3.3. Supposed mechanism of pinane-2-ol isomerization

Pinane-2-ol molecule can pass into excited state with vibrational energy enough for homolytic breaking of C–C bond (~420 kJ/mol) because of absorption of infra-red radiation emitted by the heated catalyst surface or impact of the molecule with the heated catalyst surface or some molecule of gas phase. The resulting biradical can initiate growth of the radical chain in pinane-2-ol conversion. However, some experimental results cannot be explained by a radical chain mechanism. These are high selectivity of breaking of two particular C–C bonds of pinanyl ring and formation of a negligible amount of low-molecular hydrocarbons C$_1$–C$_6$. To estimate the mean energy acquired by pinane-2-ol molecule when passing through the heated catalyst, we obtained the dependence of watt consumption on the rate of reaction mixture feed into reactor (Fig. 7). The results obtained show that when passing through the heated reactor pinane-2-ol molecule acquires mean energy as low as 31 (±1.4) kJ/mol. This corresponds to thermal excitation only translational, rotational and three vibrational degrees of freedom. It is unlikely that pinane-2-ol molecule acquires energy enough for C–C bond destruction with free radical formation. Obviously, pinane-2-ol isomerization must proceed by
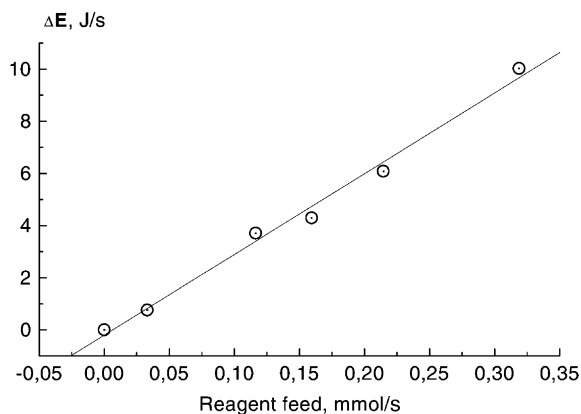
Fig. 7. Dependence of watt consumption of the electroconductive unit-type catalyst on reagent feed. Reaction conditions: $T = 560\,°C$; mixture composition: pinane-2-ol (8 mol%), butanol (90.5 mol%), pyridine (1.5 mol%); contact time $(\tau) = 0.055\,s$.

energetically beneficial pathway. Note that selective opening of 4-membered cycle of pinanyl ring readily proceeds under the influence of even weak acids [13].
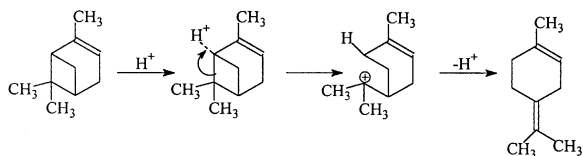

Thermal excitation of O–H bond vibration level must facilitate proton separation. Molecule adsorption at the pyrolytic carbon surface, which has mobile π-electrons, can facilitate redistribution of electron density in the molecule. Thus at high temperature, reactions of intramolecular protonation/deprotonation with participation of O–H group proton are possible.
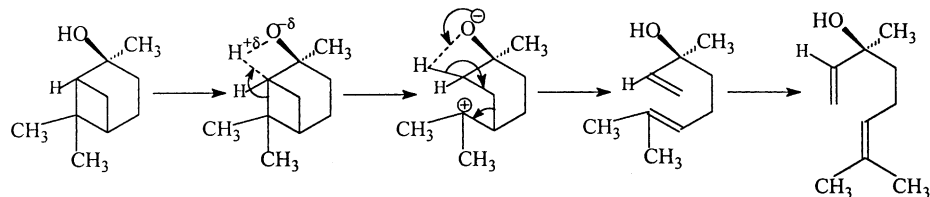
Intramolecular attack of tertiary carbon atom by O–H group proton results in breaking of C–C bond of 4-membered ring. Further redistribution of electron density results in breaking of C–C bond of 6-membered ring, formation of two olefin bonds and recovering of O–H bond.

3.4. Scheme of pinane-2-ol transformation

On the basis of results obtained the general scheme of linalool as well as side products formation have been suggested.
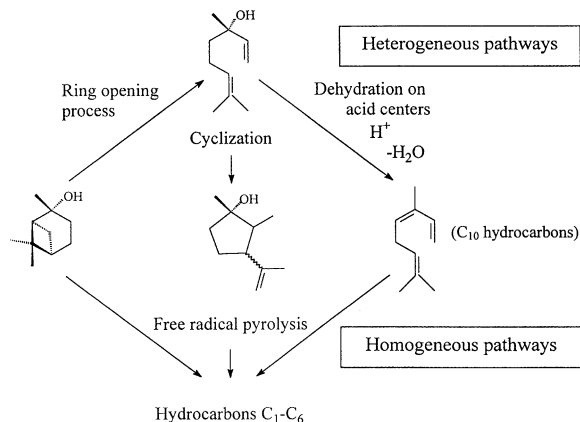
The scheme consists of heterogeneous and homogeneous pathways of irreversible routs of reagent and intermediates conversion. Heterogeneous pathway includes the ring opening reaction of pinane-2 molecule giving the aimed product linalool. Subsequent linalool conversion proceeds by two parallel routes: (i) cyclization to the mixture of 5-membered hydroxyolefines and (ii) dehydration on acid centers of catalyst surface giving C_{10} hydrocarbons.

Homogeneous pathway includes the pyrolysis of pinane-2-ol, linalool, 5-membered hydroxyolefines and C_{10}—hydrocarbons by free radical mechanism resulting in C_1–C_6 hydrocarbons formation as well as coke deposition on the catalyst surface.

4. Conclusions

1. The effect of heterogeneous and homogeneous pathways on the process of pinane-2-ol isomeriza-

tion has been studied and the scheme of pinane-2-ol transformation has been suggested.

2. The kinetics of pinane-2-ol isomerization has been studied and the mechanism of linalool formation is suggested. The key factors determining the selectivity of linalool formation have been clarified.

3. The results obtained can be used for development of an effective method for preparation of linalool—the key semiproduct for synthesis of vitamins and fragrant compounds.

References

[1] W. Schmidt-Renner, Mitteilungsblatt Chemische Gesellschaft der DDR 33 (8) (1986) 175.

[2] J.M. Coxon, R.P. Garland, M.P. Hartshorn, Aust. J. Chem. 25 (1972) 353.

[3] V.A. Semikolenov, I.I. Ilyna, I.L. Simakova, Appl. Catal. A 211 (1) (1991) 91.

[4] V.A. Semikolenov, I.I. Ilyna, in: Proceedings of the Fifth International Symposium on Heterogeneous Catalysis and Fine Chemicals, Lyon, August 30–September 3, 1999, p. 62.

[5] G. Weygand, G. Hilgetag, Organische-Chemische Experimentierkunst, Verlag, Leipzig, 1964, p. 671.

[6] R.A. Kalinenko, S.G. Shvedova, N.S. Nametkin, Neftekhimia 19 (3) (1979) 415.

[7] R.A. Kalinenko, L.V. Shevel'kova, V.B. Titov, Neftekhimia 16 (1) (1976) 100.

[8] R.B. Satanova, R.A. Kalinenko, N.S. Nametkin, Kinet. Katal. 22 (2) (1981) 291.

[9] J. Tanaka, T. Katagiri, K. Ozawa, Bull. Chem. Soc. Jpn. 44 (1971) 130.

[10] G. Ohloff, E. Klein, Tetrahedron 18 (1962) 37.

[11] V.G. Cherkaev, Trudy VNIISHD 7 (1965) 96.

[12] H. Strickler, G. Ohloff, E.Sz. Kovats, Helv. Chim. Acta 50 (78) (1967) 759.

[13] D.V. Banthorpe, D. Whittaker, Quart. Rev. 20 (3) (1966) 373.