

Allyl rearrangement of 3-methyl-1-penten-4-yn-3-ol

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The paper is concerned with kinetic study of the allyl rearrangement of 3-methyl-1-penten-4-yn-3-ol catalyzed by sodium hydrogensulfate in aqueous solution. The influence of temperature in the interval 70—100°C and of catalyst concentration in the range 0.225—1.275 mol dm⁻³ in reaction mixture on the rearrangement of 3-methyl-1-penten-4-yn-3-ol has been evaluated.

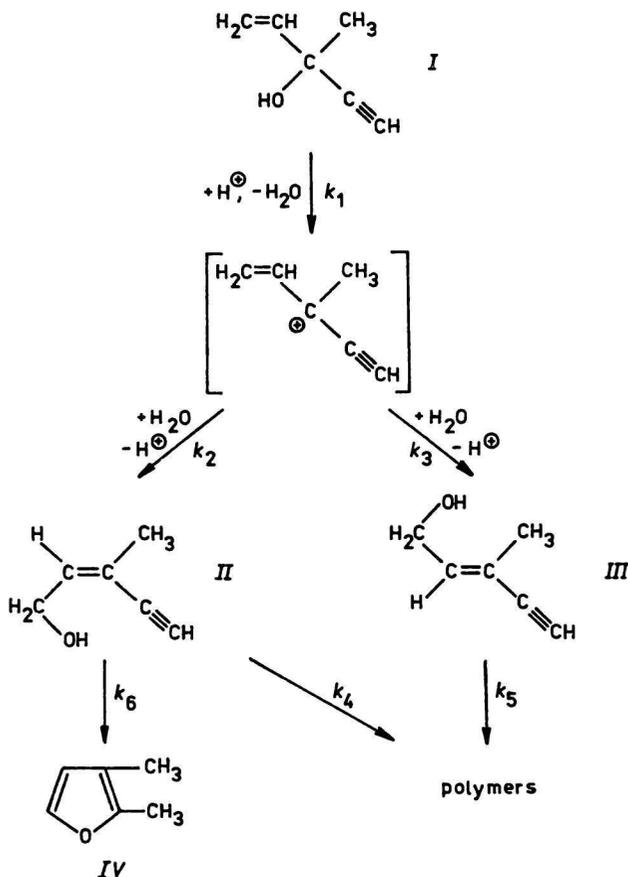
The time dependence of the component concentrations in reaction mixture, *i.e.* 3-methyl-1-penten-4-yn-3-ol, and *cis* and *trans* isomers of 3-methyl-2-penten-4-yn-1-ol was determined experimentally. These relationships were evaluated by using the system of rate equations describing the transformations and origination of individual components.

В работе проводится кинетическое исследование аллильной перегруппировки 3-метил-1-пентен-4-ин-3-ола в водном растворе при катализе бисульфатом натрия. В работе оценивается влияние температуры в интервале 70—100°C, а также концентрации катализатора в интервале 0,225—1,275 моль дм⁻³ в реакционной смеси на перегруппировку 3-метил-1-пентен-4-ин-3-ола.

Экспериментально установлены временные зависимости концентраций компонентов реакционной смеси, 3-метил-1-пентен-4-ин-3-ола, *цис*- и *транс*-изомеров 3-метил-2-пентен-4-ин-1-ола, которые затем были описаны с помощью системы уравнений скоростей преращения и образования отдельных компонентов.

The product of the allyl rearrangement of 3-methyl-1-penten-4-yn-3-ol (*I*) is the *cis* isomer of 3-methyl-2-penten-4-yn-1-ol (*II*) which is an intermediate of industrial production of retinyl acetate (vitamin A-acetate) by the Isler method [1—3].

The allyl rearrangement proceeds under catalysis by strong mineral acids [4—7]. The compound *II*, the *trans* isomer of 3-methyl-2-penten-4-yn-1-ol (*III*) [4—10], 2,3-dimethylfuran (*IV*) [10, 11], and further products of polymerization [10] were determined in the reaction mixture (Scheme 1).



Scheme 1

The rate of isomerization is significantly affected by the properties of reaction medium, especially by the polarity of the solvent [10, 12] and is higher in polar solvents.

The formation of primary alcohols *II* and *III* is in agreement with the theory of monomolecular nucleophilic substitution [12, 13]. The authors of paper [13] suggested the reaction mechanism of the rearrangement of *I* according to which they put this rearrangement into the class of anomalous, nucleophilic, monomolecular substitution reactions of the type $\text{S}_{\text{N}}1'$ [12]. The analysis of the energy diagram of structures of the suggested mechanism of the rearrangement has shown that the activation energy of formation of *II* is lower than that of *III*, which means that the probability of origination of *II* is higher.

It results from the present-day literature knowledge that not only the proper reaction conditions but also the polarity of reaction medium, acidity, and the

concentration of catalyst have influence on selectivity of the transformation of *I* into *II*.

We paid attention to the isomerization of *I* under conditions of homogeneous catalysis with sodium hydrogensulfate in aqueous medium. This catalyst is frequently used for isomerizations of allyl systems [4]. However, its application to the allyl rearrangement of *I* is little-known from available literature.

Experimental

For our experiments we used 3-methyl-1-penten-4-yn-3-ol (purum) (Fluka, Buchs, Switzerland) purified by distillation at reduced pressure 1.5 kPa (purity 99.7 mass %), cyclohexanol (anal. grade), sodium hydrogensulfate (anal. grade), sodium hydrogencarbonate (anal. grade), and carbon tetrachloride (purum) (Lachema, Brno).

GLC analyses were performed on Chrom-5 instrument equipped with FID detector by using a glass column of 3 m length and 4 mm diameter. Carbowax 20 M (10 %) on Chromaton N-AW-DMCS of granularity 0.125–0.16 mm was used as packing. The measurements were carried out at the column temperature of 130 °C, injection port temperature of 140 °C, and detector temperature of 160 °C. The flow of carrier gas (nitrogen) was 50 cm³ min⁻¹ at inlet overpressure of 0.25 MPa, the flow of hydrogen was 26 cm³ min⁻¹ at inlet overpressure of 0.15 MPa, and the flow of air was 500 cm³ min⁻¹ at inlet overpressure of 0.25 MPa. The inlet temperature of gases was 20 °C. The method of internal standard (cyclohexanol) was employed, the mean relative error of determination of concentration of components *I–III* being below 2 %.

Isomerization of compound I

The aqueous solution of sodium hydrogensulfate was dosed into a sulfonation flask of 2.5 dm³ volume which was equipped with necessary accessories and placed in a thermostat. After rinsing the apparatus with nitrogen, the overpressure of nitrogen under liquid seal was adjusted and kept constant for the whole time of experiment. Then compound *I* was added into the reactor.

During experiment the samples of reaction mixture were taken in regular time intervals. They were cooled and neutralized by adding sodium hydrogencarbonate. The organic fraction of the reaction mixture was extracted with carbon tetrachloride (efficiency of extraction exceeded 99 %). The extracts were analyzed by gas chromatography and the content of components *I–IV* was determined.

Results and discussion

In this study the influence of temperature in the interval 70–100 °C and of sodium hydrogensulfate concentration ranging from 0.22 to 1.3 mol dm⁻³ on

the course of isomerization of substance *I* was investigated. The experiments were carried out in nitrogen atmosphere in the course of 240 min.

The time dependence of dimensionless concentrations of substances *I*, *II*, and *III* $C' = c c_0^{-1}$ with respect to the initial concentration of substance *I* (c_{I0}) at the temperature of reaction mixture of 80 °C and for the sodium hydrogensulfate concentration $c_K = 0.225 \text{ mol dm}^{-3}$ is represented in Fig. 1.

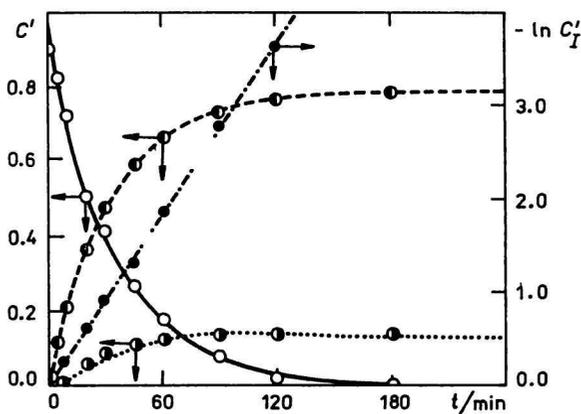


Fig. 1. Time dependence of the measured (points) and calculated (curves) values of dimensionless concentrations $C' = c c_0^{-1}$ of 3-methyl-1-penten-4-yn-3-ol (*I*), *cis* isomer of 3-methyl-2-penten-4-yn-1-ol (*II*), and *trans* isomer of 3-methyl-2-penten-4-yn-1-ol (*III*) and of logarithm of the degree of conversion of *I* ($X_I = (1 - C_I')$) for isomerization of *I* at 80 °C using sodium hydrogensulfate concentration $c_K = 0.225 \text{ mol dm}^{-3}$

—○— *I*, —●— *II*, ●●● *III*, —●— $-\ln C_I' = f(t)$.

It results from primary evaluation of the measured values that the rate of transformation of substance *I* is governed by the rate equation of the first-order reactions. In Fig. 1 the corresponding time dependence of the degree of transformation of substance *I* $X_I = (1 - C_I')$ is given in the form $-\ln(1 - X_I) = f(t)$. The relationship has the form of straight line, the correlation coefficient equals 0.991. The observed irreversibility of the allyl rearrangement of substance *I* may be explained by the energetically favourable interaction of the double and triple bond with *p*-electrons of the hydroxyl group in substances *II* and *III*.

An increase in reaction temperature complicates the course of isomerization of substance *I*. Besides the reactions producing substances *II* and *III*, some consecutive reactions of substances *II* and *III* can be observed. In Fig. 2 the time dependence of dimensionless concentrations of substances *I*—*III* at 98 °C is represented for the concentration of sodium hydrogensulfate $c_K = 0.225 \text{ mol dm}^{-3}$

For evaluating the experimental results, a system of rate equations which was most consistent with the measured concentration relationships for substances *I*—*III* was to be found. Since substance *IV* was not found in measurable quantity in reaction mixture under experimental conditions used, the rate of its formation was much lower than that of substances *II* and *III*. A model comprising simple reactions according to Scheme 1 was used for calculation. The rates

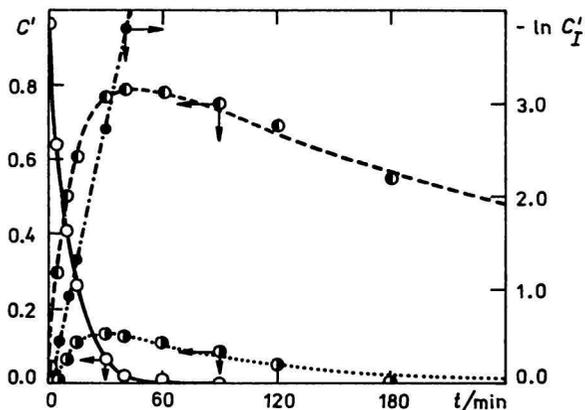


Fig. 2. Time dependence of the measured (points) and calculated (curves) values of dimensionless concentrations $C' = c c_0^{-1}$ of 3-methyl-1-penten-4-yn-3-ol (*I*), *cis* isomer of 3-methyl-2-penten-4-yn-1-ol (*II*), and *trans* isomer of 3-methyl-2-penten-4-yn-1-ol (*III*) and of logarithm of the degree of conversion of *I* ($X_I = (1 - C_I')$) for isomerization of *I* at 98°C using sodium hydrogensulfate concentration $c_K = 0.225 \text{ mol dm}^{-3}$

—○— *I*, —○— *II*, ···●··· *III*, —●— $\ln C_I' = f(t)$.

of conversion of substance *I* and formation of substances *II* and *III* v_I , v_{II} , and v_{III} at constant volume of reaction mixture (eqns (1—3)) were expressed. In accordance with literature [10], a linear dependence of rate constants of particular reactions on the concentration of catalyst c_K (eqn (4)) was assumed.

$$v_I = \frac{dc_I}{dt} = -k'_{v1} c_I \quad (1)$$

$$v_{II} = \frac{dc_{II}}{dt} = k'_{v2} c_I - k'_{v4} c_{II} \quad (2)$$

$$v_{III} = \frac{dc_{III}}{dt} = k'_{v3} c_I - k'_{v4} c_{III} \quad (3)$$

$$k'_{vi} = k_{vi} c_K \quad (4)$$

Table 1

Values of rate constants of the particular reactions taking place in isomerization of 3-methyl-1-penten-4-yn-3-ol as a function of sodium hydrogensulfate concentration c_K and reaction temperature

c_K mol dm ⁻³	$k'_{v1} \cdot 10^3$ min ⁻¹	$k'_{v2} \cdot 10^3$ min ⁻¹	$k'_{v3} \cdot 10^3$ min ⁻¹	$k'_{v4} \cdot 10^3$ min ⁻¹	$k'_{v5} \cdot 10^3$ min ⁻¹
Temperature 71 °C					
0.225	15.2 ± 0.3	11.8 ± 0.3	2.2 ± 0.2	—	—
0.312	21.1 ± 0.4	17.2 ± 0.3	3.7 ± 0.2	—	—
0.625	35.7 ± 0.6	27.8 ± 0.5	6.7 ± 0.2	—	—
0.937	59.2 ± 1.3	45.5 ± 0.9	9.2 ± 0.5	—	—
1.275	69.6 ± 1.2	53.9 ± 0.8	11.2 ± 0.6	0.6 ± 0.1	3.0 ± 0.6
Temperature 80 °C					
0.225	30.8 ± 0.9	24.5 ± 0.7	4.4 ± 0.6	—	—
0.312	33.1 ± 1.8	26.6 ± 1.1	6.4 ± 0.9	—	—
0.625	63.2 ± 1.0	52.1 ± 0.7	9.9 ± 0.5	—	—
0.937	93.7 ± 2.1	74.5 ± 1.5	16.1 ± 1.0	1.1 ± 0.1	4.8 ± 0.7
1.275	134.6 ± 3.3	107.1 ± 2.3	23.7 ± 1.4	1.2 ± 0.1	6.2 ± 0.8
Temperature 88 °C					
0.225	56.2 ± 1.0	47.0 ± 0.6	7.2 ± 0.5	—	—
0.312	75.0 ± 1.9	56.9 ± 1.2	14.0 ± 0.8	0.6 ± 0.2	2.7 ± 0.8
0.625	121.3 ± 2.4	96.3 ± 1.9	25.1 ± 2.1	1.2 ± 0.3	5.1 ± 0.8
0.937	202.5 ± 6.1	160.9 ± 5.0	37.9 ± 3.8	2.4 ± 0.2	7.5 ± 0.7
1.275	237.7 ± 9.1	187.0 ± 6.3	42.0 ± 4.1	2.7 ± 0.8	10.6 ± 0.8
Temperature 98 °C					
0.225	85.6 ± 3.4	75.8 ± 2.6	15.0 ± 2.0	2.5 ± 0.5	9.7 ± 2.7
0.312	125.6 ± 4.6	86.6 ± 2.9	18.2 ± 2.1	2.7 ± 0.5	9.9 ± 1.6
0.625	257.2 ± 3.7	205.0 ± 2.5	44.2 ± 1.8	2.9 ± 0.5	10.4 ± 2.0
0.937	416.5 ± 6.4	319.6 ± 4.3	72.3 ± 2.8	3.2 ± 0.8	17.2 ± 1.6
1.275	524.2 ± 6.8	396.6 ± 4.5	94.1 ± 3.0	3.8 ± 0.9	25.9 ± 2.8

Index $i = 1-5$ denotes the rate constant k_i valid for the corresponding particular reaction, c_I , c_{II} , and c_{III} are molar concentrations of substances *I*, *II*, and *III*, and c_K is concentration of sodium hydrogensulfate.

The constants $k'_{v1}-k'_{v5}$ were calculated from the determined concentration relationships on a computer SM-4/20 by using the program KINET for calculating the parameters of the system of linear differential equations. The optimization was achieved by the use of the Gauss—Newton—Marquardt method. The calculated values of dimensionless concentrations of the com-

ponents of the reaction mixture are expressed by graphs in Figs. 1 and 2. The rate constants k'_{v1} — k'_{v5} of the particular reactions involved in isomerization of substance *I* are given as a function of temperature and sodium hydrogensulfate concentration c_K in Table 1.

In Fig. 3 the relationships between the calculated values of rate constants of the particular reactions involved in isomerization of substance *I* and catalyst concentration c_K at 98 °C are represented.

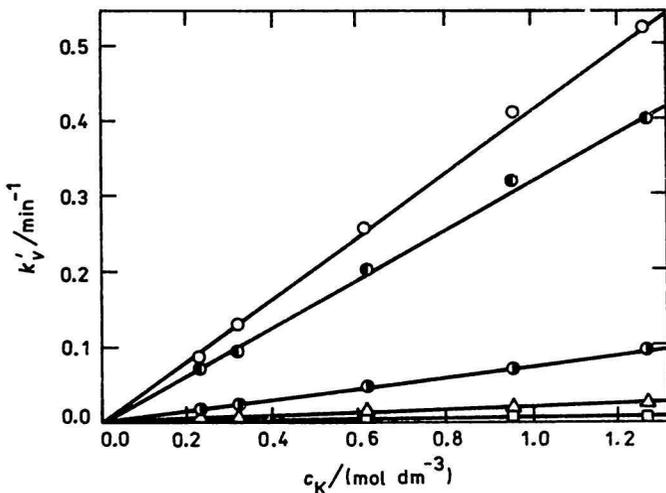


Fig. 3. Variation of rate constants of the particular reactions taking place in isomerization of 3-methyl-1-penten-4-yn-3-ol with sodium hydrogensulfate concentration c_K at 98 °C.

○ k'_{v1} , ● k'_{v2} , ● k'_{v3} , □ k'_{v4} , △ k'_{v5} .

In the investigated interval of experimental conditions the rate constants k'_t are linearly dependent on catalyst concentration. The values of parameters k'_t calculated from eqn (4) are listed in Table 2.

The relationships between the rate constants and temperature for the isomerization of substance *I* at constant catalyst concentration $c_K = 1.275 \text{ mol dm}^{-3}$ are represented in the form $\ln k'_t = f(T^{-1})$ in Fig. 4.

Table 2

Values of constants k_t calculated from the dependence of the observed rate constants k'_t on catalyst concentration ranging from 0.225 to 1.275 mol dm⁻³ at 98 °C

Particular reaction	1	2	3	4	5
$\frac{k_{vi} \cdot 10^3}{\text{dm}^3 \text{ min}^{-1} \text{ mol}^{-1}}$	417 ± 5	319 ± 4	73 ± 2	3 ± 1	19 ± 2

These relationships were used for calculating the apparent activation energies E of the reactions involved in the isomerization of substance *I* (Table 3).

These results show that the side reaction giving rise to substance *III* and the consecutive reactions responsible for transformations of substances *II* and *III* in the course of isomerization of substance *I* exhibit higher apparent activation

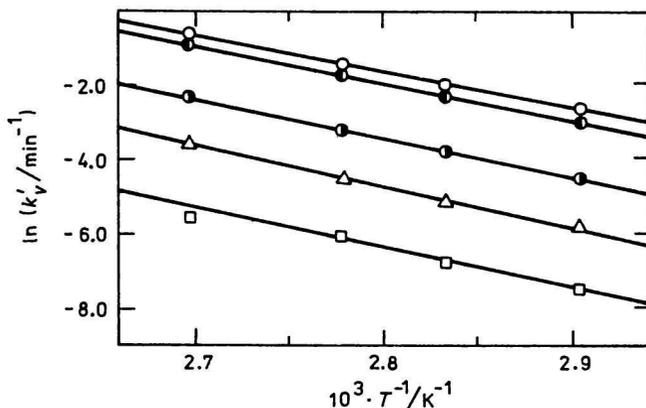


Fig. 4. Variation of logarithm of rate constants of the particular reactions taking place in isomerization of 3-methyl-1-penten-4-yn-3-ol with the inverse value of absolute temperature at constant sodium hydrogensulfate concentration $c_K = 1.275 \text{ mol dm}^{-3}$

○ k'_{1} , ● k'_{2} , ● k'_{3} , □ k'_{4} , △ k'_{5} .

Table 3

Values of apparent activation energies E_i of the particular reactions taking place in isomerization of 3-methyl-1-penten-4-yn-3-ol obtained from experimental data at constant sodium hydrogensulfate concentration $c_K = 1.275 \text{ mol dm}^{-3}$

Particular reaction	1	2	3	4	5
$\frac{E_i}{\text{kJ mol}^{-1}}$	81 ± 1	80 ± 1	86 ± 1	106 ± 20	86 ± 1

energies than the reaction producing the required product *II*. Therefore the conditions involving lower reaction temperatures (below 80°C) and sodium hydrogensulfate concentration under 0.6 mol dm^{-3} shall be profitable for the selectivity of the transformation of *I* into *II*. The above-mentioned procedure enables us to accomplish the isomerization of substance *I* with a high degree of conversion of *I* and with the optimum ratio of the desirable product *II* to the

undesirable side product *III*. Besides, the consecutive reactions of substances *II* and *III* can thus be restrained.

Presented accomplishments can be used in Slovakofarma, Hlohovec for preparing the industrial production of the *cis* isomer of 3-methyl-2-penten-4-yn-1-ol which is an intermediate of vitamin A-acetate.

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