HYDROGENATION OF AN AQUEOUS SOLUTION OF BUT-2-YNE-1,4-DIOL ON RANEY NICKEL CATALYST

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But-2-yne-1,4-diol (I) has always attracted the attention of research workers as a simple model of the stereoselective hydrogenation of acetylenic glycols, and as an object for an industrial application of its hydrogenation products, in particular, the cis-isomer of but-2-ene-1,4-diol (II), in the oxazole synthesis of pyridoxine [1]. The hydrogenation of I on a Raney nickel catalyst in water has the practical aim of using a commercial sample of I (a 35% aqueous solution) and a cheap hydrogenation catalyst. However, the activity of Raney nickel in water is very low. It increases with a decrease in concentration [2] and an increase in hydrogen pressure [3]. The reaction does not cease with absorption of 1 mole of hydrogen, but proceeds further at a rate depending on the initial concentration of I. One of the methods of increasing the selectivity of Raney nickel is the adsorption displacement by pyridine of compound II formed in the course of the hydrogenation process. The action of pyridine on the activity of a Raney nickel catalyst was studied in an alcoholic medium only, with qualitative analysis of the hydrogenizate [2].

It was interesting to obtain a quantitative characteristic of the activity and selectivity of the Raney nickel catalyst depending on the method of leaching of nickel-aluminum alloy, the size of its particles (1 to 2-mm chips and dust-like fraction – the by-products), the nature of the tertiary amine and the conditions of hydrogenation of the aqueous solution of I.

We therefore developed a modified procedure to carry out the gas-liquid chromatography for determining the composition of the hydrogenizate and studied the action of the following amines: pyridine, dimethylaniline (DMA), tetramethylethylenediamine (TMEDA) and triethylamine (TEA) in the concentration range of 0.1-10% and temperature range of 25-45°C, taken in the following per weight ratio: for 0.12 g or 0.21 g of Raney nickel, 0.7 g of I for a 10% aqueous solution of I.

For determining the composition of the hydrogenizate in the form of the acetyl derivatives of I and II and trans-isomer of but-2-ene-1,4-diol as well as butane-1,4-diol, a known procedure [4] was used. The diols are acetylated by this method in the presence of sulfuric acid, followed by neutralization of the reaction mixture by sodium bicarbonate and extraction with ether. To simplify the method for determining the diols and for the quantitative estimation of the yield of the cis-isomer of II, we acetylated the mixture of diols with acetic anhydride in the presence of pyridine, using diphenyl as the internal standard.

To identify the peaks corresponding to the acetylated cis- and trans-but-2-ene-1,4-diols, we prepared the samples of the corresponding acetates.

The results of hydrogenation on different samples of nickel-aluminum alloy are shown in Table 1.

Table 1 shows that the yield of the cis-isomer of II remains practically constant when less than 1 mole of hydrogen has been absorbed. However, in the hydrogenizates there are already present small amounts of the trans-isomer of but-2-ene-1,4-diol (III) and butane-1,4-diol (IV). After the disappearance of I during further hydrogenation, the cis-isomer II partially converts into trans-isomer III and compound IV. In the presence of pyridine, the hydrogenation of II is suppressed, but not completely ($W_{max}/W_{fin} = 18$).

During hydrogenation, the catalyst potential φ_{st} is established, which changes little with time, but at the moment of absorption of 1 mole of hydrogen, it comparatively rapidly

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TABLE 1. Comparative Properties of Different Samples of Raney Nickel Catalysts

Catalyst*	Reaction temperature, °C	Amount of pyridine, g	W_{max}/W_{fin}	A, liter/(g·h)	Composition of hydrogenate, %				Yield of II, %†	v_{fin}/v_{theor}
					I	II	III	IV		
Stored for 18 h under alkali, prepared from main fraction of nickel-aluminum alloy	25	—	3,8	0,45	16	79	2	4	94	0,86
	45	—	3,8	0,34	17	79	2	2	96	0,86
Leached at 40°C	25	0,36	5,0	0,38	14	80	2	3	94	0,85
Freshly prepared from by-products of nickel-aluminum alloy	25	0,36	9,0	0,34	14	81	3	3	94	0,85
Freshly prepared from main fraction	25	—	2,0	0,66	11	80	3	6	90	0,94
Stored under alkali for 18 h, prepared from main fraction	25	—	2,9	0,56	—	56	24	19	56	1,18
Freshly prepared from main fraction	25	0,36	18,0	0,69	—	90	3	7	90	1,05
	35	0,36	8,2	0,40	—	95	2	3	95	1,08
Stored for 18 h under alkali, leached byproducts	25	0,36	18,5	0,58	—	91	3	6	91	1.08
Freshly prepared, leached in presence of SAS/surface active substance/(0.01%) from main fraction	25	0,36	18,8	0,76	—	91	3	6	91	1,05

Note. Here and in Table 2: W_{max}/W_{fin} is the ratio of the maximal and final rates of hydrogenation; A is the activity of the catalyst, expressed as an amount of absorbed hydrogen per unit time and related to 1 g of leached catalysts; v_{fin}/v_{theor} is the ratio of the amount of the absorbed to hydrogen to the theoretical, calculated for half-hydrogenation.

*Amount of catalyst 0.21 g.

†Yield of cis-isomer II is given as calculated per reacted I.

shifts to the cathode side (Fig. 1). In the presence of amine this action is more strongly marked since the hydrogenation of II is hindered and the catalyst becomes additionally saturated with hydrogen. The final value of potential (φ_{fin}) is in the region ($\varphi_{fin}-\varphi_{st}$ = 40-50 mV) which is more negative than in the absence of amine ($\varphi_{fin}-\varphi_{st}$ = 10-15 mV). A decrease in the catalyst/I ratio causes a decrease in the activity of the catalyst, probably because of the displacement of a large part of the reactive hydrogen by I, as indicated by a shift of 150-170 mV in φ_{st} into anode region, compared with φ_{st} during the hydrogenation with a large amount of the catalyst.

When the catalyst is stored for 15-20 h under alkali, its activity becomes 15% lower.

The catalytic action of leached by-products (the dust fraction) is similar to that of the catalyst from the main fraction of the nickel-aluminum alloy.

Increase in the leaching temperature and leaching of the nickel-aluminum alloy in the presence of a surface active substance (SAS) increases the activity of the catalyst. This agrees with the known data in the literature [5] and is explained by an increase in the surface of the nickel contact.

Increase in the hydrogenation temperature of I leads to a decrease in the activity of the catalyst (see Table 1 and Fig. 2) and is accompanied by a shift in the potentiometric curve to the anode region, which indicates that the catalyst surface becomes depleted of hydrogen. The value of the apparent activation energy obtained is 5 kcal/mole, while that calculated from the formula in [6] is close to the known value (4.2 kcal/mole) [3].

In the series of amines investigated, only pyridine does not cause a decrease in the activity of the catalyst (see Table 2 and Fig. 1). Other amines, even in negligible concentrations (0.1%), deactivate the catalyst and suppress the hydrogenation of both the

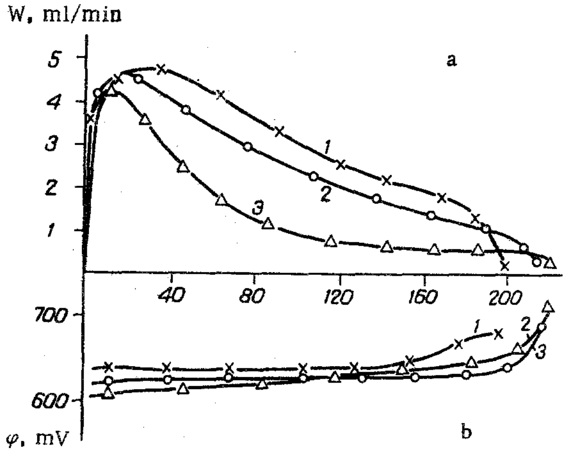

Fig. 1

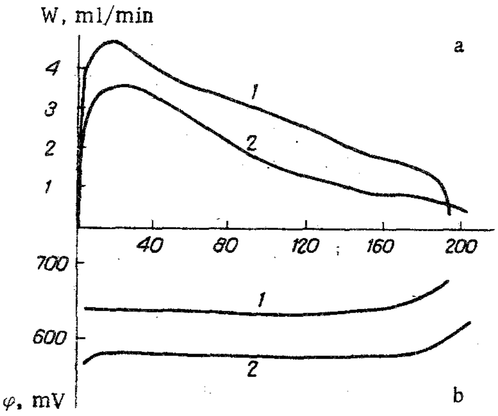

Fig. 2

Fig. 1. Kinetic (a) and potentiometric (b) curves of the hydrogenation of an aqueous solution of I in the presence of 0.66 g (1), 0.36 g (2) of pyridine, and 0.098 g of TMEDA (3) on a freshly prepared catalyst from the main fraction (1, 3) and byproducts (2) of the nickel-aluminum alloy.

Fig. 2. Kinetic (a) and potentiometric (b) curves of the hydrogenation of aqueous solution of I in presence of 0.36 g (1) of pyridine at 25°C (1) and 35°C (2) on freshly prepared catalyst from main fraction of nickel-aluminum alloy. Abscissa — volume of hydrogen (ml).

triple and the double C—C bonds. Thus, if the process is not discontinued at the absorption of 1 mole of hydrogen, an accumulation of the trans-isomer III and butane-1,4-diol is observed (see the action of DMA). An increase in the concentration of pyridine in the solution from 2.5 to 10% is accompanied by an increase in the activity of the catalyst. The activating influence of pyridine is probably due to its ability to form a complex with nickel and I, whose catalytic activity is higher than that of the metal. With decrease in the concentration of I in the solution, the concentration of the active complex also decreases; pyridine blocks the freed surface, displacing compound II formed into the solution. The possibility of adsorption displacement of II was confirmed by the authors of [2] in the case of hydrogenation of mixtures. The final value of the potential which becomes established depends on the basicity of the amine and its blocking ability.

We thus detected the activating action of pyridine and showed that in the series of amines studied it is the best for the selective hydrogenation of I. Increase in the activity of Raney nickel catalyst can be achieved by raising the leaching temperature of the alloy, using SAS-10, optimal ratio of pyridine to I (1:1), and maintaining an optimal hydrogenation temperature of not less than 35°C. We showed that the dust byproducts of the nickel-aluminum alloy can be used for the hydrogenation reaction and the potentiometric method for the control of the process.

EXPERIMENTAL

Preparation of the Catalyst. A weighed portion (0.4-0.7 g) of nickel-aluminum alloy (30-35% of nickel) was introduced in portions (4-6 times) to a 25% aqueous solution of sodium hydroxide heated to 80°C (ratio of the alloy/aqueous solution of the alkali 1:5) and the mixture was held for 2 h at 92-94°C. The catalyst obtained was washed by decantation with hot (not less than 70°C) water, avoiding direct contact with atmospheric oxygen, to a neutral reaction (pH 6.0-6.5). The catalyst suspended in water was quickly transferred to a vessel for hydrogenation.

During leaching of the dust fraction (by-products), a suspension of the nickel-aluminum alloy in water was added to an aqueous solution of alkali, without permitting the concentration of the alkali to fall below 20%.

Experiments on Hydrogenation. These were carried out according to known procedure [7] in a special long-necked hydrogenation flask, fitted with a thermostating jacket and a pair of measuring electrodes. The hydrogenation flask was shaken by a special device to ensure elimination of diffusional limitations.

TABLE 2. Influence of Tertiary Amines on Catalytic Properties of Raney Nickel Catalyst during Hydrogenation of a 10% Aqueous Solution of But-2-yne-1,4-diol at 25°C

Amine	Amount of amine, g	W_{max}/W_{fin}	A, liter (g · h)	Composition of hydrogenizate				Yield of II, %	v_{fin}/v_{theor}
				I	II	III	IV		
TEA	0,290	6,3	0,20	47	50	1	2	98	0,55
	0,073	8,0	0,22	50	47	2	2	96	0,51
	0,008	10,0	0,27	41	56	2	2	96	0,58
	0,080	6,7	0,42	—	78	11	11	78	1,20
TMEDA	0,098	22,0	0,23	—	93	4	4	93	1,15
	0,028	5,0	0,32	1	93	2	2	94	1,15
	0,200	17,5	0,52	—	93	2	2	93	1,07
Pyridine	0,360	18,0	0,69	—	90	3	7	90	1,05
	0,660	19,5	0,76	—	91	2	6	91	1,08

Note. The catalyst is freshly prepared from the main fraction of nickel-aluminum alloy, amount of catalyst 0.21 g.

For the hydrogenation, we used electrolytic hydrogen, freshly distilled amines, and a sample of I obtained by evaporating a 35% aqueous solution, and recrystallized from a mixture of ethanol and benzene (1:1). This melted at 56-57°C and was chromatographically pure according to the GLC data.

The catalyst, a given volume of amine, and I were successively added to the hydrogenation flask. The system was purged with hydrogen, thermostated, and hydrogenated, with simultaneous volumetric and potentiometric control of the reaction course. At the end of the process, the hydrogenizate was separated from the catalyst by filtration. A given sample of the filtrate (0.15 g of diols) was evaporated on a rotor evaporator at reduced pressure (20 mm Hg) at a temperature below 50°C and analyzed by the GLC method by modified procedure.

Method for Determining the Composition of But-2-yne-1,4-diol Hydrogenizate. An accurately weighed portion of diphenyl (180-200 mg) was introduced into a steam-treated probe of the hydrogenizate and 1 ml of acetic anhydride, 2 ml of pyridine, and 2 ml of benzene were added. The solution was left to stand for 5 min at 40°C and chromatographed.

Conditions of chromatography: chromatograph LKhM-8MD (5th model), length of column 3 m, stationary phase 5% of polyethylene glycol adipate on polychrome-1 (0.15-0.32 mm), rate of consumption of the helium gas carrier 15 ml/min, temperature of thermostat linearly programmed, 1°/min from 120 to 190°C. Retention times: diphenyl — 51 min 00 sec; acetylated I — 54 min 00 sec; II — 39 min 45 sec; IV — 36 min 45 sec. The amounts of the diols in the probe are calculated from the mean values of the ratios between the peak areas, corresponding to I, II, III, IV, and a standard, taking into account the parameters of a calibrated graph.

Cis-But-2-ene-1,4-diol (II). A solution containing 16.0 g of O-ethylidenebut-2-ene-1,4-diol, 12 ml of ethanol, 32 ml of water and 2 g of oxalic acid was heated at the boiling point for 20 h. The mixture was neutralized with a saturated aqueous solution of sodium bicarbonate, the precipitate was filtered, and the filtrate was diluted with 100 ml of ethanol. The salt that separated was filtered, the filtrate was evaporated *in vacuo* at 40°C (20 mm), and the residue was distilled *in vacuo* at 118-121°C (1 mm). Yield, 2.11 g (17%) of compound II. Found, %: C 53.88; H 9.34. $C_4H_8O_2$. Calculated, %: C 54.51; H 9.17.

Diacetate of Trans-but-2-ene-1,4-diol. The compound was obtained by a procedure described in [8] from 1,3-butadiene. It boiled at 112-114°C (12 mm), n_D^{20} 1.4426 (according to literature data [8], bp 115°C(12 mm), n_D^{20} 1.4420).

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POLAROGRAPHIC INVESTIGATION OF D-RIBONO-γ-LACTONE

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The reduction of D-ribono-γ-lactone (RL) by electrolysis in the presence of alkali metal salts is a method for the industrial preparation of D-ribose, an intermediate product in the synthesis of riboflavin (vitamin B_2) [1]. At the start of the first investigations [2-5] we used mercury as the cathode. When other metals were used as the cathode material the results were not successful, and a low yield of ribose on solid electrodes was obtained only when their surface was amalgamated [6, 7]. This was confirmed in several other papers also [8, 9], and is explained by the fact that the reducing agent in this process must be an amalgam of alkali metal formed on a mercury cathode [10] during electrolysis. The conclusion on this preferential indirect reduction, compared with direct reduction of RL on a mercury electrode, was based on the considerable shift of the zero charge point to the negative potentials on passing from mercury to the amalgam, and increase in the adsorbability of RL on the surface of the electrode under these conditions [7].

Because of the importance of this conclusion for understanding the reduction mechanism of RL and for clarifying the role of the electrode material in the synthesis of D-ribose, we undertook a polarographic study of RL. Information on the polarographic behavior of this compound was limited to incomplete data only, obtained for relatively concentrated (0.01 M) solutions [11].

Besides polarography, we also used cyclic voltamperometry.

On the polarograms obtained with a background of tetraalkylammonium salts in aqueous, alcoholic, or aqueous-alcoholic media, the RL gives only one wave in the vicinity of the background discharge (Fig. 1). The halfwave potential ($E_{1/2}$) depends on the concentration of the electrolyte (C_{el}), and was shifted to the region of less negative potentials when its concentration was increased (see Table 1, Nos. 1-4). The slope $\Delta E_{1/2}/\Delta \log C_{el} \simeq$ 80 mV somewhat exceeds the theoretical value ($\simeq$60 mV) for irreversible reduction in the case of an uncharged depolarizer [12]. The deviation may be due to the difficulty of accurately determining $E_{1/2}$ because of its closeness to the discharge of the electrolyte. In contrast, replacement of Et_4N^+ (see Table 1, Nos. 2, 5, 6, 8) for Bu_4N^+, and increase in the proportion of organic solvent (transition from aqueous solutions to alcoholic-aqueous and alcoholic solutions) leads to a shift of $E_{1/2}$ to more negative potentials, which agrees with the literature data on the influence of the solvent on $E_{1/2}$ of other compounds [12]. The influence of the charge in the alcohol content on the limiting current (i_{lim}) of RL is relatively small; in the region of 30-90% of alcohol, the i_{lim} value varies by nearly 30% (maximum i_{lim} is at an alcohol content of ∿70%).

After we had obtained these data indicating the polarographic activity of RL, we attempted to clarify the nature of RL wave; further experiments were carried out with a background of 0.07 M Et_4NClO_4 in 90% ethanol (saturated solution).

We first studied the dependence of the value of i_{lim} on the concentration of RL. Thus, a directly proportional dependence was found to exist between i_{lim} and C_{RL} values (Fig. 2).

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