Thermolysis of α-pinene in supercritical lower alcohols*

A. M. Chibiryaev,[a,b]★ *V. I. Anikeev,*[c] *A. Yermakova,*[c] *P. E. Mikenin,*[c] *I. V. Kozhevnikov,*[b] *and O. I. Sal´nikova*[a]

[a]*N. N. Vorozhtsov Novosibirsk Institute of Organic Chemistry, Siberian Branch of the Russian Academy of Sciences,*
9 prosp. Akad. Lavrent´eva, 630090 Novosibirsk, Russian Federation.
Fax: +7 (383) 330 9752. E-mail: chibirv@nioch.nsc.ru
[b]*Department of Natural Sciences, Novosibirsk State University,*
2 ul. Pirogova, 630090 Novosibirsk, Russian Federation
[c]*G. K. Boreskov Institute of Catalysis, Siberian Branch of the Russian Academy of Sciences,*
5 prosp. Akad. Lavrent´eva, 630090 Novosibirsk, Russian Federation

Thermal isomerization of α-pinene in supercritical solvents, *viz*., ethanol, methanol, and propan-1-ol, was carried out, and differences in the rate and selectivity of the process were revealed. In supercritical ethanol the reaction rate increases sharply and the selectivity remains unchanged with an increase in the temperature (from 290 to 390 °C) or pressure (from 90 to 270 atm). The main reaction products are limonene, isomeric alloocimenes, and pyronenes. The selectivity for limonene in propan-1-ol is higher than in other alcohols when the conversion of α-pinene not higher than 50%. In supercritical ethanol (430 °C, 120 atm, 140 s) limonene is more stable than α-pinene (conversion 8%).

Key words: thermal isomerization, thermolysis, supercritical media, monoterpenes, α-pinene, limonene, alloocimene, pyronene, alcohols.

Organic synthesis in supercritical media is a modern, dynamically developing branch of organic chemistry.[1—4] However, transformations of terpenoid hydrocarbons and their functional derivatives in supercritical media remain virtually unstudied. Only single examples for the catalytic hydrogenation of terpenoids in supercritical CO_2 [5] and subcritical water[6] are known, as well as the esterification of some terpenoid alcohols.[7]

The purpose of the present work is to study transformations of α-pinene in supercritical alcohols (methanol, ethanol, and propan-1-ol) and reveal a relationship of the temperature and pressure to the reaction rate and the influence of the residence time on the conversion.

Experimental

(+)-α-Pinene (≥98%) and (+)-limonene (≥97%) were purchased from Aldrich.

Thermal isomerization under supercritical conditions was carried out in a laboratory setup using a tubular flow-type reactor 6 m long and 1.75 mm in diameter (the reactor volume was about 14 cm^3). A solution of the starting substance was supplied by a piston pump to the reactor from which the reaction mixture was transferred to a heat exchanger for subsequent cooling and further to a separator where samples for analysis were taken.

The composition of the reaction products was analyzed by the GC-MS method on a Hewlett-Packard 5890/II gas chromatograph with an HP MSD 5971 quadrupole mass spectrometer as a detector. An HP-5 quartz column (30 m × 0.25 mm) was used (copolymer of 5% diphenyl- and 95% dimethylsiloxane as the stationary phase, the film thickness 0.25 μm); the carrier gas was helium with a constant flow rate of 1 mL min^{-1}; the injector temperature was 280 °C; temperature programming: 50 °C (2 min), 50—200 °C (4 °C min^{-1}), 200—300 °C (20 °C min^{-1}), 300 °C (20 min); the energy of ionizing electrons was 70 eV. Qualitative analysis was performed comparing retention indices of components and their complete mass spectra with the corresponding data for pure compounds if any and with the data of the Wiley7 library of mass-spectrometric data (375000 mass spectra) and catalogue.[8] The percentage composition of mixtures was calculated from the surface areas of chromatographic peaks using no correction coefficients.

Results and Discussion

The behavior of α-pinene in supercritical 96% ethanol was studied at T = 290—390 °C and P = 90—270 atm, which are higher than the critical parameters of the alcohol (T_{cr} = 519.3 K (~246 °C), P_{cr} = 67.6 atm). The experimental data are presented in Tables 1 and 2 and Figs 1—3.

The temperature and pressure intervals of the process were chosen taking into account the following. It was experimentally found that the noticeable conversion of α-pinene was observed at the temperature and pressure higher than the critical parameters of the alcohol. Therefore, the lower boundary of the T and P values is deter-

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Table 1. Composition of the reaction mixture for α-pinene thermolysis in supercritical MeOH, EtOH, and PrOH at different residence times τ (300 °C, 100 atm, 0.1 mol L^{-1})

Component of mixture	Alcohol	Content (%) at τ/s				
		30	70	140	200	300
α-Pinene	MeOH	99.6	96.2	91.3	87.2	75.8
	EtOH	98.7	94.7	86.9	77.6	59.7
	PrOH	97.6	—	67.3	51.3	28.7
Limonene	MeOH	0	2.5	5.8	9.0	15.0
	EtOH	0.9	3.6	9.9	16.3	25.2
	PrOH	2.4	—	27.5	39.4	40.0
α-Pyronene	MeOH	0	0	0.1	0.2	0.3
	EtOH	0	0	0.2	0.4	0.8
	PrOH	0	—	0.6	1.3	1.0
β-Pyronene	MeOH	0	0	0	0	0.1
	EtOH	0	0	0	0	0.2
	PrOH	0	—	0.2	0.5	0.6
Alloocimene	MeOH	0	1.1	2.2	2.6	7.0
	EtOH	0	1.2	2.1	4.4	10.1
	PrOH	0	—	0	1.5	2.7
neo-Alloocimene	MeOH	0	0.2	0.4	0.6	1.4
	EtOH	0	0.5	0.9	1.3	4.0
	PrOH	0	—	0	0.5	1.9
Other products (total)	MeOH	0.4	0	0.2	0.4	0.4
	EtOH	0.4	0	0	0	0
	PrOH	0	—	4.4	5.5	25.1

Table 2. Composition of the reaction mixture for limonene thermolysis in supercritical ethanol at different temperatures (residence time 140 s, 120 atm, 0.1 mol L^{-1})

Component	Content (%)	
	330 °C	430 °C
α-Pinene	2.9	4.3
Limonene	97.0	92.1
α-Pyronene	0	0.6
β-Pyronene	0	0.9
Alloocimene	0	0
neo-Alloocimene	0	0
Other products (total)	0.1	2.1

mined by the required rate of α-pinene conversion. The upper limit of the *T* and *P* values of the process is restricted by thermal stability of the solvent. For instance, in the isothermal regime (330 °C) at pressures higher than 200 atm or in the isobaric regime (120 atm) at temperatures above 370 °C, gaseous substances, *viz.*, products of alcohol decomposition, are formed, and this process is intensified with the further increase in the temperature and pressure in the reactor.

Experiments in supercritical ethanol showed that the single transformation of α-pinene under these conditions was its thermolysis (Scheme 1).

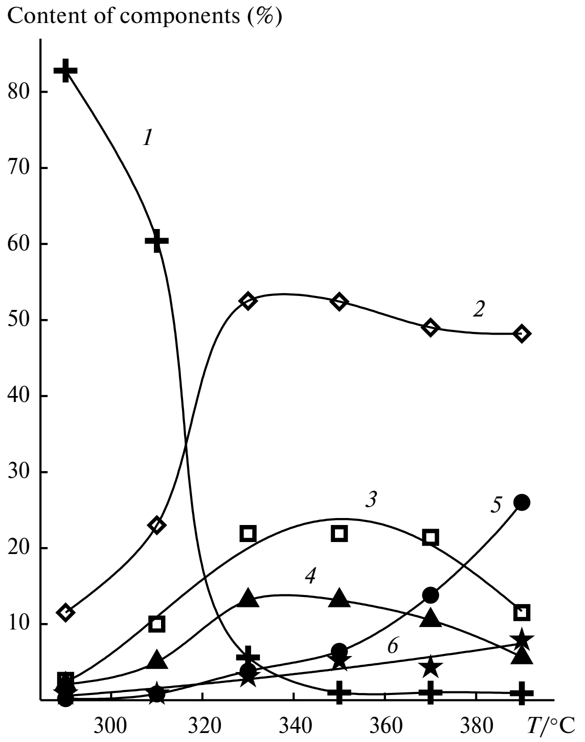


Fig. 1. Temperature effect on the isomerization rate of α-pinene in supercritical ethanol (residence time 70 s, 120 atm, 0.1 mol L^{-1}): pinene (*1*), limonene (*2*), alloocimene (*3*), *neo*-alloocimene (*4*), pyronenes (*5*), and other products (*6*).

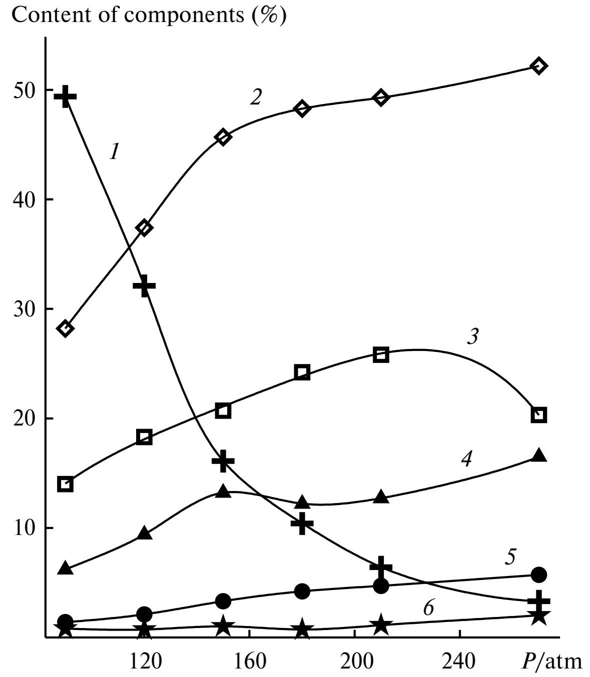


Fig. 2. Pressure effect on the isomerization rate of α-pinene in supercritical ethanol (residence time 70 s, 330 °C, 0.1 mol L^{-1}): pinene (*1*), limonene (*2*), alloocimene (*3*), *neo*-alloocimene (*4*), pyronenes (*5*), and other products (*6*).

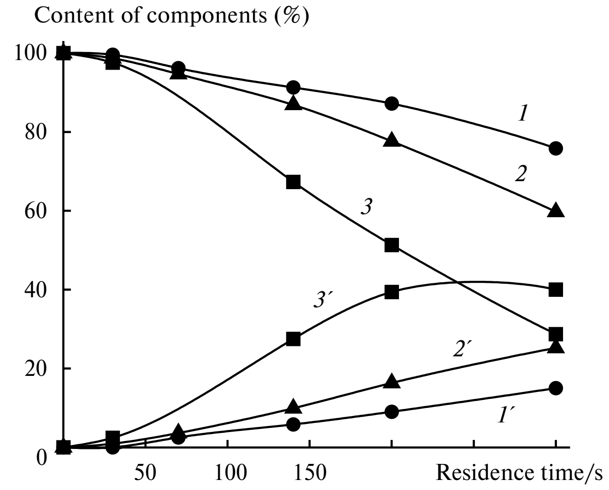
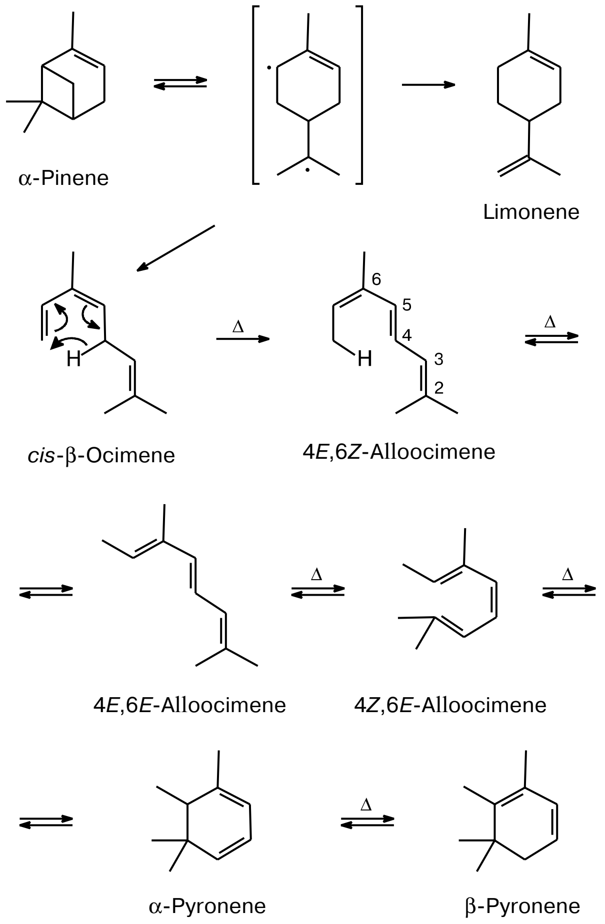


Fig. 3. Effect of the residence time on the degree of α-pinene isomerization in supercritical alcohols (300 °C, 100 atm, 0.1 mol L^{-1}): MeOH (*1*, *1*′), EtOH (*2*, *2*′), and PrOH (*3*, *3*′); curves *1*—*3* indicate the consumption of α-pinene, and curves *1*′—*3*′ show the accumulation of limonene.

Scheme 1



A similar composition of the conversion products was obtained earlier during the gas-phase[9—16] and liquid-phase[12,13,17—19] thermal isomerization of α-pinene, which was studied in the temperature interval from 180 to 500 °C and at residence times from several hours (gas-phase reaction) to several days (liquid-phase process). Published data show that prolong heating at a high temperature is required for α-pinene to achieve the 90—95% conversion, and the heating is inevitably followed by an increase in the fraction of by-products. The effect of the pressure in the reactor on the thermolysis rate of α-pinene has not been studied earlier.

Taking into account industrial significance of α-pinene and limonene,[20] we believe that the study of the effect of the supercritical medium on the direction and selectivity of the transformation and search for conditions for the enhancement of the limonene yield are of practical interest.

Temperature effect. In the isobaric regime (P_{const} = 120 atm) the conversion of α-pinene increases from 17 up to ~99% with an increase in the reaction temperature from 290 to 390 °C (see Fig. 1). In this case, the yield (concentration) of transformation products (limonene and isomeric alloocimenes) reaches the maximum value at 350±20 °C (53 and 35%, respectively), after which their concentration decreases.

On the contrary, the content of α- and β-pyronenes in the mixture tends to increase in the chosen temperature range and achieves the maximum value (26%) at 390 °C. This is somewhat lower than the yield attained in the gas-phase reaction at 410±15 °C (35—45%).[10,18,21] At 290 and 310 °C the reaction mixture contains ~0.4% *cis*-β-ocimene, which can indirectly confirm the proposed mechanism (see Scheme 1). The absence of noticeable amounts of this triene during thermolysis is usually related to the fact that the triene is rapidly transformed into 4*E*,6*Z*-allooocimene due to the 1,5-hydride shift.[19,22,23]

It should be noted that the amount of other by-products, which are omitted in Scheme 1, also increases with the temperature increase: at 390 °C their overall content is ~8%.

Pressure effect. Based on general considerations only, it is difficult to predict *a priori* the character of the pressure effect on the rate of the transformation under study. The amount of consumed α-pinene is equal to the molar amount of the products (see Scheme 1), *i.e.*, the reaction should not be pressure-sensitive. At the same time, some literature data indicate the acceleration of several reactions in supercritical media with the pressure increase.[24,25]

Experiments showed that under isothermal conditions ($T_{\rm const}$ = 330 °C) the pressure increase from 90 to 270 atm increases the conversion of α-pinene from 51 to 97% (see Fig. 2). The content of limonene in the mixture increases from 28 to 52% and becomes close to the maximum value described for the gas-phase process. The concentration of pyronenes also increases with the pressure increase but more slowly than that for the temperature change. The greatest distinctive features of the isothermal process (as compared to the isobaric process) are related to a change in the content of alloocimenes. Although the maximum total concentration of the latter is higher only by 4% (39%), the dynamics of their individual accumulation is different. At ~210±10 atm the maximum of the allo-ocimene concentration is achieved, while the content of *neo*-alloocimene still continues to grow. In the isobaric process for a change in the reaction temperature, the both indicated isomers had the concentration maximum at the same temperature (see Fig. 1).

The isobaric and isothermal processes differ from each other by the dynamics of accumulation of by-products: their concentration increases more rapidly with a pressure change.

Influence of the solvent nature and residence time. Comparative studies of the influence of the nature of the solvent, *viz*., MeOH, EtOH, and PrOH, on the isomerization rate of α-pinene were performed. The critical parameters of methanol and propan-1-ol differ insignificantly from those for ethanol: $T_{\rm cr}$ = 512.6 K (~239 °C), $P_{\rm cr}$ = 79.9 atm and $T_{\rm cr}$ = 536.7 K (~263 °C), $P_{\rm cr}$ = 51.0 atm, respectively, *i.e.*, on going from methanol to propan-1-ol the critical temperature increases from 239 to 263 °C and the critical pressure decreases from 80 to 51 atm. Ethanol occupies an intermediate position in the series of these alcohols.

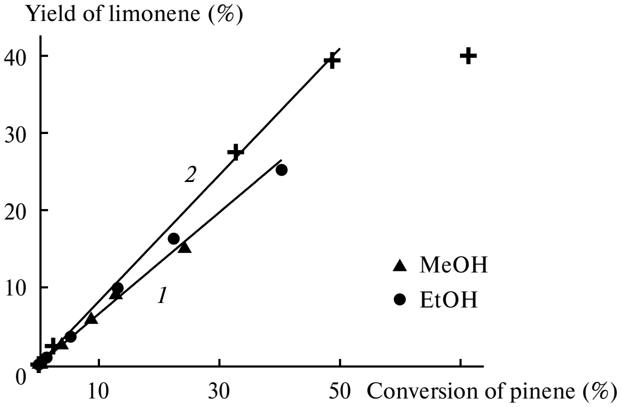


Fig. 4. Selectivity of the conversion for limonene in supercritical alcohols: MeOH and EtOH (*1*) and PrOH (*2*).

In experiments at constant temperature and pressure ($T_{\rm const}$ = 300 °C, $P_{\rm const}$ = 100 atm), the residence time was varied within 30—300 s, which was calculated as the ratio of the reactor volume (cm^3) to the volume consumption (cm^3 s^{-1}) of an alcoholic solution of α-pinene.

The isomerization rates in supercritical alcohols were shown to differ noticeably (see Table 1 and Fig. 4). The conversion of α-pinene at equal *T* and *P* values increases in the series of alcohols C_1—C_3. The maximum concentration of limonene in propan-1-ol is lower than that in the experiment with ethanol in isothermal and isobaric regimes (40% against 52%), and the content of by-products increases to 25% compared to the reactions in methanol and ethanol where the contents of the latter are close to zero (<1%).

Thus, the replacement of one alcohol by another strongly affects the conversion rate. In propan-1-ol (compared to ethanol) the isomerization of pinene to limonene along with other parallel transformations are accelerated (see Table 1).

The selectivity of conversion for limonene, which is determined as the ratio of the yield of limonene to the conversion of α-pinene, is shown in Fig. 4.

The selectivity for limonene in the region of α-pinene conversion $X \leq 0.4$ is the same for methanol and ethanol and equals ~0.66 (see Fig. 4, slope of straight line *1*). In the same conversion range, the selectivity in propan-1-ol is higher and equal to 0.88 (see Fig. 4, line *2*). The selectivity for limonene in propanol decreases with an increase in the conversion of α-pinene (X > 0.5). The yield of by-products increases simultaneously from 13 to 35%.

Thermolysis of limonene in supercritical ethanol. To continue the study of thermolysis of α-pinene with the purpose of possible optimization of the conditions of limonene preparation, it was necessary to elucidate whether limonene underwent any transformations in the supercritical medium or not. It was known beforehand that for the gas-phase transformation of limonene its conversion rate below 415 °C is low but already at 450 °C limonene is consumed completely within the same reaction duration.[26] It can be assumed that at temperatures below 400 °C limonene, which is formed from α-pinene in the supercritical medium, does not react further. This assumption required additional studies, especially after a mixture of products similar to the pyrolysis products of α-pinene has been reported to form from limonene at high temperatures.[27]

To estimate the conversion of limonene, we carried out the thermolysis of its ethanolic solution (see Table 2).

At 330 °C the conversion of limonene is not higher than 3% and the main product of its transformation is α-pinene, which can be formed from limonene as a result of ene reaction.[15] When the temperature increases to 430 °C, the conversion increases insignificantly (~8%) and α- and β-pyronenes appear along with α-pinene; however, alloocimenes are entirely absent in the reaction mixture. According to the proposed mechanism (see Scheme 1), pyronenes are formed from alloocimenes due to intramolecular cyclization.[14,21,28] The absence of alloocimenes in the reaction mixture is related, most likely, to the fact that at 430 °C they are rapidly transformed into α- and β-pyronenes and other pyrolysis products. This is indirectly indicated by the earlier observed decrease in the maximum concentration of alloocimenes in experiments on α-pinene thermolysis at elevated temperatures and pressures (see above).

Thermolysis of α-pinene in the presence of phenol. To study additional possibilities of the process in supercritical media, we carried out the thermolysis of α-pinene (the initial concentration in EtOH is 0.1 mol L^{-1}) in the presence of phenol (concentration 0.3 mol L^{-1}) at T_{const} = 380 °C, three different pressure values (100, 150, and 200 atm), and a residence time of 140 s. However, a phenol additive exerted no noticeable effect on the reaction course. Pinene is consumed completely (residual concentration <0.5%), the concentration of limonene that formed remains close to the maximum value (47—49%), and the content of phenol does not virtually change with the pressure increase. No other compounds, except for the starting phenol and isomerization products of α-pinene, were found in the reaction mixture.

The presence of phenol exerts no effect on the radical character of thermal isomerization of α-pinene (see Scheme 1). This fact confirms available information that the reaction is insensitive to the presence of inhibitors of radical species.[12]

In the conclusion, it has been found that the thermolysis of α-pinene in supercritical alcohols results in the same products as gas-phase and liquid-phase thermal isomerizations. At the same time, the supercritical reaction medium makes it possible to enhance the conversion rate by several orders of magnitude with retention of the reaction selectivity for limonene and isomeric allooocimenes, whose maximum yield is 52 and 38%, respectively. The efficient parameters controlling the reaction rate are the temperature and pressure. A comparative study of the influence of the solvent nature on the isomerization shows that the conversion of α-pinene at the same parameters increases in the series of alcohols C_1—C_3. In the range of chosen temperatures and pressures, limonene is thermally more stable than α-pinene.

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