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EFFECT OF THE NATURE OF THE SOLVENT ON THE RATE AND MECHANISM  
OF THE CATALYTIC HYDROGENATION OF DIFURFURYLIDENEACETONE

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It was established that the hydrogenation of difurfurylideneacetone on a skeletal Ni-Ti-Al catalyst at atmospheric pressure proceeds nonselectively. The rate of hydrogenation in both aprotic and protic solvents increases as their overall electrophilicity increases. The process is realized selectively under hydrogen pressure. By changing the type of solvent one can obtain a catalyzate enriched in various reaction products.

One of the most obscure problems in heterogeneous catalysis is the effect of the nature of the solvent on the rate and mechanism of the hydrogenation of organic compounds. It is known [1] that, depending on the type of solvent catalyst used, hydrogenation may lead to the formation of various reaction products.

The aim of the present research was to investigate the effect of the nature of various solvents on the rate and mechanism of hydrogenation of difurfurylideneacetone (I) on a skeletal nickel-titanium-aluminum catalyst and to determine the conditions for the selective hydrogenation of dienone I. It is known [2] that to characterize the nonspecific solvation capacity of solvents one uses two parameters, viz., the polarity and polarizability, which are expressed by functions of the dielectric constant or the refractive index. Scales of the overall acidity (electrophilicity)  $E$  of the solvents are used as the one-parameter characteristic of the polarities of solvents. The dependence of the rate of hydrogenation of dienone I on the electrophilicities of the solvents is shown in Table 1. It is apparent from the data presented for the hydrogenation of dienone I at 20°C in both aprotic and protic dipolar solvents that the reaction rate increases as the electrophilicity of the solvent increases. This dependence is displayed particularly distinctly in the hydrogenation of I at 50°C and atmospheric pressure.

The study showed that the hydrogenation of dienone I at atmospheric pressure in various solvents leads to the formation of a mixture of hydrogenated products.

It is apparent from the data presented that in the hydrogenation of dienone I at 20°C the reaction rate increases from 1.2 (in n-heptane) to 14 ml of H<sub>2</sub> per minute (in ethanol). As the temperature is increased to 50°C, the rate of hydrogenation ranges from 1.5 to 25 ml of H<sub>2</sub>/min; the reaction rate increases in a different manner in various solvents. This phenomenon is evidently explained by the change in the coefficient of distribution of the substance undergoing hydrogenation between the solvent and the catalyst surface. The reason for the insignificant increase in the rate of hydrogenation of dienone I in n-heptane as the temperature is increased is the limited solubility of starting dienone I in this solvent. This also limits the hydrogenation process. After 300 min of hydrogenation of dienone I at

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TABLE 1. Dependence of the Rate of Hydrogenation of Difurfurylideneacetone (I) on the Overall Electrophilicity (E) of the Solvent (at atmospheric pressure)

Solvent	E [2]	Rate of H <sub>2</sub> absorption, ml/min	
		20°	50°
n-Heptane	0	1,2	1,5
Ethyl acetate	—	3,0	6,5
DMF	2,6	4,0	6,5
1,4-Dioxane	4,2	2,5	9,5
2-Propanol	8,7	8,0	11,0
1-Butanol	10,3	3,5	20,5
Ethanol	11,6	14,0	20,6
Methanol	14,9	10,0	22,2

atmospheric pressure in the solvents indicated above at 50°C, the degree of conversion ranges from 66.8 to 90%, and the catalyzate contains a mixture of hydrogenated products.

We have previously shown [3, 4] that the hydrogenation of difurfurylideneacetone (I) on a Raney nickel catalyst at atmospheric pressure takes place via the successive formation of 1,5-difurypent-1-en-3-one (II), 1,5-difuryl-3-pentanone (III), 1,5-ditetrahydrofuryl-3-pentanone (IV), and 1,5-ditetrahydrofuryl-3-pentanol (V).

We established that the hydrogenation is zero-order in the concentration of starting dienone I. The apparent activation energy for the temperature range 20–65°C is 23–26 kJ/mole. As the temperature is raised, the reaction rate increases particularly appreciably during hydrogenation of the ethylene bonds in the side chain. The rate-determining step of the process is the reduction of the carbonyl group in the 1,5-ditetrahydrofuryl-3-pentanone (IV) molecule.

Further study showed that intermediate furan ketone III is consumed during hydrogenation via two parallel pathways: On the one hand, it is converted to ketone IV, while, on the other, it is converted to 1,5-difuryl-3-pentanol (VI), which are then hydrogenated to give final alcohol V.

The maximum yield of alcohol VI (1–5% of the total mass of the hydrogenated products) is observed in the hydrogenation of dienone I, enone II, and ketone III in methanol, 96% ethanol, 1,4-dioxane, and DMF at 50°C and atmospheric pressure; the principal pathway in this case is the formation of tetrahydrofuran ketone IV. This reaction pathway is in agreement with the energy calculations of the multiplet theory of catalysis, according to which hydrogenation of the double bonds of the furan ring precedes reduction of the carbonyl group in the hydrogenation of furan ketones [4].

The dependences of the reaction rates and the degree of conversion on the polarity of the solvent in the hydrogenation of dienone I under a hydrogen pressure of 60 atm are presented in Table 2. In Table 2 the solvents are arranged in the order of increasing dipole moments. It is apparent from Table 2 that the optimum solvents for the preparation of 1,5-ditetrahydrofuryl-3-pentanol are the lower aliphatic alcohols such as ethanol and the propanols. At both atmospheric and increased hydrogen pressures the hydrogenation of dienone I proceeds more rapidly in the lower aliphatic alcohols than in the other solvents. A further increase in the molecular weight and the dipole moment, as well as a transition from alcohols to a different class of solvents, viz., tetrahydrofuran (THF), leads to a decrease in the rates of hydrogenation of the ethylene bonds and the carbonyl group, as a result of which the yield of final product V and, correspondingly, the degree of conversion decrease. The hydrogenation of the ethylene bonds in dienone molecule I is realized at a high rate [ $(4.3\text{--}7.0) \cdot 10^{-3}$  mole/min] when the process is carried out in ethanol, propanols, THF, and ethyl acetate. The hydrogenation of the carbonyl group in the 1,5-ditetrahydrofuryl-3-pentanone molecules is realized at the highest rate [ $(0.39\text{--}0.72) \cdot 10^{-3}$  mole/min] in ethanol, propanols, isobutyl alcohol, and aqueous ethanol.

When the hydrogenation is carried out in 1,4-dioxane, isoamyl alcohol, ethyl acetate, and DMF under a hydrogen pressure of 20–120 atm and at 20–120°C, the process stops spon-

TABLE 2. Dependence of the Reaction Rates and Degree of Conversion on the Nature of the Solvent\*

Solvent	Dipole moment, D	Degree of conversion, %	Rate		Yield of V, %
			consumption of I, $10^{-3}$ mole/min	formation of V, $10^{-3}$ mole/min	
1,4-Dioxane	0,45	39	2,34	0	0
Isobutyl alcohol	1,64	95,3	2,70	0,52	71,8
2-Propanol	1,66	100	4,66	0,71	99,7
Ethanol (96%)	1,66	100	7,0	0,54	98,2
1-Propanol	1,68	100	6,36	0,72	98,5
Tetrahydrofuran	1,75	61,1	4,32	0,09	11,5
1-Hexanol	1,77	80	2,26	0,34	51,5
Isoamyl alcohol	1,82	33	2,12	0	0
Ethyl acetate	1,88	36	4,37	0	0
Water	1,90	43	0,60	0,26	32,0
Tetrahydrofuryl alcohol	2,33	60	2,33	0,15	33,1
DMF	3,86	34	2,35	0	0
Ethanol-water (3:4)	—	85	3,48	0,39	5,05

\*Conditions: 15 g (0.07 mole) of dienone I, 1.5 g of the catalyst, 250 ml of the solvent, a hydrogen pressure of 60 atm, a reaction temperature of 100°C, and a reaction time of 2 h.

taneously at the step involving the formation of furan ketone III in 80-98% yield. In conformity with the theoretical prerequisites of D. V. Sokol'skii [1, 5], this is explained by the higher adsorptive capacity of the solvent as compared with reaction product III on the active centers of the catalyst. Thus by changing the solvent one can obtain a catalyzate that is enriched in various products of a specific type.

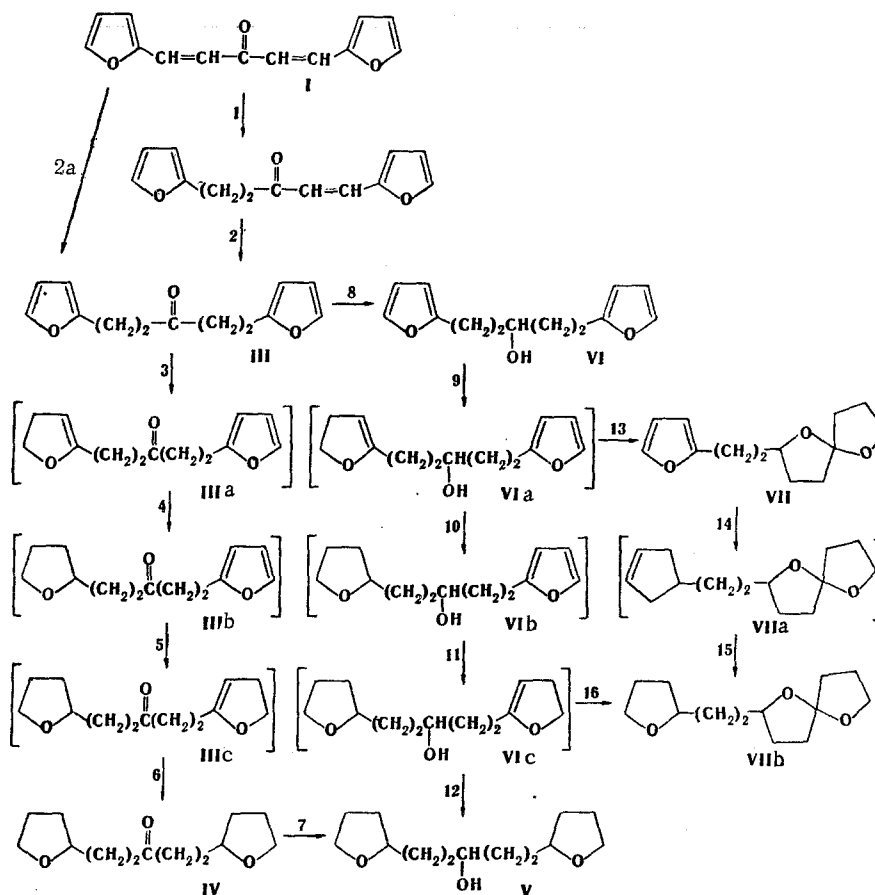
The structure of the solvent used has an appreciable effect on the rate and mechanism of the hydrogenation of dienone I. When the process is carried out in alcohols with a normal structure, the rate of formation of ketone III and final product V is higher than the rate of hydrogenation in iso alcohols. For example, the rate of formation of ketone III in the hydrogenation of dienone I in 1-propanol is  $6.36 \cdot 10^{-3}$  mole/min, whereas it is  $4.66 \cdot 10^{-3}$  mole/min in 2-propanol.

Considering the complexity of the mechanism of the catalytic hydrogenation of dienone I at both atmospheric and increased hydrogen pressures, we studied the kinetics of the hydrogenation of intermediates II-IV and a model compound, viz., 1-( $\alpha$ -furyl)-5-( $\alpha$ -tetrahydrofuryl)pentan-3-one (IIIb). All other things being equal (60 atm and 100°C), the trends of the kinetic curves for the hydrogenation of I and II are absolutely identical, and the rates of their consumption are  $7.12 \cdot 10^{-3}$  and  $7.63 \cdot 10^{-3}$  mole/min, respectively. In the case of hydrogenation of dienone I under hydrogen pressure intermediate enone II does not accumulate in the catalyzate as a consequence of the fact that the rate of the II  $\rightarrow$  III reaction is higher than the rate of the I  $\rightarrow$  II reaction.

The hydrogenation of ketones III and IIIb separately leads to the formation of ketone IV. Their rates of consumption are low and amount to  $4.50 \cdot 10^{-3}$  and  $1.34 \cdot 10^{-3}$  mole/min, respectively. Ketone IV is subsequently hydrogenated to give final product V. The hydrogenation of furan ketone III to tetrahydrofuran IV probably takes place through the formation of intermediates: Ketone III by adding a mole of hydrogen is hydrogenated to give dihydro product IIIa, and the latter is rapidly hydrogenated to give ketone IIIb, which in turn is converted to ketone IV through intermediate dihydro product IIIc.

It should be noted that the formation of small amounts (0.5-3.0%) of 1,6-dioxaspiro[3.5]nonanes is observed in the hydrogenation of I-III and IIIb. These products are formed through cyclization of intermediate dihydrofuran alcohol VIa. The formation of 1,6-dioxaspiro[3.5]nonanes is indirect evidence for the stepwise hydrogenation of the double bonds of the furan ring, which was also noted in [6].

On the basis of the data obtained the stepwise character of the hydrogenation of difurfurylideneacetone (I) on a skeletal nickel-titanium-aluminum catalyst can be expressed by the following scheme:



All of the compounds indicated in the scheme, except for the dihydro products, were isolated, and their structures were confirmed by their IR, PMR, and mass spectra [4].

It follows from the scheme that the hydrogenation of the double bonds of the furan ring takes place through a step involving the formation of the intermediate dihydro product. This step is realized slowly because of the existence of an energy barrier of the conjugated furan ring of 72 kJ/mole [7]. The intermediate dihydro product is hydrogenated rapidly to give the tetrahydro product, since conjugation is absent in the dihydro product.

Thus in the hydrogenation of dienone I at atmospheric pressure over a broad range of temperatures in various protic and aprotic solvents with various electrophilicities the process does not take place selectively, and the catalyzate contains a mixture of hydrogenation products. At the same time, the hydrogenation of dienone I under hydrogen pressure is realized selectively. Aprotic solvents that display a lower degree of electrophilicity (2.6-4.2) direct the hydrogenation process to favor (to the extent of 80-98%) the formation of 1,5-difuryl-3-pentanone, while protic solvents with overall electrophilicities of 8.7-11 direct the process to favor (to the extent of 71.8-99.7%) the formation of the final product, viz., 1,5-ditetrahydrofuryl-3-pentanol. An increase in the temperature has a more pronounced effect on the step involving the hydrogenation of the ethylene bonds in the side chain both at atmospheric and increased hydrogen pressures in methanol, ethanol, propanols, 1-butanol, and ethyl acetate.

#### EXPERIMENTAL

The solvents used in this research were purified by known methods [8, 9]. Hydrogenation at atmospheric pressure and analysis of the reaction products were carried out by the methods described in [4]. Hydrogenation under pressure was realized in a Vishnevskii autoclave with vigorous stirring under static conditions. At 15-min intervals samples were collected from the catalyzate without disrupting the conditions and were analyzed by gas-liquid chromatography (GLC). The rates were expressed with allowance for the vapor pressure of the solvent (Table 1).

The IR spectra were recorded with an IKS-14 spectrometer. The PMR spectra were recorded with a Jeol C-60 spectrometer with hexamethyldisiloxane as the internal standard.

1-( $\alpha$ -Furyl)-5-( $\alpha$ -tetrahydrofuryl)pentan-3-one (IIIb). This compound had bp 135°C (2 mm),  $n_D^{20}$  1.4905, and  $d_4^{20}$  1.0710. IR spectrum: 890, 927, 1511 (furan ring); 1014, 1150 (tetrahydrofuran ring); 1715  $\text{cm}^{-1}$  (C=O). The PMR spectrum contains three types of protons related to the  $\alpha'$ ,  $\beta'$ , and  $\beta$  protons of the furan ring centered at 7.25, 6.10, and 5.90 ppm with  $J_{\beta',\beta} = 3.60$ ,  $J_{\alpha',\beta'} = 1.80$ , and  $J_{\alpha',\beta} = 0.82$  Hz, in agreement with the literature data [10]. In addition, the spectrum contains signals related to the methylene groups of the tetrahydrofuran ring centered at 1.70 and 3.60 ppm in the form of multiplets and at 2.50 ppm from the side chain in the form of a quartet with  $J_{\text{CH}_2,\text{CH}_2} = 6.10$  Hz. Found: C 69.87; H 8.0%;  $M^+$  223.  $\text{C}_{13}\text{H}_{18}\text{O}_3$ . Calculated: C 69.95; H 8.0%; M 223.

1,5-Difuryl-3-pentanol (VI). This compound had bp 141°C (1 mm),  $n_D^{20}$  1.5090, and  $d_4^{20}$  1.1001. IR spectrum: 725, 883, 935, 1035, 1600 (furan ring); 3440  $\text{cm}^{-1}$  (OH). According to the data in [11], this compound has bp 112-114°C (0.14 mm),  $n_D^{25}$  1.5092, and  $d_4^{20}$  1.1006. The PMR spectrum contains signals of three types of protons centered at 7.20, 6.15, and 5.85 ppm, which are related to the  $\alpha'$ ,  $\beta'$ , and  $\beta$  protons of the furan rings with  $J_{\beta,\beta'} = 3.60$ ,  $J_{\alpha',\beta'} = 1.80$ , and  $J_{\alpha',\beta} = 0.87$  Hz, as well as a signal at 3.55 ppm (s, OH). The proton of the secondary carbon atom (>CH) shows up in the form of an unresolved multiplet centered at 2.50 ppm. The protons of four methylene groups appear in the form of a quartet centered at 2.55 ppm with respect to hexamethyldisiloxane with  $J_{\text{CH}_2,\text{CH}_2} = 6.09$  Hz. Found:  $M^+$  221.  $\text{C}_{13}\text{H}_{16}\text{O}_3$ . Calculated: M 221.

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