

## Thermal transformations of monoterpene compounds in supercritical lower alcohols

V.I. Anikeev \*, A. Yermakova, I.V. Kozhevnikov

Boreskov Institute of Catalysis SB RAS,  
prosp. Akad. Lavrentieva 5, Novosibirsk 630090, Russian Federation

\*E-mail: anik@catalysis.nsk.su

### Introduction

Thermal chemical transformations of phytogetic (mono)terpene compounds are of considerable practical interest for the production of alkyl-substituted benzenes — aromatic C<sub>7</sub>–C<sub>10</sub> hydrocarbons, various mono- and polyoxygenated compounds for medical industry, unsaturated diene and triene compounds — intermediates of fine organic synthesis, and monomers for synthesis of polymers (oligomers). Thus, bicyclic monoterpene hydrocarbons  $\alpha$ - and  $\beta$ -pinenes, which are the main components of turpentine, are used in noncatalytic thermolysis to obtain limonene and  $\beta$ -myrcene necessary for manufacturing of cosmetics, perfumery and household chemicals.

*$\alpha$ -Pinene,  $\beta$ -pinene, verbenol and refined sulfate turpentine* were chosen for the study of thermal transformations of monoterpene compounds in supercritical solvents. Chemical transformations of these monoterpene compounds are multivarious and have been much studied. In particular, the thermal isomerization reaction, which is generally carried out at low or atmospheric pressure in the gas [1-5] or liquid [6, 7] phase, has been studied in detail for  $\alpha$ - and  $\beta$ -pinenes. In this case, the reaction mixture contact time necessary to provide the 90-95% conversion of  $\alpha$ -pinene may range from several to tens hours. So large contact times strongly restrict wide industrial application of the available technologies of thermal isomerization of terpene compounds for the production of polyunsaturated aliphatic compounds and main aromatic hydrocarbons.

Thermal isomerization of terpene compounds can be accelerated by the use of catalysts [8] or application of new reaction media, among which supercritical solvents are most promising. Analysis of the literature shows the lack of studies on thermal isomerization of monoterpene compounds in supercritical solvents. There are only few works devoted to catalytic hydrogenation of  $\alpha$ -pinene in supercritical CO<sub>2</sub> [9-11] and synthesis of esters (the *esterification* reactions) of terpene alcohols [12].

## 1. Experimental procedure and chemical analysis of reaction products

Experiments were performed with (+)- $\alpha$ -pinene (> 98%, Aldrich), (-)- $\beta$ -pinene ( $\geq$  99%, Fluka), (+)-limonene ( $\geq$  99%, Aldrich), and (S)-cis-Verbenol (verbenol) (95%, Aldrich). Sulfate turpentine used in the study was a commercial product containing  $\alpha$ -pinene (76-80%), camphene (1.2%),  $\beta$ -pinene (4.1%), 3-carene (10.8%), limonene (3%) and other compounds (0.9%).

Thermal isomerization of terpene compounds in supercritical solvents was investigated using a laboratory setup with a tubular flow reactor of ca. 7 cm<sup>3</sup> capacity. Temperature and pressure were varied over the range of 530-700 K and 80-300 atm. Depending on the chosen solvent, reaction mixture was supplied to the reactor inlet by one or two liquid streams. In the latter case, a solution of monoterpene compound in alcohol was the first stream, and distilled water was the second one. These two independent liquid streams mixed directly at the reactor inlet. Contact time determined as a ratio of reactor volume to the reaction mixture feed rate under the input conditions  $T_0, P_0$ :  $\tau = V_D/Q_{cm}$  was ca. 70-140 s.

At the reactor outlet, reaction mixture was cooled and sent for analysis after separation into gas and liquid phases.

## 2. Mathematical methods for experimental data processing and kinetic modeling

The studies of kinetic regularities of complex reactions carried out in plug-flow reactors generally give the dependences of reaction mixture composition on contact time under isothermal and isobaric conditions at a specified inlet composition of feed mixture. In the present study, kinetic regularities of chemical transformations were found by variation of temperature at a fixed contact time and constant pressure. Mathematical processing of experimental data showed that thus obtained composition-temperature dependences (ignition curves) provide essential information about reaction scheme and allow a correct determination of the temperature dependence of kinetic constants. A mathematical model of plug-flow reactor is presented as a set of ordinary differential equations. Identification of the kinetic model includes determination of unknown values of the rate constants and activation energies that provide the best agreement of experimental and calculated data. For that, the target function is formulated, which is subjected to minimization of parameters.

## 3. Reaction kinetics of monoterpene compounds thermal isomerization in supercritical solvents

### *Isomerization of $\alpha$ -pinene in supercritical lower alcohols*

Lower alcohols: methyl, ethyl and propanol-1 were used as supercritical solvents for the study of  $\alpha$ -pinene isomerization. Fig. 1 shows the  $\alpha$ -pinene conversion (curves 1-3) and formation

of main product, limonene (curves 1'-3'), in supercritical solvents: methyl, ethyl and 1-propyl versus contact time at constant temperature and pressure.

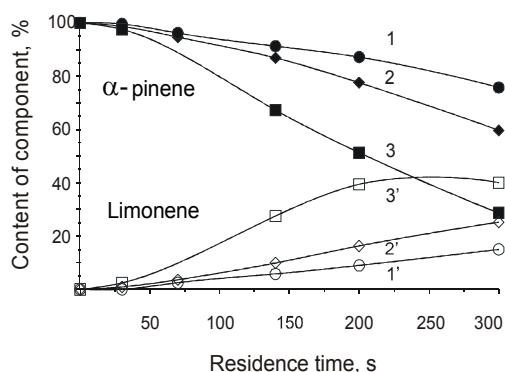


Fig. 1. The content of  $\alpha$ -pinene (1-3) and limonene (1'-3') in the products of  $\alpha$ -pinene isomerization in supercritical alcohols (methyl (1), ethyl (2) and 1-propyl (3)) as a function of contact time. Temperature 300°C, pressure 100 atm.

### Isomerization of $\alpha$ -pinene in supercritical ethanol

The experimental data on thermal isomerization of  $\alpha$ -pinene in supercritical ethanol were obtained in two series of experiments performed at constant contact time  $\tau = 70$  s: (1) data on changes in the reaction mixture composition at temperature varied in the range of 560-660 K and constant pressure  $P = 120$  atm; (2) data about the effect of reaction medium pressure on the rate of  $\alpha$ -pinene chemical transformations at constant temperature  $T = 600$  K.

The temperature dependences of reaction mixture composition at thermal isomerization of  $\alpha$ -pinene obtained at constant pressure (dots on the plot) are shown in Fig. 2. Based on the experimental and literature data [1, 2, 6, 7], main reaction routes of  $\alpha$ -pinene isomerization in supercritical alcohols are presented as a scheme, Fig. 3, similar to the scheme of  $\alpha$ -pinene thermal isomerization in the gas or liquid phase [1, 2, 6, 7]. Reaction rate of each step is expressed by the first order kinetic equations.

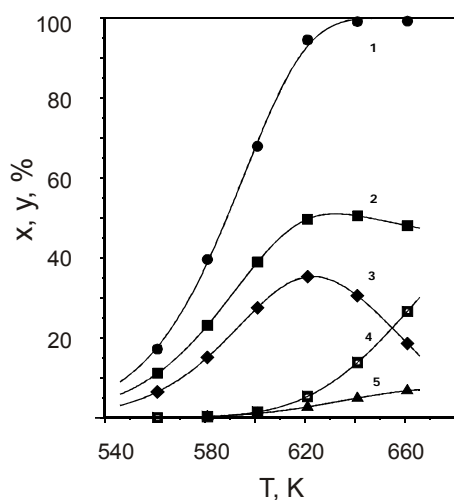


Fig. 2.  $\alpha$ -Pinene conversion and formation of isomerization products versus temperature ( $P = 120$  atm,  $\tau = 70$  s). Comparison of experimental (dots) and calculated (lines) data. 1 –  $\alpha$ -pinene, 2 – limonene, 3 – 4E,6Z-alloocimene, 4 – 4E,6E-alloocimene, 5 – isomeric pyrenenes.

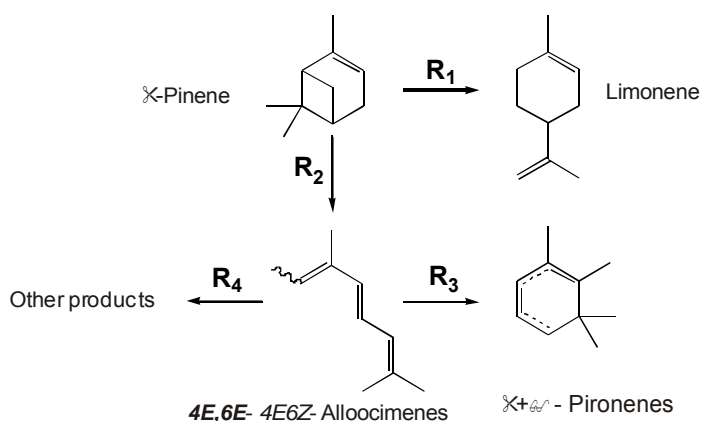


Fig. 3. A scheme of reaction routes for  $\alpha$ -pinene thermal isomerization

The calculated constants and their confidence intervals resulting from this model identification are listed in Table 1, good agreement between experimental and calculated data is demonstrated in Fig. 2.

Table 2. Results and statistical characterization of constants presented in the scheme (Fig. 3)

Rate constants and confidence intervals			
Rate constant, 1/s		Activation energy, J/mol	
$k_{0,1}$	$8.51E+07 \pm 1.38E+07$	$E_1$	$1.18E+05 \pm 8.07E+03$
$k_{0,2}$	$2.73E+09 \pm 4.99E+08$	$E_2$	$1.37E+05 \pm 9.21E+03$
$k_{0,3}$	$1.08E+08 \pm 6.15E+07$	$E_3$	$1.29E+05 \pm 3.10E+04$
$k_{0,4}$	$1.23E+03 \pm 1.37E+03$	$E_4$	$7.43E+04 \pm 6.06E+04$
Root-mean-square absolute error			0.97%

#### Isomerization of $\alpha$ -pinene in supercritical ethanol with water addition

Interest in studying the thermal isomerization of  $\alpha$ -pinene in supercritical mixture of ethanol and water (isomerization of monoterpenes was carried out in ethyl alcohol containing ca. 5% of water) is caused by the intention to reveal effect of water on the reaction mechanism, selectivity and rate of the overall transformation. This is related with the fact that water in the critical region of its parameters is strongly dissociated [13] and can manifest the properties of acid or base catalyst, which provides advantages in the performance of some chemical transformations [14, 15].

The experimental data on  $\alpha$ -pinene thermal isomerization in supercritical ethanol-water mixture are presented in Fig. 4 (dots) as the dependences of molar fractions of the reaction products (limonene, isomeric alloocimenes, pyronenes, and the sum of all other products) on water content in

the feed mixture, other conditions being equal. One may see from this Figure that a higher yield of limonene at increased concentration of water in supercritical solvent is related with the growth of  $H^+$  ions concentration due to stronger dissociation of water [13].

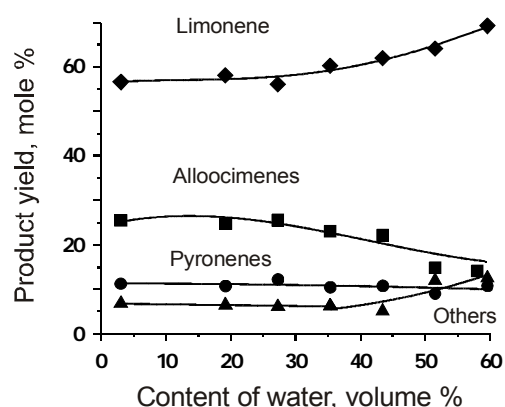


Fig. 4. The yield of organic products versus water content in the reaction mixture. 1 – limonene; 2 – the sum of 4E,6Z- and 4E,6E-alloocimenes; 3 – the sum of pyronenes; 4 – other products. The concentrations are normalized to the initial concentration of  $\alpha$ -pinene in solution.  $T = 657\text{ K}$ ,  $P = 230\text{ atm}$ .

Figure 5 displays the most likely schemes of radical (route **A**) and ionic (route **B**) mechanisms of  $\alpha$ -pinene isomerization. At the first step, route **A** includes the formation of an intermediate biradical of *n*-menthane structure, which converts into limonene formally as a result of the [1,5]-shift of  $H^\bullet$  atom.

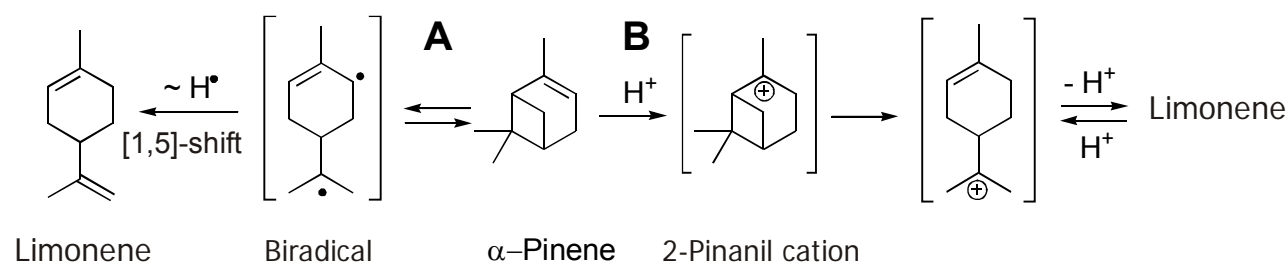


Fig. 5. Schemes of radical (route **A**) and ionic (route **B**) mechanisms of  $\alpha$ -pinene isomerization.

#### *Isomerization of $\beta$ -pinene and a mixture of $\alpha$ - and $\beta$ -pinenes in supercritical ethanol*

In the gas-phase reaction,  $\beta$ -pinene, similar to  $\alpha$ -pinene, undergoes thermal isomerization yielding  $\beta$ -myrcene as the main reaction product. It seems interesting to compare the reactivities of both pinenes and the kinetic features of their transformations in *sc*-ethanol, other things being equal.

In this study, we considered the effect of temperature upon its variation in the range of 280 – 420°C on the conversion and selectivity of  $\beta$ -pinene thermolysis in *sc*-ethanol at pressure 120 atm and  $\tau = 70\text{ s}$ . As seen from Fig. 6,  $\beta$ -pinene conversion in *sc*-ethanol exceeds 99% even at 410°C. The products of  $\beta$ -pinene transformation were similar to those obtained at thermal isomerization of  $\beta$ -pinene in the gas or liquid phase [4, 5, 16-19]. Since the products of  $\beta$ -pinene transformation in

*sc*-ethanol contain no compounds differing from those at its thermal isomerization in the gas phase, this suggests that  $\beta$ -pinene thermolysis in *sc*-ethanol and in the gas phase proceeds by the same mechanism (see the scheme in Fig.7). This mechanism implies the formation of intermediate biradical I, which further converts either into limonene and *p*-mentha-1(7),8-diene or into biradical II yielding  $\beta$ -myrcene.

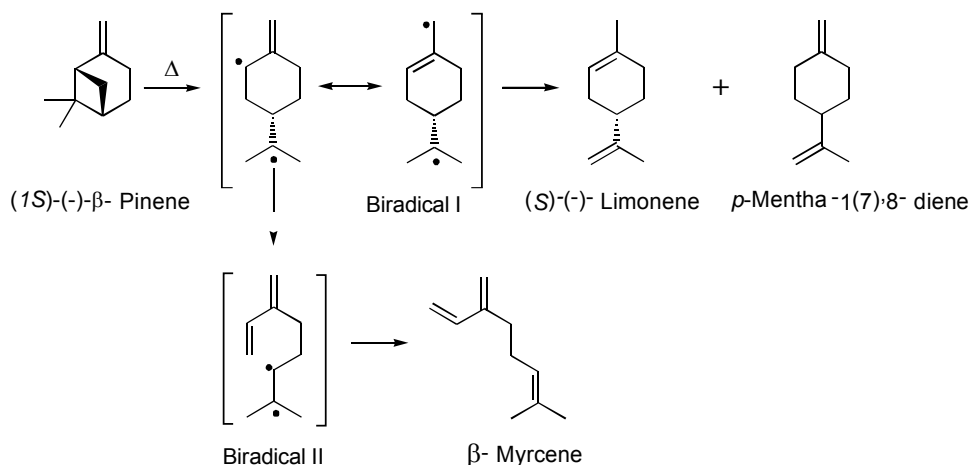
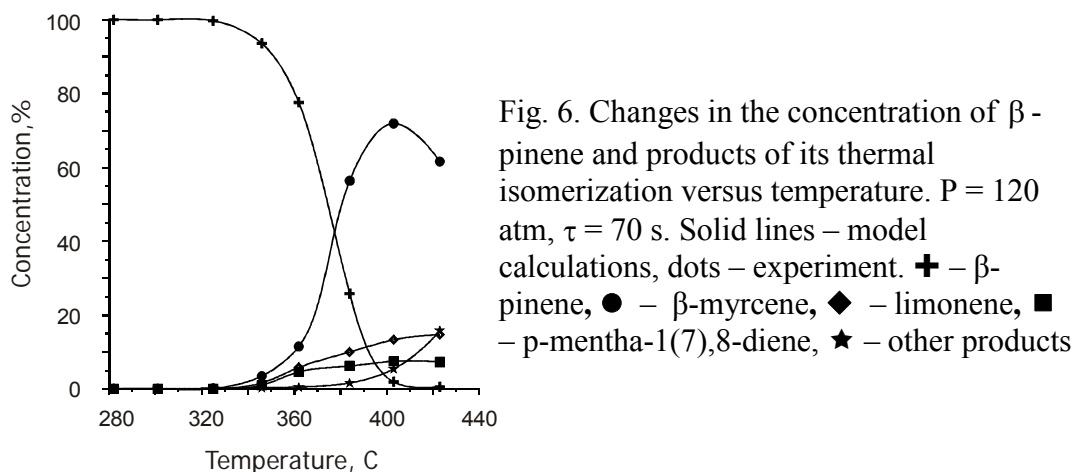


Fig. 7. The mechanism of  $\beta$ -pinene thermal isomerization in supercritical ethanol

#### Isomerization of a mixture of $\alpha$ - and $\beta$ -pinenes in supercritical ethanol

It was found that the products of co-thermolysis of an equimolar mixture of  $\alpha$ - and  $\beta$ -pinenes are represented solely by the species that are obtained at independent thermolysis of individual  $\alpha$ -pinene [20, 21] and  $\beta$ -pinene [22] in *sc*-ethanol. The reaction mixture contained no other products that could have formed by the interaction of a)  $\alpha$ - and  $\beta$ -pinene thermolysis products with each other or b) these products with each of pinenes. This confirms that under the conditions

of experiment  $\alpha$ - and  $\beta$ -pinenes undergo thermolysis independently of each other, although they have some common products — limonene and a group of compounds denoted as ‘other products’.

#### *High-pressure thermolysis of sulfate turpentine*

Sulfate turpentine used as the initial reactant in our study contained  $\alpha$ -pinene (75-80%), camphene (1.2-1.5%),  $\beta$ -pinene (3-5%), 3-carene (11-14%), limonene (2-4%), and other compounds. The content of sulfur in sulfate turpentine was ca. 0.03-0.05%.

The quantitative analysis of the reaction products revealed that, similar to the case of  $\alpha$ -pinene, thermolysis of sulfate turpentine gives limonene, isomeric alloocimenes and pyronenes as main reaction products. Analysis of the experimental data allowed us to propose a kinetic model of sulfate turpentine thermolysis. A comparison of the dependences of  $\ln k_{\Sigma}$  on  $1000/T$  for  $\alpha$ -pinene transformations in turpentine (line 1) and in *sc*-ethanol (line 2), Fig. 8, demonstrates, first, that at similar pressures the total rate constant of the  $\alpha$ -pinene reaction in turpentine exceeds that in *sc*-ethanol. Second, activation energy  $E$  of the  $\alpha$ -pinene reaction in turpentine is higher than that in *sc*-ethanol:

$$\text{In turpentine: } k_{\Sigma 0} = 2.69 \times 10^{11} \text{ 1/s} \quad E = 149.4 \text{ kJ/mol}$$

$$\text{In sc-ethanol: } k_{\Sigma 0} = 5.46 \times 10^7 \text{ 1/s} \quad E = 113.3 \text{ kJ/mol}$$

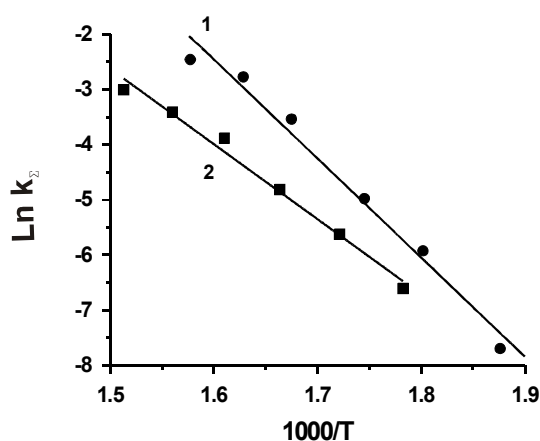


Fig. 8. Arrhenius lines  $\ln k_{\Sigma} - 1000/T$ . Line 1 – turpentine; line 2 – *sc*-ethanol.  $P = 120$  atm;  $\tau = 70$  s.

#### *Thermal transformations of cis-verbenol in supercritical ethanol*

In the further study of reactions of terpene compounds in supercritical solvents, thermal isomerization of verbenol was carried out in supercritical ethyl alcohol at variation of temperature and constant pressure. This gave a dependence of verbenol conversion on the reaction temperature, Fig. 9. The experimental data demonstrate, first, that isomerization of *cis-trans* verbenol in

supercritical ethanol considerably increases the reaction rate and provides virtually a complete conversion of *cis-trans* verbenol even at 380°C (whereas the gas-phase isomerization of verbenol shows no detectable conversion of *cis-trans* verbenol at this temperature [23]). Second, the yield (selectivity) of the target product, *cis*- and *trans*-citral, increases from 8 to 38% compared to the gas-phase reaction [23].

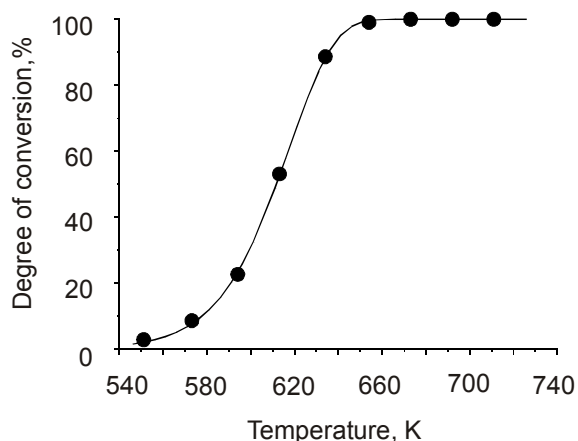


Fig. 9. Conversion of *cis*-verbenol as a function of temperature. Pressure 120 atm, contact time 70 s. Dots – experimental data, solid line – processed data.

#### 4. Effect of pressure on the rate of thermal isomerization of monoterpene compounds in supercritical alcohols

The experiments on  $\alpha$ -pinene thermal isomerization in supercritical ethanol showed also a pronounced effect of the reaction mixture pressure on the rate of parallel chemical transformations of  $\alpha$ -pinene, Fig. 10. However, variation in the reaction mixture pressure has no detectable effect on selectivity of the reaction.

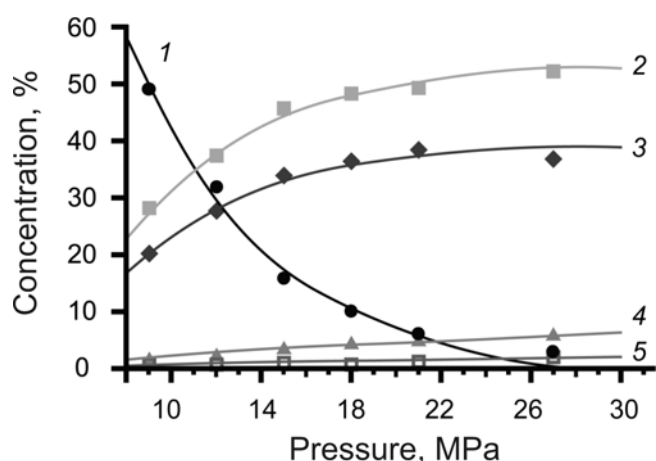


Fig. 10. Conversion of  $\alpha$ -pinene (x) and yield of isomerization products versus pressure.  $T = 600$  K, contact time 70 s. Comparison of experimental (dots) and calculated (lines) data.

1 –  $\alpha$ -pinene, 2 – limonene, 3 – isomeric alloocimenes, 4 – isomeric pyronenes, 5 – other products

Transition state theory was used for interpretation and quantitative description of the pressure (density) effect of solvent on the apparent rate constants of  $\alpha$ -pinene thermal isomerization. As a result, apparent rate constants of the reaction in equations (3) are already the function of pressure:



$$k_{i,\text{app}} = k_i(T_0, P_0) \exp\left(-\frac{\Delta\tilde{V}^\#(P)}{RT}(P - P_0)\right)$$

The proposed model adequately describes the experimental data concerning the constancy of selectivity of  $\alpha$ -pinene thermal isomerization versus pressure, Fig. 24.

We studied also the pressure effect on the rate of thermal isomerization of  $\alpha$ -pinene in turpentine without solvent.

*Effect of pressure on the rate of  $\alpha$ -pinene isomerization in supercritical ethanol with addition of water. The ionic mechanism*

As was shown above, the ionic product of water,  $K_w$ , increases in proportion to the growth of water density according to relationship (7); hence, the concentration of  $H^+$  ions also increases, thus increasing the chemical reaction rate. Raising the pressure in the system *sc*-ethanol + water +  $\alpha$ -pinene at a constant temperature increases the density of supercritical media according to its state equation, which increases the concentration of ions. Although ethanol contains only 4-5% of water, the growth of  $H^+$  ions concentration with pressure increases the reaction rate by the ionic mechanism of  $\alpha$ -pinene isomerization, according to equation (16).

## Conclusion

The report systematizes the results of basic studies on thermal transformations of phytogetic terpene compounds ( *$\alpha$ - and  $\beta$ -pinenes, turpentine, cis-verbenol*) carried out in supercritical fluid solvents, mainly in supercritical lower alcohols. The main result is the demonstration of a considerable increase in the rate of terpene compounds thermal isomerization in supercritical media — lower alcohols, with the retained selectivity toward target reaction products as compared to the rate of similar reactions conducted in the gas or liquid phase.

The kinetic studies and thermodynamic calculations of the phase states and critical parameters of selected multicomponent and multiphase systems containing terpene compounds provided a deep insight into isomerization mechanism of these compounds and elucidated the role of supercritical solvent in a dramatic increase of the reaction rate compared to the same compounds in the gas or liquid phase. The pressure of supercritical solvent was found to facilitate acceleration of the reactions under study.

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