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Abstract

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ON THE MECHANISM OF THE REACTION OF CATALYTIC HYDROGENOLYSIS OF THE FURAN RING

In studying the hydrogenolysis reaction of furan and its derivatives, various authors have raised the question of whether this reaction can proceed through a stage of hydrogenation of the double bonds in the ring, followed by cleavage of the resulting tetrahydrofuran ring at one of the C–O bonds. A negative answer to this question was given by studies of the comparative hydrogenolysis of furan and its derivatives, on the one hand, and of the corresponding tetrahydro derivatives, on the other, under identical reaction conditions. Thus, Kaufmann and Adams (^{1}), as a result of studying the behavior of furyl and tetrahydrofuryl alcohols under conditions of hydrogenating them in the liquid phase on a platinum catalyst, concluded that the formation of 1,2-pentanediol and 1,5-pentanediol during hydrogenation of furyl alcohol cannot pass through the stage of reduction of the double bonds in the ring, since tetrahydrofuryl alcohol does not undergo hydrogenolysis in appreciable quantities.

Smith and Fuzek (^{2}) arrived at similar ideas concerning the mechanism of the hydrogenolysis reaction of the furan ring when studying the comparative hydrogenolysis of furan and tetrahydrofuran in acetic acid solution on the same platinum catalyst. Connor and Adkins (^{3}) investigated the hydrogenolysis of silvan and tetrahydrosilvan, furyl and tetrahydrofuryl alcohols on copper chromite in the liquid phase and established a sharply different relation to hydrogenolysis between the furan and tetrahydrofuran rings. Tetrahydrofuryl alcohol, undergoing hydrogenolysis to an insignificant extent, gave almost exclusively 1,5-pentanediol, whereas furyl alcohol under the same conditions was converted into a mixture of almost equal amounts of 1,2-pentanediol and 1,5-pentanediol. Under identical hydrogenation conditions, silvan gave 70% hydrogenolysis products, while tetrahydrosilvan remained unchanged by 74%.

Thus, the works listed above proved that the tetrahydrofuran ring under conditions of liquid-phase hydrogenation completely lacks the capacity for hydrogenolysis that is characteristic to a high degree of the furan ring. This difference in the behavior of the furan and tetrahydrofuran rings under conditions of catalytic hydrogenation also occurs when the reaction is carried out in the vapor phase on nickel (4) and skeletal nickel-aluminum (5) catalysts. Wilson (4) studied the comparative hydrogenolysis of silvan and tetrahydrosilvan in the vapor phase on a nickel catalyst and found that tetrahydrosilvan remains unchanged at 100°, while at 250° it undergoes deep decomposition with formation of gaseous products. Consequently, in the vapor phase as well, hydrogenation of the double bonds in the furan ring does not precede hydrogenolysis of the ring.

Recently we (6) showed that on Pt carbon at 250–300° homologues of tetrahydrofuran are isomerized into aliphatic ketones. However, this reaction proceeds much more slowly than the direct hydrogenolysis

of the alkylfurans themselves under these same conditions, and therefore it is impossible to regard tetrahydrofurans as intermediate compounds in the hydrogenolysis reaction of furan compounds. Thus, all these studies lead to the conclusion that hydrogenolysis of the C—O bond may occur either in the ring of furan itself or in the ring of dihydrofuran. The formation of the latter as an intermediate product is proved by the conversion of sylvan into γ-acetopropyl alcohol upon hydrogenation in the presence of water (7):

$$\text{[reaction scheme: 2-methylfuran]} \xrightarrow{H_2} \text{[[dihydro-2-methylfuran]]} \begin{array}{l} \xrightarrow{H_2} \text{[tetrahydro-2-methylfuran]} \\ \xrightarrow{H_2O} \mathrm{CH_3C(O)CH_2CH_2CH_2OH} \end{array}$$

Indirect evidence for stepwise hydrogenation of bonds in the furan ring is also provided by the formation of spirans under the conditions of hydrogenation of 3-furylalkanols over nickel and copper-chromium catalysts. Alexander et al. (8) propose the following scheme for the formation of spirans:

$$\text{[furylalkanol]} \longrightarrow \text{[[dihydrofurylalkanol]]} \longrightarrow \text{[spiro compound]}$$

On the basis of these experimental data, some investigators (4,9) regard the formation of dihydrofuran as an intermediate stage in the reaction of hydrogenolysis of the furan ring. At the same time, Bredig (10), measuring the rate of hydrogenation of furan on a platinum catalyst, found that the addition of 3 moles of hydrogen does not proceed stepwise, since all the hydrogenation curves were smooth. In connection with what has been set forth above, this fact may be interpreted to mean that hydrogenation in the presence of water creates conditions favorable for a different course of the process and that, consequently, the question of one or another mechanism of the hydrogenolysis reaction of the furan ring cannot be decided from the results of hydrogenation of the furan ring in the presence of water.

In the present work we investigated the hydrogenation of dihydrosylvan in the gas phase on platinized carbon and on nickel on zinc oxide at 250-260°. As is known, sylvan under these conditions is completely cleaved at the C—O bond 1-5 with formation of methyl propyl ketone ([11]). Tetrahydrosylvan remains unchanged on Ni—ZnO, while on Pt—C it undergoes isomerization to pentan-2-one ([6]), the rate of formation of the ketone in this case being considerably lower than the rate of its formation as a result of the hydrogenolysis of sylvan:

$$\text{[dihydrosylvan]} \xrightarrow[250-260^\circ]{\text{Pt—C, Ni—ZnO}} CH_3CH_2CH_2C(O)CH_3$$

Dihydrosylvan, if it is formed as an intermediate compound in the hydrogenolysis of sylvan, should be converted into methyl propyl ketone with the same ease and just as completely as sylvan. However, the experiments carried out by us show that the principal reaction in the hydrogenation of dihydrosylvan on Pt—C and Ni—ZnO at 250-260° is not hydrogenolysis of the C—O bond, but hydrogenation of the C-C bond in the ring:

$$\text{[dihydrosylvan]} \xrightarrow[250-260^\circ]{\text{Pt—C}} \text{[tetrahydrosylvan]}\ (90\%) + CH_3CH_2CH_2C(O)CH_3\ (\sim 10\%)$$

and $$\text{[dihydrosylvan]} \xrightarrow[250-260^\circ]{\text{Ni—ZnO}} \text{[tetrahydrosylvan]}\ (\sim 50\%) + CH_3CH_2CH_2C(O)CH_3\ (15-20\%)$$

The formation of methyl propyl ketone during the hydrogenation of dihydrosilvan on Pt—C may occur as the result of a secondary isomerization reaction of tetrahydrosilvan. On Ni—ZnO, tetrahydrosilvan is not isomerized into methyl propyl ketone; therefore, in this case it must be assumed that dihydrosilvan undergoes hydrogenolysis at the C—O bond 1-5 to give pentan-2-one. In the hydrogenation of dihydrosilvan on Ni—ZnO, in addition to tetrahydrosilvan and methyl propyl ketone, compounds with high boiling points are also formed in considerable amounts (30-35%).

The ability of the C=C bond in the dihydrofuran ring to be readily reduced on Pt—C and Ni—ZnO is evidently connected with the fact that this bond essentially has the properties of a simple olefinic bond. Consequently, it should be hydrogenated with approximately the same ease as the double bond in the side chain of alkenylfurans, and much more readily than the C—O bond in the dihydrofuran ring. At the same time, according to the conclusions of multiplet theory (12), the hydrogenation of the first double bond in the furan ring proceeds much more difficultly than the hydrogenation of an olefinic bond, and approximately as difficultly as the hydrogenolysis of the C—O bond in the furan ring. It follows from this that cleavage of the C—O bond should occur with considerably greater probability in the ring of furan itself, which is fully confirmed in our experiment.

The results obtained by us can also be given another interpretation. Namely, it may be assumed that the silvan ring, while in the adsorbed state, is first hydrogenated at one C=C bond, and then such adsorbed dihydrosilvan may subsequently be hydrogenated to tetrahydrosilvan, undergo hydrogenolysis, or, finally, add the elements of water at the double bond. Experiment shows that if only one C=C bond in the furan ring can be hydrogenated at first, then such a product of partial reduction must, without desorbing, undergo further transformations in the directions indicated above. In general, however, the method of proving the mechanism of hydrogenolysis of the furan ring, consisting in the study of the behavior of possible intermediate forms (in our case, dihydrosilvan and tetrahydrosilvan) under identical reaction conditions, cannot answer the question of the sequence in which the hydrogenation processes proceed on the catalyst surface, since it essentially includes consideration of stages of desorption and adsorption of intermediate compounds. Taking into account all that has been said above, on the basis of our experiments it may be asserted that the formation of dihydrofuran is not an intermediate stage in the hydrogenolysis reaction of the furan ring. In other words, from the catalyst surface, after a number of elementary acts of the process of hydrogenation of the furan ring, either tetrahydro derivatives or products of hydrogenolysis of the ring at the ether bond are desorbed:

$$\text{[furan ring]}\text{—R+H}_2 \xrightarrow{\text{adsorption}} \text{Adsorption complex} \xrightarrow{\text{desorption}} \begin{cases} \text{[tetrahydrofuran ring]—R,} \\ \text{hydrogenolysis products.} \end{cases}$$

Experimental Part

Catalysts. Platinized charcoal was prepared by impregnating activated charcoal with the calculated amount of a solution of chloroplatinic acid, followed by reduction with hydrogen in the reaction tube at 200-250°. The catalyst contained 5% finely dispersed platinum. Ni—ZnO, containing 30% Ni, was obtained by coprecipitation with caustic potash of nickel and zinc hydroxides from a solution of their nitrates, followed by reduction with hydrogen at 200-300°.

Starting materials. Dihydrosilvan was obtained by dehydration of acetopropyl alcohol according to the method of Kirrmann and Cienty (13). After

after rectification on an efficient column it had the following constants: b.p. 79-80°/750 mm, d_4^{20}0.9039 and n_D^{20}1.4297. Found MR 24.02; for C_5H_8O calculated MR 24.26. Pure silvane (b.p. 64-66°/750 mm, d_4^{20}0.9121, n_D^{20}1.4320) was isolated from a commercial preparation by treating the latter with sodium and rectifying on an efficient column. Experiments on the comparative hydrogenation of silvane and dihydrosilvane were carried out by the flow method at 250-260° and normal pressure. The temperature was measured with a chromel-alumel thermocouple in the middle of the catalyst bed. The substance was fed into the reaction zone at a space velocity of 0.1 hr^{-1}. The catalysts were dried with potash and rectified on a column with an efficiency of 40 theoretical plates.

The results of the experiments are presented in Table 1.

Table 1

Hydrogenation products of silvane and dihydrosilvane on Pt–C and Ni–ZnO at 250-260°

Starting substance	Hydrogenation products on Pt–C	Hydrogenation products on Ni–ZnO
Silvane	Pentan-2-one (~100%):b.p. 109-101.5° d_4^{20} 0.8080, n_D^{20} 1.3912	Pentan-2-one (95-100%)
Dihydrosilvane	Tetrahydrosilvane (90%)b.p. 79-80° d_4^{20} 0.7582, n_D^{20} 1.4060Pentan-2-one (~10%)	Tetrahydrosilvane (50%),pentan-2-one (15-20%),compounds with b.p. above 105°(30-35%)

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