

CHEMICAL KINETICS  
AND CATALYSIS

## The Thermal Isomerization of Terpene Compounds in Supercritical Alcohols

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**Abstract**—The experimental data obtained were used to construct a kinetic model of the isomerization of  $\alpha$ -pinene in supercritical ethanol. The model took into account the influence of both temperature and pressure on the rate and selectivity of the reaction.

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### INTRODUCTION

Supercritical fluids are an attractive medium for the chemical transformations of organic compounds. Thanks to the special properties of substances in the critical region of their parameters, supercritical solvents sometimes multiply increase the rate of a chemical reaction and its controlled selectivity [1].

Among supercritical fluid solvents suitable for conducting chemical transformations in them, we should mention water, CO<sub>2</sub>, alcohols, and several saturated and unsaturated hydrocarbons. In certain instances, preference is given to supercritical water and CO<sub>2</sub>. At the same time, the lower alcohols are also extensively used for performing organic reactions, including reactions under supercritical conditions. Alcohols are strong solvating agents and reach the supercritical state under comparatively mild conditions (for ethanol, the critical temperature and pressure are  $T_c = 516.2$  K and  $p_c = 63$  atm). This is why they are finding ever increasing use as supercritical solvents.

Among many reactions of organic compounds performed in supercritical fluids, the transformations of terpene compounds of plant origin ( $\alpha$ -pinene,  $T_c = 646.0$  K and  $p_c = 27.6$  atm, and turpentine) are of great interest for practical applications, because the products of such transformations (limonene and other monoterpene hydrocarbons) are used in the production of cosmetics and perfumes, polymeric materials, and household chemicals.

Mixtures of monoterpene compounds are contained in turpentines prepared from conifers. The major turpentine components are  $\alpha$ - and  $\beta$ -pinenes, 3-carene, and limonene [2].

The thermal isomerization of  $\alpha$ -pinene under usual conditions (without a solvent) at 180–250 (liquid-phase reaction [3]) or 226–256°C (gas-phase reaction [4–6])

requires contact times of from several hours to several days to obtain a 90–95% degree of conversion. This is a substantial limitation on the industrial application of such a technology.

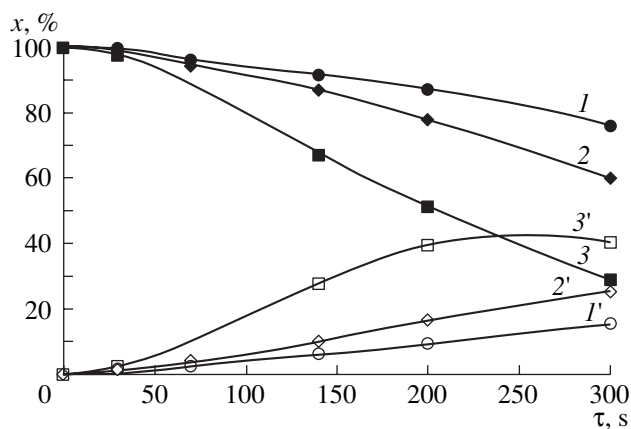
At the same time, there are no data on the thermal isomerization of terpene compounds in supercritical solvents. Only the catalytic hydrogenation of  $\alpha$ -pinene in supercritical CO<sub>2</sub> [7] and the formation of terpene alcohol esters [8] have been studied.

Our main goal was to experimentally study the reactivity of supercritical C<sub>1</sub>–C<sub>3</sub> alcohols in the thermal isomerization of  $\alpha$ -pinene and turpentine.

### EXPERIMENTAL

The thermal decomposition of terpene compounds in supercritical solvents was studied experimentally on a laboratory unit similar to that described in [9] in a flow reactor. The reaction mixture at the exit of the reactor was cooled, separated into the gas and liquid phases, and analyzed. The composition of liquid reaction products was determined by chromatography on a Hewlett-Packard 5890/II gas chromatograph with an HP MSD 5971 quadrupole mass spectrometer as a detector. Analyses were performed using an HP-5 quartz column (5%-diphenyl-95%-dimethylsiloxane copolymer) of length 30 m and inside diameter 0.25 mm. The stationary phase film thickness was 0.25  $\mu$ m.

We studied the influence of temperature and pressure on the degree of conversion and selectivity of isomerization of  $\alpha$ -pinene and turpentine in supercritical alcohols.



**Fig. 1.** Degrees of ( $1'$ – $3'$ )  $\alpha$ -pinene transformation and ( $1$ – $3$ ) limonene formation in supercritical ( $1$ ,  $1'$ ) methanol, ( $2$ ,  $2'$ ) ethanol, and ( $3$ ,  $3'$ ) 1-propanol depending on contact time at temperature  $300^\circ\text{C}$  and pressure 100 atm.

## RESULTS AND DISCUSSION

### *The Isomerization of $\alpha$ -Pinene in Supercritical Alcohols*

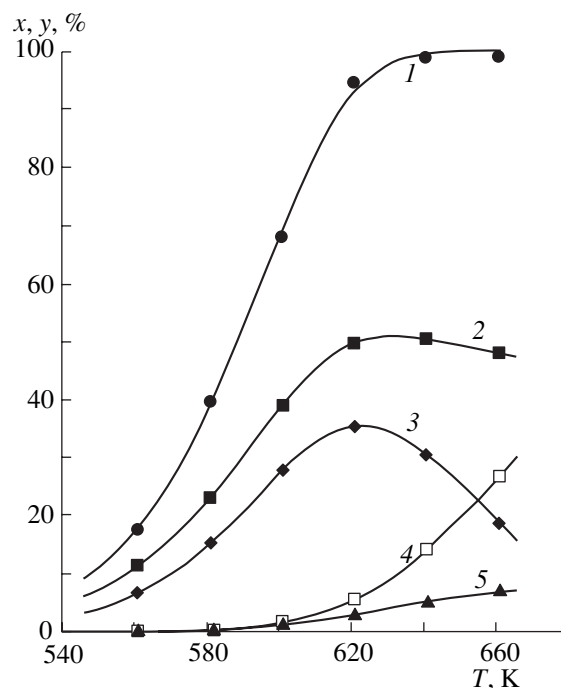
The lower alcohols are extensively used as solvents for many organic compounds. They have comparatively low critical parameters and are stable toward thermal decomposition in this region. These alcohols are therefore of interest as supercritical solvents for performing chemical transformations. We used lower alcohols such as methanol, ethanol, and 1-propanol to study the isomerization of  $\alpha$ -pinene.

The dependences of the degree of conversion of  $\alpha$ -pinene (curves  $1$ – $3$ ) and formation of the main product, limonene (curves  $1'$ – $3'$ ), in supercritical methanol, ethanol, and 1-propanol on the duration of contact at constant temperature and pressure are shown in Fig. 1. We found that, first, the reactivity of alcohols as supercritical solvents increased as the number of alcohol molecule CH groups grew. Secondly, the chemical composition of reaction products did not change. Next, none of the selected supercritical alcohols interacted with  $\alpha$ -pinene and its isomerization products. Lastly, none of the alcohols influenced reaction selectivity substantially.

Separate experiments showed that limonene, which was the major  $\alpha$ -pinene isomerization product, was stable in supercritical alcohols under similar conditions.

### *The Isomerization of $\alpha$ -Pinene in Supercritical Ethanol*

Ethanol in the supercritical state was selected for a more detailed study of the isomerization of  $\alpha$ -pinene depending on temperature and pressure. Changes in reaction mixture composition caused by the thermal isomerization of  $\alpha$ -pinene in the alcohol as the temper-

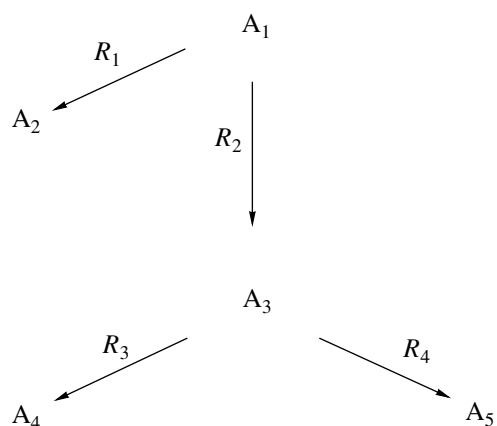


**Fig. 2.** Degrees of  $\alpha$ -pinene transformation and formation of isomerization products as functions of temperature; comparison of experimental data (symbols) and calculation results (lines);  $p = 120$  atm; ( $1$ )  $\alpha$ -pinene, ( $2$ ) limonene, ( $3$ ) alloocimene, ( $4$ ) neoalloocimene, and ( $5$ ) ( $\alpha + \beta$ )-pyrenenes.

ature was varied from 560 to 660 K at a constant pressure of  $p = 120$  atm are shown in Fig. 2.

Kinetic studies of complex reactions in flow ideal displacement reactors are as a rule performed to obtain the dependences of reaction mixture composition on contact time under isothermal and isobaric conditions at a given mixture composition at the entrance of the reactor. The resulting integral composition–contact time curves contain sufficient information for constructing a scheme of mutual transformation paths and for advancing primary hypotheses concerning the kinetic functions for describing the rates of separate reactions. Subsequent mathematical data processing is performed to determine numerical kinetic equation constants.

In certain instances, preference is, however, given to obtaining the dependences of reaction mixture composition on temperature or pressure at a constant contact time. This approach was used in the present work to study the thermal isomerization of  $\alpha$ -pinene. Note that data processing for constructing kinetic models then requires the use of a mathematical model in which the number of constants to be determined (rate constants (preexponential factors) and activation energies) is at least two times larger than the number of reaction paths. Because activation energies are exponents of exponential functions, this complicates parametric identification and may cast doubt on the reliability of the param-



**Fig. 3.** Scheme of  $\alpha$ -pinene thermal isomerization paths;  $A_1$ ,  $\alpha$ -pinene;  $A_2$ , limonene;  $A_3$ , (allo + neoallo)-ocimenes;  $A_4$ , ( $\alpha + \beta$ )-pyronenes; and  $A_5$ , other products.

eters found. Solving this problem is therefore accompanied by an a posteriori analysis of the results obtained from the point of view of their statistical significance.

The experimental (Fig. 2) and literature [3–6] data allow  $\alpha$ -pinene isomerization reaction paths in the supercritical alcohols used to be described by the scheme shown in Fig. 3, which is similar to the scheme of the thermal isomerization of  $\alpha$ -pinene in the gas or liquid phase.

The mathematical model of an ideal displacement reactor used for data processing can be written in the form of a system of ordinary differential equations as

$$\frac{dy_i}{d\tau} = \sum_{j=1}^{N_R} z_{ji} R_j(y) \quad \tau = 0: \quad (1)$$

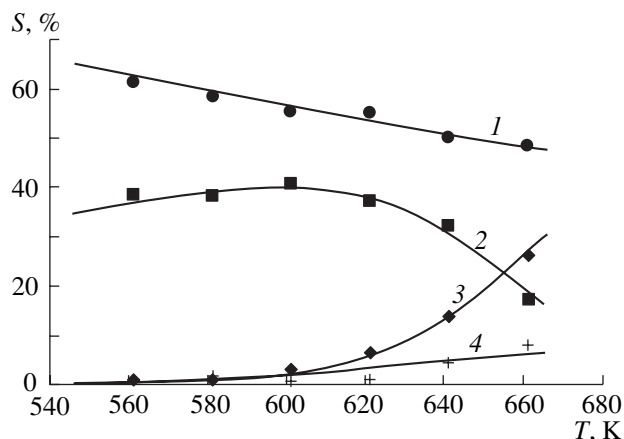
$$y_1^0 = 1, \quad y_i^0 = 0, \quad i = 2, \dots, N_S,$$

where  $y_i = c_i/c_1^0$ ;  $c_i$  is the current component concentration;  $c_1^0$  is the initial component concentration;  $N_S$  is the number of components;  $N_R$  is the number of chemical reactions included into the scheme of transformation under consideration, Fig. 3;  $z_{ji}$  is the  $ij$ th element of the stoichiometric matrix corresponding to the reaction scheme assumed ( $i$  is the matrix column and  $j$  matrix row number);  $R_j(y)$  is the first-order reaction rate; and  $\tau$  is the contact time. The volume of the reactor ( $\text{cm}^3$ ) is  $V_R$ , and the flow rate ( $\text{cm}^3/\text{s}$ ) is  $Q$ .

System (1) was used to identify model parameters. The results are presented in Table 1.

#### Reaction Selectivity

The temperature dependence of reaction selectivity with respect to the yields of its major products is shown in Fig. 4. Here, selectivity is determined as an integral



**Fig. 4.** Reaction selectivity  $S$  with respect to (1) limonene, (2) (allo + neoallo)-ocimenes, (3) ( $\alpha + \beta$ )-pyronenes, and (4) other products as a function of temperature.

value, as the ratio between the product yield and the amount of transformed  $\alpha$ -pinene under given conditions. It follows from Fig. 4 that the major product of the thermal isomerization of  $\alpha$ -pinene in supercritical ethanol is limonene. Its yield reaches 50–60%. The yield, however, decreases somewhat as the temperature increases. Reaction selectivity with respect to limonene can be written as the ratio between rate constants in the form

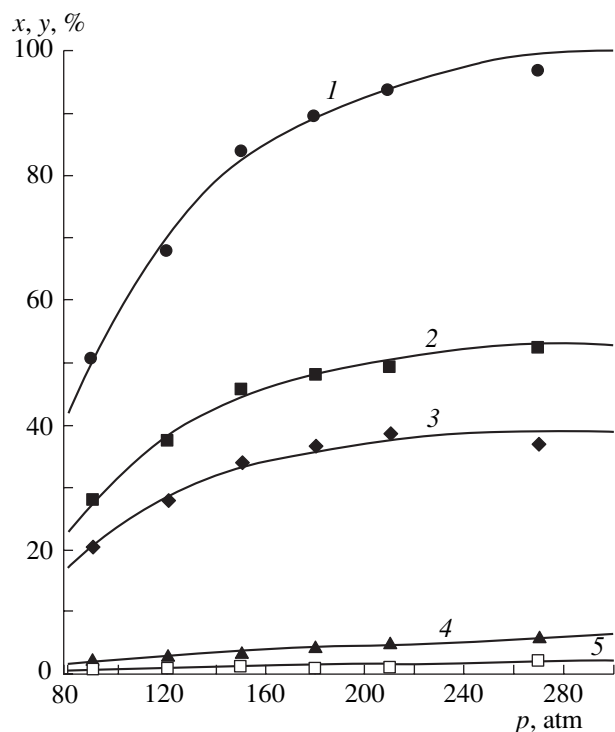
$$S_{\text{Li}} = \frac{k_{10} \exp(-E_1/RT)}{k_{10} \exp(-E_1/RT) + k_{20} \exp(-E_2/RT)}. \quad (2)$$

Because  $E_2 > E_1$ , selectivity decreases slightly as the temperature grows. Accordingly, the contribution of path 2 (Fig. 3) increases. As a result, the yield of isomeric alloocimenes grows. The reactions that yield  $A_4$  (the sum of pyronenes) and  $A_5$  (other side products), however, begin to prevail in reaction sequences  $A_1 \rightarrow A_3 \rightarrow A_4$  and  $A_1 \rightarrow A_3 \rightarrow A_5$  as the temperature grows higher. It follows that heating decreases selectivity with respect to the  $A_3$  intermediate because of an increase in the yields of  $\alpha$ - and  $\beta$ -pyronenes and  $A_5$  products.

**Table 1.** Results and statistical characteristics of estimates of the constants of the model presented in Fig. 3

$n$	$k_{0, n}, \text{s}^{-1}$	$E_n, \text{J/mol}$
1	$8.505 \times 10^7 \pm 1.381 \times 10^7$	$1.180 \times 10^5 \pm 8.069 \times 10^3$
2	$2.727 \times 10^9 \pm 4.993 \times 10^8$	$1.366 \times 10^5 \pm 9.195 \times 10^3$
3	$1.083 \times 10^8 \pm 6.149 \times 10^7$	$1.294 \times 10^5 \pm 3.095 \times 10^4$
4	$1.229 \times 10^3 \pm 1.371 \times 10^3$	$7.425 \times 10^4 \pm 6.061 \times 10^4$

Note: Root-mean-square absolute error is 0.97%.



**Fig. 5.** Degree of  $\alpha$ -pinene transformation ( $x$ ) and isomerization product formation as a function of pressure; comparison of experimental data (symbols) and calculation results (lines); (1)  $\alpha$ -pinene, (2) limonene, (3) (allo + neoallo)-ocimenes, (4) ( $\alpha$  +  $\beta$ )-pyrenenes, and (5) other products.

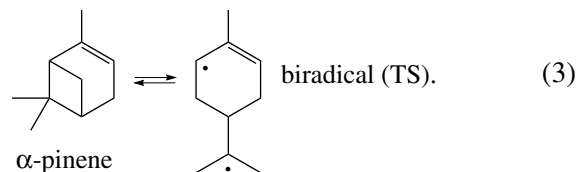
#### The Influence of Pressure on Reaction Rate Constants

Our experiments (the isomerization of  $\alpha$ -pinene in supercritical ethanol) showed that reaction mixture pressure substantially influenced the rate of chemical transformations at a constant temperature, Fig. 5. Such pressure effects on chemical reaction rate constants are characteristic of reactions in solutions, including solutions in supercritical solvents [10–13]. The rates of certain reactions increase as the pressure (medium density) grows [10, 14–19], whereas the rates of other reactions may decrease [14, 20–23] or pass an extremum as the pressure changes [14, 24].

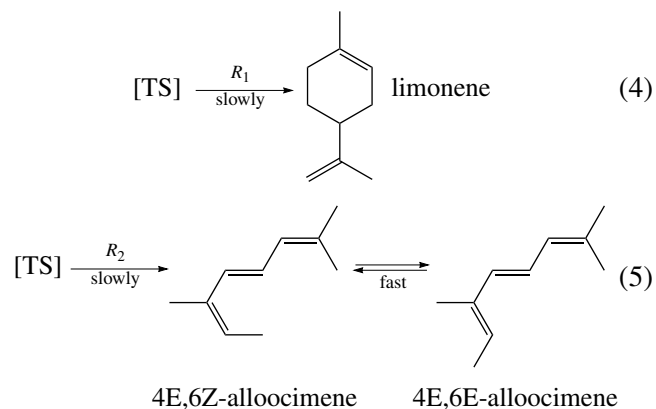
Generally, the influence of solvent pressure on reaction rate constants is determined by specific solvent interactions with the chemical components reacting in it and depends on the nature and properties of the supercritical solvent and the character of solute molecule interactions with it.

It is sometimes suggested that the influence of solvent pressure (density) on the apparent rate constants for chemical reactions can be explained and quantitatively described using transition state theory [25]. According to this theory, motion along a chemical reaction coordinate overcomes a potential energy barrier whose top corresponds to the potential energy of the activated complex (transition state, TS), which is the transition state of the molecule between its initial and

final states. According to this theory, the initial and fast stage of  $\alpha$ -pinene transformation is the formation of the transition state, which is assumed to be a biradical existing at equilibrium with initial  $\alpha$ -pinene; that is,



Next, presumably irreversible decomposition of the transition state along two directions occurs,



The rates of reactions (4) and (5) at a reference temperature of  $T_0 = 600$  K, at which experiments with pressure changes were performed, can be represented as

$$\begin{aligned} R_1(T_0, p) &= k_1(T_0, p)y^\#, \\ R_2(T_0, p) &= k_2(T_0, p)y^\#, \end{aligned} \quad (6)$$

where  $y^\#$  is the dimensionless concentration of the transition state.

The dependence of the apparent rate constants on pressure can be described by the equation [26]

$$\begin{aligned} &\frac{\partial}{\partial p} \left( \ln \frac{k_{i, \text{app}}(T_0, p)}{k_i(T_0, p_0)} \right) \\ &= \frac{1}{RT} \left( \frac{\partial \ln \Phi_{A_i}}{\partial p} - \frac{\partial \ln \Phi_{\text{TS}}}{\partial p} \right) = \frac{-\Delta \bar{V}^\#}{RT}, \end{aligned} \quad (7)$$

$$i = 1, 2,$$

where  $k_{i, \text{app}}$  stands for the apparent rate constants of reactions (4) and (5). The  $k_1(T_0, p_0)$  and  $k_2(T_0, p_0)$  values at  $T_0 = 600$  K and  $p_0 = 120$  atm were calculated using the data presented in Table 1. The  $\Phi_i = \Phi_i(y, T, p)$  fugacity coefficients are functions of temperature, pressure, and critical and other parameters of the pure components and the molar composition of the mixture. The  $\Delta \bar{V}^\# = \bar{V}_{\text{TS}} - \bar{V}_{A_i}$  value, which is the difference of the partial molar volumes of the transition complex and reagent, is usually called “activation volume.”

The  $\Delta\bar{V}^\ddagger$  value depends on both the intrinsic system properties (reagent properties) and the properties of the solvent. The  $\Delta\bar{V}^\ddagger$  value can be both negative and positive.

The integration of (7) from  $p_0$  to  $p$  ( $p_0 = 120$  atm) yields the dependence of the apparent chemical reaction constants on pressure,

$$\ln k_{i, \text{app}}(T_0, p) = \ln k_i(T_0, p_0) - \frac{1}{RT} \int_{p_0}^p \Delta\bar{V}^\ddagger(p) dp, \quad (8)$$

$$i = 1, 2.$$

#### The Problem of Parameter Identification: Solution with the Use of a Series of Variable Pressure Data

Equation (8) is difficult to use for solving the inverse problem of calculating the apparent constants if we do not have a simple explicit equation for describing the dependence of  $\Delta\bar{V}^\ddagger(p)$  on  $p$ . At the same time, the mean-value theorem can be used in discrete  $p_1-p_0$ ,  $p_2-p_0$ , ...,  $p_k-p_0$  intervals of pressure variations in our experiments. The integrals in (8) can then be written as

$$\ln k_{i, \text{app}}(T_0, p_k) = \ln k_i(T_0, p_0) - \frac{\Delta\tilde{V}_k^\ddagger}{RT} \int_{p_0}^{p_k} dp \quad (9)$$

$$= \ln k_i(T_0, p_0) - \frac{\Delta\tilde{V}_k^\ddagger}{RT} (p_k - p_0),$$

where  $\Delta\tilde{V}_k^\ddagger$  is the mean  $\Delta\bar{V}^\ddagger(p)$  integral value over the  $p_k-p_0$  pressure interval. Clearly, this value is also a function of pressure. A preliminary analysis of the experimental data showed that the dependence of  $\Delta\tilde{V}_k^\ddagger$  on  $p$  could be described by the empirical equation

$$\Delta\tilde{V}^\ddagger = b_0 + b_1 p + b_2 p^2. \quad (10)$$

The inverse problem was solved using the scheme of reaction paths presented in Fig. 3, through minimizing the objective function with calculating concentrations by the numerical integration of system (1). The apparent rate constants as functions of pressure were written as

$$k_{i, \text{app}} = k_i(T_0, p_0) \exp\left(-\frac{\Delta\tilde{V}_k^\ddagger(p)}{RT} (p - p_0)\right). \quad (11)$$

The sought model parameters are then the coefficients of (10), because the preexponential factors  $k_i(T_0, p_0)$  ( $i = 1, 2$ ) were calculated using the Arrhenius dependence with the activation energies determined earlier.

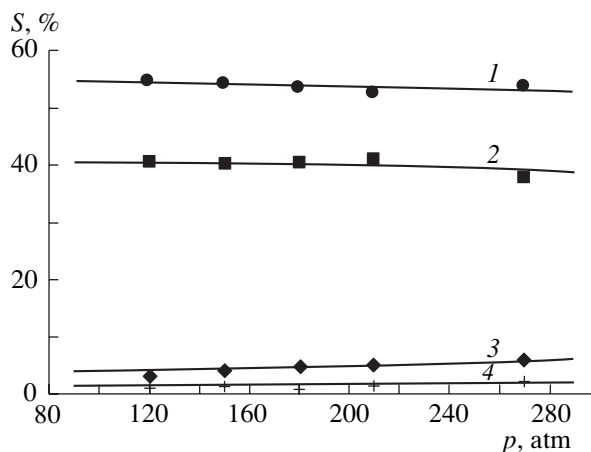


Fig. 6. Reaction selectivity  $S$  with respect to (1) limonene, (2) (neoallo + allo)-ocimenes, (3) ( $\alpha + \beta$ )-pyronenes, and (4) other products as a function of pressure.

The coefficients of (10) obtained this way were

$$\begin{aligned} b_0 &= -1974.63 \pm 136.85, \\ b_1 &= 13.15 \pm 0.91, \\ b_2 &= -0.022 \pm 0.002. \end{aligned} \quad (12)$$

We see that the influence of pressure should be taken into account for two rate constants only, which correspond to paths 1 and 2 in Fig. 3. This influence, however, certainly affects the concentration of the  $A_3$  component (the sum of alloocimene and neoalloocimene), which, in turn, determines the yields of  $A_4$  (the sum of pyronenes) and  $A_5$  (other side products).

The  $\Delta\tilde{V}^\ddagger$  value calculated over the interval of pressures studied is negative. It follows that rate constants increase as the pressure grows. Agreement between the experimental data and calculation results is illustrated by Fig. 5. The largest gradient of constant growth is observed over the pressure range 90–120 atm; these pressures are closest to the critical pressure of ethanol.

The influence of pressure on reaction selectivity is illustrated by Fig. 6, which shows that the corresponding pressure effects are insignificant. This is in agreement with the model suggested above, because the  $k_1(T, p)/k_2(T, p)$  ratio between the constants does not change as the pressure increases. Only  $A_1 \rightarrow A_2$  and  $A_1 \rightarrow A_3$  reaction rates increase.

#### The Decomposition of Turpentine in Supercritical Ethanol

The initial reagent was sulfate turpentine, a side product of cellulose production. Its composition is given in Table 2. The experimental conditions were as follows: the concentration of turpentine in 96% ethanol was 56 wt %, contact time 140 s, and pressure 120 atm.

**Table 2.** Products of sulfate terpentine decomposition in supercritical ethanol

Composition	Content	330°C	380°C
$\alpha$ -Pyronene	–	2.2	8.2
Tricyclene	0.3	0.3	0.3
$\alpha$ -Pinene	79.4	2.6	–
$\alpha$ -Fenchene	0.3	0.3	0.4
Camphene	1.2	1.4	1.4
$\beta$ -Pinene	4.1	2.5	–
$\beta$ -Myrcene	–	0.9	0.7
$\beta$ -Pyronene	–	2.4	14.7
3-Carene	10.8	11.0	11.1
<i>p</i> -Cymene	0.2	0.8	1.0
Limonene	2.9	44.0	44.7
Alloocimene	–	21.3	4.3
Nealloocimene	–	7.2	4.2
Other products	0.8	5.5	9.0

The qualitative and quantitative composition of the products of turpentine conversion in supercritical ethanol is listed in Table 2 for two temperatures. First, we see that virtually complete transformation of  $\alpha$ -pinene occurs above 330°C. Secondly, an increase in the temperature of the reaction substantially increases the yield of  $\alpha$ - and  $\beta$ -pyronenes and decreases the yield of alloocimene.

To summarize, our experimental study and mathematical data processing showed that supercritical C<sub>1</sub>–C<sub>3</sub> alcohols are an effective reaction medium for the thermal isomerization of terpene compounds. For instance, the rate of  $\alpha$ -pinene isomerization in supercritical ethanol is higher than the rate of isomerization in the gas or liquid phase by several orders of magnitude, the selectivity with respect to the desired reaction products remaining unchanged.

#### ACKNOWLEDGMENTS

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