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Kinetics of 2-Pinanol Isomerization to Linalool on the Monolith Carbon-Containing Catalyst

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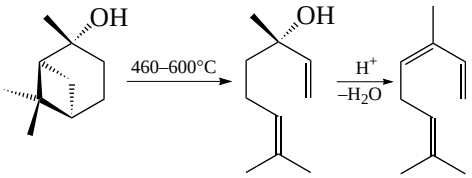
Abstract—Isomerization of 2-pinanol into linalool is studied on a monolith carbon-containing catalyst at 733–893 and a total pressure of 2–40 torr. The rate constants of *cis*(*trans*)-2-pinanol transformation into linalool and linalool cyclization are determined. Experimental data are described by the consecutive kinetic scheme. The mechanism of linalool formation is proposed according to which pinane ring opening occurs in an intramolecular reaction. A highly selective process of linalool synthesis by the thermal isomerization of 2-pinanol is shown to be possible.

INTRODUCTION

Linalool is an important fragrance compound and a reagent in the syntheses of other fragrance compounds and vitamins [1].

A promising method for linalool synthesis is the opening of four- and six-membered cycles in the thermal isomerization of 2-pinanol [2, 3] according to the following scheme:



(I)

However, this process is accompanied by intensive side reactions: dehydration to form a set of unsaturated isomeric C_{10} hydrocarbons, cyclization resulting in numerous 5-membered hydroxyolefins, and deep pyrolysis with carbon deposition on the reactor walls and the formation of light paraffins [2]. The practical implementation of the above scheme of linalool synthesis would be possible if we could know factors affecting the rate of linalool formation and the yields of by-products.

Side reactions can largely be suppressed by carrying the reaction in the reactor with short contact times. Earlier, we proposed a monolith catalyst for the processes of thermal isomerization. This catalyst is heated by passing the electric current through it [3].

The goal of this work was to study the kinetics of 2-pinanol isomerization on the conducting monolith carbon-containing catalyst.

EXPERIMENTAL

The thermal isomerization of 2-pinanol was carried out in a vacuum in a heat-insulated flow-type reactor with a diameter of 30 mm (Fig. 1). The conducting monolith composite catalyst was placed inside the reactor. The catalyst was made of stainless steel with a diameter of 30 mm and a height of 50 mm. The average diameter of pores was 2 mm. The geometric surface area of pores was 30 cm^2. The monolith surface was made of pyrolytic carbon. The construction of the monolith ensured the constant density of electric energy distributed over the whole bulk of the catalyst. The energy consumption of the monolith was 0.5 kW at a voltage of 0–220 V. The maximal working temperature was 1000°C. The catalyst surface temperature was controlled using a mobile thermocouple mounted into a

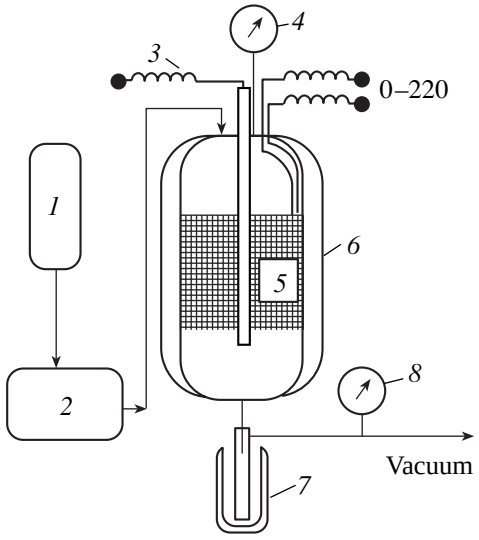


Fig. 1. Schematic of the flow-type reactor for 2-pinanol pyrolysis: (*1*) burette with 2-pinanol; (*2*) dosing pump; (*3*) thermocouple; (*4*, *8*) vacuum gauge; (*5*) conducting monolith composite catalyst; (*6*) thermal insulator; and (*7*) trap cooled with liquid nitrogen.

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thermocouple well along the vertical axis of the monolith. The reactant pressure before passing through the monolith was controlled by a mercury pressure gauge.

A solution of 2-pinanol (or linalool) in butanol-1 was dosed into a vaporizer on the top of the reactor. After passing through the heated monolith catalyst, products were collected in a liquid-nitrogen-cooled trap connected to a vacuum pump. The pressure at the reactor outlet (P_0) was set by the reduction gear connected to the vacuum-pump line and measured with a mercury gauge.

Products were identified by chromatography coupled with mass spectrometry using a VG-7070 instrument. Data from [2] were taken into account.

The concentrations of products in the reaction mixture were analyzed by chromatography (flame-ionization detector, 7 m × 3 mm column packed by Silicone SE 30 on Chromaton (0.16–0.20-mm fraction)), nitrogen carrier gas supplied at a rate of 30 ml/min. The retention times of the main components (T = 100–200°C, 4°C/min) were as follows: linalool, 970 s; *trans*-2-pinanol, 1140 s; and *cis*-2-pinanol, 1190 s.

RESULTS AND DISCUSSION

Choice of Conditions for 2-Pinanol Conversion

The products of the thermal isomerization of the mixture of *cis*- and *trans*-2-pinanol contained the initial reactant, target linalool, and three groups of by-products: unsaturated 5-membered cyclic alcohols (pyrolysis alcohols), hydrocarbons with the formula $C_{10}H_{16}$, and a set of light C_1–C_6 hydrocarbons. The ratio between the products substantially depended on reaction conditions. With an increase in P_0 above 25 torr, we observed a drastic increase in the formation of light C_1–C_6 hydrocarbons due to the transformation of the initial 2-pinanol via the mechanism of deep pyrolysis. The pyrolysis of cyclic hydrocarbons occurs via the branched chain mechanism [4, 5], and the rate of radical decay on reactor walls is determined by the ratio of the free path of molecules and the distance between reactor walls. Assuming that the effective diameter of 2-pinanol σ is 0.7 nm and that the reaction temperature T is 825 K, the average free path λ can be estimated using the formula

$$\lambda = kT/(2^{1/2}\pi\sigma^2 P_{\text{eff}}),$$

where P_{eff} is the effective pressure and k is the Boltzmann constant.

Our estimates show that for $P_{\text{eff}} \approx 20$ torr, λ is approximately 2 mm, which corresponds to the average diameter of monolith catalyst pores. Thus, a decrease in the yield of light C_1–C_6 hydrocarbons with a decrease in the pressure is stipulated by suppressing the radical route of deep 2-pinanol pyrolysis.

The intensive formation of $C_{10}H_{16}$ hydrocarbons probably occurs due to the dehydration of terpene alcohols on acid microadmixtures, which are present on the reactor walls or on the monolith surface. The introduction of pyridine in small amounts (1.5–2 mol %) results in a substantial increase in the selectivity to linalool (the selectivity to linalool S is measured as a ratio of linalool to the sum of all products in moles; it is measured in percents) as shown in Fig. 2. The selectivity increases due to a decrease in the yield of hydrocarbons $C_{10}H_{16}$ to ~5%. When the molar fraction of pyridine is varied within 0–16%, the concentration of *cis*- and *trans*-2-pinanol in reaction products remains virtually the same. This points to the fact that the formation of hydrocarbons $C_{10}H_{16}$ largely occurs via the dehydration of linalool rather than from initial 2-pinanol (Scheme (I)).

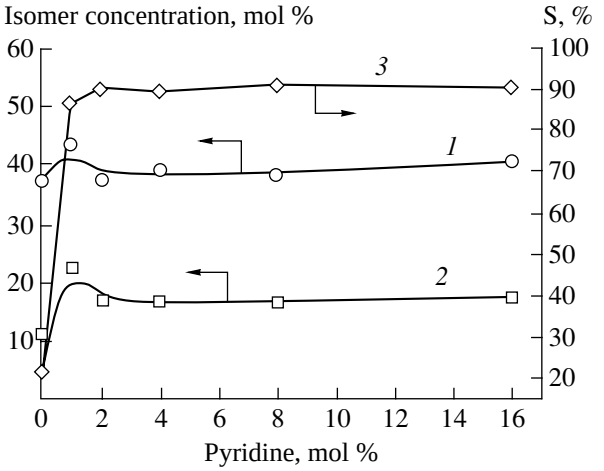


Fig. 2. Dependence of the concentration of (*1*) *cis*- and (*2*) *trans*-2-pinanol and (*3*) selectivity to linalool on the concentration of pyridine in the mixture. Reaction conditions: T = 560°C; composition of the reaction mixture: *n*-butanol/2-pinanol = 9/1 mol/mol, *cis*/*trans*-2-pinanol = 3.0; the rate of mixture supply w = 1.0 ml/min.

Further experiments were carried out using the mixture containing 1.5–2 mol % pyridine, which suppressed linalool dehydration almost completely.

Influence of Effective Pressure in the Reaction Zone

When the process is carried out in a flow-type reactor, the value of P_{eff} is the sum of pressures at the reactor outlet P_0 and the pressure difference ΔP between outlet and inlet of the reactor bed:

$$P_{\text{eff}} = P_0 + \Delta P.$$

When the process is carried out in a vacuum ($P_0 \cong 0$), the effective pressure is largely determined by ΔP, which in turn is related to the flow of substance N (mol/min) through the reaction zone:

$$N = D\Delta P,$$

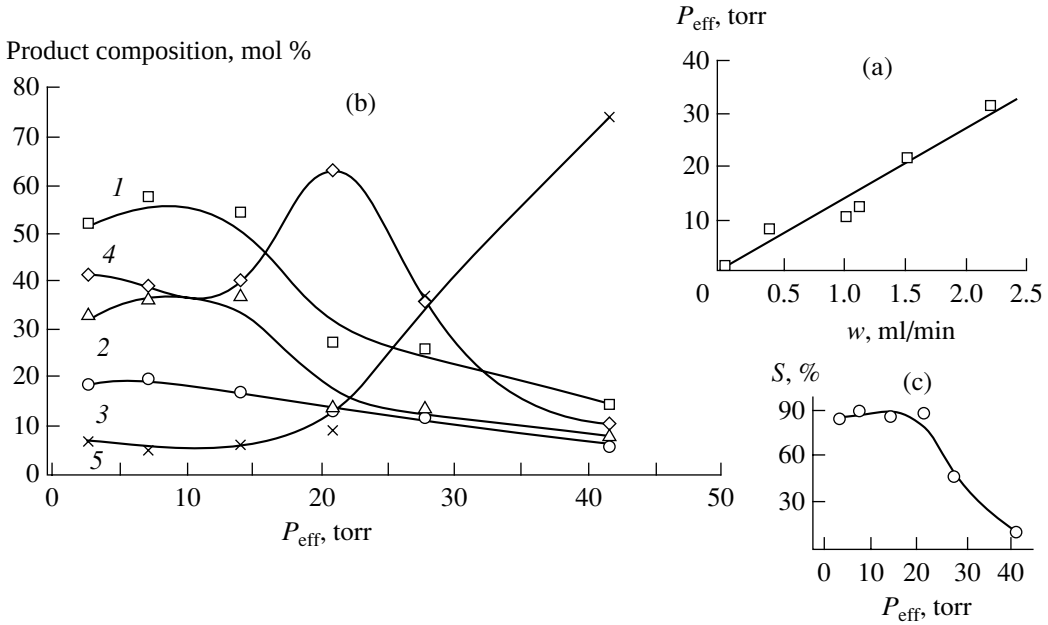


Fig. 3. Dependence of (a) the effective pressure in the reaction zone on the rate of mixture supply w, (b) the composition of the reaction mixture, and (c) the selectivity to linalool on the effective pressure in the reaction zone: (*1*) sum of *cis*- and *trans*-2-pinanols; (*2*) *cis*-2-pinanol; (*3*) *trans*-2-pinanol; (*4*) linalool; and (*5*) hydrocarbons C_1–C_6. Reaction conditions: T = 560°C; composition of the reaction mixture: pinanol, 8 mol %; butanol, 90.5 mol %; pyridine, 1.5 mol %; the contact time τ, 0.055 s.

where D is the hydrodynamic resistance of the reaction zone. Then, the effective pressure in the reaction zone would depend on the rate of 2-pinanol supply:

$$P_{eff} = P_0 + N/D = P_0 + \alpha w/D,$$

where α is the overall concentration of components in the reaction mixture (mol/l) and w is the rate of reaction mixture supply (ml/min).

Indeed, the experimental dependence of the effective pressure on the rate of reaction mixture supply (Fig. 3a) is described by the linear function

$$P_{eff} = 0.268 + 13.76w.$$

Thus, by varying the rate w of reaction mixture supply, one can obtain data on the effect of P_{eff} on the process of the thermal isomerization of 2-pinanol (Fig. 3b). In the general case, the contact time τ is determined as a ratio of the reaction zone volume (V_{Cat}) and the space velocity of reagent supply (V) at the reaction temperature (T). Therefore, the contact time depends on w. After simple rearrangements, we obtain using $V = NRT/P_{eff}$ that

$$\tau = V_{Cat}(P_0 + \alpha w/D)/(\alpha wRT).$$

Analysis of this expression shows that the value τ decreases with an increase in w in the region of higher values of P_0 ($P_0 \gg \alpha w/D$) and tends to a constant value in the region of low values of P_0 ($P_0 \ll \alpha w/D$). Therefore, in the studied range of the flow rates of regent mixture supply, the contact time remains virtually constant, and the apparent effect on the process of the thermal isomerization of 2-pinanol is due to P_{eff} (Fig. 3b). At low P_{eff} (3–15 torr), the relative concentration of reactants and products remains constant. This points to the apparent first order of the reaction rate with respect to the 2-pinanol pressure. With an increase in the effective pressure to 20 torr, a drastic decrease in the 2-pinanol concentration is observed (this is largely due to the conversion of the *cis* isomer) and the yield of linalool increases. A further increase in P_{eff} results in a gradual decrease in the 2-pinanol concentration and a drastic increase in the yield of by-products (C_1–C_6 hydrocarbons). The selectivity to linalool remains at the level of 90% at P_{eff} = 3–25 torr and decreases to 10% at higher values of P_{eff} (Fig. 3c).

The kinetics and mechanism of the pyrolysis of cyclic aliphatic hydrocarbons have been studied earlier [4–6]. Three-, four-, and five-membered ring opening occurs via a unimolecular mechanism at temperatures below 600°C and a lowered pressure [4]. At a temperature higher than 700°C and pressures of 30–760 torr, cyclohexane ring opening occurs via a radical chain mechanism [5]. Molecular reactions are not excluded.

Apparently, the thermal isomerization of penane-2-ol occurs mostly via the unimolecular mechanism at P_{eff} = 3–15 torr (Fig. 3b) which enables the high selectivity to linalool. At a higher value of $P_{eff} \geq 20$ torr, the contribution from the radical chain mechanism for four- and six-membered ring opening in pinane increases. This results in an increase in 2-pinanol conversion and the yield of C_1–C_6 hydrocarbons whose formation is characteristic of the radical chain processes of pyrolysis [4–6].

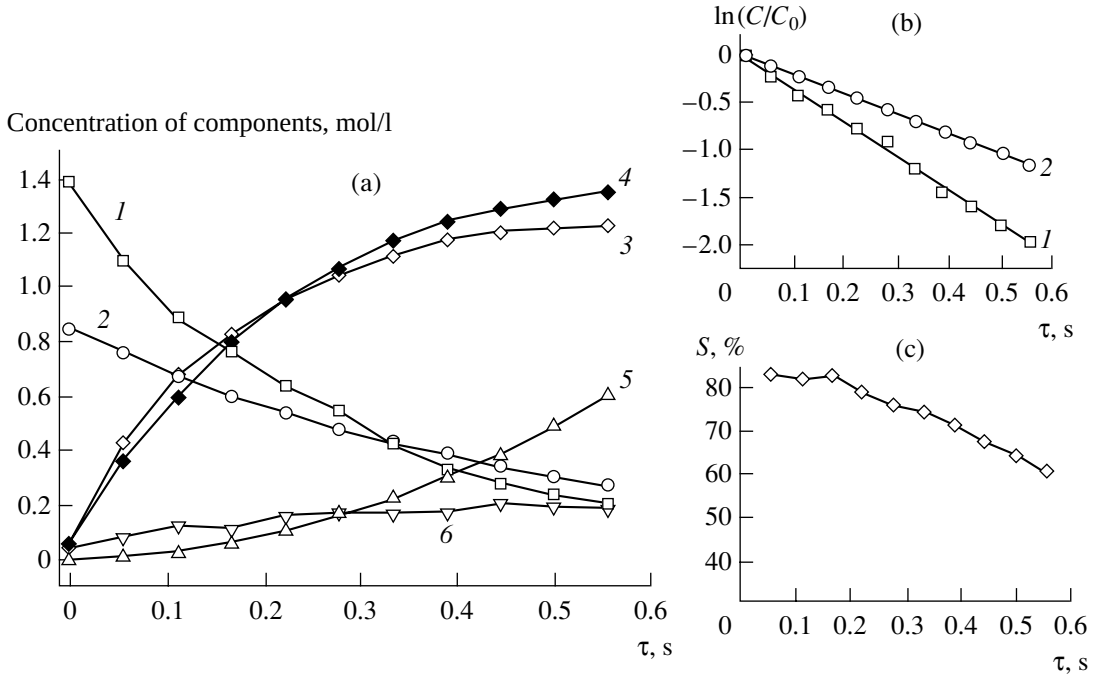
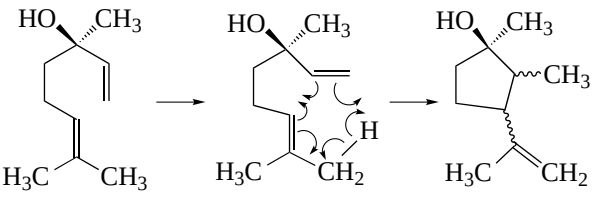


Fig. 4. Dependence of the composition of the reaction mixture on the contact time (τ) in 2-pinanol pyrolysis: (a) a plot of concentration vs. contact time: (*1*) *cis*-2-pinanol, (*2*) *trans*-2-pinanol, (*3*) linalool, (*4*) calculated concentration of linalool, (*5*) five-membered pyrolysis alcohols, and (*6*) hydrocarbons; (b) the same plot in semilogarithmic coordinates: (*1*) *cis*-2-pinanol and (*2*) *trans*-2-pinanol; (c) selectivity to linalool. Reaction conditions: $T = 560°C$; $P_{eff} = 10–15$ torr, the initial composition of the reaction mixture: pinanol, 20 mol %; butanol, 78 mol %; pyridine, 2 mol %.

Effect of the Contact Time

To obtain the dependence of the product composition on the contact time (Fig. 4a), we carried out the following series of experiments. A portion of the reactant mixture passed at a constant rate through a reactor heated to a desired temperature. Products at the reactor outlet were collected in a trap cooled with liquid nitrogen. Then, the samples were withdrawn for GLC analysis, and the rest of the products were used to pass additionally through a reactor under identical conditions (the same temperature and effective pressure). A change in the product composition from the reactor inlet to its outlet corresponded to the reaction extent for the contact time τ. After *n* passes through the reactor, the product composition corresponded to the contact time *n*τ.

The concentrations of *cis*-2-pinanol and *trans*-2-pinanol in the reaction products monotonically decrease with an increase in the contact time (Fig. 4a). The dependences of the relative concentrations of these isomers on τ in semilogarithmic coordinates are linear. This fact suggests the apparent first order of the reaction with respect to the concentration of isomers (Fig. 4b). The calculated values of the apparent rate constant of *cis*-2-pinanol k_{cis} is 3.56 s^{-1} and the respective constant of *trans*-2-pinanol k_{trans} is 2.06 s^{-1}. The concentration of linalool increases and reaches the maximum at τ = 0.5–0.6 s and further gradually decreases. The concentration of by-product 5-membered hydroxyolefins monotonically increases with an increase in τ (Fig. 4a). A decrease in the selectivity to linalool with an increase in τ (Fig. 4c) points to the fact that the kinetic scheme of the thermal isomerization of 2-pinanol includes the route of linalool conversion into 5-membered hydroxyolefins. The authors of [2, 7, 8] believe that linalool cyclization into 5-membered hydroxyolefins occurs via the intramolecular migration of hydrogen according to the scheme



We studied kinetics of linalool conversion under the conditions identical to the conditions of 2-pinanol thermal isomerization (Fig. 5a). With an increase in the contact time, a monotonic decrease in the concentration of initial linalool and accumulation of stoichiometric amounts of 5-membered hydroxyolefins are observed. The absence of 2-pinanol in the products points to the irreversibility of the thermal isomerization of 2-pinanol to linalool. In semilogarithmic coordinates, a change in the relative concentration of linalool with time is well described by a straight line. This fact points to the first

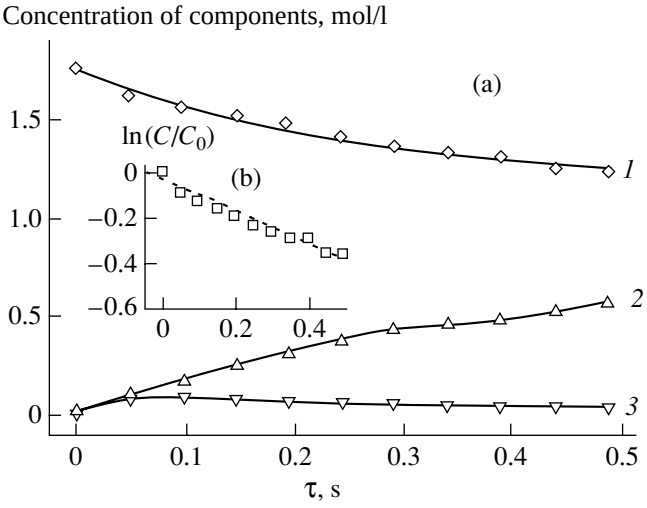
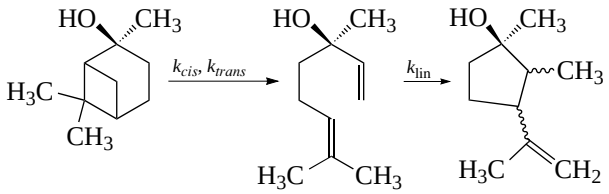


Fig. 5. (a) Dependence of the composition of the reaction mixture on the contact time τ in linalool pyrolysis: (*1*) linalool, (*2*) five-membered pyrolysis alcohols, (*3*) hydrocarbons; (b) dependence of the relative concentration of linalool on time in semilogarithmic coordinates. Reaction conditions: T = 540°C; P_{eff} = 10–15 torr, the initial composition of the reaction mixture: linalool, 20 mol %; butanol, 78 mol %; pyridine, 2 mol %.

order of linalool cyclization reaction with respect to its concentration (Fig. 5b). The value of the apparent rate constant of linalool isomerization k_{lin} is 0.69 s^{-1}. We assume that the thermal isomerization of 2-pinanol into 5-membered hydroxyolefins occurs via the following consecutive kinetic scheme:



Then, the kinetics of isomerization of the mixture of *cis* and *trans* isomers of 2-pinanol can be described by the following set of equations

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

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

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

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

where C_{cis}, C_{trans}, C_{lin}, and C_{hol} are the concentrations of *cis*-2-pinanol, *trans*-2-pinanol, linalool, and 5-membered hydroxyolefins, respectively.

If we neglect the routes of light C_1–C_6 hydrocarbon formation (whose overall yield is lower than 10% based on reacted 2-pinanol) and hydration reactions, the following material balance equation is applicable:

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

where $C_{0,\,cis}$ and $C_{0,\,trans}$ are the initial concentrations of *cis*- and *trans*-2-pinanol. The solution to this set of equations gives the value of linalool concentration:

$$C_{lin} = \frac{k_{cis}C_{0,\,cis}\exp(-k_{cis}\tau)}{k_{lin} - k_{cis}} + \frac{k_{trans}C_{0,\,trans}\exp(-k_{trans}\tau)}{k_{lin} - k_{trans}} + \left(C_{0,\,lin} - \frac{k_{cis}C_{0,\,cis}}{k_{lin} - k_{cis}} - \frac{k_{trans}C_{0,\,trans}}{k_{lin} - k_{trans}}\right)\exp(-k_{lin}\tau).$$

Taking into account the initial concentrations and the obtained values of k_{lin}, k_{cis}, and k_{trans}, we obtain

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

Analysis of this expression suggests that the maximal concentration of linalool in the reaction products may reach 59.05% at a contact time of 0.63 s. This agrees well with experimental data (54% at 0.56 s).

Effect of Temperature

The formation of linalool at a noticeable rate occurs at a temperature beginning from 480°C. The products of the partial opening of the pinane ring, such as terpineol, were not found. With an increase in temperature, a decrease in the concentration of 2-pinanol and an increase in the concentration of linalool (Fig. 6a) are observed. At 510–600°C, the selectivity to linalool decreases from a maximal value of 83% at 560°C to 69% at 620°C (Fig. 6b). The Arrhenius plots of the rate constants of *cis*- and *trans*-2-pinanol are linear (Fig. 7a). The apparent activation energy of *cis*- and *trans*-2-pinanol conversion differ insignificantly: $E_{a,\,cis}$ = 215.1 and $E_{a,\,trans}$ = 190.3 kJ/mol. Apparently, the configuration of the 2-pinanol molecule does not affect the energy of its transition to the activated state. The values of $E_{a,\,cis}$ and $E_{a,\,trans}$ are significantly lower than the activation energy found for cyclohexane pyrolysis at 725–850°C (357.4–385.8 kJ/mol), which occurs via the radical chain mechanism [5]. This difference in the activation energy is probably due to the difference in the mechanisms. The isomerization of 2-pinanol into linalool occurs most likely via the molecular mechanism that does not require substantial energy expenses for the homolytic cleavage of chemical bonds with the formation of free radicals.

The Arrhenius plot for the rate constant of linalool cyclization into 5-membered hydroxyolefins is linear.

The activation energy is $E_{a,\,lin}$ = 86.2 kJ/mol (Fig. 7a). This low value of activation energy agrees with the proposed synchronous mechanism of linalool cyclization that involves the polymerization of C=C bonds and proton migration [2, 7].

Comparison of the values of $E_{a,\,cis}$, $E_{a,\,trans}$, and $E_{a,\,lin}$ suggests that an increase in temperature should result in an increase in the selectivity to linalool. The apparent decrease in the selectivity at 620°C is stipulated by an increase in the contribution from the radical processes resulting in the formation light C_1–C_6 hydrocarbons (Fig. 6b).

In the isomerization of *cis*- and *trans*-2-pinanol, the contact time and other conditions are identical for both isomers in each experiment in the studied temperature range. Then, taking into account the first order of the reaction with respect to reactant concentrations, the ratio of the apparent rate constants of *cis*- and *trans*-2-pinanol can be expressed in terms of their initial and current concentrations:

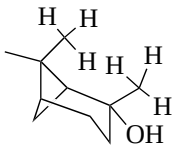
$$k_{cis}/k_{trans} = [\ln(C_{cis}/C_{0,\,cis})]/[\ln(C_{trans}/C_{0,\,trans})].$$

The ratio k_{cis}/k_{trans} remains constant with an increase in temperature (Fig. 7b). The average value of k_{cis}/k_{trans} is 1.5, which is close to the value obtained at 560°C in the experiments with different contact times: k_{cis}/k_{trans} = 1.7.

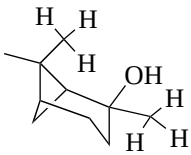
The Reactivity of cis- and trans-2-Pinanol

The close values of $E_{a,\,cis}$ and $E_{a,\,trans}$ point to the fact that, for the transition into the activated state, about the same energy is required for both *cis*- and *trans*-2-pinanol. The higher value of k_{cis} compared to k_{trans} is probably stipulated by the preexponential factor that characterizes the probability of the transition of an activated molecule into the products. The most probable reasons associated with the geometry of *cis*- and *trans*-isomers are

(1) Weakening of C–C bonds in the pinane ring because of the repulsion of bulky CH_3 groups oriented in the same direction in the *cis*-2-pinanol molecule:



(2) Steric shielding of the neighboring tertiary carbon atoms in the pinane ring by the CH_3 group from the alcohol group proton attack:



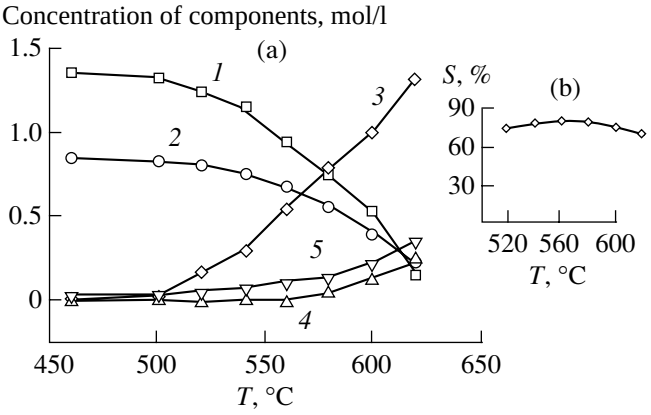


Fig. 6. Temperature dependences of (a) the composition of the reaction mixture ((*1*) *cis*-2-pinanol; (*2*) *trans*-2-pinanol; (*3*) linalool; (*4*) five-membered pyrolysis alcohols; and (*5*) hydrocarbons); (b) the selectivity to linalool. Reaction conditions: P_{eff} = 10–15 torr, the initial composition of the reaction mixture: pinanol, 20 mol %; butanol, 78 mol %; pyridine, 2 mol %; contact time τ, 0.055 s.

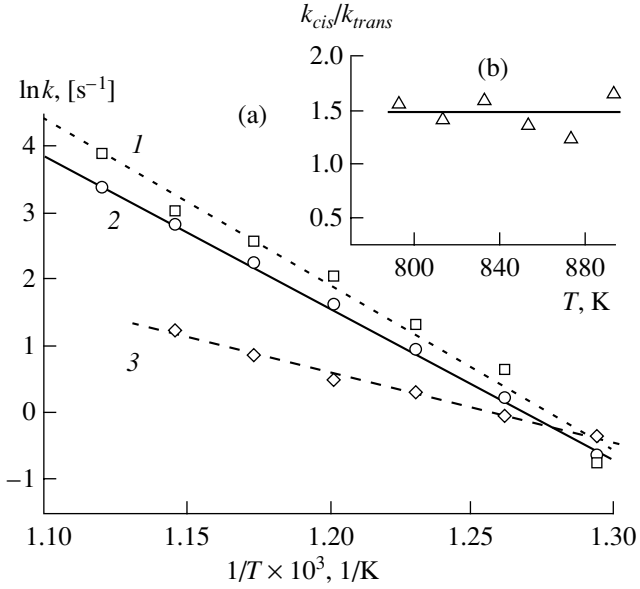


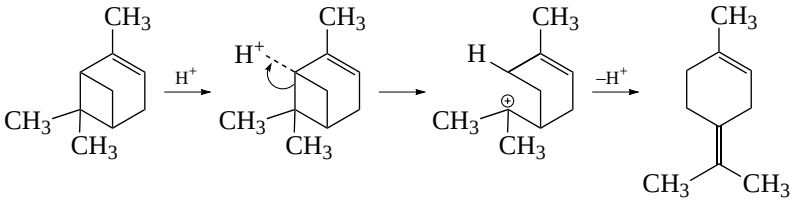
Fig. 7. (a) The Arrhenius plot of the apparent rate constant *k* of the rate of conversion of (*1*) *cis*-2-pinanol; (*2*) *trans*-2-pinanol; and (*3*) linalool; and (b) dependence of the ratio of constants of *cis*-2-pinanol and *trans*-2-pinanol on temperature. Reaction conditions: P_{eff} = 10–15 torr, the initial composition of the reaction mixture: pinanol, 20 mol %; butanol, 78 mol %; pyridine, 2 mol %; contact time τ, 0.055 s.

Assumed Mechanism of 2-Pinanol Isomerization

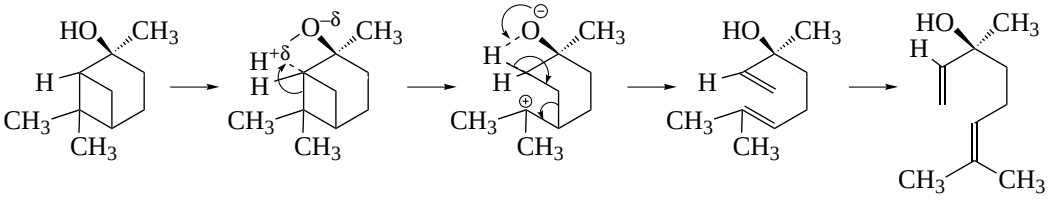
The 2-pinanol molecule has 81 degrees of freedom. When the first vibrational level is completely populated, 2-pinanol can accumulate vibrational energy equal to 81*RT*. In the studied temperature range (480–600°C), this energy is 506.8–587.6 kJ/mol. The

2-pinanol molecule can be excited to accumulate the vibrational energy that is sufficient for the homolytic cleavage of the C–C bond (~420 kJ/mol) due to the consumption of IR radiation emitted by the heated surface of the monolith. Another source of energy can be the collision with the heated surface or any gas-phase molecule. A biradical formed in this process may initiate the propagation of a radical chain of 2-pinanol conversion. However, some experimental data cannot be explained by the radical chain mechanism: the high selectivity of the cleavage of the two C–C bonds in the pinane ring, and the low yields of light C_1–C_6 hydrocarbons.

Note that the selective opening of the four-membered pinane ring readily occurs even under the action of weak acids [9]:



The thermal excitation of the vibrational level of the O–H bond should favor proton abstraction. Thus, intramolecular protonation and OH-group proton-assisted deprotonation are possible at a high temperature:



The intramolecular attack of the OH-group proton results in the cleavage of the C–C bond in the four-membered ring. The further redistribution of the electron density results in a cleavage of the C–C bond in the six-membered ring, the formation of olefin bonds, and the restoration of the O–H bond.

CONCLUSION

Results obtained in this work make it possible to create the highly selective process for the synthesis of linalool, which is a valuable fragrance compound. This process could be based on the thermal isomerization of 2-pinanol. 2-Pinanol can be obtained according to the scheme involving the catalytic hydrogenation of α- and β-pinane, pinane oxidation by air to pinane hydroperoxide, and its further hydrogenation to 2-pinanol.

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