CATALYTIC HYDROGENATION OF FURFURYLIDENEACETONE

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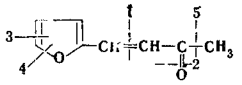
The stepwise character of the hydrogenation of furfurylideneacetone on a Raney nickel catalyst at 50°C and atmospheric pressure was investigated. It is shown that the intermediate – 1-(α-furyl)-3-butanone – is primarily hydrogenated to 1-(α-tetrahydrofuryl)-3-butanone.

Furan compounds and their hydrogenation products are an important form of raw material for the organic synthesis industry and for obtaining polymeric materials. This explains the interest that has been shown in the study of the hydrogenation of furan and its derivatives [1, 2]. The bonds can be arranged in a definite order with respect to the difficulty of hydrogenation in furan compounds: hydrogenation of the C=C (1) and C=O (2) bonds in the side chain, hydrogenation of the C=C bonds (3) in the furan ring, and hydrogenolysis of the C–O bond (4) in the furan ring, and hydrogenolysis of the C–O and then C–C (5) bonds. This sequence of reactions is explained by the energy relationships of Balandin's multiplet theory of catalysis [3]. From the point of view of confirmation of the assumptions of the theory, the hydrogenation of furfurylideneacetone, which has all of the types of bonds indicated above, is of great interest.



Furfurylideneacetone is the major component of the "FA" monomer produced by Soviet industry. In addition, it can also be obtained and used as a pure product [4]. The transformations of furfurylideneacetone to 1-(α-furyl)-3-butanone [5], 1-(α-tetrahydrofuryl)-3-butanol [6], and to 2-methyl-1,6-dioxaspiro[4.4]-nonane [7], as well as the conversion of 1-(α-furyl)-3-butanol to 1-(α-tetrahydrofuryl-3-butanol [8] and 2-methyl-1,6-dioxaspiro[4.4]nonane [8], which confirm the assumption of the multiplet theory, have been reported. However, cases of disparity between the experimental data and theory are also known. For example, the hydrogenation of furfurylideneacetone over nickel gave 1-(α-tetrahydrofuryl)-3-butanone [9], i.e., hydrogenation occurs more readily at the ring double bond (3) than at the carbonyl bond (2). In individual studies, the hydrogenation of furfurylideneacetone was directed to obtain definite products, and the experimental conditions differed considerably. For this reason, although the major products of the hydrogenation of furfurylideneacetone were previously known, the stepwise hydrogenation, which is required by multiplet theory, has not been investigated. The goal of the present research was a study of the stepwise character of the hydrogenation of furfurylideneacetone on a nickel catalyst together with an accurate determination of the sequence of the transformations predicted by Balandin's multiplet theory of catalysis.

It was first found that the reaction rate (the volume of H_2 absorbed in the first 10 min) does not change when the mixing intensity is increased above 650 oscillations of the long-necked hydrogenation flask per minute (Fig. 1). It is apparent from Fig. 2, in which the dependence of the reaction rate increases in proportion to the amount of catalyst as the amount of catalyst increases from 0.1 to 0.7 g. A further increase in the amount of catalyst induces a certain slowing down of the reaction rate. These results demonstrate

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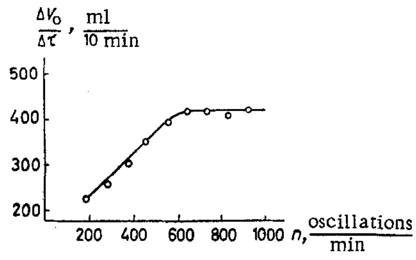


Fig. 1

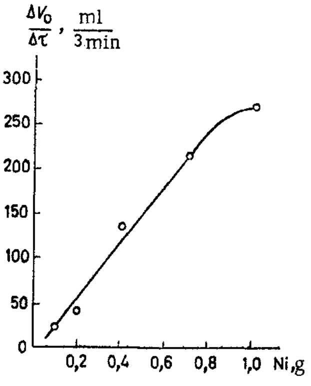


Fig. 2

Fig. 1. Effect of the mixing intensity on the rate of hydrogenation of furfurylideneacetone (for 2 g of furfurylideneacetone and 0.4 g of Ni in 30 ml of ethanol at 50°C).

Fig. 2. Effect of the amount of catalyst on the rate of hydrogenation of furfurylideneacetone (for 2 g of furfurylideneacetone in 30 ml of ethanol at 50°C).

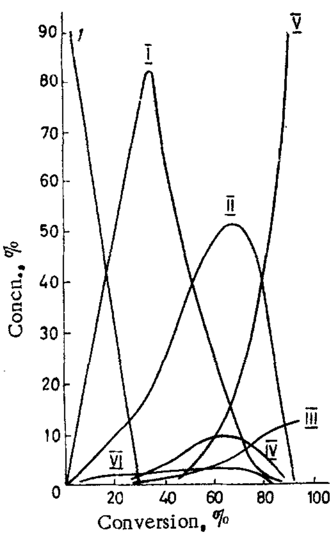


Fig. 3. Curves of the consumption of furfurylideneacetone (1) and of the buildup of hydrogenation products during the hydrogenation. (The Roman numerals next to the curves correspond to the Roman numerals in the reaction scheme, while VI is an unidentified component.)

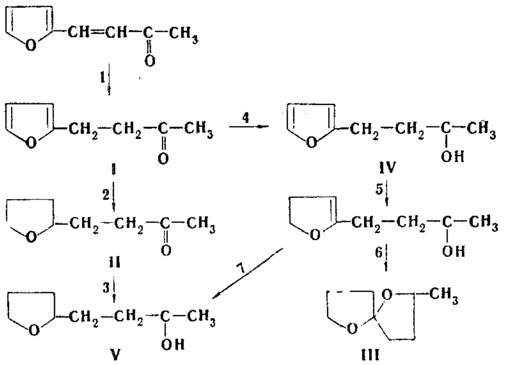
that diffusion factors do not play a substantial role under the conditions used in the research (700-800 oscillations per minute, 0.1-0.7 g of catalyst).

A chromatographic investigation demonstrated that five major reaction products, two of which are ketones (reaction with hydroxylamine) and two of which are alcohols (formation of esters), are formed under the investigated conditions. To isolate the individual products, we utilized the fact that the process is quite selective under the conditions that we chose, and, by stopping the process at different stages of the hydrogenation, we were able to obtain a catalyzate enriched in the desired product. As a result of an analysis of the IR spectra, we were able to identify the following components of the catalyzate, corresponding to the peaks on the chromatogram: 1-(α-furyl)-3-butanone (I), 1-(α-tetrahydrofuryl)-3-butanone (II), 2-methyl-1,6-dioxaspiro[4.4]nonane (III), 1-(α-furyl)-3-butanone (IV), and 1-(α-tetrahydrofuryl)-3-butanol (V). The structures of the indicated compounds were also confirmed by comparison of their refractive indexes (n_D^{20}) with the literature values: 1.4703 and 1.4700 [11] for I, 1.4500 and 1.4485 [12] for II, 1.4426 and 1.4428 [10] for III, 1.4748 and 1.4743 [10] for IV, and 1.4550 and 1.4550 [10] for V.

Curves of the change in the percentage of the individual components of the catalyzate during the hydrogenation were constructed from the results of chromatographic analysis. It is apparent from Fig. 3 that the amount of starting substance decreases rapidly during the reaction and is used up when a conversion of 30% is reached (1.2 mole H_2). The formation of II begins practically simultaneously with the formation of I (see the scheme on following page), and the formation of IV, the percentage of which in the catalyzate is considerably less than the percentage of II, begins only in later stages of the process. The formation of compound III commences as IV is formed. At higher degrees of conversion, V is formed from II and partially from IV. At the end of the reaction, after the absorption of ~4 mole of H_2, the catalyzate contains ~90% V and ~10% III.

On the basis of our results, the sequence of the formation of the products of the hydrogenation of furfurylideneacetone can be represented by the scheme on the following page.

Thus the 1 → 2 → 3 path predominates during the hydrogenation of furfurylideneacetone under our conditions, while the 1 → 4 → 5 → 6, 7 sequence required by the multiplet theory is realized to a lesser degree.



The energy barriers for the hydrogenation of the C=O bond and the first C=C bond in the furan ring, calculated in accordance with the multiplet theory, differ only slightly and are, respectively, 10.7 and 11.4 kcal/mole [3]. In our case, both of these processes (2 and 4 in the scheme above) are realized in parallel rather than successively as assumed by the multiplet theory. It should further be noted that, according to our data, not only the ethylene bond but also the carbonyl bond and furan ring are hydrogenated in furfurylideneacetone at 50° C and atmospheric pressure, while there are reports (for example, see [10]) that the furan ring is hydrogenated on nickel only under pressure and at elevated temperatures (120-160° C).

EXPERIMENTAL

The furfurylideneacetone (mp 39-40° C) used in this research was synthesized by the method in [10]. The Raney nickel catalyst was obtained by leaching a Ni–Al alloy (1 : 1) with 20% alkali solution at 20 and 50° C for 1 h at each temperature. The hydrogenation was carried out at 50° C in a long-necked hydrogenation flask at atmospheric pressure. The hydrogenation flask was charged with 2 g of the substance to be hydrogenated in 30 ml of ethanol and 0.4 g of catalyst suspended under a layer of solvent. Electrolytic hydrogen without additional purification was used for the hydrogenation. The beginning of the experiment was considered to be the instant at which the oscillator was switched on. Samples (0.1 ml) for analysis were selected from the hydrogenation flask at definite intervals, and the absorbed hydrogen was measured with a gas burette. The catalyzate samples were analyzed with a KhROM-2 chromatograph with a flame-ionization detector. The column was 2-m long with a diameter of 4 mm, and the stationary phase was 15% E-301 silicone elastomer on 60-80-mesh Chromosorb W. The gas-carrier (nitrogen) flow rate was 30 ml/min, and the column temperature was 123° C. The IR spectra were recorded with UR-10 and IKS-22 spectrometers.

LITERATURE CITED

1. A. A. Ponomarev and V. V. Zelenkova, Usp. Khim., 20, 589 (1951).
2. I. F. Bel'skii and N. I. Shuikin, Usp. Khim., 32, 6 (1963).
3. A. A. Balandin, Multiplet Theory of Catalysis [in Russian], Izd. MGU (1964), Chap. 2, pp. 135, 138.
4. Belgian Patent No. 656,273 (1965); Chem. Abstr., 65, No. 4 (1966).
5. A. A. Ponomarev, Candidate's Dissertation [in Russian], MGU (1954).
6. US Patent No. 1,903,850 (1927); Chem. Zentralblatt, 2, 281 (1933).
7. A. Hinz, G. Meyer, and G. Schücking. Ber., 76, 676 (1943).
8. K. Alexander, L. Hafner, and L. Schniepp, J. Am. Chem. Soc., 73, 2725 (1951).
9. H. Wienhaus and H. Leonhardi, Chem. Zentralblatt, 1, 224 (1930).
10. A. A. Ponomarev, Syntheses and Reactions of Furan Compounds [in Russian], Izd. Saratovsk. Gos. Univ. (1960).
11. A. A. Ponomarev and Z. V. Til', Zh. Obshch. Khim., 27, 1075 (1957).
12. A. A. Ponomarev, Z. V. Til', I. Markushina, and K. Sapunar, Dokl. Akad. Nauk SSSR, 93, 297 (1953).