

The kinetics of thermal isomerization of β -pinene and a mixture of β - and α -pinenes in supercritical ethanol

A. Yermakova^a, A.M. Chibiryayev^{b,c}, I.V. Kozhevnikov^a, V.I. Anikeev^{a,*}

^a Borekov Institute of Catalysis SB RAS, Novosibirsk 630090, Russian Federation

^b N.N. Vorozhtsov Institute of Organic Chemistry SB RAS, Novosibirsk 630090, Russian Federation

^c Novosibirsk State University, Novosibirsk 630090, Russian Federation

Received 15 September 2007; received in revised form 22 November 2007; accepted 7 December 2007

Abstract

Thermal isomerization of β -pinene and equimolar mixture of α - and β -pinenes in supercritical ethanol was studied experimentally. The reactivity of structurally similar α - and β -pinenes were compared in the same supercritical solvent. It was shown that both pinenes undergo thermal transformations independently of one another upon co-thermolysis in supercritical (SC) ethanol. Conversion of α -pinene yields monocyclic limonene as the main product, and β -pinene gives acyclic β -myrcene. This study allowed developing the first kinetic model of β -pinene thermolysis in SC ethanol.

© 2007 Elsevier B.V. All rights reserved.

Keywords: Thermal isomerization; Monoterpenes; α - and β -pinenes; Supercritical ethanol; Kinetic

1. Introduction

Thermal isomerization of monoterpene compounds conducted with or without heterogeneous catalysts is a promising technology for obtaining the liquid fractions of aromatic C_7 – C_{10} hydrocarbons and other unsaturated compounds, which are the intermediates for organic synthesis and production of polymeric materials. Non-catalytic thermolysis of bicyclic monoterpene hydrocarbons (α - and β -pinenes) yields limonene and β -myrcene, the essential components of artificial perfume compounds.

Our previous studies [1–3] demonstrated that thermolysis of terpene compounds could be carried out in supercritical (SC) media, for instance, in lower alcohols (methanol, ethanol, and 1-propanol) [1,2]. It was shown that thermal isomerization of α -pinene in SC ethanol increases the reaction rate by several orders of magnitude as compared to the gas-phase or liquid-phase thermolysis. This result may underlie the development of novel technologies for industrial processing of turpentine, a conventional source of monoterpenic hydrocarbons.

To get a deeper insight into thermal transformations of terpene compounds in SC media, it seems interesting to compare the reactivity of structurally similar α - and β -pinenes in the same supercritical solvent, to develop kinetic models of the reactions, and to determine their rate constants.

2. Experimental

Experimental studies on thermolysis of monoterpene compounds in SC ethanol were performed with a lab-scale setup comprising a tubular plug-flow continuous reactor. The setup construction, reactor parameters, and methods of the feed mixture analysis are thoroughly described elsewhere [1–3].

2.1. Experimental results

The study was aimed at elucidating the effect of reaction temperature ($T = 550$ – 690 K) on conversion and selectivity of isomerization of β -pinene and equimolar mixture of α - and β -pinenes in SC ethanol at a constant pressure $P_{\text{const}} = 120$ atm. The feed mixture contact time τ comprised 70 s and was determined as a ratio of the reactor volume V_R (14 cm^3) to the volumetric flow rate $Q(T_0, P_0)$ (cm^3/s) calculated at $T_0 = 25^\circ\text{C}$ and $P_0 = 1$ atm. Initial experimental data are presented in Tables 1 and 2 as the

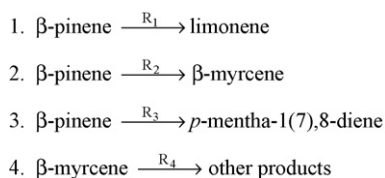
* Corresponding author. Tel.: +7 383 339 74 47.

E-mail address: anik@catalysis.nsk.su (V.I. Anikeev).

Table 1
Thermal isomerization of β -pinene in supercritical ethanol at the different temperatures

Compound (%)	Temperature (°C)							
	280	300	320	340	360	380	400	420
β -Pinene	100.0	100.0	99.7	93.6	77.6	25.8	1.9	0.6
Limonene	–	–	–	1.6	5.8	10.0	13.3	14.7
β -Myrcene	–	–	0.1	3.5	11.5	56.4	71.9	61.6
<i>p</i> -Mentha-1(7),8-diene	–	–	–	1.0	4.6	6.2	7.5	7.3
Sum of the other products	–	–	0.2	0.3	0.5	1.6	5.4	15.8

Residence time, 70 s; $P = 120$ atm; $C_0 = 0.1$ M.



Scheme 1.

temperature dependencies of molar fractions of the reaction products.

2.1.1. Development of kinetic models

The experiments on β -pinene thermolysis in SC ethanol and a possible reaction mechanism are thoroughly discussed by the authors in Ref. [4], which shows that under the conditions of experiment, β -pinene conversion proceeds mainly as three routes in Scheme 1.

As seen from Table 1, main transformation of β -pinene in SC ethanol is the thermal opening of bicyclic pinane system (bicyclo[3.1.1]heptane) to form acyclic β -myrcene, with its maximum yield (72%) attained at 400 °C. A further temperature elevation considerably decreases the yield of this product, which is accompanied by a sharp increase in the yield of “other products” of unidentified structure (mainly the other monoterpenic hydrocarbons $C_{10}H_{16}$). The temperature dependency of “other products” accumulation and decrease in β -myrcene yield give ground to suggest that main contribution to the formation of “other products” is made by chemical transformations of β -myrcene, for instance, by the reactions of [4 + 2]-cycloaddition [5] and/or polymerization [6].

The analysis of enantiomeric composition of the products obtained at separate thermolysis of α - and β -pinenes in SC ethanol [4] indicates that limonene can form only directly from β -pinene. Neither *p*-mentha-1(7),8-diene nor α -pinene can be the limonene precursors in the reaction of β -pinene thermolysis. Besides, the retention of initial enantiomeric purity of β -pinene upon its thermolysis excludes the reverse steps of reactions 2 and 3 in Scheme 1. These results allowed us to reduce greatly the number of elementary reactions for the development of kinetic model.

2.1.2. A kinetic model of β -pinene thermolysis

The above scheme of thermal transformations of β -pinene (Scheme 1) was taken as a basis of kinetic model. Reaction rates of all the routes are represented by the first order equations:

$$\begin{aligned} R_i &= k_i C_i \quad i = 1 - 3 \\ R_4 &= k_4 C_2 \end{aligned} \quad (1)$$

where C_1 and C_2 are respectively the concentrations of β -pinene and β -myrcene (g mol/cm^3), and k_i are the corresponding rate constants (1/s) represented as the Arrhenius temperature dependence

$$k_j(T) = k_{j0} \exp\left(\frac{-E_j}{RT}\right), \quad j = 1, 2, \dots, 4 \quad (2)$$

where E_j is the activation energy (J/mol), and R is the universal gas constant.

Table 2
Co-thermolysis of an equimolar mixture of α - and β -pinenes in supercritical ethanol at different temperatures

Compound (%)	Temperature (°C)							
	282	301	325	346	362	384	403	423
α -Pinene	46.7	42.2	28.1	16.0	4.2	–	–	–
β -Pinene	53.3	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
Sum of α - and β -pyrenenes	–	0.1	0.4	2.0	3.4	8.1	16.0	23.8
Sum of 4 <i>E</i> ,6 <i>Z</i> - and 4 <i>E</i> ,6 <i>E</i> -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
<i>p</i> -Mentha-1(7),8-diene	–	–	–	–	–	1.8	2.6	4.1
Sum of the other products	–	–	–	0.9	1.3	4.2	5.6	10.3

Residence time, 70 s; $P = 120$ atm; $C_0 = 0.1$ M. Initial mixture: α -pinene, 49.3%; β -pinene, 50.7%.

Table 3
Results of kinetic model identification

No	Reaction	k_0 (1/s)	E (J/mole)	Rate constant at $T=360^\circ\text{C}$
1	β -Pinene \rightarrow limonene	$(2.075 \pm 0.428) \times 10^{19}$	$(2.753 \pm 0.175) \times 10^5$	0.000387
2	β -Pinene \rightarrow β -myrcene	$(1.310 \pm 0.267) \times 10^{20}$	$(2.76 \pm 0.167) \times 10^5$	0.002098
3	β -Pinene \rightarrow p -menthadiene	$(2.639 \pm 0.601) \times 10^{13}$	$(2.153 \pm 0.192) \times 10^5$	0.000044
4	β -Myrcene \rightarrow others	$(2.319 \pm 0.870) \times 10^9$	$(1.575 \pm 0.328) \times 10^5$	0.000230
5	α -Pinene \rightarrow limonene	$(8.505 \pm 0.138) \times 10^7$	$(1.180 \pm 0.081) \times 10^5$	0.015390
6	α -Pinene \rightarrow alloocimenes	$(2.727 \pm 0.499) \times 10^8$	$(1.366 \pm 0.092) \times 10^5$	0.001438
7	Alloocimenes \rightarrow pyronenes	$(1.083 \pm 0.615) \times 10^7$	$(1.294 \pm 0.310) \times 10^5$	0.000224
8	Alloocimenes \rightarrow others	$(1.229 \pm 1.371) \times 10^3$	$(7.425 \pm 6.061) \times 10^4$	0.000911
9	β -Pinene \rightleftharpoons α -pinene		Not available to identify	

2.1.3. Mathematical description of lab-scale reactor

A mathematical model of the plug-flow reactor is presented as a set of ordinary differential equations:

$$\frac{dC_i}{d\tau} = \sum_{j=1}^{N_R} z_{ji} R_j \quad (3)$$

with the initial conditions:

$$\tau = 0: C_i = C_i^0; \quad C_i^0 = 0, \quad i = 2, \dots, N_S \quad (4)$$

Here, C_i^0 denotes the inlet concentrations of components, $N_S = 5$ is the number of components, $N_R = 4$ is the number of chemical reactions included in the transformation scheme under consideration, and z_{ji} denotes the j -th row and i -th column of the stoichiometric matrix corresponding to the reaction scheme accepted above.

Taking into account the equivalent transformations by introducing dimensionless concentrations $y_i = C_i/C_1^0$, a set of Eq. (3) can be presented as:

$$\frac{dy_i}{d\tau} = \sum_{j=1}^{N_R} z_{ji} R_j(y); \quad \tau = 0: y_1^0 = 1, y_i^0 = 0, i = 2, \dots, N_S \quad (5)$$

A set of Eq. (5) was used to identify the model parameters.

2.1.4. Identification of the model

The identification problem includes determination of unknown values of the rate constants and activation energies providing the best fit of experimental and calculated data. For this purpose, we formulated a target function to be minimized by parameters:

$$Q = \sum_{k=1}^{N_{\text{EXP}}} \left(\mathbf{y}_k^{\text{exp}} - \mathbf{y}_k^{\text{calc}}(\mathbf{p}) \right)^T \mathbf{W}_k^{-1} \left(\mathbf{y}_k^{\text{exp}} - \mathbf{y}_k^{\text{calc}}(\mathbf{p}) \right) \rightarrow \min(\mathbf{p}) \quad (6)$$

where $\mathbf{y}_k^{\text{exp}}$ is the N_S -dimensional column vector composed of the concentrations of i -th component measured in each k -th experiment; $\mathbf{y}_k^{\text{calc}}$ is the vector of calculated concentrations obtained by integrating a set of differential equations of model (5) in the range of 0–70 s at the corresponding temperature T_k in the k -th

experiment with regard to (1) and (2); and \mathbf{p} denotes the N_P -dimensional column vector of the desired parameters ($N_P = 16$):

$$\mathbf{p} = [k_{10}, k_{20}, \dots, k_{40}, E_1, E_2, \dots, E_4] \quad (7)$$

Target function (6) was minimized using a classic Gauss–Marquard iteration method [7]. The concentrations were calculated at each iteration step by numerical integration of a set of differential Eq. (6) at current values of the constants.

Other essential details of the identification procedure and method of statistical validation of the results are thoroughly described in our previous work [3]. All rate constants obtained as a result of the kinetic model identification are statistically significant. Numerical values of the constants are listed in Table 3.

For the proposed kinetic model of β -pinene thermolysis in SC ethanol, based on the reactions of Scheme 1, a good agreement between experimental and calculated data is observed, which is demonstrated in Fig. 1.

It was found that the products of co-thermolysis of an equimolar mixture of α - and β -pinenes (see Table 2) are represented

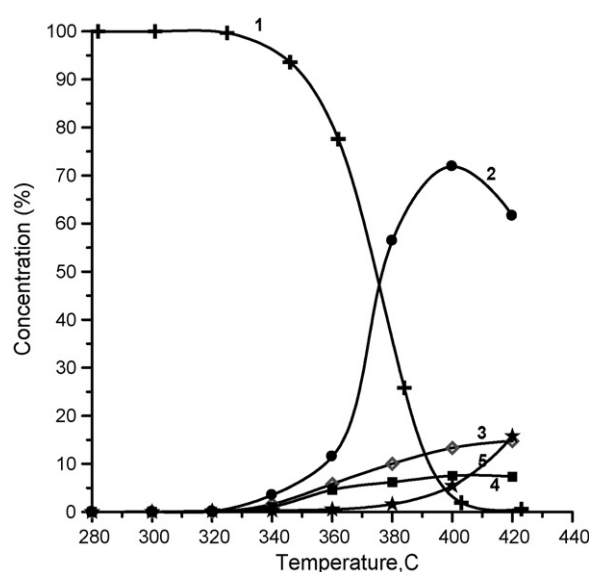


Fig. 1. The temperature dependence of the reagent concentrations of thermal isomerization of β -pinene. $P=120$ atm. Solid lines—calculated data, points—experiment: 1, β -pinene; 2, β -myrcene; 3, limonene; 4, p -menthadiene; 5, other products.

exclusively by the same substances that form upon independent thermolysis of individual α -pinene [1–3] and β -pinene [4] in SC ethanol. The reaction mixture under consideration contained no other compounds that could form due to the interaction of (a) the products of α - and β -pinene thermolysis with each other or (b) these products with each of pinenes. Thus, in the mathematical description of experiments on co-thermolysis of an equimolar mixture of α - and β -pinenes (see Table 2), the kinetic scheme of transformations was based on routes 1–4 of Scheme 1 and on the reactions of α -pinene thermolysis in SC ethanol [1–3]. A general scheme of thermal transformations of the α - and β -pinene mixture is presented in Fig. 2.

In addition to the reactions shown in Fig. 2, the kinetic model of the total co-thermolysis was supplemented with a reversible reaction of prototropic isomerism “ α -pinene \rightleftharpoons β -pinene”, which may occur under the conditions of experiment [8,9]. However, during the identification of kinetic model, these reactions (forward and reverse) were not identified, i.e., under the experiment conditions, interconversion of α - and β -pinenes seems to proceed much more slowly than other conversions of these compounds. This conclusion is supported, first, by the fact that thermolysis of α -pinene yields no β -myrcene, which is the main product of β -pinene thermolysis. It means that thermolysis of the α - and β -pinene mixture does not include the “ α -pinene \rightarrow β -pinene” transformation. Second, limonene that forms upon thermolysis of β -pinene has the same enantiomeric purity as the initial β -pinene. Hence, the “ β -pinene \rightarrow α -pinene” reaction does not occur during thermolysis, since otherwise α -pinene would give racemic limonene (dipentene) [4], which decreases the enantiomeric purity of limonene obtained at thermolysis of β -pinene.

The mathematical description of a complex scheme of thermal isomerization of the α - and β -pinene mixture (Fig. 2) was represented also by a set of differential equations of (3) and (4) type with the number of reactions $N_R = 8$ and the number of components $N_S = 8$. The obtained values of constants are listed in Table 3. Comparison of the calculation results with the exper-

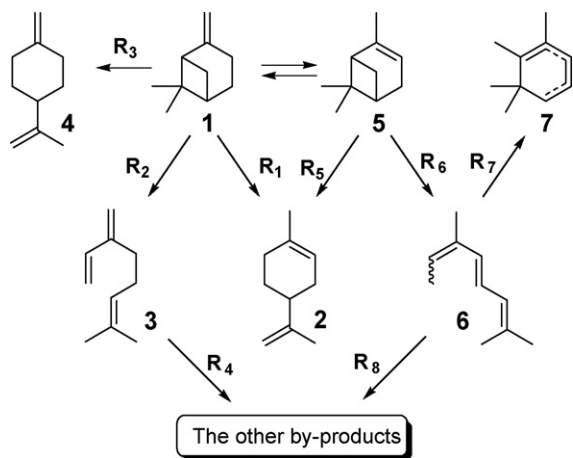


Fig. 2. General scheme of β - and α -pinenes thermal isomerization. 1, β -pinene; 2, limonene; 3, β -myrcene; 4, *p*-menthadiene; 5, α -pinene; 6, alloocimenes; 7, pyrenenes.

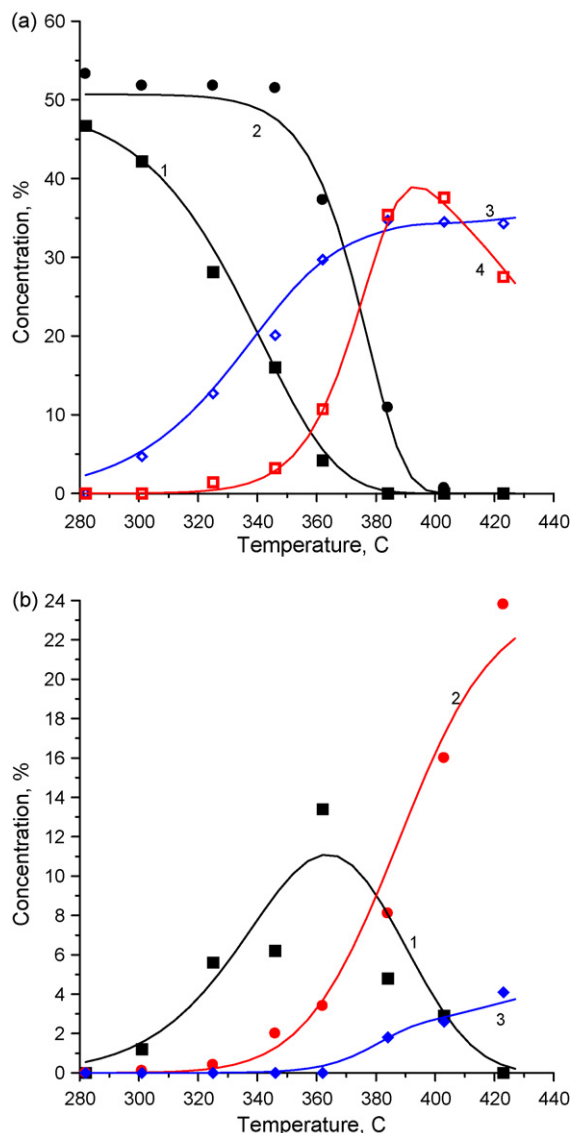


Fig. 3. (a) Comparison of experimental and calculated data. Solid lines—calculations, points—experiment. 1, α -pinene; 2, β -pinene; 3, limonene; 4, β -myrcene. (b) Comparison of experimental and calculated data. Solid lines—calculations, points—experiment: 1, alloocimenes; 2, pyrenenes; 3, *p*-menthadiene.

imental data of Table 3 is shown in Fig. 3a and b. One may see that the accepted kinetic model adequately describes the experimental data.

Rate constants of β -pinene thermolysis obtained at identification of the kinetic model (the scheme in Fig. 2) coincide, within confidence intervals, with the constants found earlier when processing the experimental data on thermolysis of individual β -pinene. This additionally supports our assumption that, under the experiment conditions, α - and β -pinenes undergoes thermolysis independently of one another, although they have common products—limonene and a group of compounds denoted as “other products”.

Note that the reaction of β -pinene conversion starts at higher temperatures as compared to α -pinene.

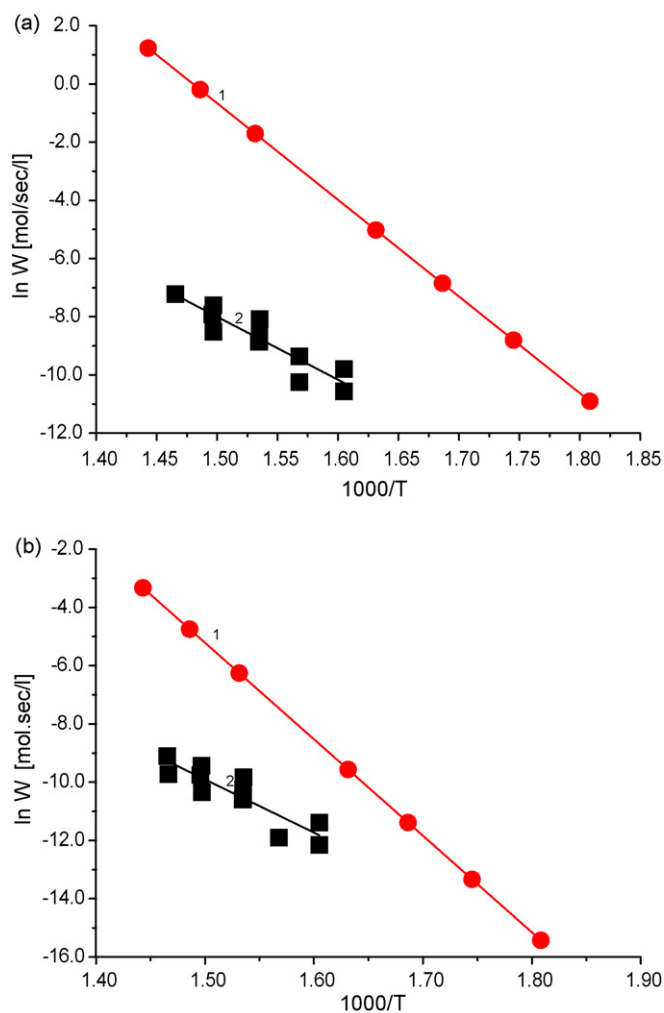


Fig. 4. (a) Comparison of our experimental data with the literary data for reaction β -pinene \rightarrow β -myrcene. Line 1, data of present work; line 2, data of [8]. (b) Comparison of our experimental data with the literary data for reaction β -pinene \rightarrow limonene. Line 1, data of present work; line 2, data of [10].

2.2. Comparison of the obtained results with the literature data

Before comparing our data with the literature experimental data, it is necessary to consider the related methodological problems. In the known works devoted to thermal isomerization of α - or β -pinene in the gas-phase, e.g. [10], experiments were performed using the “standard pyrolysis equipment” [11], which amounts to a plug-flow continuous reactor operating under isothermal and isobaric conditions. The effect of temperature on conversion of pinenes and yield of the reaction products was studied at a constant feed rate of the initial reagent fed as vapors of a substance (pinene) in a carrier gas (N_2).

The mathematical description of such reactor was represented by a set of differential equations similar to Eq. (5). To determine the reaction rate constants, the authors of [10] used analytical forms of solution of the corresponding differential equations, assuming the first order of the reactions, which is basically true. In this case, integration of the first order equation, e.g., with respect to several reaction routes gives the total rate constant for

the transformation of initial substance in the form:

$$k_{\Sigma} = \frac{\ln(y_{10}/y_1)}{\tau} \quad (8)$$

where y_{10}, y_1 are the concentrations of the initial substance at the reactor inlet and outlet. Evidently, the y_{10}/y_1 ratio is independent of the units used in the initial equations of the model. Since the product of $k_{\Sigma} \times \tau$ is a dimensionless quantity, numerical value and dimensionality of the constants calculated by Eq. (8) will depend on the way of representation of the “fictitious” contact time τ . However, different authors treat this subject differently. For instance, in Ref. [10] residence time is determined as a ratio of

$$\tau^{(1)} = \frac{V_R}{Q(T, P)} \quad (9)$$

where V_R is the reactor volume (cm^3), and $Q(T, P)$ is the consumption of vapor/gas (cm^3/s) calculated for current values of temperature and pressure. On the other hand, to determine numerical values of the reaction rate constants, residence time τ entering the mathematical representation of the constant can be expressed as

$$\tau^{(2)} = \frac{V_R}{Q(T_0, P_0)} \quad (10)$$

where T_0, P_0 are certain reference values of temperature and pressure (for instance, $T_0 = 298$ K, $P_0 = 1$ atm), and accordingly $Q(T_0, P_0)$ is a constant value.

Since the product of $k_{\Sigma} \times \tau$ is a dimensionless quantity, it is clear that different ways of τ representation give different values of the rate constants and hence different values of activation energies of the reaction. Thus, the rate constants derived from expression (8) and expressions (9) and (10) are incomparable to each other, as are the values of activation energy calculated from the temperature dependence of these constants.

To resolve this contradiction and perform a comparative analysis, it is reasonable to bring the rate constants of thermal isomerization of α - or β -pinene reported by different authors to the common dimensions. This can be accomplished by multiplying expressions (9) and (10) (or dividing expression (8)) into the corresponding molar volume of the reacting medium ($V_m(T, P)$, L/mol). The resulting rate constant will have the mol/(L s) dimensions, the same as the dimensions of the reaction rate, which is conventionally defined as the number of moles of the substance reacting per unit time in a unit reaction volume. The interpretation of numerical value of such constant having the mol/(L s) dimensions is physically substantiated: it characterizes a “specific” reaction rate (\bar{W}) at a unit (dimensionless) concentration of the reacting substance [12].

Therefore, to compare the rate constants reported, for example, in Ref. [10] with the constants obtained in the present work, values of the first constants should be divided by a variable quantity $V_m(T, P) = RT/P$, where T and P are the values of temperature and pressure in respective experiment. Concurrently, values of the rate constants listed in Table 3 should be divided by a constant quantity $V_m(T_0, P_0) = M/\rho_L = 0.575$ L/mmol, where ρ_L is the density of initial mixture of ethanol and pinene (α - or β -

pinene) at T_0 and P_0 (g/L), and M is the average molecular weight (g/g-mol).

Specific rates \bar{W} of the reactions “ β -pinene \rightarrow β -myrcene” and “ β -pinene \rightarrow limonene”, obtained in the gas-phase in Ref. [10] and in SC ethanol, are compared in Fig. 4a and b in the $\ln \bar{W} - 1000/T$ coordinates. Curves 1 in both figures reflect the data acquired in the present work, while curves 2 were plotted with the experimental data of [10] converted by the method described above. The plots show that in the gas-phase the reaction starts at higher temperatures as compared to the reaction in SC ethanol. Nevertheless, specific rates of the reactions in SC ethanol are by several orders of magnitude higher than in the gas-phase. The activation energies are also different, being lower in the gas-phase process.

3. Conclusion

Experimental study followed by mathematical processing of the data demonstrates that SC ethanol is an efficient reaction medium for thermal thermolysis of α - and β -pinenes. It was found that both pinenes undergo thermal isomerization independently of one another upon co-thermolysis in SC ethanol. α -Pinene conversion gives monocyclic limonene as the main product, and β -pinene gives acyclic β -myrcene. Numerical values of the activation energy and pre-exponential factor of β -pinene conversion into acyclic β -myrcene were shown to strongly exceed those for α -pinene conversion into limonene.

This study allowed us to develop the first kinetic model of β -pinene thermolysis in SC ethanol. The data obtained may be used as a basis for calculating and designing a pilot-scale indus-

trial reactor for thermal conversion of such wood chemicals as turpentine.

References

- [1] A.M. Chibiryayev, V.I. Anikeev, A. Yermakova, P.E. Mikenin, I.V. Kozhevnikov, O.I. Sal'nikova, Thermolysis of α -pinene in supercritical lower alcohols, *Russ. Chem. Bull. Int. Ed.* 55 (6) (2006) 987–992.
- [2] V.I. Anikeev, A. Yermakova, A.M. Chibiryayev, I.V. Kozhevnikov, P.E. Mikenin, Thermal isomerization of terpene compounds in supercritical alcohols, *Russ. J. Phys. Chem.* 81 (5) (2007) 711–716.
- [3] A. Yermakova, A.M. Chibiryayev, I.V. Kozhevnikov, P.E. Mikenin, V.I. Anikeev, Thermal isomerization of α -pinene in supercritical ethanol, *Chem. Eng. Sci.* 62 (9) (2007) 2414–2421.
- [4] A.M. Chibiryayev, A. Yermakova, I.V. Kozhevnikov, O.I. Sal'nikova, V.I. Anikeev, Comparative thermolysis of β - and α -pinenes in supercritical ethanol: the reaction characterization and enantiomeric ratio of products, *Russ. Chem. Bull. Int. Ed.* 56 (6) (2007) 1234–1238.
- [5] T. Sasaki, S. Eguchi, T. Ishii, Reactions of isoprenoids. IV. Reactivity of myrcene in 1,4-cycloaddition reactions, *J. Org. Chem.* 34 (12) (1969) 3749–3753.
- [6] A.J. Johanson, F.L. McKennon, L.A. Goldblatt, Emulsion polymerization of myrcene, *Ind. Eng. Chem.* 40 (3) (1948) 500–502.
- [7] D.W. Marquard, An algorithm for least-squares estimation of nonlinear parameters, *J. Soc. Ind. Appl. Math.* 11 (1963) 431–441.
- [8] D.V. Banthorpe, D. Whittaker, The preparation and stereochemistry of pinane derivatives, *Chem. Rev.* 66 (6) (1966) 643–656.
- [9] W.R. Rocha, H.M.S. Milagre, W.B. De Almeida, On the isomerization of β -pinene: a theoretical study, *J. Mol. Struct. (Theochem)* 544 (2001) 213–220.
- [10] J.E. Hawkins, J.W. Voght, The rate of the thermal isomerisation of β -pinene in the vapor phase, *J. Phys. Chem.* 57 (9) (1953) 902–905.
- [11] I.A. Goldblatt, S. Palkin, Vapor phase thermal isomerisation of α - and β -pinene, *J. Am. Chem. Soc.* 63 (12) (1941) 3517–3522.
- [12] V.I. Dimitrov, *The Simple Kinetics*, Novosibirsk, Nauka, 1982.