Comparative thermolysis of β- and α-pinenes in supercritical ethanol: the reaction characterization and enantiomeric ratios of products*

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The thermolysis of β-pinene and the co-thermolysis of an equimolar mixture of β- and α-pinenes in supercritical ethanol were carried out. The reaction of β-pinene affords β-myrcene as the major product (>70%). Considerable differences in the temperature dependence of the reaction rate were revealed for the transformations of β-pinene into β-myrcene and of α-pinene into limonene. The pre-exponential factors and the activation energies were calculated. The enantiomeric ratios of the thermolysis products of β- and α-pinenes and limonene were estimated. The starting monoterpenes do not undergo racemization during thermolysis. The thermolysis of enantiomerically pure α-pinene affords racemic (±)-limonene, whereas (−)-β-pinene gives (−)-limonene. The enantiomeric ratio in the latter remains equal to the enantiomeric purity of the starting β-pinene.

Key words: thermolysis, supercritical media, ethanol, monoterpenes, pinenes, β-myrcene, limonene.

Thermal transformations of terpene hydrocarbons provide the basis for the synthesis of polyunsaturated compounds (dienes, trienes, and aromatics), which are widely used in organic synthesis and in the production of polymer adhesive materials. Limonene and β-myrcene, which are the major components of many essential oils and the key substances of artificial perfumery-cosmetic composites, can be synthesized by the thermolysis of the bicyclic monoterpenes, such as α- and β-pinenes.

Earlier, we have demonstrated[1] that the thermolysis of terpenes can be performed in supercritical media. For example, it was found that the thermolysis of α-pinene in supercritical alcohols (methanol, ethanol, or propan-1-ol) gives acyclic and monocyclic unsaturated nonaromatic compounds, whereas limonene does not undergo thermal transformations under these conditions. In continuing studies of transformations of terpenes in supercritical media, it was of interest to compare the reactivity of structurally similar α- and β-pinenes in the same supercritical solvent.

The aim of the present study was to investigate the thermolysis of β-pinene in supercritical ethanol, to find the temperature dependence of the reaction rate, to reveal the differences in thermal transformations of β- and α-pinenes, and to determine the enantiomeric ratios of the thermolysis products of pinenes and limonene.

Experimental

(−)-β-Pinene (≥99%, sum of enantiomers, Fluka), (+)-α-pinene (≥98 %, sum of enantiomers, Aldrich), and (+)-limonene (≥99 %, sum of enantiomers, Aldrich) were used in experiments.

The thermolysis of terpenes in supercritical ethanol was carried out in a laboratory apparatus using a tubular flow-type reactor with a length of 3 m and a diameter of 1.75 mm; the volume of the reaction zone was 7 mL. A solution of pinene (or a mixture of pinenes) in 96% ethanol was fed to the reactor using a piston pump. Then the reaction mixture was successively passed to a heat exchanger for cooling and to a separator, where samples were taken for analysis. In all cases, the compounds were kept in the active zone of the reactor (the residence time τ) for 70 s. This time was calculated as the ratio of the reaction zone volume (mL) to the volumetric rate, at which the reaction mixture was fed to the reactor (mL min^{-1}).

The compositions of the reaction products were analyzed by gas chromatography mass spectrometry on a Hewlett—Packard 5890/II gas chromatograph equipped with an HP MSD 5971 quadrupole mass spectrometer as the detector. A 30-m HP-5

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quartz column with an inner diameter of 0.25 mm was used; the film thickness of the stationary phase (5% diphenylsiloxane—95% dimethylsiloxane copolymer) was 0.25 μm; helium with a constant flow rate of 1 mL min^{-1} was used as the carrier gas; the injector temperature was 280 °C; the temperature mode: 50 °C (2 min), 50—200 °C (4 °C min^{-1}), 200—300 °C (20 °C min^{-1}), and 300 °C (20 min); the ionizing electron energy was 70 eV. The qualitative analysis was carried out by comparing the retention indices (Kovats indices) of the components and their complete mass spectra with the corresponding data for the pure compounds and with the data from the NIST (190825 compounds) and Wiley (621600 mass spectra) mass spectral libraries and the catalogue.[2] The percentage compositions of the mixtures were calculated from the chromatographic peak areas without using the sensitivity correction coefficients.

The enantiomeric ratios of the starting compounds and the thermolysis products were analyzed by gas chromatography mass spectrometry on a Agilent 6890 gas chromatograph equipped with a 5975 Inert quadrupole mass-selective detector. The mixtures were separated on a 30-m capillary column with an inner diameter of 0.25 mm; the film thickness of the stationary phase (the chiral phase CycloSil-B) was 0.25 μm; helium with a constant flow rate of 1 mL min^{-1} was used as the carrier gas; the injector temperature was 250 °C; the interface temperature was 250 °C; the temperature mode: 50 °C (2 min), 50—180 °C (2 °C min^{-1}), 180—220 °C (5 °C min^{-1}), and 220 °C (20 min); the ionizing electron energy was 70 eV; the scan range was 29—500 a.u.m. The cathode was switched on within 3.5 min after the injection of the sample; the volume of the sample was 0.2 μL.

Results and Discussion

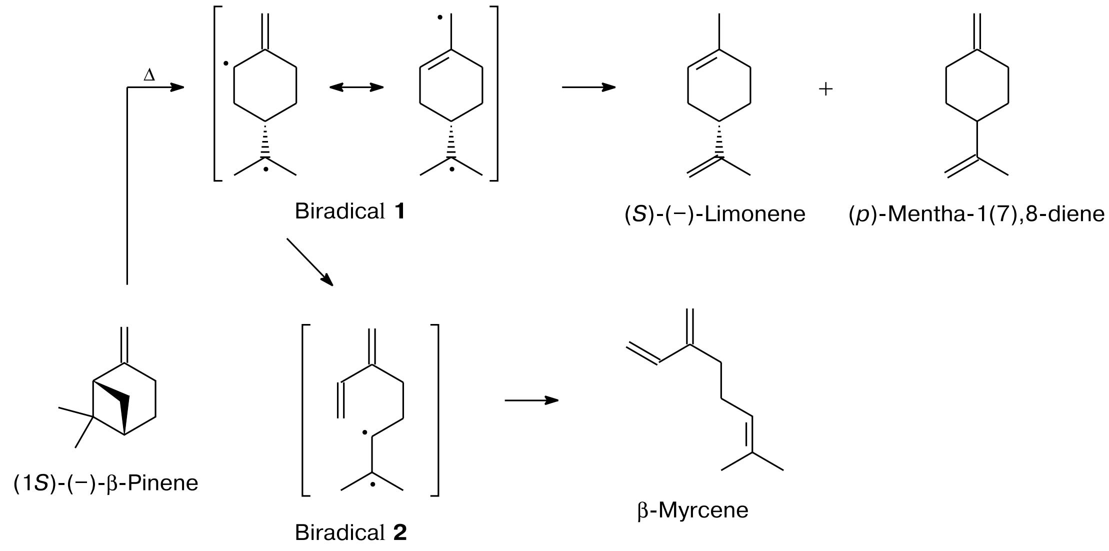
Data on thermal transformations of β-pinene under high pressure are lacking in the literature. In the present study, we performed the reaction of β-pinene in supercritical ethanol at 120 atm and 280—420 °C and investigated the reactivity of this compound under the simultaneous action of high temperature and pressure. The temperature range of the reaction in supercritical ethanol overlaps with that of the thermal isomerization of β-pinene studied earlier.[3—7] This choice helped in locating the possible influence of a supercritical medium and, in particular, in revealing the pressure effect.

In supercritical ethanol, the maximum conversion of β-pinene (>99%) at a constant pressure and a constant residence time is achieved at 410 °C. As in the case of α-pinene,[1] the thermolysis of β-pinene is the major process in supercritical ethanol. The thermolysis affords a mixture of monocyclic and acyclic compounds with the empirical formula $C_{10}H_{16}$, *viz*., β-myrcene, limonene, and *p*-mentha-1(7),8-diene (Scheme 1). These products are analogous to those prepared by the gas-[4—7] and liquid-phase[3] thermal isomerization of β-pinene.

The temperature dependence of the yield (the concentration in the reaction mixture) of β-myrcene, which is the major transformation product, has a pronounced maximum (72% at 400 °C), after which the curve sharply descends (Fig. 1). Monocyclic limonene and *p*-mentha-1(7),8-diene were produced in 15% (420 °C) and 8% yields (400 °C), respectively, their total concentration being no higher than 22% throughout the temperature range under investigation.

A sharp increase in the amount (the percentage in the reaction mixture) of other products (by 10.4%) occurs at 400—420 °C (the upper limit of the temperature range under study), and it is consistent with the decrease in the amount of β-myrcene by 10.3%. High reactivity of β-myrcene in the cycloaddition[8] and polymerization[9] reactions, particularly at high temperatures,[10] suggests that the chemical transformations of β-myrcene make the main

Scheme 1



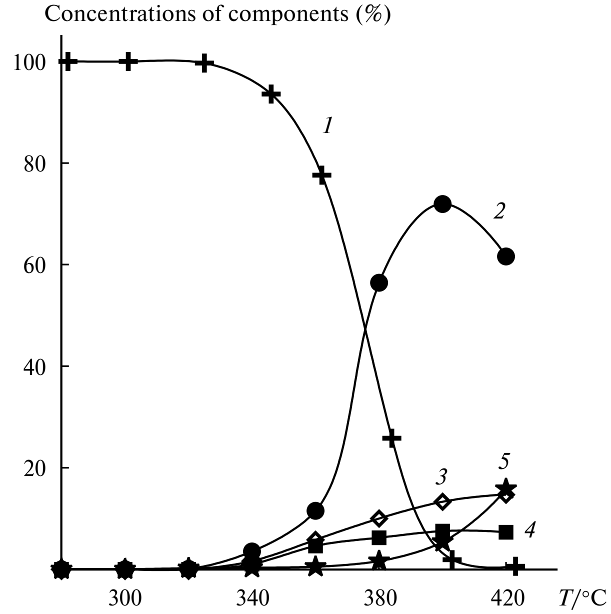


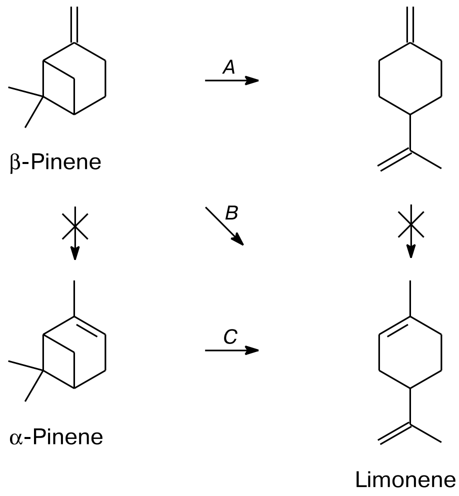
Fig. 1. Temperature dependences of the rate of thermolysis of β-pinene in supercritical ethanol (the residence time was 70 s, $P_{\text{const}} = 120$ atm, $C_0 = 0.1$ mol L^{-1}): β-pinene (*1*), β-myrcene (*2*), limonene (*3*), *p*-mentha-1(7),8-diene (*4*), and other products (*5*).

contribution to the formation of other products in this temperature range.

The fact that the reaction mixture contains no products associated with the use of supercritical ethanol[11] suggests that the mechanism of thermolysis of β-pinene in supercritical ethanol is analogous to that of the gas-phase thermal isomerization[12] (see Scheme 1). This mechanism involves the formation of intermediate biradical **1**, which is transformed either into a mixture of limonene and *p*-mentha-1(7),8-diene or into biradical **2** followed by the formation of β-myrcene.

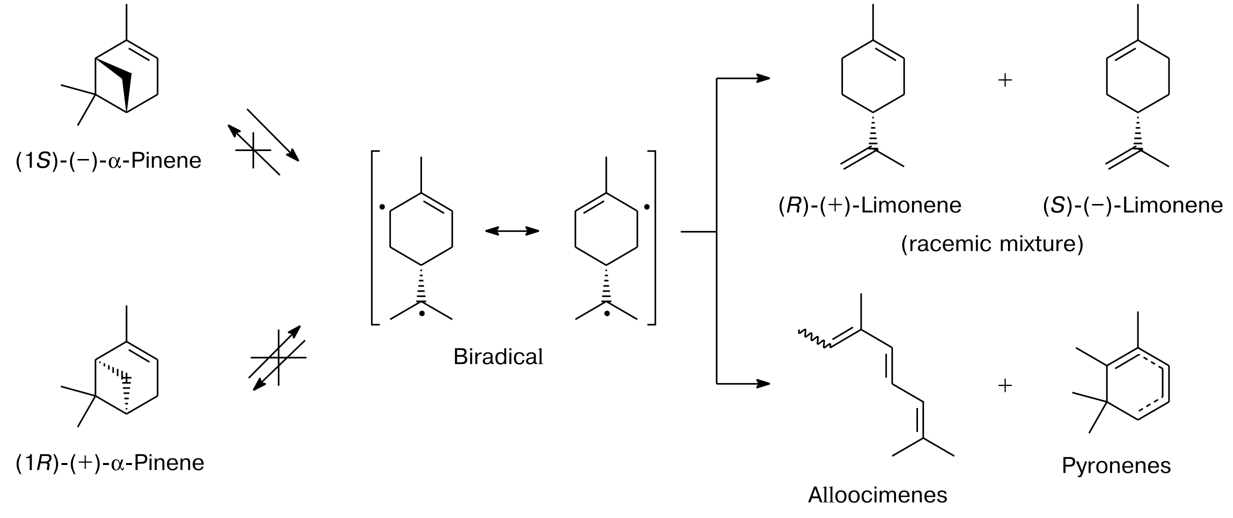
The formation of limonene from β-pinene can proceed through the following three independent pathways (Scheme 2): from *p*-mentha-1(7),8-diene as a result of its thermal prototropic tautomerism (*A*), directly from β-pinene through biradical **1** (*B*), or from α-pinene, which can be generated under the reaction conditions as a result of the prototropic rearrangement of β-pinene (*C*).[13,14] The absence of α-pinene in the reaction mixtures does not rule out the pathway *C*, because α-pinene can undergo fast thermal transformations under the above-mentioned conditions of thermolysis of β-pinene to give limonene[1] (Schemes 2 and 3).

Scheme 2



To validate this hypothesis, we performed the co-thermolysis of an equimolar mixture of α- and β-pinenes in supercritical ethanol (Fig. 2, Table 1).

Scheme 3



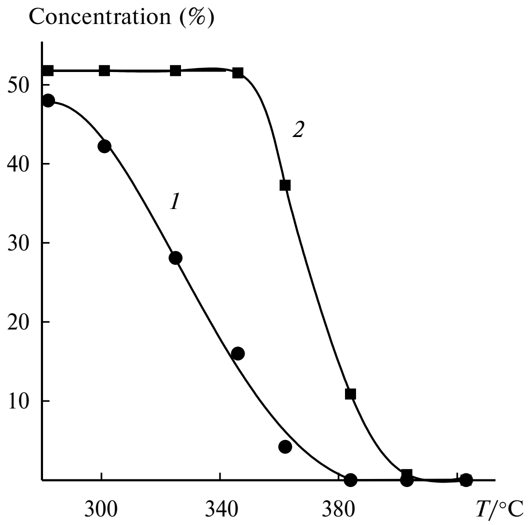


Fig. 2. Temperature dependences of the co-thermolysis of α- (*1*) and β-pinenes (*2*) in supercritical ethanol (the residence time was 70 s, P_{const} = 120 atm, C_0 = 0.1 mol L^{-1} for each pinene).

The co-thermolysis affords exclusively those compounds, which are generated in the independent thermolysis of individual α-pinene[1] and β-pinene in supercritical ethanol, whereas the percentage of the products in the reaction mixture (their concentrations) at the chosen temperature is determined by the initial concentration of the starting α- and β-pinenes.

At a pressure of 120 atm and a residence time of 70 s, α-pinene begins to undergo thermal transformations at 280 °C, whereas β-pinene remains stable under these conditions up to 340 °C. At the same time, the conversion of α-pinene higher than 99% is achieved at 380—390 °C (ΔT = 100—110 °C); the analogous conversion of β-pinene, at 410—420 °C (ΔT = 70—80 °C). The following pre-exponentional factors and activation energies were determined from the experimental data on the temperature dependence of the concentrations of the reaction products: $k_0 = (1.310\pm0.267)\cdot10^{20}$ s^{-1} and E_a = 276.1±16.7 kJ mol^{-1} for the β-pinene → β-myrcene reaction; $k_0 = (8.505\pm0.138)\cdot10^{7}$ s^{-1} and E_a = 118.0±8.1 kJ mol^{-1} for the α-pinene → limonene reaction.

Table 1. Percentage of the co-thermolysis products of α- and β-pinenes in supercritical ethanol at different temperatures (C_0 = 0.1 mol L^{-1} for each pinene, the initial ratio of α/β pinenes was 48.2 : 51.8)

Component	T/°C							
	282	301	325	346	362	384	403	423
α-Pinene	48.0	42.2	28.1	16.0	4.2	—	—	—
β-Pinene	51.8	51.8	51.8	51.5	37.3	10.9	0.7	—
Limonene	—	4.7	12.7	20.1	29.7	34.7	34.5	34.3
Pyronenes	—	0.1	0.4	2.0	3.4	8.1	16.0	23.8
Alloocimenes	—	1.2	5.6	6.2	13.4	4.8	2.9	—
β-Myrcene	—	—	1.4	3.2	10.7	35.4	37.6	27.5
Other products*	—	—	—	0.9	1.3	6.0	8.2	14.4

* The sum taking into account *p*-mentha-1(7),8-diene.

At 404 °C, the rate of the β-pinene → β-myrcene transformation is equal to that of the α-pinene → limonene transformation. At 350 °C, the conversion of β-pinene is at most 5%, whereas the conversion of α-pinene is 85%, and the rate of the transformation of α-pinene into limonene is 12 times higher than that of the transformation of β-pinene into β-myrcene. This demonstrated that the pathway *C* resulting in the formation of limonene from α-pinene (see Scheme 2) cannot be ignored based exclusively on the fact that α-pinene is absent in the reaction mixtures.

An additional information on the reactivity of disubstituted octatrienes having the same carbon skeleton, *viz.*, β-myrcene with two conjugated and one isolated C=C bonds and isomeric alloocimenes containing three conjugated C=C bonds, in supercritical ethanol was obtained from the data on the co-thermolysis of pinenes. The maximum concentration of alloocimenes in the reaction mixture is two times lower than that of β-myrcene and it is achieved at lower temperature (~350 °C), after which the concentration rapidly decreases.[1] Apparently, β-myrcene in supercritical ethanol is more stable to thermal transformations than alloocimenes.

An important information for elucidating the mechanism of formation of limonene in the reaction of β-pinene in supercritical ethanol can be extracted by analyzing the enantiomeric purity of the products. The quantitative ratios of enantiomers (the enantiomeric excess *ee*) in the starting compounds (α- and β-pinenes and limonene) and the reaction mixtures were determined by gas chromatography mass spectrometry on a chromatographic column with a chiral phase. The thermolysis temperatures for all monoterpenes were chosen so that the conversion was no higher than 80—85% (315 °C for α-pinene, 380 °C for β-pinene, and 430 °C for limonene). The data are summarized in Table 2.

At 430 °C, the conversion of (*R*)-(+)-limonene in supercritical ethanol was demonstrated to be no higher than 1%, and unconsumed limonene does not undergo racemization and retains its initial optical purity.

During the thermolysis of (1*S*)-(−)-α-pinene, its initial optical purity also remains unchanged (see Table 2 and Scheme 3). This means that the rate of the limonene → α-pinene backward reaction, for which a biradical is postulated as an intermediate species, is very low and can be ignored.

Limonene generated upon thermolysis of (1*S*)-(−)-α-pinene is racemic (the so-called dipentene). The formation of a racemic mixture of enantiomers of limonene is quite understandable provided that an intermediate species exists as a biradical (see Scheme 3).

Table 2. Enantiomeric ratios of the starting monoterpenes and their thermolysis products[a]

Reaction	Component	Before the reaction (%)			After the reaction (%)			
		Composition	Both enantiomers	*ee*[b]	Composition	Both enantiomers	*ee*[b]	Conversion
Thermolysis of limonene	(*R*)-(+)-Limonene	99.1	99.5	99	97.8	98.8	98	0.8
	(*S*)-(–)-Limonene	0.4			1.0			
Thermolysis of α-pinene	(1*S*)-(–)-α-Pinene	74.9	92.2[c]	62	59.0	71.0	66	21.2
	(1*R*)-(+)-α-Pinene	17.3			12.0			
	(*S*)-(–)-Limonene	—	—	—	7.2	14.0	3	—
	(*R*)-(+)-Limonene	—			6.8			
Thermolysis of β-pinene	(1*S*)-(–)-β-Pinene	96.7	99.9	94	19.0	19.7	93	80.3
	(1*R*)-(+)-β-Pinene	3.2			0.7			
	(*S*)-(–)-Limonene	—	—	—	12.3	12.9	91	—
	(*R*)-(+)-Limonene	—			0.6			

[a] Only the compounds, which can exist as enantiomers, are given.

[b] The enantiomeric excess.

[c] The remaining 7.8% account for the residual amounts of other monoterpene hydrocarbons of composition $C_{10}H_{16}$.

As in the case of the reaction of (–)-α-pinene, the optical purity of β-pinene remains unchanged during its thermolysis (see Table 2). However, limonene generated in the course of thermolysis of (–)-β-pinene is optically active. The enantiomeric excess of (*S*)-(–)-limonene is equal to that of the starting (1*S*)-(–)-β-pinene. The formation of this enantiomer of limonene would be expected from (1*S*)-(–)-β-pinene through the pathway *B* (see Schemes 1 and 2).

Taking into account that *p*-mentha-1(7),8-diene is achiral and that racemic limonene is derived from α-pinene, none of these compounds could be a precursor of optically active limonene in the thermolysis of β-pinene. Hence, of the three pathways presented in Scheme 2, the reaction follows only the pathway *B*.

To summarize, we found that the rates of thermolysis of β- and α-pinenes in supercritical ethanol are substantially different in the temperature range of 280—420 °C at a constant pressure of 120 atm. Both transformations afford limonene as the common product. However, β-pinene gives this compound as the minor product. The thermolysis of β-pinene affords β-myrcene as the major product, whose maximum yield (72%) is achieved at 400 °C. The activation energies and the pre-exponentional factors for the major thermal transformations β-pinene → β-myrcene and α-pinene → limonene were determined from the experimental data. Investigations of the enantiomeric ratios of the thermolysis products of β- and α-pinenes and limonene provided deeper insight into the mechanism of thermolysis of these monoterpenes.

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