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Abstract

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CATALYTIC HYDROGENATION OF FURAN COMPOUNDS UNDER PRESSURE IN A FLOW SYSTEM

The present work presents the results of a study of the hydrogenation of various furan compounds in a flow system at elevated hydrogen pressures over Pt—C and skeletal Ni—Zn and Ni—Al catalysts. Comparison of these results with experimental data obtained earlier in the hydrogenation of furan derivatives in the vapor phase at normal pressure makes it possible to determine the influence of pressure on the ability of the furan ring to be hydrogenated to a tetrahydrofuran ring or to undergo hydrogenolysis, and on the sequence and selectivity of reduction of different unsaturated bonds in a furan compound.

1. As is known (^{1}), hydrogenation of sylvan over Pt—C at normal pressure and 275° leads to complete hydrogenolysis of the furan ring with formation of methyl propyl ketone (reaction II); tetrahydrosylvan is not formed under these conditions. An entirely different course of the reaction is observed in the hydrogenation of sylvan over Pt—C in a flow system at the same temperature, but at a hydrogen pressure increased to 50 atm. In this case the main direction of the reaction is hydrogenation of sylvan to tetrahydrosylvan (reaction I), while hydrogenolysis of the furan ring proceeds to a much smaller extent (about 25%):

$$\text{sylvan} \xrightarrow[\text{Pt—C, } 275^\circ]{H_2,\ 50\ \text{atm}} \begin{cases} \text{tetrahydrosylvan} & 75\% \quad (\text{I}) \\ CH_3CH_2CH_2{-}C(=O){-}CH_3 & 20\% \\ CH_3CH_2CH_2CH(OH){-}CH_3 & \sim 5\% \quad (\text{II}) \end{cases}$$

2. Recently we found (^{2}) that in the hydrogenation of 2-methyl-5-acetylfuran over Pt—C at normal pressure the primary reaction is predominantly hydrogenolysis of the ring at the $C-O$ bond adjacent to the carbonyl group. The heptanedione-2,5 formed in this process cyclizes with elimination of water to 1-methylcyclohexen-1-one-3, which then, depending on the temperature, is converted either into 3-methylcyclohexanone or into *m*-cresol. Primary reduction of the carbonyl group with subsequent hydrogenation and hydrogenolysis of the resulting 2-methyl-5-ethylfuran occupies a subordinate place under these conditions (about 20%). However, this reac-

tion becomes practically the only one in the hydrogenation of 2-methyl-5-acetylfuran over Pt—C at 230—250° and a hydrogen pressure of 50 atm:

$$CH_3\text{—furan—}C(=O)\text{—}CH_3 \rightarrow CH_3\text{—furan—}CH_2CH_3 \rightarrow CH_3\text{—tetrahydrofuran—}CH_2CH_3 \quad 55\%$$

$$CH_3\text{—furan—}CH_2CH_3 \begin{cases} \downarrow\ 10\% & \text{heptanol-3} \\ & \text{heptanone-3} \\ \downarrow\ 22\% & \text{heptanol-2} \\ & \text{heptanone-2} \end{cases}$$

3. Under the same hydrogenation conditions on Pt—C (250°, 50 atm), the hydroxyl group in alkylfurylcarbinols, analogously to the carbonyl group, is reduced before the furan ring is hydrogenated. For example, hydrogenation of isopropylfurylcarbinol gives a catalyzate containing about 30% α-isobutylfuran and about 50% α-isobutyltetrahydrofuran:

$$\text{[furyl]–}CH(OH)\text{–}CH(CH_3)_2 \longrightarrow \text{[furyl]–}CH_2CH(CH_3)_2 \longrightarrow \text{[tetrahydrofuryl]–}CH_2CH(CH_3)_2$$

4. The properties of the skeletal Ni—Zn catalyst were studied by us, in particular, in the hydrogenation of sylvan in the vapor phase at normal pressure. Over a wide temperature interval (150-300°), sylvan underwent hydrogenolysis—by 70-75% at 150° and quantitatively at 270-300°. At lower temperatures an insignificant amount of tetrahydrosylvan is formed (not more than 20% at 150°). The use of elevated pressure in the hydrogenation of sylvan on skeletal Ni—Zn promotes the reaction of hydrogenation of multiple bonds in the furan ring and suppresses the hydrogenolysis reaction. However, this effect is less pronounced than on the platinum catalyst. At 250-260° and 50 atm hydrogen pressure, sylvan on skeletal Ni—Zn gives 35-40% tetrahydrosylvan, 20-25% 2-pentanone, and about 40% 2-pentanol.

5. As we have shown earlier (3), the skeletal Ni—Al catalyst, unlike other nickel catalysts, has the distinctive property of carrying out the so-called "conjugated" hydrogenolysis of the furan ring under hydrogenation conditions in a flow system at normal pressure. Already at 235-250° the furan ring in α-alkylfurans is completely cleaved with formation of ketones of three series: 2-alkanones, 3-alkanones, and 4-alkanones. α-Alkyltetrahydrofurans are not formed at this temperature. An increase in pressure also very substantially changes the direction of hydrogenation of the furan ring. Thus, as a result of hydrogenation of sylvan in a flow system at 270° and 50 atm hydrogen pressure in the presence of a Ni—Al catalyst, about 50% tetrahydrosylvan, 45% aliphatic ketones and alcohols (2-butanol, methyl ethyl ketone, methyl propyl ketone), and about 5% n-pentane were obtained.

Thus, in all cases, increasing the hydrogen pressure during hydrogenation in a flow system favors the course of the reaction of hydrogenation of multiple bonds in the furan ring. This is most strongly expressed when carrying out the reaction on platinized carbon, and least on nickel catalysts (skeletal Ni—Zn and Ni—Al). The increase in pressure also contributes to the fact that, on Pt—C, reduction of the hydroxyl and carbonyl groups before hydrogenation of the furan ring becomes the principal or even the only primary reaction in the hydrogenation of alkylfurylcarbinols and alkylfurylketones.

Experimental Part

Catalysts. Platinized carbon containing 10% Pt was prepared by impregnating birch activated carbon with a solution of chloroplatinic acid and subsequently reducing it with hydrogen in the reaction tube at 250-320°. Skeletal Ni—Zn and Ni—Al catalysts were obtained by incomplete removal of aluminum or zinc from alloys of these metals with nickel by treating pieces of the alloy with a solution of caustic soda. To remove zinc, the use of a concentrated alkali solution and prolonged heating are required, whereas to dissolve part of the aluminum from the alloy with nickel, a 10% NaOH solution was used.

Starting substances. Pure sylvan was isolated from the technical product by distillation on a column: b.p. 62-64° (750); n_D^{20} 1.4320; d_4^{20} 0.9120. 2-Methyl-5-acetylfuran was obtained by acetylation of sylvan with acetic anhydride in the presence of phosphoric acid: b.p. 68-69° (7); n_D^{20} 1.5095; d_4^{20} 1.0655. Its yield was 45% of theory.

Isopropylfurylcarbinol was synthesized by the Grignard reaction from furfural and isopropyl bromide in a yield of 70% of theory: b.p. 66-68° (5), n_D^{20} 1.4791; d_4^{20} 1.0297.

Experimental conditions. The hydrogenation of sylvan, 2-methyl-5-acetylfuran, and isopropylfurylcarbinol over Pt—C, skeletal Ni—Zn, and skeletal Ni—Al was carried out in a flow-type apparatus ( ) at 230-275° and a hydrogen pressure of 50 atm. The reaction products were distilled on an efficient column. The substances obtained had the following properties:

Tetrahydrosylvan, b.p. 79-79.2° (747); n_D^{20} 1.4060; d_4^{20} 0.8582.

Pentanone-2, b.p. 100-102° (750); n_D^{20} 1.3912; d_4^{20} 0.8081; semicarbazone, m.p. 110°.

Pentanol-2, b.p. 118-119° (750); n_D^{20} 1.4060; d_4^{20} 0.8097.

2-Methyl-5-ethyltetrahydrofuran, b.p. 116.5-117° (742); n_D^{20} 1.4130; d_4^{20} 0.8403.

α-Isobutylfuran, b.p. 128-128.5° (750); n_D^{20} 1.4415; d_4^{20} 0.8785.

α-Isobutyltetrahydrofuran, b.p. 149-150° (755); n_D^{20} 1.4265; d_4^{20} 0.8484.

Tetrahydrosylvan and methylethyl ketone, obtained in the hydrogenation of sylvan over skeletal Ni—Al, were contained in the fraction with b.p. 78-80°.

The amounts of these compounds in the fraction were determined on the basis of the refractive-index values.

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REFERENCES

1. N. I. Shuikin, I. F. Bel' skii, DAN, **115**, 330 (1957).
2. N. I. Shuikin, I. F. Bel' skii, DAN, **127**, 359 (1959).
3. N. I. Shuikin, I. F. Bel' skii, Izv. AN SSSR, OKhN, 1958, No. 3, 309.
4. N. I. Shuikin, E. D. Tulupova, Z. P. Polyakova, Izv. AN SSSR, OKhN, 1958, No. 12, 1476.

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

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