

## ГИДРОГЕНИЗАЦИЯ ЗАМЕЩЕННЫХ НИТРО-, АЗОБЕНЗОЛОВ, ИХ СМЕСИ И ЗАМЕЩЕННОГО НИТРОАЗОБЕНЗОЛА НА СКЕЛЕТНОМ НИКЕЛЕ В ВОДНЫХ РАСТВОРАХ 2-ПРОПАНОЛА

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*Статья посвящена гидрогенизации 4-нитроанилина, 4-амино-2'-гидрокси-5'-метилазобензола, их смеси и 4-нитро-2'-гидрокси-5'-метилазобензола на скелетном никеле в водном растворе 2-пропанола азеотропного состава ( $x_2 = 0,68$ ) и данном растворителе с добавкой кислоты (0,01 М  $\text{CH}_3\text{COOH}$ ) или гидроксида натрия (0,01 М  $\text{NaOH}$ ). Выяснение причин и разработка подходов к селективному управлению стадийностью превращений замещенных нитроазобензолов, содержащих в молекуле две реакционные группы, в условиях гидрогенизации представляют интерес с теоретической и практической точек зрения. Скорость образования промежуточных продуктов при гидрогенизации нитроазобензолов во многом определяется активацией нитро- и азогрупп. Цель работы – проведение сравнительного анализа скоростей превращения нитро- и азогрупп в индивидуальных соединениях со скоростями гидрогенизации их смеси и скоростью превращения нитроазобензола, имеющего в своем составе одновременно нитро- и азогруппу, обсуждение причин влияния состава растворителя на скорость превращений моно- и дизамещенных бензолов. Данные УФ-спектроскопии свидетельствуют о том, что электронное состояние гидрируемых соединений в используемых составах растворителя не претерпевает существенных изменений, так как максимумы поглощения смещаются не более чем на 1 нм как при введении добавки кислоты, так и основания. Напротив, наблюдаемые скорости гидрогенизации моно- и дизамещенных бензолов изменяются в достаточно широких пределах. Сравнительный анализ скоростей гидрогенизации индивидуальных соединений, их смеси и дизамещенного бензола позволяет сделать вывод о том, что первоочередность восстановления той или иной группы в составе 4-нитро-2'-гидрокси-5'-метилазобензола можно сделать на основании расчета количественного соотношения образующихся продуктов реакции. При гидрогенизации смеси соединений, содержащих нитро- и азогруппы первостепенную роль начинает играть их адсорбционная, а не реакционная способность.*

**Ключевые слова:** жидкофазная гидрогенизация, скелетный никель, кинетическая кривая, скорость реакции, 4-нитро-2'-гидрокси-5'-метилазобензол, 4-нитроанилин, 4-амино-2'-гидрокси-5'-метилазобензол, смесь соединений, 2-пропанол, уксусная кислота, гидроксид натрия, водород, формы водорода, селективность

## HYDROGENIZATION OF SUBSTITUTED NITRO-, AZOBENZENES, THEIR MIXTURE AND SUBSTITUTED NITROAZOBENZENE ON SKELETAL NICKEL IN AQUEOUS 2-PROPANOL SOLUTIONS

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*The article is devoted to the investigation of the hydrogenation of 4-nitroaniline, 4-amino-2'-hydroxy-5'-methylazobenzene, their mixture and 4-nitro-2'-hydroxy-5'-methylazobenzene on skeletal nickel in an aqueous solution of 2-propanol with azeotropic composition ( $x_2 = 0.68$ ) and this solvent with the addition of acid (0.01 M  $\text{CH}_3\text{COOH}$ ) or sodium hydroxide (0.01 M  $\text{NaOH}$ ). The elucidation of the reasons and the development of approaches to the selective control of the staged transformations of substituted nitroazobenzenes containing two reactive groups in a molecule under the conditions of hydrogenation are of interest from theoretical and practical points of view. The rate of formation of intermediate products during the hydrogenation of nitroazobenzenes is largely determined by the activation of nitro and azo groups. The aim of the work is to conduct a comparative analysis of the rates of conversion of nitro- and azogroups in individual compounds with the rates of hydrogenation of their mixture and the rate of conversion of nitroazobenzene, which simultaneously contains nitro- and azogroups, to discuss the reasons for the influence of the solvent composition on the conversion rates of mono- and disubstituted benzenes. UV-spectroscopic data indicate that the electronic state of the hydrogenated compounds in the solvent compositions used does not undergo significant changes, since the absorption maxima are shifted by no more than 1 nm, both with the addition of acid and base. On the contrary, the observed rates of hydrogenation of mono- and disubstituted benzenes vary within fairly wide limits. A comparative analysis of the rates of hydrogenation of individual compounds, their mixtures and disubstituted benzene allows us to conclude that the priority of reduction of one or another group in 4-nitro-2'-hydroxy-5'-methyl-azobenzene can be made on the basis of calculating the quantitative ratio of the reaction products. When a mixture of compounds containing nitro and azo groups is hydrogenated, their adsorption rather than reactivity begins to play the primary role.*

**Key words:** liquid-phase hydrogenation, skeletal nickel, kinetic curve, reaction rate, 4-nitro-2'-hydroxy-5'-methylazobenzene, 4-nitroaniline, 4-amino-2'-hydroxy-5'-methyl-azobenzene, mixture of compounds, 2-propanol, acetic acid, sodium hydroxide, hydrogen, forms of hydrogen, selectivity

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The processes of the liquid-phase hydrogenation are the basis of effective technologies for obtaining products in the fine organic synthesis. However, in the original literature, information concerning the hydrogenation of mixtures of substances or compounds with several reactive groups with respect to hydrogen is extremely limited [1, 2]. It is not possible to make reasonable predictions about the selectivity of the hydrogenation of disubstituted benzenes when the reaction conditions change.

The purpose of the work is to perform a comparative analysis of the rates of conversion of nitro and azogroups in individual compounds with the rates of hydrogenation of their mixture and the rate of conversion of nitroazobenzene, which simultaneously contains nitro and azogroups, and the reasons for the influence of the solvent composition on the rate of transformations of mono- and disubstituted benzenes.

It is known that the rates and rate constants of reactions in heterogeneous catalysis are determined by a number of factors [1]. In particular, the medium as a homogeneous component of the catalytic system determines the reaction rate through a change in the solubility of the compound to be hydrogenated, their adsorption value, hydrogen reproduction rate, the solvent can determine the macrokinetic region of the process, etc. In this work, an azeotropic composition of 2-propanol is used as media ( $x_2 = 0.68$ ) and this solvent with the addition of acid (0.01 M  $\text{CH}_3\text{COOH}$ ) and base (0.01 M  $\text{NaOH}$ ).

The starting compounds used were 4-nitroaniline (4HA), 4-amino-2'-hydroxy-5'-methylazobenzene (4AAB) and 4-nitro-2'-hydroxy-5'-methylazobenzene (4NAB). 4HA and 4AAB were chosen as individual compounds not only because of the presence of nitro and azo groups in them, respectively, but also because they are products of hydrogenation of 4NAB.

4-nitro-2'-hydroxy-5'-methylazobenzene was synthesized by the method of traditional synthesis of azo dyes in described [3]. After diazotization, 4-nitroaniline followed by decomposition of the diazonium salt and combination with 4-cresol, 4-nitro-2'-hydroxy-5'-methyl-azobenzene was separated by filtration, dried and then re-precipitated from DMF, followed by recrystallization from ethanol.

4-amino-2'-hydroxy-5'-methylazobenzene was obtained by reduction of 4-nitro-2'-hydroxy-5'-methylazobenzene with sodium sulfide with an excess of the latter. The resulting product was recrystallized twice from ethanol. The structure of the synthesized compounds was confirmed by the methods of elemental analysis, NMR, IR and mass spectrometry.

In kinetic studies, skeletal nickel [4] served as a catalyst with an average particle size of 4 μm with their distribution over a radius close to monodisperse.

The reaction was monitored by the amount of absorbed hydrogen, the observed reaction rates were calculated from the change in the amount of hydrogen per unit time. In all cases, a correspondence was observed between the amount of absorbed hydrogen and the reaction stoichiometry corresponding to the complete conversion of the individual compounds or their mixtures. Additionally, the completeness of the conversion of the starting compounds and the selectivity of the reaction with respect to the final products were confirmed by thin-layer chromatography.

Spectral studies were performed on a spectrophotometer "CARY 50 scan UV-Visible Spectrophotometers" in the UV region of the spectral scale. The wavelengths corresponding to the absorption maxima of the individual compounds were found by mathematical processing of the spectral curves.

Quantitative analysis of the samples taken during hydrogenation of 4NAB was performed using HPLC on a brandchromatograph "Shimadzu LC-6A" with a 25 cm long stainless steel packed column, spectrophotometric detector with deuterium and tungsten

elements for the UV and visible spectral regions. The detector device made it possible to carry out measurements in the scale range from 175 to 700 nm. The management of the analysis conditions and the processing of the obtained results were performed using a personal computer. "Lichrosorb RP-18" with a particle diameter of 5 μm was used as the stationary phase; aqueous solutions of acetonitrile of various concentrations were used as eluent: in the analysis of 4HA – 20%, 4NAB and 4AAB – 60%. The column temperature, eluent feed rate, and wavelength were selected experimentally.

Qualitative analysis by ascending thin layer chromatography was carried out on Sorbfill plates using the toluene: ethyl acetate binary mixture as a eluent in a 7: 3 volume ratio and nitrogen oxides as an identifying agent. Identification of the reaction products was performed by comparing the working chromatograms with chromatograms of individual witness substances.

#### EXPERIMENTAL SECTION

UV-spectroscopic data indicate that the electronic state of 4HA, 4AAB and 4NAB in the solvent compositions used does not undergo significant changes, since the absorption maxima are shifted by no more than 1 nm, both when introducing an acid additive and a base. At the same time, the solubility of the compounds varies in different ways depending on the composition of the solvent – see Table 1.

It should be noted that the solubility of 4HA does practically not change, while for 4AAB it increases noticeably when going from a neutral solvent, respectively, to a solvent with the addition of sodium hydroxide and acetic acid. No correlation between the change in solubility and the observed reaction rate for different media is observed. The solubility of hydrogen was assumed to be unchanged and was assumed to be equal to the solubility of gas in an aqueous solution of 2-propanol with an azeotropic composition of  $1.8 \cdot 10^{-3} \text{ cm}^3/\text{cm}^3$  liquid phase.

Table 1

**Solubilities (α) and wavelengths of absorption maxima (λ, nm) in UV spectra of solutions of hydrogenated compounds**  
**Таблица 1. Растворимости (α) и значения длин волн максимумов поглощения (λ, нм) в УФ-спектрах растворов гидрируемых соединений**

Compound	Solvent					
	2-propanol-water -0.01 M CH <sub>3</sub> COOH, pH = 4.2		2-propanol-water pH = 8.0		2-propanol-water-0.01 M NaOH, pH = 13.2	
	α, g/100 cm <sup>3</sup>	λ, nm	α, g/100 cm <sup>3</sup>	λ, nm	α, g/100 cm <sup>3</sup>	λ, nm
4NA[5]	3.51 ± 0.20	380	3.40 ± 0.20	379	3.28 ± 0.20	380
4AAB[5]	2.88 ± 0.20	385	0.42 ± 0.05	384	1.48 ± 0.10	386
4NAB	-	338; 418	0.14 ± 0.02	338; 418	-	338; 418

There is a change in the rates of hydrogenation of 4HA, 4AAB over fairly wide limits. Fig. 1-3 show

the dependences of the hydrogenation rate of 4HA, 4AAB, their mixtures and 4NAB on the reaction time

for various media. For the convenience of comparing the kinetic curves in Fig. 1-3, the initial sections of the dependences are shown to the degree of conversion for each of the hydrogenated compounds 0.55-0.65.

In [1, 6-8], it was shown that on skeletal nickel under the conditions of hydrogenation of substituted benzenes, the rate of azo group conversion increases with the presence of an acid in the solvent, while for the nitro group this change occurs under the influence of sodium hydroxide. The results obtained, shown in Fig. 1-3 and Table 2, do not contradict this provision.

The kinetic curves shown in Figure 1 allow the following conclusions. In a neutral solvent, the rate of hydrogenation of the azo group in 4AAB is higher than the rate of reduction of the nitro group in 4HA. When hydrogenating 4NAB and mixture 4NA with 4AAB, the rate is within the error of the experimental results at 4AAB reduction rates.

A different picture is observed with the hydrogenation of 4HA, 4AAB, their mixture and 4NAB in a solvent with the addition of sodium hydroxide and acetic acid.

Fig. 2 shows the initial sections of the kinetic curves illustrating the transformation of the hydrogenated compounds in the presence of a base. In this solvent composition, in contrast to the neutral medium, in the initial phase of the reaction, the hydrogenation rates for a mixture of 4HA and 4AAB, as well as 4NAB, are in good agreement with each other and respond within the error limits of the hydrogenation rate 4HA. This allows us to conclude that both in a mixture of nitro and azo compounds, and in 4NAB, the conversion of the nitro group is of paramount importance. Indeed, according to the quantitative analysis of samples of the reaction mass during hydrogenation of 4NAB, the yield of 4AAB is 85%. As shown above, in a neutral solvent, the rates of hydrogenation of 4NAB are close to the conversion rate of 4AAB. It can be assumed that the yield of 4AAB in comparison with the solvent in which the base is present should decrease, which is observed in the experiment – the yield of 4AAB decreases to 65%.

The coincidence of the rates of hydrogenation of the mixture and 4HA within the experimental error indicates that the adsorption capacity of 4HA is higher than for 4AAB. According to the data given in [9-13], the adsorption coefficients for intermediate reduction products of nitrobenzene containing various unsaturated groups, including the nitro and azo group, can differ by more than two orders of magnitude, which ensures the primary reduction of the nitro compound. A similar pattern was observed when hydrogenating a mixture of nitrobenzene with azoxybenzene on skeletal

nickel in an aqueous solution of 2-propanol with azeotropic composition was example [15].

In the presence of acid in the solvent (Fig. 3) the observed rates of hydrogenation for the mixture, and especially 4NAB, decrease from the values characteristic of the conversion of 4AAB to values close to the rates of reduction of the nitro group in 4HA. It can be assumed that in this solvent the addition of hydrogen both in 4NAB and in the mixture of compounds will mainly occur along the azo group. Indeed, when 4NAB is hydrogenated, the 4AAB yield, as compared with neutral solvent, decreases from 65% to 2%. In addition, according to TLC, during the hydrogenation of a mixture of 4HA with 4AAB, the appearance of 2-amino-4-methylphenol, which is the product of double bond hydrogenation in 4AAB, is observed from the beginning of the reaction. The sequence of transformation of the reactive groups during the hydrogenation of 4NAB and in the mixture of individual compounds is given in Table 2.

It can be stated that the conclusion about the priority of the restoration of one or another group in the composition of a disubstituted compound can be made on the basis of the analysis of the formed reaction products and the calculation of their quantitative ratio. When hydrogenating a mixture of compounds containing similar groups, one can come to the wrong conclusion, since not only the reactivity of one group or another, but also the adsorption capacity of the compound begins to play the primary role [9-15].

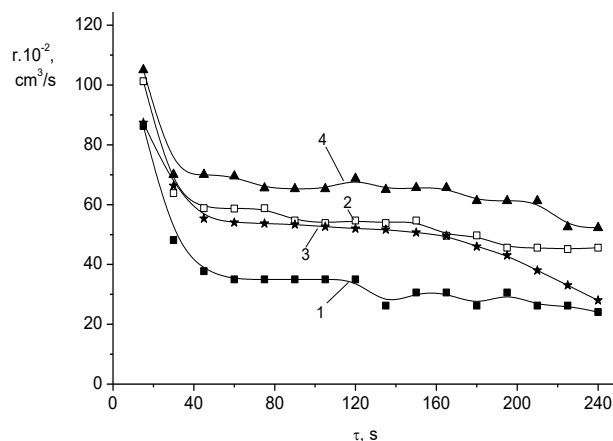


Fig. 1. The change in the observed rates of hydrogenation of 4NAB and a mixture of 4NA and 4AAB on skeletal nickel in an aqueous solution of 2-propanol with azeotropic composition at  $T = 303 \text{ K}$ ,  $g_{\text{cat}} = 0.625 \text{ g}$ ,  $g_{4\text{NAB}} = (1.950 \pm 0.005) \text{ mmol}$ ,  $g_{4\text{HA}} = (1.950 \pm 0.005) \text{ mmol}$ ,  $g_{4\text{AAB}} = (1.950 \pm 0.005) \text{ mmol}$ ,  $V_{\text{liquidphase}} = 100 \text{ cm}^3$ , hydrogen pressure is 0.1 MPa. 1- 4NA, 2- 4AAB, 3 - mixtures, 4 - 4NAB  
Рис. 1. Изменение наблюдаемых скоростей гидрогенизации 4НАБ и смеси соединений 4НА и 4ААБ на скелетном никеле в водном растворе 2-пропанола азеотропного состава при  $T = 303 \text{ K}$ ,  $g_{\text{кат}} = 0,625 \text{ г}$ ,  $g_{4\text{НАБ}} = (1,950 \pm 0,005) \text{ ммоль}$ ,  $g_{4\text{НА}} = (1,950 \pm 0,005) \text{ ммоль}$ ,  $g_{4\text{ААБ}} = (1,950 \pm 0,005) \text{ ммоль}$ ,  $V_{\text{ж.ф.}} = 100 \text{ см}^3$ , давление водорода 0.1 МПа. 1 – 4НА, 2 – 4ААБ, 3 – смеси, 4 – 4НАБ

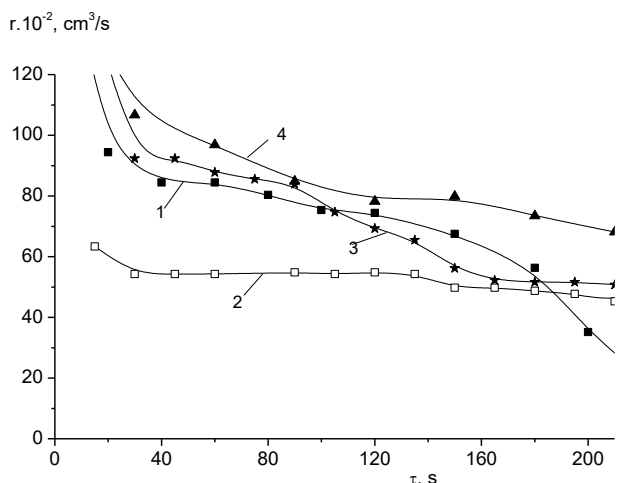


Fig. 2. The change in the observed rates of hydrogenation of 4NAB and a mixture of 4NA and 4AAB compounds on skeletal nickel in an aqueous solution of 2-propanol with the addition of sodium hydroxide at  $T = 303\text{ K}$ ,  $g_{\text{cat}} = 0.625\text{ g}$ ,  $g_{4\text{NAB}} = (1.950 \pm 0.005)\text{ mmol}$ ,  $g_{4\text{NA}} = (1.950 \pm 0.005)\text{ mmol}$ ,  $g_{4\text{AAB}} = (1.950 \pm 0.005)\text{ mmol}$ ,  $V_{\text{liquidphase}} = 100\text{ cm}^3$ , hydrogen pressure is 0.1 MPa. 1 - 4NA, 2 - 4AAB, 3 - mixtures, 4 - 4NAB

Рис. 2. Изменение наблюдаемых скоростей гидрогенизации 4НАБ и смеси соединений 4НА и 4ААБ на скелетном никеле в водном растворе 2-пропанола с добавкой гидроксида натрия при  $T = 303\text{ K}$ ,  $g_{\text{кат}} = 0,625\text{ г}$ ,  $g_{4\text{НАБ}} = (1,950 \pm 0,005)\text{ ммоль}$ ,  $g_{4\text{НА}} = (1,950 \pm 0,005)\text{ ммоль}$ ,  $g_{4\text{ААБ}} = (1,950 \pm 0,005)\text{ ммоль}$ ,  $V_{\text{ж.ф.}} = 100\text{ см}^3$ , давление водорода 0.1 МПа. 1 - 4НА, 2 - 4ААБ, 3 - смеси, 4 - 4НАБ

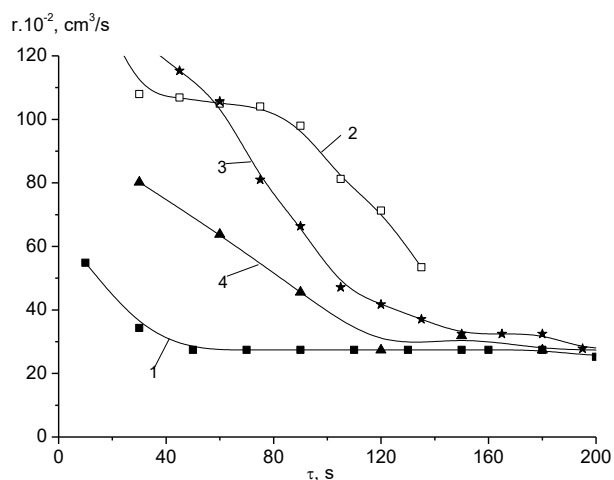


Fig. 3. The change in the observed rates of hydrogenation of 4NAB and a mixture of 4NA and 4AAB compounds on skeletal nickel in an aqueous solution of 2-propanol with the addition of acetic acid at  $T = 303\text{ K}$ ,  $g_{\text{cat}} = 0.625\text{ g}$ ,  $g_{4\text{NAB}} = (1.950 \pm 0.005)\text{ mmol}$ ,  $g_{4\text{NA}} = (1.950 \pm 0.005)\text{ mmol}$ ,  $g_{4\text{AAB}} = (1.950 \pm 0.005)\text{ mmol}$ ,  $V_{\text{liquidphase}} = 100\text{ cm}^3$ , hydrogen pressure is 0.1 MPa. 1 - 4NA, 2 - 4AAB, 3 - mixtures, 4 - 4NAB

Рис. 3. Изменение наблюдаемых скоростей гидрогенизации 4НАБ и смеси соединений 4НА и 4ААБ на скелетном никеле в водном растворе 2-пропанола с добавкой уксусной кислоты при  $T = 303\text{ K}$ ,  $g_{\text{кат}} = 0,625\text{ г}$ ,  $g_{4\text{НАБ}} = (1,950 \pm 0,005)\text{ ммоль}$ ,  $g_{4\text{НА}} = (1,950 \pm 0,005)\text{ ммоль}$ ,  $g_{4\text{ААБ}} = (1,950 \pm 0,005)\text{ ммоль}$ ,  $V_{\text{ж.ф.}} = 100\text{ см}^3$ , давление водорода 0.1 МПа. 1 - 4НА, 2 - 4ААБ, 3 - смеси, 4 - 4НАБ

Table 2

Some characteristics of the hydrogenation of substituted benzenes on skeletal nickel in aqueous solutions of 2-propanol

Таблица 2. Некоторые характеристики гидрогенизации замещенных бензолов на скелетном никеле в водных растворах 2-пропанола

Characteristic reactions	Solvent		
	2-propanol-water -0.01 M CH <sub>3</sub> COOH, pH = 4.0	2-propanol-water pH = 8.0	2-propanol-water-0.01 M NaOH, pH = 13.2
The average value of the reaction rate, $r \cdot 10^2, \text{ cm}^3/\text{s}$ :			
4NA	30 ± 5	40 ± 5	90 ± 10
4AAB	110 ± 10	60 ± 5	55 ± 10
4NAB	80 → 40 ± 5	70 ± 5	100 ± 10
Mix 4NA + 4AAB	120 → 40 ± 5	55 → 40 ± 5	90 → 55 ± 5
Transformation sequence -N=N- and -NO <sub>2</sub> groups:			
in the mix in NAB	-N=N->-NO <sub>2</sub> -N=N->-NO <sub>2</sub>	-N=N-<- -NO <sub>2</sub> -N=N->- -NO <sub>2</sub>	-N=N-<- -NO <sub>2</sub> -N=N-<<- -NO <sub>2</sub>
The sequence of transformation of the reactive groups during hydrogenation 4NAB, %:			
4NA	98	35	15
4AAB	2	65	85

Different rates of hydrogenation of compounds used in the work in the forms of hydrogen adsorbed on the catalyst surface. In the works [1, 16-20] it is noted that in the hydrogenation of double bonds the weakly bound molecular form is most active, the molecular form of adsorbed hydrogen is  $\alpha$ -form ( $\text{H}_2^{\delta+}$ ), for the transformation of the nitro group, strongly bonded forms - non-ionized  $\gamma$ -form (H) and ionized  $\beta$ -forms ( $\text{H}^{\delta+}$  and  $\text{H}^{\delta-}$ ) adsorbed hydrogen are more preferable. Analysis of the data presented in [2, 16-20] allows a quantitative assessment of the content of various forms of adsorbed hydrogen on the surface of skeletal nickel, depending on the pH of an aqueous solution of alcohol. Data illustrating the content of the active forms of hydrogen and their ratio depending on the pH of the aqueous-alcoholic solution are given in Table 3.

Table 3

The content of adsorbed forms of hydrogen on the surface of skeletal nickel in aqueous solutions of ethanol ( $x_2 = 0.78$ )

Таблица 3. Содержание адсорбированных форм водорода на поверхности скелетного никеля в водных растворах этанола ( $x_2 = 0,78$ )

pH of an aqueous solution of ethanol	5.5	8.2	14.0
Content of active forms $\text{H}_2, \text{ cm}^3/\text{g}_{\text{kat}}$ [1, 10, 11]:			
$\alpha$ - form	3.69	2.72	1.89
( $\beta + \gamma$ ) - forms	16.44	17.89	17.39
$\alpha / (\beta + \gamma), \%$	22.30	15.20	10.50

According to the data shown in Fig. 1-3 and Table 2, the conversion rate of the nitro group increases with the transition from neutral to solvent with the addition of sodium hydroxide, while the rate of hydrogenation of azo gamma increases with decreasing pH. This position is consistent with the change in the selectivity of the reaction with respect to 4HA and 4AAB during hydrogenation of 4NAB – Table 2.

The obtained experimental data confirm the assumption that the rates of conversion of nitro and azo

groups to 4HA and 4AAB on skeletal nickel are in good agreement with the change in the ratio of weakly bound and strongly bound forms of adsorbed hydrogen depending on the pH of the solvent. Thus, by varying the composition of the solvent, it is possible to change the rates of transformation of reactive groups in mono- and disubstituted benzenes.

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