Chemistry

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Abstract

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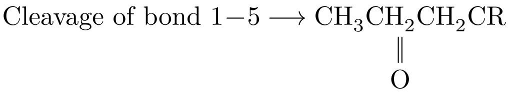
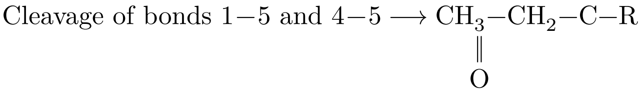
CATALYTIC HYDROGENOLYSIS OF SYLVAN ON VARIOUS CATALYSTS

The hydrogenolysis reaction of furan homologues depends on three factors: the conditions under which it is carried out, the nature of the catalyst, and the temperature. In the hydrogenation of sylvan in the liquid phase over copper chromite, the furan ring is cleaved to almost the same extent at the ether bonds 1-2 and 1-5, as a result of which pentanol-1 and pentanol-2 are formed, respectively ([1]). In contrast to this, hydrogenolysis of sylvan in the liquid phase over Adams' platinum catalyst proceeds in the direction of cleavage only of the C—O bond 1-5 ([2]). Hydrogenolysis of sylvan in the vapor phase over nickel ([3]) and copper ([4]) catalysts also proceeds at the C—O bond 1-5, but the reaction product in this case is not an alcohol, but a ketone (pentanone-2).

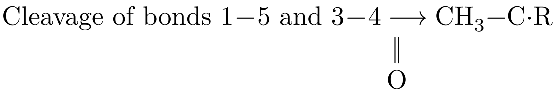
We ([5]-[7]) have investigated the hydrogenolysis reaction of furan homologues in the vapor phase over a skeletal nickel-aluminum catalyst and have shown that on this catalyst hydrogenolysis takes place not only of the ether bonds, but also of the carbon-carbon bonds in the furan ring. All furan homologues having an alkyl or alkenyl substituent in the α-position undergo hydrogenolysis in three directions:



$$\text{Cleavage of bond } 1-5 \longrightarrow CH_3CH_2CH_2\underset{\substack{\| \\ O}}{C}R \qquad (I)$$



$$\text{Cleavage of bonds } 1-5 \text{ and } 4-5 \longrightarrow CH_3-CH_2-\underset{\substack{\| \\ O}}{C}-R \qquad (II)$$



$$\text{Cleavage of bonds } 1-5 \text{ and } 3-4 \longrightarrow CH_3-\underset{\substack{\| \\ O}}{C}\cdot R \qquad (III)$$

At 175° and lower temperatures the furan ring undergoes hydrogenolysis only in directions (I) and (II), while at a higher temperature (235°) it also proceeds in direction (III). In the present article we give the results of a study of the hydrogenolysis of sylvan in the presence of various catalysts: platinum on carbon

(15% Pt), palladium on carbon (10% Pd), Adkins copper chromite, nickel on aluminum oxide (30% Ni), and a skeletal nickel-aluminum catalyst.

The latter was prepared by leaching 10-15% of aluminum from a Ni—Al alloy containing 27% Ni. The reaction was carried out in the vapor phase in a flow-type apparatus at 275°. The rate of passage of sylvan was 0.1 hr^{-1}. The reaction products were fractionated on a column with an efficiency of 30 theoretical plates, and then identified by determining physical constants and by converting the ketones formed into semicarbazones.

Hydrogenolysis of sylvan on a skeletal Ni—Al catalyst. After passing 120 g of sylvan over the Ni—Al catalyst in a stream of hydrogen at 275°, 92 g of catalyzate was obtained, from which the following compounds were isolated:

1. Acetone (35%). Semicarbazone, m.p. 186°.
2. Methyl ethyl ketone (24%), b.p. 78.5-79.5° (743 mm), d_4^{20}0.8068, n_D^{20}1.3796. Semicarbazone, m.p. 146-147°.
3. Methyl propyl ketone (36%), b.p. 100.5-101° (743), d_4^{20} 0.8071, n_D^{20} 1.3912. Semicarbazone, m.p. 110°.

The higher-boiling portion of the catalyzate (in an amount of about 5%) was not investigated. The gaseous reaction products, after removal of hydrogen from them, were analyzed by the chromatographic method. They contained methane (3%), ethane (64%), propane (22%), and butane (11%).

Hydrogenation of sylvan on a Ni/Al_2O_3 catalyst. 100 g of sylvan after hydrogenation at 275° gave 67 g of catalyzate and 16 g of water. In pure form, unconverted sylvan (36%), *n*-pentane (10%), and methyl propyl ketone (9%) were isolated from the catalyzate.

A fraction with b.p. 77-80° (753 mm) and n_D^{20} 1.3930, obtained in an amount of 8%, gave a semicarbazone with m.p. 147°, which indicates the presence of methylethyl ketone in it. After treatment of this fraction with sodium bisulfite, pure tetrahydrosylvan was obtained.

A considerable part of the catalyzate (37%) boiled within 60-150° (8 mm) and was not subjected to further investigation. It apparently represented a mixture of glycols and condensation products.

120 g of sylvan was subjected to hydrogenation at 400°. In this process 78 g of catalyzate and 16 g of water were obtained. The catalyzate contained unconverted sylvan (24%), *n*-pentane (8%), acetone (10%), methylethyl ketone (6%), tetrahydrosylvan (6%), methyl propyl ketone (6%), and a higher-boiling residue (40%).

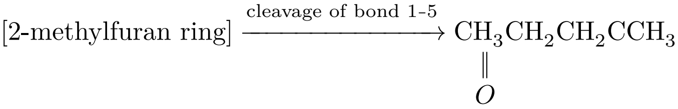
Hydrogenolysis of sylvan on copper chromite. The copper chromite catalyst proved to be only slightly active in the hydrogenation of sylvan in the vapor phase at 275°. After a single passage of sylvan over the catalyst, about 80% of it did not enter into the reaction. The reaction products consisted of pentanone-2 (yield 75%, calculated on converted sylvan) and a residue with b.p. above 150°.

Hydrogenolysis of sylvan on platinized carbon. 120 g of sylvan, after a single passage over a platinum catalyst at 275°, gave 116 g of catalyzate, which contained pentanone-2 (85%) and unconverted sylvan (15%).

Hydrogenolysis of sylvan on palladized carbon. As a result of hydrogenating 120 g of sylvan at 275° over palladium deposited on activated carbon, 118 g of catalyzate was obtained, which consisted of tetrahydrosylvan (71%) and pentanone-2 (29%).

The results of the present investigation lead to the conclusion that the direction and depth of hydrogenolysis of the furan ring depend substantially on the nature of the catalyst.

Platinum deposited on carbon has the selective capacity to bring about hydrogenolysis of the ring in sylvan only at the ether bond 1-5:



$$\text{[2-methylfuran ring]} \xrightarrow{\text{cleavage of bond 1-5}} CH_3CH_2CH_2\underset{\underset{O}{\|}}{C}CH_3$$

The presence in the reaction products exclusively of pentanone-2 and unconverted sylvan shows that at 275° on the platinum catalyst the hydrogenolysis reaction proceeds at an incomparably greater rate than the hydrogenation of the double bonds in the ring. Pentanone-2 is formed practically in quantitative yield, calculated on the sylvan that entered into reaction. Conversely, the palladium catalyst proves effective in the reaction of hydrogenating the double bonds in the ring and exhibits only slight activity with respect to hydrogenolysis of the ether bond. As on platinum, the furan ring in the presence of the palladium catalyst undergoes hydrogenolysis only at the C–O bond 1-5, as a result of which pentanone-2 is formed. The copper chromite catalyst exhibits a very low ac-

activity in the hydrogenation and hydrogenolysis reactions of the furan ring at 275°. In contrast to hydrogenolysis of sylvan over copper chromite in the liquid phase, leading to the formation of two alcohols ([1]), the reaction in the vapor phase over this catalyst proceeds only in the direction of cleavage of the ether bond not adjacent to the side group.

Skeletal nickel-aluminum catalyst and nickel on alumina exhibit a profound difference with respect to their ability to carry out the hydrogenolysis reaction of the furan ring. On the nickel-alumina catalyst at 275° only about 15% ketones are formed; 85% of the catalyzate consists of unchanged sylvan, *n*-pentane, and compounds with a high boiling point. This shows that nickel on alumina promotes processes of deep decomposition of the furan ring and the formation of molecules of more complex composition.

On the skeletal nickel-aluminum catalyst the furan ring undergoes hydrogenolysis in three directions:

[2-methylfuran ring, positions 1–5 indicated]

Cleavage of bond 1—5 ⟶ $CH_3CH_2CH_2C(=$

Cleavage of bonds 1—5 and 4—5 ⟶ $CH_3CH_2C(=O)CH$

Cleavage of bonds 1—5 and 3—4 ⟶ $CH_3C(=O)CH_3$

These results are in agreement with our earlier observations ([5]-[7]) on the hydrogenolysis of higher homologs of furan on a skeletal nickel-aluminum catalyst. Thus, of all the catalysts investigated, only the skeletal nickel-aluminum catalyst possesses the ability to smoothly carry out hydrogenolysis of the furan ring both in the direction of cleavage of the ether bond 1—5 and in the direction of conjugated cleavage of bonds 1—5 and 4—5 and 1—5 and 3—4. This property of the catalyst gives a practical possibility of obtaining aliphatic ketones of various structures as a result of hydrogenolysis of alkylfurans.

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

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.