SELECTIVE HYDROGENATION OF 6,10-DIMETHYLUNDECA-3,5,9-TRIEN-2-ONE ON RANEY NICKEL CATALYST

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The study of the influence of the concentration of the substrate and catalyst is important for determining the region in . .ch the reaction proceeds and the optimization of the process.

The influence of the concentration of the hydrogenated compound on the reaction rate has been studied in several papers [4, 7]. A decrease in the rate of the reaction was detected when the content of the unsaturated compound in the solution was increased from 10 to 50%. The authors of [7] explain this by increase in the adsorption of the unsaturated compound 6-methylhepta-3,5-dien-2-one, and displacement of hydrogen from the catalyst surface. The authors of [4] explain that they obtained a similar experimental result because the reaction products are more strongly adsorbed on the contact surface than are the initial compounds. Information on the order of reaction with respect to the unsaturated compound is contradictory. In [4] it was stated that the order with respect to the substrate in ethanol is zero, while in isopropanol it is close to one.

The amount of the heterogeneous catalyst is one of the factors determining the region in which a catalytic reaction [2], including hydrogenation, proceeds. Up to now, there are no data in the literature on the influence of the concentration of the substrate and the catalyst on the course of the reduction of 6,10-dimethylundeca-3,5,9-trien-2-one (I). Therefore, the aim of the present work was to fill this gap. Compound I was hydrogenated on a Raney nickel catalyst in the presence of a modifier. The method and the analysis are given in [6]. The overall scheme of the reaction can be represented as follows:

 $I \xrightarrow{k_1} II \xrightarrow{k_2} III \xrightarrow{k_3} IV \xrightarrow{k_4} V,$ 

where II is 6,10-dimethylundeca-3,9-dien-2-one; III is 6,10-dimethylundeca-9-en-2-one; IV is 6,10-dimethylundecan-2-one; and V is 6,10-dimethylundecan-2-ol.

To clarify the character of the adsorption of the components, we compared the IR spectra of I and I coordinated with the catalyst, and of IV and IV coordinated with the the catalyst, obtained on a UR-20 spectrophotometer. The spectra shown in Fig. 1 indicate an inappreciable adsorption of I and IV by the catalyst; thus, the model given in [6] for a palladium catalyst is correct.

Influence of Concentration of I. An isopropanol solution with a 0.4-1.6 M content of I was hydrogenated in the presence of 15 wt. % modified Raney nickel catalyst, at 30°C and at a partial hydrogen pressure of 8.1 MPa. We should note that in this series of experiments, the modifier/catalyst ratio was retained constant. It was found that with increase in the concentration of I from 0.4 to 1 M, the time of formation of IV sharply increases (Fig. 2). Further increase in the content of I in the solution does not affect the reaction so notice-ably.

Increase in the concentration of I leads to increase in the amount of intermediate products of hydrogenation and to their slower consumption.

The fact that the amount of V in the catalysate is approximately the same, 4.5%, while the yield of IV, at an initial concentration of I of 0.4 M is 95%, and at a concentration of 1.6 M 60%, is noteworthy. We believe that this is because the modifier influences not only the contact, but also the substrate, which we and other authors [1, 3, 5] have already observed for processes with the participation of hydrogen. It is possible that during hydrogenation, a mixed ligand reactive complex is formed (catalyst-solvent-substrate-modifier), which is responsible for the selective course of the process.

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Fig. 2

Fig. 1. IR spectra of I and IV and surface compounds I and IV with the catalyst. IV + kt, I + kt - adsorbed by catalyst, respectively. IV + kt, I + kt - IV and I, adsorbed catalysts respectively.

Fig. 2. Dependence of composition of catalysate on amount of catalyst. 1, 6, 11, 16, 21) 7.5% by weight relative to I (in wt.%); 2, 7, 12, 17, 22) 12 wt.%; 2, 8, 13, 18, 23) 15 wt %; 4, 9, 14, 19, 24) 18 wt. %; 5, 10, 15, 20, 25) 22.5 wt. %; 1, 2, 3, 4, 5) III; 6, 7, 8, 9, 10) II; 11, 12, 13, 14, 15) IV; 16, 17, 18, 19, 20) V. Abscissa — time (in min); ordinate — composition of catalysate (in %).

Analysis of the observed rate constants of the hydrogenation stages of ethylene bonds at the 3, 4 ( $k_2$ ), 9, 10 ( $k_3$ ) positions and of the C=O group ( $k_4$ ) of I, shown in Table 1 indicates a complex character of the influence of the concentration factor on the course of the process. The values of the observed constants constants  $k_2$  and  $k_3$  sharply decrease with increase in the content of I from 0.4 to 1.6 M, and then remain practically constant. In contrast,  $k_4$  increases considerably with increase in the concentration of I, and this tendency is retained over the whole range of concentrations of I studied. This indirectly confirms our supposition on the interaction between the modifier and the substrate, which leads to a change in the selectivity of the process. Interaction of the substrate with the modifier in the bulk of the solution is directly confirmed by a 40 cm<sup>-1</sup> decrease in the frequency of the stretching vibrations of the C=O group in the IR spectrum (see Fig. 1).

Decrease in the observed rate constants of the separate reaction stages can be explained by several factors. Firstly, with increase in the content of I in the solution, the coating of the catalyst surface by the organic compound considerably increases, which may hinder access of hydrogen to the active centers of the contact. Secondly, as a result of capillary condensation, the concentration of I in the pores of Raney nickel should be still higher than that on the contact surface and in the solution. This leads to an intradiffusional inhibition with respect to the reagent gas.

These two phenomena should considerably decrease the working surface of the catalyst, as evident from the observed decrease in the values of the reaction rate constants.

The third reason for the decrease in the values of the hydrogenation rate constants of I may be the decrease in the solubility of hydrogen in the reaction medium because of increase in the viscosity of the medium.

Thus, during the catalytic reduction of I, we should take into account the possible inhibition of the process with respect to hydrogen medium.

Influence of Amount of Catalyst. The experiments were carried out at 30°C and at a hydrogen pressure of 8.1 MPa (zero order with respect to the reagent gas). An isopropanol solution with a 0.4 M content of I was hydrogenated. The amount of Raney nickel varied over the range of 7.5-22.5% (by weight, relative to 1). The modifier/I ratio remained constant in this medium.

TABLE 1. Influence of Concentration of I on its Hydrogenation

Concentra- tion of I, M	Specific rate constants of stages, min <sup>-1</sup>				
	kg • 104	k <sub>3</sub> · 10 <sup>4</sup>	k4 · 104	k3/k4	
0,4 1,0 1,4 1,6	16,62 5,7 6,78 5,14	6,75 3,45 2,53 2,64	0,07 0,3 0,5 0,6	96,4 11,5 5,06 4,4	

## TABLE 2. Influence of Amount of Raney Nickel on the Selectivity of Hydrogenation of I

Concentration of Raney nickel, wt.% relative to I	Content of I at 120th min from the beginning of process, %	S <b>elect</b> ivity S
7,5	1,7	0,95
12,0	2,3	0,95
15,0	4,9	0,95
18,0	5,7	0,94
22,5	6,6	0,93

TABLE 3. Influence of Amount of Raney Nickel on Hydrogenation

Amount of catalyst, wt.% relative to I	Specific rate constants of hydrogenation stages, min <sup>-1</sup>				
	k <sub>1</sub> · 10 <sup>4</sup>	$k_z \cdot 10^4$	k <sub>3</sub> · 104	k4 • 104	
7,5 12,0 15,0 18,0 22,5	135,90 116,58 — — —	16,96 16,58 16,62 28,98 —	4,05 4,30 6,75 8,82 12,45	0,05 0,05 0,07 0,09 0,14	



Fig. 3. Dependence of composition of catalysate on concentration of I. 1, 5, 9, 13) 0.4 M; 2, 6, 10, 14) 1 M; 3, 7, 11, 15) 1.4 M; 4, 8, 12, 16) 1.6 M; 1, 2, 3, 4) III.) 5, 6, 7, 8) II; 9, 10, 11, 12) IV; 13, 14, 15, 16) V. Abscissa — time (in min); ordinate — composition of catalysate (in %).

It was found that increase in the concentration of the catalyst from 7.5 to 15% sharply intensified the reduction of the ethylene bonds of I. Compound I was detected in the catalysate only at these amounts of the contact. Further increase in the Raney nickel content in the reaction medium did not show any influence on the hydrogenation of the ethylene bonds (Fig. 3).

The formation of V in the presence of 7.5-12% of Raney nickel proceeded very slowly. With increase in the amount of contact, the content of V increased, while the selectivity of the reaction decreased (Table 2).

By analyzing the values of the specific rate constants of the reduction of the 5, 6  $(k_1)$ , 3, 4  $(k_2)$ , 9, 10  $(k_3)$  bonds and the C=O group  $(k_4)$  calculated according to [6] (Table 3), it was noted that increase in the concentration of the catalyst led to increase in the observed rate constants of the reaction stages. This is possibly because under otherwise equal conditions, with increase in the amount of the active metal, the catalyst/modifier ratio also increased (the activity of the catalytic system increased).

It is known that increase in the activity of the contact, while other process parameters remain unchanged, causes a transition of the reaction from the kinetic into the diffusion region with respect to the reagent gas [2]. We observed this phenomenon in the range of the catalyst concentrations of 18% or higher.

The data obtained in the present work and the results listed in [6] show that the modified Raney nickel catalyst can be proposed for replacing palladium catalysts in the hydrogenation of I.

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OXIDATION OF EFFLUENT HYDROGEN BROMIDE. II. OXIDE CATALYSTS OF THE DEACON PROCESS IN THE OXIDATION OF HYDROGEN BROMIDE

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In the production of levomyceti, ornide, bromocamphor, and other medications, where bromination is carried out by molecular bromine, HBr is liberated. The widely used method for the decontamination of the effluent HBr by an alkali solution has a simple apparatus design, but the method is unsuitable for setting up a closed production cycle with respect to bromide. We believe that utilization of HBr by catalytic oxidation to bromine has more prospects. In contrast to the Deacon process of the oxidation of HCl, the oxidation of HBr has been insufficiently studied. The literature data are available mainly in patent publications, in which the final result of the research work is only shown, without disclosing the principles for producing the oxidation catalysts of HBr. Therefore, at the initial stage of producing the catalyst, because the reactions are of the same type, and to reveal the differences in the course of the process, it was interesting to study the Deacon oxide catalysts in the oxidation of HBr.

## EXPERIMENTAL

<u>Method of Testing the Catalysts</u>. The oxidation of HBr was studied on a copper-aluminum catalyst prepared by mixing aluminum hydroxide with basic copper carbonate, followed by heat treatment [6], and also on copper-chromium and copper-cobalto-chromium oxide catalysts obtained by impregnating brand ShN-2  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> with a specific surface of 105 m<sup>2</sup>/g and brand KSN high-temperature  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> with a surface of area of 2.5 m<sup>2</sup>/g [2].

The catalysts were tested on a laboratory flow-type apparatus described in [1]. The catalytic reactor was prepared from a thermostable glass and was equipped with a housing for a thermocouple for measuring the temperature at the catalyst layer. To decrease the influence of the longitudinal temperature gradient, arising because of the exothermicity of the process, the volume of the catalyst was limited to 1 ml, and the height of the layer was 7 mm. For uniform distribution of the gas flow and heating of the incoming reaction mixture to the process temperature, the catalyst was covered by quartz glass (the 1-1.6 mm fraction) up to a height of 10 mm. Before starting the experiment, the contact was conditioned in an

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