CHARACTERISTICS OF THE CATALYTIC HYDROGENATION OF 5-METHYLFURFURAL

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The hydrogenation of 5-methylfurfural in the vapor and liquid phases was studied in the presence of catalysts: Pd/C (KDF), Pd/Al$_2$O$_3$, copper-chromite (GIPKh-105) and Raney-Ni. The chief characteristics of the conversion of the aldehyde group of 5-methylfurfural depending on the nature of the catalyst and the reaction conditions were established. The greater reactivity of 5-methylfurfural in the hydrogenation reaction, compared with furfural, was revealed.

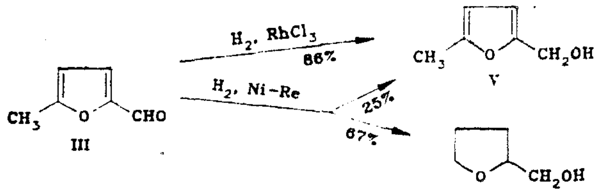
Contact hydrogenation of furfural (I) series as the basis of the production of 2-methylfuran, furfuryl and tetrahydrofurfuryl alcohols. Several papers have been devoted to the hydrogenation of furfural to furfuryl alcohol (II) and 2-methylfuran, and also to the subject of the study of kinetics and mechanism of this process.

The hydrogenation of 5-methylfurfural (III) has been less investigated. The results are given in [5] of the investigation of the kinetics and mechanism of the hydrogenation of 5-methylfurfural to 2,5-dimethylfuran (IV) on Pd/Al$_2$O$_3$. The hydrogenation of the aldehyde group of compound III to the methyl group of compound IV is also carried out on copper–chromate catalysts [6, 7]. Using a mixture of copper and chromium oxides, in addition to 2,5-dimethylfuran, 5-methylfurfuryl alcohol (V) was also detected [8, 9]. Compounds IV and V, which are obtained from readily available starting material (still residues of the rectification of furfural), are used as solvents and intermediates in the synthesis of heterocyclic compounds.

We carried out a systematic investigation of the hydrogenation of 5-methylfurfural in the presence of various catalysts in liquid and vapor phases, and the data obtained were compared with the data for the hydrogenation of furfural.

In the liquid phase in the presence of RhCl$_3$ at 60°C and at a hydrogen pressure of 0.3 MPa, the hydrogenation of the aldehyde group of compound III to a carbinol group proceeds selectively, and the yield of alcohol V reaches 86% (Scheme 1). On Raney-Ni under the same conditions, together with the unsaturated alcohol V (25%), tetrahydrofurfuryl alcohol is formed, in 67% yield, which indicates the simultaneous occurrence of the hydrogenation of the aldehyde group, demethylation and hydrogenation of the furan ring.

Scheme 1



In the vapor phase on a Pd/C catalyst at a temperature above 200°C, the main direction of the conversion of furancarboxaldehyde III and I is the decarbonylation reaction, as a result of which 2-methylfuran (VI) and furan (VII), respectively, are formed. With decrease in the reaction temperature and increase in the concentration of hydrogen in the reaction mixture, the rate of hydrogenation of the aldehyde group of compounds I, III to the methyl group of compounds VI, IV increases (Scheme 2).

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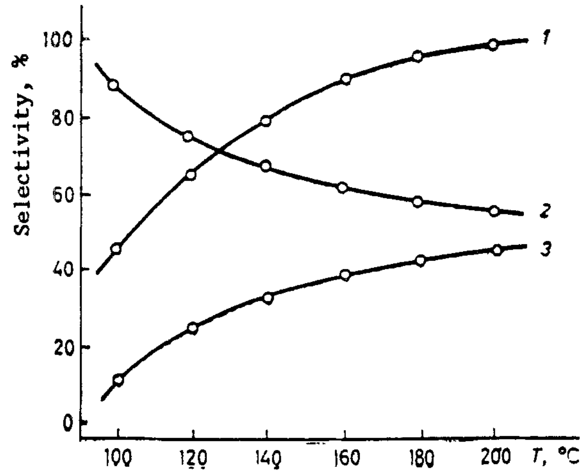
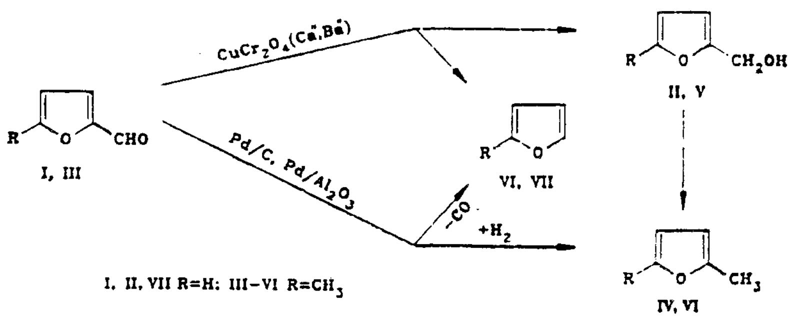


Fig. 1. Dependence of conversion of 5-methylfurfural (1) and selectivity of formation of 2,5-dimethylfuran (2) and 2-methylfuran (3) on temperature on a Pd/Al_2O_3 catalyst. Flow rate of aldehyde III) 1200 (g/h)/liter of catalyst, hydrogen:aldehyde III = 25:1, moles.

TABLE 1. Hydrogenation of 5-Methylfurfural on Pd/C Catalyst

T, °C	Flow rate of III (g/h)/liter of catalyst	H_2:III ratio, moles	Conversion, %	Selectivity of formation, %		Efficiency with respect to IV (g/h)/liter of catalyst
				IV	VI	
200	400	2,1	100	33,3	65,8	116
200	920	9,4	99,2	55,6	42,2	440
160	1760	12,0	94,6	56,0	43,1	814
120	1600	20,9	46,8	74,9	24,2	490
110	190	47,3	70,4	84.2	14.8	98

Scheme 2



The selectivity of the formation of 2,5-dimethylfuran from 5-methylfurfural at 110°C is high, since at this temperature the conversion, and hence the efficiency of the process, decrease (Table 1).

Similar characteristics of the conversion of 5-methylfurfural are also observed on Pd/Al_2O_3 (Fig. 1). The conversion values of the starting material and the selectivities of the formation of furans IV and VI on the Pd/C and Pd/Al_2O_3 catalysts are similar.

On copper-chromite catalysts promoted by alkaline earth metal salts (of calcium or barium) (FIPKh-105K, GIPKh-105B, GIPKh-105F) furancarboxaldehydes I and III convert into products of complete or partial hydrogenation of the aldehyde group of II, IV-VI (Scheme 2). The specific weight of the decarbonylation reactions is low.

The hydrogenation of 5-methylfurfural was carried out on GIPKh-105B (Table 2). With a small excess of hydrogen in the 200-250°C range, the hydrogenation of the aldehyde group of compound III to the methyl group of compound IV proceeds with high efficiency and selectivity. A further increase in the temperature accelerates the deactivation process of the catalyst,

TABLE 2. Hydrogenation of 5-Methylfurfural on a GIPKh-105B Catalyst

T, °C	Flow rate of III (g/h)/liter of catalyst	H_2:III ratio, moles	Conversion, %	Selectivity of formation, %		
				IV	V	VI
200	800	3,0	99,6	89,6	3,3	3,8
225	800	3,0	99,9	90,4	0,6	5,1
250	800	3,0	99,1	89,3	0,2	5,9
275	800	3,0	95,3	87,6	0,0	7,3
300	800	3,0	88,7	85,1	1,4	8,5
175	1200	23,5	36,4	14,8	78,4	1,3
200	1200	23,5	48,0	16,7	75,4	2,2
225	1200	23,5	52,7	34,2	56,4	3,6
225	400	20,6	99,7	90,6	1,2	1,3
225	800	10,3	99,5	88,8	2,4	1,3
225	1100	7,4	99,3	87,5	3,5	1,5
225	1700	5,5	98,9	86,0	5,3	1,7
225	2400	3,6	98,2	84,8	7,1	2,0
220	800	3,0	100,0	81,6	0,0	4,6
220	800	3,0	100,0	83,4	0,0	3,0
220	800	3,0	100,0	86,3	1,2	2,8
220	800	3,0	100,0	85,9	1,8	2,7
220	800	3,0	99,8	86,0	2,1	2,5
220	800	3,0	99,6	85,9	2,7	2,3
220	800	3,0	99,4	87,0	2,6	2,5
220	800	3,0	99,3	86,0	6,2	1,9
220	800	3,7	99,4	81,5	8,4	2,0
220	800	3,7	99,5	82,2	8,3	1,8
220	800	3,7	99,2	81,2	8,7	1,9

which results in a decrease in the conversion and formation of 2-methylfuran. At high concentrations of 5-methylfurfural and hydrogen at 175-225°C, the conversion of the starting compound decreases and the selectivity of formation of alcohol V increases. At a constant temperature of contacting at 225°C, increase in the charge of the aldehyde from 400 to 2400 (g/h)/liter slightly decreases the conversion of the initial III and increases the selectivity of formation of alcohol V and 2-methylfuran. The selectivity of formation of alcohol V also increases sharply on lowering the hydrogen:aldehyde III ratio to <2:1. The latter is explained by the fact that, according to stoichiometry, one molecule of hydrogen is needed for the formation of a molecule of alcohol, and two molecules for the formation of a molecule of the methyl derivatives. Since the hydrogenation of furancarboxaldehydes proceeds by a consecutive mechanism, the hydrogenation reaction stops at the first stage at a small excess of hydrogen, i.e., at the stage of formation of the alcohol.

At constant temperatures and concentrations of aldehyde III and hydrogen (Table 2), a gradual deactivation of the catalyst with time is observed. The appearance of the initial III and alcohol V in the reaction products can be regarded as an indication of a decrease in the activity of the catalyst. A gradual increase in the reaction temperature or decrease in the charge of the starting compound, makes it possible to increase the conversion of 5-methylfurfural and selectivity of formation of the methyl derivative IV to the original level, and also to increase the lifetime of the catalyst.

It follows from a comparison of the dependences of the conversion of aldehydes I and III on temperature (Fig. 2) that the two aldehydes exhibit high activity in the hydrogenation of the aldehyde group. Hydrogenation of furfural under these conditions generally stops at the stage of formation of alcohol II, while hydrogenation of 5-methylfurfural proceeds preferentially up to the stage of complete hydrogenation of the aldehyde group, i.e., to the formation of 2,5-dimethylfuran. Increase in the reactivity of aldehyde III and alcohol V is promoted by the presence of a methyl group, which has electron-donor properties and activates the occurrence of the consecutive hydrogenation reactions. The selectivity of formation of furan alcohols increases with decrease in the hydrogenation temperature, but the conversion thus decreases.

On hydrogenation of a mixture of aldehydes I and III, 1:3, in a small excess of hydrogen (H_2/aldehyde = 3:1, moles), the dependence of the conversion of the aldehydes on temperature is similar to the dependence of the conversion of the separate components. The selectivity of the hydrogenation of the aldehyde group to methyl group products is greater than 90% at 200-250°C. The decarbonylating ability of the catalyst is low (up to 6-8%), but is more strongly pronounced for a freshly prepared catalyst and increases with increase in the reaction temperature above 250°C. Similar results were also obtained in the hydrogenation of mixtures of furancarboxaldehydes with a lower content of 5-methylfurfural (50-30%) in the range of charges of total aldehydes of 400-1000 (g/h)/liter. Thus, the industrial copper-chromite catalyst, promoted by calcium or barium salts

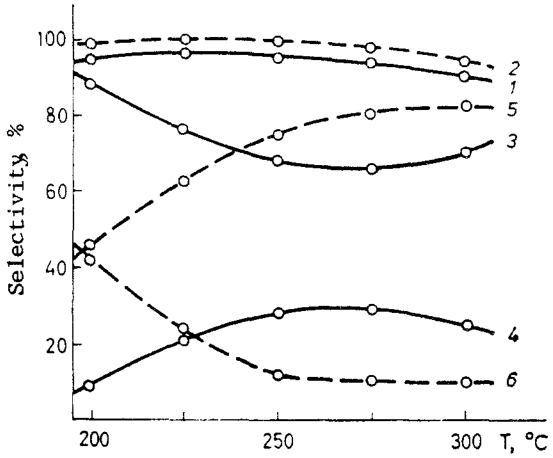


Fig. 2. Dependence of conversion of furfural (1) and 5-methylfurfural (2) and the selectivity of formation of furfuryl alcohol (3) and 2-methylfuran (4) from furfural, and of 2,5-dimethylfuran (5) and 5-methylfurfuryl alcohol (6) from 5-methylfurfural on temperature on a GIPKh-105K catalyst. Flow rate of aldehyde 400 (g/h)/liter of catalyst, hydrogen:aldehyde = 20:1, moles.

(GIPKh-105) can be considered as a very promising catalyst for the hydrogenation of 5-methylfurfural and also of mixtures of aldehydes I and III for the purpose of obtaining alcohol V and the methyl derivative IV – which are very useful reagents and solvents.

EXPERIMENTAL

The experiments on the hydrogenation of 5-methylfurfural on palladium catalysts were carried out in a gradientless flow-type reactor with a vibrofluidized layer of the catalyst (0.3-1.0 g). The experiments on the hydrogenation of the furancarboxaldehydes I and III on copper-chromite catalyst were carried out on a flow-type integral-type apparatus with 20 ml of the catalyst. The composition of the reaction mixture was analyzed on a Varian Aerograph 2800 gas–liquid chromatograph with a flame-ionization detector, a 2-m column, 2 mm in diameter, 10% dinonyl phthalate on Celite-545 (30-60 mesh), with temperature programming from 50 to 130°C at a rate of 8°C/min. The flow rate of carrier gas helium is 40 ml/min, duration of analysis – 10 min.

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REACTION OF 4-METHYL-3,4-EPOXYTETRAHYDROPYRAN WITH NUCLEOPHILES

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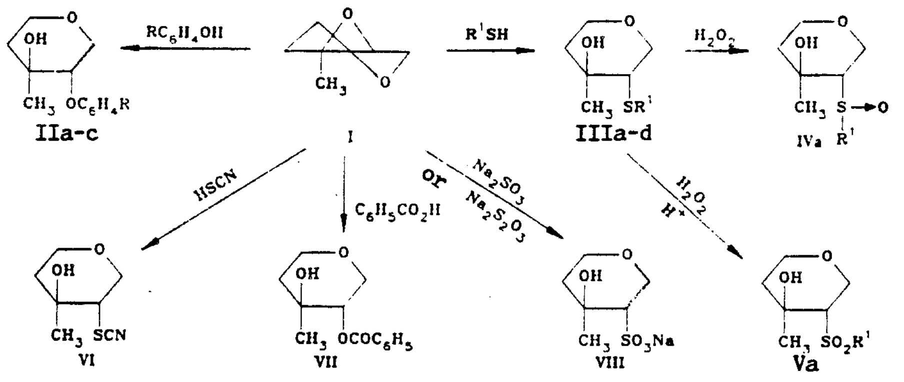
Reaction of 4-methyl-3,4-epoxytetrahydropyran with phenols, thiols, thiocyanic acid and benzoic acid, thiourea, and with sodium sulfite and thiosulfate occurs with opening of the epoxide ring. Using IR spectroscopy it was shown that the products occur via trans-diaxial opening of the oxide ring at the least-substituted carbon atom.

Reaction of nucleophilic agents with pyran epoxides is a convenient method for the stereoselective synthesis of functionally substituted derivatives of this class [1], being of interest as biologically active materials. In this connection, we have investigated the reaction of 4-methyl-3,4-epoxytetrahydropyran (I) with a series of available nucleophiles (phenols, thiols, thiocyanic and benzoic acids, sodium sulfite and thiosulfate, and thiourea.



II a $R=C_6H_5$, b $R=4\text{-}CH_3C_6H_4$; c $R=4\text{-}BrC_6H_4$; IIIa R^1=cyclohexyl, b $R^1=(CH_2)_2OH$, c R^1= piperidyl, d $R^1=CH_2CO_2H$; IVa, Va R^1= cyclohexyl

Treatment of epoxide I with phenols in aqueous NaOH solution (100°C, 4 h) gives 3-aryloxytetrahydropyrans IIa-c in 50-72% yields. Being more powerful nucleophiles, thiols react more rapidly in the same conditions (2 h) and give 3-alkylthiotetrahydropyrans IIIa-d in 65-82% yields. Treatment of sulfide IIIa with 30% hydrogen peroxide in methyl ethyl ketone gives the sulfoxide IVa and the sulfone Va in the presence of sulfuric acid. Epoxide I reacts with an ether solution of HSCN at 20°C over 48 h to give the 3-thiocyanotetrahydropyran VI in 52% yield. Heating I in $CHCl_3$ with benzoic acid in the presence of p-toluenesulfonic acid over 50 h yields the 3-tetrahydropyranyl benzoate VII (58%). Reaction of the epoxide with a

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