Kinetic scheme of homogeneous acid-catalyzed transformation of isopentenols

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The reactions occurring in an equilibrium mixture of 3-methyl-1-buten-3-ol and 3-methyl-2-buten-1-ol in 24-49 % aqueous solutions of H_2SO_4 yield isoprene, 3-methyl-3-buten-1-ol, isobutylene, formaldehyde, 3-methylbutane-1,3-diol. Isobutylene is rapidly hydrated to give 2-methylpropan-2-ol. The presence of formaldehyde in the reaction mixture indicates that the transformations involve the reverse Prins reaction. On the basis of experimental and literature data, two most probable reaction schemes were suggested.

Key words: isopentenols, reaction scheme; Prins reaction; acid catalysis; kinetics.

Previously¹ it has been shown that an equilibrium mixture of 3-methyl-1-buten-3-ol (1) and 3-methyl-2buten-1-ol (2) in 24–49 % aqueous solutions of H_2SO_4 at 25 °C is converted into isoprene (3), isobutylene (4), 3-methyl-3-buten-1-ol (5), formaldehyde, and 3-methyl-butane-1,3-diol (6). Isobutylene formed in the reaction is rapidly hydrated to 2-methylpropan-2-ol (7). The experimental detection of formaldehyde and alcohol 7 in the product mixture served as evidence of the occurrence of the reverse Prins reaction during the transformations of isopentenols 1 and 2 in acid media.

Several schemes of the transformations of unsaturated alcohols 1 and 2 in the presence of H_2SO_4 can be suggested based on published²⁻⁴ and experimental data. In the present work we attempt to elucidate the mechanism of formation of numerous reaction products by computer analysis of the previously obtained kinetic data.

Experimental

Unsaturated alcohol 1 served as the starting compound. Kinetics of dehydration of an equilibrium mixture of alcohols 1 and 2 was studied by spectrophotometry based on the increase in the optical absorption of isoprene at $\lambda = 227$ nm (Fig. 1, curve 1). The kinetics of hydration of 3-methyl-3buten-1-ol (5) was studied by withdrawing samples as the reaction proceeded. The reaction products were analyzed by GLC on a Khrom-5 instrument with a flame ionization detector (a 1 m×4 mm stainless-steel column packed with 5 % XE on Chromaton N-AW-HMDS, using nitrogen as the carrier gas (v = 30 mL min⁻¹) and temperature programming in the 60-220 °C range).

Kinetic data on the hydration of isobutylene (4) in aqueous solutions of H_2SO_4 were obtained from the spectral data, *i.e.*, the decrease in the optical density at $\lambda = 207$ nm. The experimental values of rate constants of the individual steps of

the process are listed in Table 1. The computer analysis of the kinetic data was performed using the KINETIKA (KINETICS) program developed by E. F. Brin and S. O. Travin⁵ (N. N. Semenov Institute of Chemical Physics of the RAS).

Results and Discussion

Previously,¹ based on GLC analysis of the products of transformation of an equilibrium mixture of isopentenols 1 and 2 in acid media, we suggested Scheme 1, according to which the final product, 3-methylbutane-1,3-diol (6), is produced only from unsaturated alcohol 5. In conformity with the literature data,^{4,10} the formation of glycol 6 may occur both by hydration of alcohol 5 according to Scheme 1 and by hydration of 5 and 2 according to Scheme 2 (steps (6) and (7)).



Fig. 1. The kinetic curves of the formation of isoprene (1) and 3-methyl-2-buten-1-ol (2) from isopentenol 1 in 30 % H_2SO_4 at 25 °C.

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Step	Type of reaction	Reaction equation	k_{exp}/min^{-1}	Refer- ence	k^{l}_{calc} /min ⁻¹	k_{calc}^2 /L mol ⁻¹ min ⁻¹
(1)	Isomerization	$\begin{array}{c} 1 \rightarrow 2 \\ 2 \rightarrow 1 \end{array}$	0.9 6.3	6 6	0.9 6.3	
(2)	Dehydration Hydration	$\begin{array}{c} 1 \rightarrow 3 \\ 3 \rightarrow 1 \end{array}$	1.9 0.23	2 2	1.8 0.17	
(3)	Decomposition Condensation	$\begin{array}{l} 2 \rightarrow 4 + \mathrm{CH}_2\mathrm{O} \\ 4 + \mathrm{CH}_2\mathrm{O} \rightarrow 5 \end{array}$			$3.0 \cdot 10^{-2}$	
(4)	Hydration Dehydration	$\begin{array}{l} 4 + \mathrm{H_2O} \rightarrow 7 \\ 7 \rightarrow 4 + \mathrm{H_2O} \end{array}$	1.8	1	2.0	
(5)	Condensation Decomposition	$\begin{array}{l} 4 + \mathrm{CH}_{2}\mathrm{O} \rightarrow 5 \\ 5 \rightarrow 4 + \mathrm{CH}_{2}\mathrm{O} \end{array}$				$2 \cdot 10^{-5}$
(6)	Hydration Dehydration	$5 + H_2O \rightarrow 6$ $6 \rightarrow 5 + H_2O$	$9.5 \cdot 10^{-2}$ $5 \cdot 10^{-4}$	3 3	$9.5 \cdot 10^{-2}$ $8.5 \cdot 10^{-5}$	
(7)	Hydration Dehydration	$\begin{array}{l} 2 + \mathrm{H_2O} \rightarrow 6 \\ 6 \rightarrow 2 + \mathrm{H_2O} \end{array}$	$3.6 \cdot 10^{-3}$ $5.0 \cdot 10^{-4}$	4 4	$2.7 \cdot 10^{-3}$ $8.5 \cdot 10^{-5}$	
(8)	Condensation	$2 + \mathrm{CH}_{2}\mathrm{O} + \mathrm{H}_{2}\mathrm{O} \rightarrow 8$				0.15

Table 1. The values for the rate constants of individual steps of the transformation of 3-methyl-1-buten-3-ol in 30 % H_2SO_4 at 25 °C

Note: k_{exp} refers to experimental data, and k_{calc} are values calculated according to Scheme 2.

In both cases, unsaturated alcohol 2 is the source of isobutylene and formaldehyde (see Schemes 1 and 2, step (3)); the third isomer, isopentenol 5, may be produced by condensation of formaldehyde with olefin 4 (step (5)) or, simultaneously, by dehydration of diol 6 according to Scheme 2.

We attempted to establish the sequence of the reactions of intermediate products formed in the transformation of an equilibrium mixture of isopentenols 1 and 2 in acid media using the previously obtained kinetic data for individual steps. Using the KINETIKA program we calculated the rate constants of reactions (3), (5), and (7) for both schemes; the rate constants of reactions (1), (2), (4), and (6) were taken from the literature.^{2-4,6} In addition, we used the experimental kinetic curves for the consumption of an equilibrium mixture of isopentenols 1 and 2 and for the formation and consumption of isoprene in 10, 20, and 30 % solutions of H_2SO_4 at 25 °C.





The results of the calculations indicate that of the two mechanisms of the process presented above, the mechanism illustrated by Scheme 2 is realized. Processing of the kinetic data of the transformation of isopentenols 1 and 2 in 30 % H_2SO_4 at 25 °C has shown that the kinetic curves of their consumption differ from the calculated curves, *i.e.*, one more pathway of the consumption of these compounds should be taken into account.

While investigating the dependence of the composition of products on the duration of the process¹ by GLC, we detected a high-boiling compound, *viz.*, 5-hydroxyisopropyl-1,3-dioxane, which, in conformity with the literature data,⁶ may result from acetalization of 3-methyl-2-hydroxymethylbutane-1,3-diol (triol 8). This allowed us to conclude that the triol can be produced by the reaction (δ) of unsaturated alcohol 2 with formaldehyde. The results of the calculation are given in Table 1 and in Figs. 1 and 2.

According to Scheme 2, the acid-catalyzed transformations of isopentenol 1 consist of a set of parallelconsecutive steps: isomerization of unsaturated alcohols 1 and 2 (step (1)), dehydration of isopentenol 1 and diol 6 (reactions (2) and (7)), hydration of unsaturated compounds (reactions (2), (4), (6), and (7)), decomposition of isopentenol 2 – discovered for the first time (step (3)), and condensation of unsaturated compounds with formaldehyde (reactions (5) and (8)). Knowledge of kinetic parameters of these steps makes it possible to judge the reactivity of the compounds involved in the process. By comparing the rate constants of hydration of unsaturated compounds (see Table 1) one can arrange these compounds in the following series in terms of their reactivity: isobutylene > alcohol 2 > alcohol 5 > alcohol 1.

We found that isopentenols 1 and 2 exhibit dissimilar reactivities with respect to decomposition to isobutylene and formaldehyde (steps (3) and (5)). Whereas the firstorder rate constant of the decomposition of isopentenol 2 increases by two orders of magnitude over the 10-30 % range of H₂SO₄ concentration, the rate constant for decomposition of alcohol 5 was not estimated due to the extremely low rate of the reaction; thus, alcohol 5 is the more stable isomer.

The rate constant of the Prins reaction was estimated for the first time using the reaction of isobutylene with formaldehyde to yield isopentenol 5 (reaction (5)) under homogeneous conditions as an example; in 30 % H₂SO₄ at 25 °C, $k_5 = 2 \cdot 10^{-5}$ L mol⁻¹ min⁻¹.



Fig. 2. The calculated kinetic curves of the formation of isobutylene (1), 3-methyl-3-buten-1-ol (2), and 3-methylbutane-1,3-diol (3) from isopentenol 1 in 30 % H_2SO_4 at 25 °C according to Scheme 2.

According to a fairly common opinion, Prins reaction occurs very rapidly and irreversibly. The question of what primary products are formed in the condensation of isobutylene with formaldehyde has been discussed for many years. Most scientists^{7,8} believe that these are glycol, unsaturated alcohol, and 1,3-dioxane, which then react with other components resulting in a complex mixture of products.

According to Scheme 2, suggested by us, if condensation of formaldehyde with isobutylene is considered to be the initial reaction, alcohols 5 and 2 are the primary products, though, in the opinion of some authors (cf. Refs. 9, 10), this reaction yields initially only unsaturated alcohol 5. To find out the sequence of transformations of the intermediate compounds in this process is of great importance for solving technological problems in the synthesis of isoprene by the "dioxane method".

The results obtained by us imply that the rates of all the reactions involved in Scheme 2 depend on the acidity of the medium and on some thermodynamic parameters. When the temperature and the concentration of the catalyst are constant, the composition of the products varies as a function of the duration of the process and also depends on the acidity of the medium. In fact, in 5–15 % H₂SO₄, isopentenols 1 and 2 and isoprene (3) are the main final products, and the reaction in 30 % H_2SO_4 yields mostly diol 6 and triol 8.

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