G. A. RUDAKOV, M. M. SHESTAEVA, L. S. IVANOVA

1965

SovietRxiv

reaction scheme

Figure 1: reaction scheme

Abstract

Full Text

G. A. RUDAKOV, M. M. SHESTAEVA, L. S. IVANOVA

ON THE INFLUENCE OF SUPPORTS ON THE DIRECTION OF ACID CATALYTIC ISOMERIZATION OF PINENE

(Presented by Academician A. A. Balandin, 9 XII 1964)

Heterogeneous isomerization of unsaturated hydrocarbons in the presence of acid catalysts is usually considered from the standpoint of the carbonium-ion theory. However, many features of these processes remain unclear. The carbonium-ion theory does not answer the question of why the use of different catalysts leads to reaction products of different composition, as, for example, in the catalytic isomerization of α-pinene (I). This reaction on solid acid catalysts—aluminosilicates, titanic acid, etc.—proceeds in two independent directions. Addition of a proton to the double bond leads to the formation of a carbonium ion (II), as a result of whose transformations bicyclic and tricyclic terpenes are formed: camphene, tricyclene, bornylene, and fenchene. Addition of a proton to the four-membered ring leads to the formation of ion (III), the starting product for obtaining a series of monocyclic terpenes ([1,2]).

From the standpoint of the carbonium-ion theory, at a given temperature one should expect a constant ratio between the products of both competing reactions, independent of the catalyst used. In reality, when different catalysts are used, the conversion of pinene into bi- and tricyclic terpenes, chiefly camphene, varies within the limits of 10 to 80%, and into monocyclic terpenes from 20 to 90%. Evidently, the influence of additional factors is manifested here.

To elucidate these factors, we studied the catalytic isomerization of α-pinene by sulfuric and phosphoric acids deposited on the surface of certain catalytically inactive supports. The results obtained are summarized in Table 1. They show that the ratio of the rates of the two transformations does not depend on the nature of the proton-donor acids, but is determined entirely by the support on which the acids are deposited. Both sulfuric and phosphoric acid by themselves isomerize pinene almost completely into monocyclic terpenes, but when deposited on the surface of catalytically inactive silica gel they give isomerizates of identical composition, containing about 40% camphene and other bi- and tricyclic terpenes. It is interesting that the composition of the isomerizates obtained is the same as when aluminosilicate deposited on the surface of the same gel is used as catalyst.

The same acids deposited on the surface of calcined, catalytically inactive titanium dioxide make it possible to obtain considerably higher yields of bi- and tricyclic terpenes, these yields being close to those obtained on titanic acid (^{3}). True, in this case the question arose of possible hydration of titanium dioxide by the acids—

···with the formation of catalytically active titanic acid. This was verified. It turned out that the greater part of the sulfuric acid deposited on the surface of titanium dioxide reacts with it; however, the titanium dioxide that has reacted at the surface does not acquire catalytic activity and, consequently, the activity of the catalyst derives from the presence of free acid on its surface.

Table 1

Effect of supports on the yield of products of two competing reactions in the catalytic isomerization of pinene at 155°

Support	Substances deposited on the support	Amount of deposited substance, %	Catalyst, %	Duration, h	Reacted pinene, %	Bi- and tricyclic terpenes	Monocyclic terpenes
Silica gel	–	–	10	4	0	–	–
Silica gel	H_2SO_4	4	2	7	74	44	56
Silica gel	H_3PO_4	10	3	6	69	43	57
Silica gel	Al_2O_3	17	0.25	3	100	44	56
TiO_2	–	–	2	4	0	–	–
TiO_2	H_2SO_4	4	0.5	5	100	68	32
TiO_2	H_3PO_4	10	2.5	5.5	100	63	37
Al_2O_3	–	–	2	4	0	–	–
Al_2O_3	H_2SO_4	4	0.75	6	100	65	35
Charcoal	H_3PO_4	10	5	1	100	9	91

A catalyst prepared by depositing phosphoric acid on charcoal almost completely isomerizes pinene into monocyclic terpenes. It was not possible to obtain a catalyst by depositing sulfuric acid on charcoal because of the interaction of sulfuric acid with the carbon during drying.

Catalysts were prepared by depositing sulfuric and phosphoric acids on catalytically inactive aluminum oxide. Both acids reacted with aluminum oxide; under the action of phosphoric acid a linear-acidity inactive catalyst was obtained, while under the action of sulfuric acid an active catalyst was obtained, but it is possible that its activity was caused not by a film of sulfuric acid but by acidic aluminum sulfate.

Catalysts prepared by depositing sulfuric and phosphoric acids on silica gel and titanium dioxide, although approaching in their properties the aluminosilicate catalyst and titanic acid, differ from them in a number of their properties. The differences consist in a considerably slower reaction, probably because of the hydrophilicity of the surface acid film and rapid poisoning, especially of catalysts containing sulfuric acid, apparently because of resinification in the surface layer. Catalysts containing phosphoric acid strongly polymerize terpenes, but this process begins after the bulk of the pinene has reacted.

The orienting action of the support in heterogeneous acid catalysis was not noted in the work of our predecessors (^{4}), possibly because the acid films were deposited by them on the surface of glasses rather than on particles with an ordered structure, or because reactions proceeding in only one direction were studied.

The orienting action of the support in the process of catalytic isomerization of pinene may be represented in two ways:

1) The direction of the reaction is determined by the position of the molecule on the surface of the catalyst. If the molecule is directed toward the surface of the catalyst by the double bond, bi- and tricyclic terpenes are formed; if by the four-membered ring, monocyclic terpenes are formed. The absence of orientation of molecules on charcoal (^{5}) makes it possible to understand the reason for obtaining isomerizates of sharply different composition on this support.
2) The course of the reaction on the outer and inner surfaces of the catalyst is different, since when the pinene molecule moves in sufficiently narrow pores its orientation toward the surface disappears.

Experimental Part

Silica gel containing no aluminum oxide was obtained by aqueous hydrolysis of reagent-grade silicon tetrachloride distilled in a stream of dry air (^{6}). The aged gel was dried at 60°, then at 150°, and washed until neutral wash waters were obtained. After secondary drying at 150° the gel was ground in a mortar to a powder and, before use, was calcined at 350°.

Table 2

Effect of the chemical interaction of supports with acids on their catalytic properties

Support	Acid deposited on the support	Amount of acid on 1 g of support, g	Washed-out acid from 1 g of catalyst, g	Catalytic activity before washing	Catalytic activity after washing
TiO_2	H_2SO_4	0.04	0.0025	+	–
Al_2O_3	H_2SO_4	0.04	0.04	++	–
Al_2O_3	H_3PO_4	0.10	0.016	–	–
Wood charcoal	H_2SO_4	0.04	0.005	–	–
Wood charcoal	H_3PO_4	0.10	0.077	+	–

The active specific surface area, by sorption of methylene blue, was 52 m^2/g (^{7}); suspension of 2.5 g of gel in 12.5 ml of H_2O, pH 5.6 (^{7}); exchange capacity with respect to CH_3COONa (^{8}), 0.13 mg-eq/g.

Titanium dioxide was obtained by calcining commercial metatitanic acid at a light-red heat for 2 h.

Reactive, anhydrous, "pure" aluminum oxide was used; before use it was calcined for 1.5 h.

The wood charcoal contained 2.05% H_2O, 2.10% ash, and 10.7% volatile substances. Analysis: C 94.23%, H 3.42%. Specific surface area 32 m^2/g (^{7}).

To deposit sulfuric and phosphoric acids, 10 g of support was treated with 40 ml of water containing the calculated amount of acid. The water was evaporated, and the product was dried first at 100°, finally at 125–135°.

To deposit aluminum oxide, silica gel was treated with an aqueous solution of aluminum nitrate containing the calculated amount of salt. It was evaporated to dryness and the residue was calcined at 350–400° (^{9}).

The initial α-pinene (an industrial sample), n_D^{20} 1.4665, d_4^{20} 0.8592, contained about 6% impurities, mainly β-pinene (^{3}).

The reaction was carried out in a three-necked flask with a stirrer. As inhibitor, 0.01% hydroquinone was added.

The course of the process was monitored by analyzing samples taken during the reaction (^{10}), and the final conclusions on the composition of the isomerizates were made from analytical distillations on columns of about 50 theoretical plates, followed by physical analysis of the fractions obtained (^{3}).

To avoid polymerization, in a number of cases the reaction was not carried to completion, and the analytical results were recalculated to the unreacted product. If the supports could react with the acids, the catalysts were subjected to additional investigation. The acids contained in them were washed out with water and titrated with alkali in the presence of phenolphthalein. The residue was dried and tested for activity with pinene. If the catalyst lost activity after the acid had been washed out, its activity was attributed to an acid film. The results are summarized in Table 2.

Institute of Petroleum and Coal-Chemical Synthesis
Irkutsk State University
named after A. A. Zhdanov

Received
7 XII 1964

Cited Literature

1. L. Ruzicka, *Pure and Appl. Chem.*, **6**, No. 4 (1963).
2. W. Sandermann, W. Schweers, *Tetrahedron Letters*, No. 6, 257 (1962).
3. T. A. Rudakov, *Chemistry and Technology of Camphor*, Moscow-Leningrad, 1961.
4. N. M. Chirkov, M. I. Vinnik et al., *Collection of Problems in Chemical Kinetics, Catalysis, and Reactivity*, Publ. Acad. Sci. USSR, 1955, p. 496.
5. Ya. Kh. De-Bur, *Collected Catalysis, Some Questions of the Theory and Technology of Organic Reactions*, IL, 1959.
6. A. V. Kiselev, *Koll. zhurn.*, **2**, 17 (1961).
7. T. A. Rudakov, Z. S. Khomenko, *ZhOKh*, **24**, 337 (1954).
8. Yu. A. Bittenazh, *ZhOKh*, **17**, 199 (1947).
9. T. A. Rudakov, M. M. Shestaeva, *ZhOKh*, **29**, 2062 (1959).
10. T. A. Rudakov, Z. S. Khomenko, M. M. Shestaeva, *ZhOKh*, **24**, 549 (1954).

Note: Figure translations are in progress. See original paper for figures.