

## РОЛЬ ВОДОРОДА В СЕЛЕКТИВНОСТИ ГИДРОГЕНИЗАЦИИ ЗАМЕЩЕННЫХ НИТРОАЗОБЕНЗОЛОВ НА СКЕЛЕТНОМ НИКЕЛЕ В ВОДНЫХ РАСТВОРАХ 2-ПРОПАНОЛА

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*Выяснение последовательности превращений замещенных нитробензолов, в частности, содержащих несколько реакционноспособных групп, и разработка подходов к управлению селективностью процессов с их участием представляет интерес как с теоретической, так и практической точек зрения. Статья посвящена анализу кинетики гидрогенизации 2-нитро-2'-гидрокси-5'-метилазобензола, 4-нитро-2'-гидрокси-5'-метилазобензола, 4-нитроанилина, 4-амино-2'-гидрокси-5'-метилазобензола на скелетном никеле в водных растворах 2-пропанола различного состава, в том числе с добавкой уксусной кислоты или гидроксида натрия при различных начальных количествах органического соединения. Увеличение начального количества 4-нитро-2'-гидрокси-5'-метилазобензола приводит к росту скорости превращения нитрогруппы в исходном соединении и к снижению скорости превращения азогруппы. Влияние вводимого гидроксида натрия в водный раствор 2-пропанола на скорость превращения нитро- и азогруппы в 4-нитро-2'-гидрокси-5'-метилазобензоле аналогично изменению скоростей при гидрогенизации индивидуальных соединений – 4-нитроанилина и 4-амино-2'-гидрокси-5'-метилазобензола. Полученные результаты не противоречат представлениям о параллельно-последовательной схеме превращений 4-нитро-2'-гидрокси-5'-метилазобензола. Одно из направлений связано с превращением азогруппы в 4-нитро-2'-гидрокси-5'-метилазобензоле и образованием 4-нитроанилина и 2-амино-4-метилфенола, а второе с превращением 4-нитро-2'-гидрокси-5'-метилазобензола через 4-амино-2'-гидрокси-5'-метилазобензол за счет восстановления нитрогруппы. К завершению реакции все промежуточные соединения восстанавливаются до 2-амино-4-метилфенола и 1,4-фенилендиамина. При гидрогенизации 2-нитро-2'-гидрокси-5'-метилазобензола одно из направлений приводит к образованию 2-нитро-2'-гидрокси-5'-метилгидразобензола, а второе – к продукту, содержащему триазольный цикл – N-оксиду 2-2'-гидрокси-5'-метилфенилбензотриазолу. К завершению реакции данные соединения, соответственно, восстанавливаются до 2-2'-гидрокси-5'-метилфенилбензотриазола и 2-амино-4-метилфенола и 1,2-фенилендиамина. В объеме раствора в присутствии гидроксида натрия 2-нитро-2'-гидрокси-5'-метилгидразобензол вследствие внутримолекулярной перегруппировки переходит в N-оксид 2-2'-гидрокси-5'-метилфенилбензотриазол.*

**Ключевые слова:** водород, адсорбция, активные формы водорода, 4-нитро-2'-гидрокси-5'-метилазобензол, 4-амино-2'-гидрокси-5'-метилазобензол, 2-нитро-2'-гидрокси-5'-метилазобензол, N-оксид 2-2'-гидрокси-5'-метилфенилбензотриазол, 2-2'-гидрокси-5'-метилфенилбензотриазол, 2-амино-4-метилфенол, 1,2-фенилендиамин, 1,4-фенилендиамин, 4-нитроанилин, скелетный никель, 2-пропанол, уксусная кислота, гидроксид натрия, кинетические кривые, скорость, константа скорости, селективность реакции

### Для цитирования:

Лефедова О.В., Хоанг Ань, Филиппов Д.В. Роль водорода в селективности гидрогенизации замещенных нитроазобензолов на скелетном никеле в водных растворах 2-пропанола. *Изв. вузов. Химия и хим. технология.* 2020. Т. 63. Вып. 6. С. 65–71

### For citation:

Lefedova O.V., Hoang Anh, Filippov D.V. Hydrogen role in selectivity of substituted nitro-azobenenes hydrogenization on skeletal nickel in 2-propanol aqueous solutions. *Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol.* [Russ. J. Chem. & Chem. Tech.]. 2020. V. 63. N 6. P. 65–71

## HYDROGEN ROLE IN SELECTIVITY OF SUBSTITUTED NITRO-AZOBENENES HYDROGENATION ON SKELETAL NICKEL IN 2-PROPANOL AQUEOUS SOLUTIONS

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*Elucidation of the substituted nitrobenzenes transformations sequence, in particular, containing several reactive groups and the development of approaches to the control of the selectivity of processes involving them is of interest from both theoretical and practical points of view. The article is devoted to the analysis of the hydrogenation kinetics of 2-nitro-2'-hydroxy-5'-methylazobenzene, 4-nitro-2'-hydroxy-5'-methyl-isobenzene, 4-nitroaniline, 4-amino-2'-hydroxy-5'-methylazobenzene on skeletal nickel in 2-propanol aqueous solutions of different composition, including with the addition of acetic acid or sodium hydroxide with various initial amounts of organic compound. The rise in the 4-nitro-2'-hydroxy-5'-methylazobenzene initial amount leads to increase in the nitro group transformation rate in the starting compound and to decrease in the azo-group transformation rate. The effect of sodium hydroxide additives in the 2-propanol aqueous solution on the nitro- and azo-groups conversion rate into 4-nitro-2'-hydroxy-5'-methyl-isobenzene is analogous to the change in the individual compounds hydrogenation rates (4-nitroaniline and 4-amino-2'-hydroxy-5'-methylazobenzene). Obtained results do not contradict the parallel-sequential scheme concept for the 4-nitro-2'-hydroxy-5'-methylazobenzene transformations. One of the directions is associated with the azo-group transformation into 4-nitro-2'-hydroxy-5'-methylazobenzene and 4-nitroaniline and 2-amino-4-methylphenol formation, and the second with the 4-nitro-2'-hydroxy-5'-methyl-isobenzene conversion through 4-amino-2'-hydroxy-5'-methyl-isobenzene by the nitro-group reducing. At the reaction end, all intermediate compounds are reduced to 2-amino-4-methylphenol and 1,4-phenylenediamine. When 2-nitro-2'-hydroxy-5'-methylazobenzene is hydrogenated, one of the directions leads to the 2-nitro-2'-hydroxy-5'-methylhydrazobenzene formation, and the second to the product containing the triazole cycle - N-oxide 2-2'-hydroxy-5'-methylphenylbenzotriazole. At the reaction end, these compounds are reduced to 2-2'-hydroxy-5'-methylphenylbenzotriazole and 2-amino-4-methylphenol and 1,2-phenylenediamine, respectively. In the solution at the sodium hydroxide presence, 2-nitro-2'-hydroxy-5'-methylhydrazobenzene transforms into the N-oxide 2-2'-hydroxy-5'-methylphenylbenzotriazole as a result of intramolecular rearrangement.*

**Key words:** hydrogen, adsorption, hydrogen active forms, 4-nitro-2'-hydroxy-5'-methylazobenzene, 4-amino-2'-hydroxy-5'-methylazobenzene, 4-nitroaniline, 1,4-phenylenediamine, skeletal nickel, 2-propanol, sodium hydroxide, kinetic curves, rate, rate constant, reaction selectivity

In any hydrogenation process, we have two equal participants – “oxidizing agent” – organic compound and “reducing agent” – adsorbed hydrogen. According to the results obtained by the authors of a number of papers [1-6], the total content and energy state of hydrogen can largely vary under the influence of a solvent.

The surface of skeletal nickel contains molecular and atomic forms of adsorbed hydrogen, which are in a state of dynamic equilibrium. The total amount of adsorbed hydrogen for a number of individual solvents, their aqueous solutions and aqueous solutions with different pH values, relative to the gas phase, is given in [1]. So, for DMF, this value is 2.48, for water – 3.46, for aliphatic alcohols – ranges from

2.37 in methanol, to 1.54 in 2-propanol. The hydrogen content in the gas phase corresponds to 48-50 cm<sup>3</sup>/g.

Most researchers working in the field of hydrogenation of substituted nitrobenzenes and compounds containing unsaturated “nitrogen-nitrogen” or “carbon-carbon” bonds, note the different activity of adsorption forms of hydrogen with respect to those or other unsaturated groups. It is believed that in the reduction of groups containing oxygen, for example, nitro, nitroso, azoxy, etc., the most active atomic, tightly bound forms of hydrogen. These forms include ionized – H<sup>δ+</sup>, H<sup>δ-</sup> or β-form and non-ionized H or γ-form. In contrast, in the hydrogenation of unsaturated “nitrogen – nitrogen” or “carbon – carbon” bonds,

the molecular, weakly bonded form of hydrogen,  $H_2^{\delta+}$  or  $\alpha$  form, is most active [7-9].

The purpose of the work is to clarify the role of individual forms of adsorbed hydrogen in the hydrogenation of substituted nitrobenzenes on skeletal nickel in solvents of different nature and composition.

#### EXPERIMENTAL PART

As the starting compound, 2-nitro-2'-hydroxy-5'-methylazobenzene (2NAB), 4-nitro-2'-hydroxy-5'-methylazobenzene (4NAB), which have both nitro and azo groups actively interacting with hydrogen under hydrogenation conditions, was used. 4-Nitroaniline (4HA) and 4-amino-2'-hydroxy-5'-methylazobenzene (4AAB) were used to conduct a comparative assessment of the rates of conversion of nitro and azo groups in the solvents under study.

The hydrogenation of the starting compounds was carried out in a thermostatically controlled reactor at atmospheric pressure of hydrogen and vigorous stirring (3200 rpm) of the liquid phase. This provided an exception to the influence of external mass transfer on the observed reaction rate. The reactor was equipped with a system of continuous hydrogen supply, the flow rate for which during the reaction was carried out by gas burettes. The accepted scheme of the experiment made it possible to determine the observed reaction rates with high reliability and an error not exceeding 5%.

The catalyst was skeletal nickel (Raney nickel), obtained from a nickel-aluminum alloy Ni:Al:Fe 50:48.8:0.2 % wt. according to the standard method [5, 10]. The ratio of the quantities of the compound to be hydrogenated and the catalyst was selected in such a way that the linear relationship between the observed reaction rate and the amount of catalyst used was maintained [11].

The control of the content of the starting compounds and reaction products during the reaction was carried out by taking 7-10 samples of the hydrogenation product, which were analyzed using thin-layer and liquid chromatography, as well as by the spectrophotometric method.

Analysis by ascending thin layer chromatography was carried out on "Sorbfill" plates using a toluene-ethyl acetate binary mixture as an eluent in a 7:3 volume ratio and nitrogen oxides or ammonia as a developer. Identification of the reaction products was carried out by comparing the working chromatograms with chromatograms of individual substances – witnesses.

Quantitative analysis was performed on a "Shimadzu LC-6A" liquid chromatograph in accordance with the procedure described in [11], and the calculation was performed using embedded software.

The total number of analyzed compounds in each individual experiment was not less than 98%, which made it possible to draw objective conclusions about the stagedness of the transformation of compounds during hydrogenation and confirmed the high reliability of the results obtained.

#### RESULTS AND DISCUSSION

Analysis of the data presented in [1-6, 12], allows us to state that the content of the weakly bound form of adsorbed hydrogen -  $\alpha$  in aliphatic alcohols increases when going from methanol to 2-propanol. And the ratio of this form to its strongly bound form is  $-\beta$  accordingly decreases. Similar changes are characteristic for aqueous solutions with different pH values.

Figure 1 shows the dependences of the ratio of the active forms of hydrogen –  $\alpha/\beta$  on the dielectric constant of aliphatic alcohol –  $\epsilon$  (a) and on the pH of the aqueous solution (b).

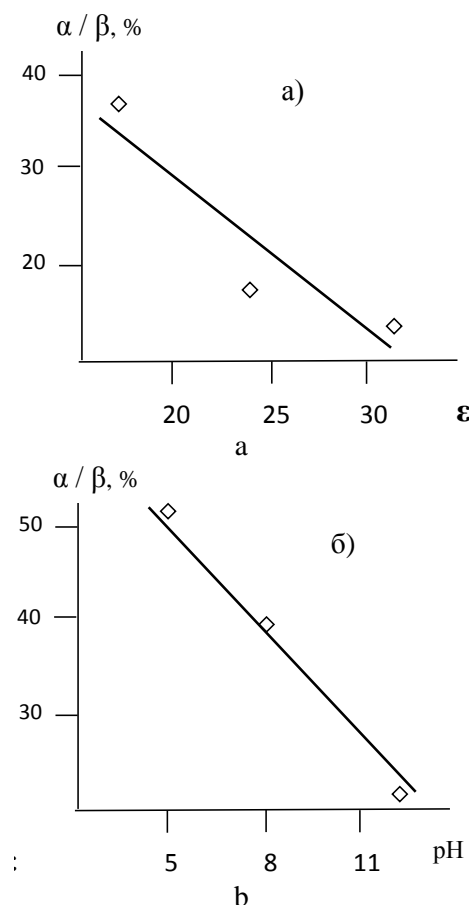


Fig. 1. Dependences of the amounts of weakly bound and strongly bound forms of hydrogen –  $\alpha/\beta$  (a) on the dielectric constant of aliphatic alcohol and the pH of an aqueous solution (b)

Рис. 1. Зависимости соотношения количеств слабосвязанной и прочносвязанной форм водорода –  $\alpha/\beta$  (а) от диэлектрической проницаемости алифатического спирта и pH водного раствора (б)

The study of the hydrogenation kinetics of 4NAB and 2NAB in aqueous solutions of aliphatic alcohols of different composition and pH values [13-14] showed that in both cases the conversion of compounds on skeletal nickel proceeds in a parallel-sequential scheme. During hydrogenation of 4NAB, 4HA, 2-methyl-4-phenol and 4AAB, respectively, are formed as reaction products in parallel stages. Upon completion of the reaction, 4HA and 4AAB are reduced to 1,4-diphenylamine and 2-methyl-4-phenol.

When hydrogenating 2NAB, the intermediate products that are formed in parallel stages are 2-nitro-2'-hydroxy-5'-methylhydrazobenzene (NHB) and the product containing the benzotriazole cycle – N-oxide 2-2'-hydroxy-5'-methylphenylbenzotriazole (NO) [12, 15, 16]. In the volume of the solution in the presence of sodium hydroxide, the NHB is able to cyclize in the NO. Upon completion of the reaction, NO is quantitatively reduced to 2-2'-hydroxy-5'-methylphenylbenzotriazole (BT), and NHB to 1,2-diphenylamine and 2-methyl-4-phenol. When discussing the results, the total yield of NO and BT was taken as the selectivity of hydrogenation of 2NAB with respect to compounds containing the benzotriazole cycle (CBTC).

It can be assumed that the ratio of the formed amounts of 4HA and 4AAB during hydrogenation of 4NAB will be related to the reactivity of the nitro and azo groups with respect to hydrogen, and in the case of 2NAB, the formation of NHB will be due solely to the interaction of the azo group with hydrogen. Therefore, it is possible that on skeletal nickel, a change in the rates of transformation of nitro and azo groups in the composition of individual compounds under the influence of a solvent will be of the same type with their transformations in the composition of 2NAB and 4NAB. A consequence of the different rates of interaction of hydrogen in the nitro and azo groups will be the change in the selectivity of the hydrogenation of these compounds with respect to the intermediate products.

Table 1 shows the average values of the ratio of the hydrogenation rates of 4HA and 4AAB, the maximum amounts of 4HA and 4AAB, as well as the yield of CBTC [12], formed, respectively, by hydrogenation of 4NAB and 2NAB for individual and binary solvents.

Comparison of changes in the amounts of weakly bound and strongly bound forms of hydrogen adsorbed on the surface of skeletal nickel (Fig. 1) with the data given in Table 1, allows us to state the following.

An increase in the activity of hydrogen with respect to the azo group leads to a decrease in the ratio of the rates of hydrogenation of 4HA to 4AAB

during the transition from 2-propanol to methanol. In the same sequence, the CBTC yield decreases upon hydrogenation of 2NAB. The highest dielectric constant is characteristic of methanol. According to Fig. 1a and the results given by the authors of [1], methanol is characterized by a higher content of weakly bound forms of adsorbed hydrogen.

*Table 1*

**The ratios of the conversion rates of 4HA/4AAB, the maximum amounts of 4HA and 4AAB, the yield of the CBTC generated during the hydrogenation of 4NAB and 2NAB for individual and binary solvents**

*Таблица 1. Соотношения скоростей превращения 4HA/4AAB, максимальных количеств 4HA и 4AAB, выход ПТЦ, образующихся при гидрогенизации 4НАБ и 2НАБ для индивидуальных и бинарных растворителей*

Solvent	$\epsilon$	$r_{4NA}/r_{4AAB}$	output CBTC, %
Methanol	32	$0.25 \pm 0.05$	25±2
Ethanol	24	$1.25 \pm 0.05$	31±2
2-propanol	18	$2.75 \pm 0.05$	35±2
Methanol-water ( $x_2 = 0.48$ )	58	$1.85 \pm 0.05$	48 → 52
Ethanol-water ( $x_2 = 0.60$ )	47	$2.25 \pm 0.05$	
2-propanol-water ( $x_2 = 0.74$ )	32	$2.90 \pm 0.20$	

Thus, an increase in the share of the weakly bound molecular form of adsorbed hydrogen increases the degree of azo group conversion in the composition of 2NAB. Indeed, with the use of a number of individual solvents, the selectivity of hydrogenation of 2NAB with respect to NHB increases with an increase in the dielectric constant of the solvent [10, 12].

It should be noted that the yield of CBTC when using aqueous solutions of aliphatic alcohols in a complex way depends on the mole fraction of alcohol. For aqueous solutions of methanol, ethanol and 2-propanol, the maximum yield of CBTC when hydrogenating 2NAB corresponds, respectively, to the molar fraction of the organic component equal to 0.48, 0.60, 0.74. For the above compositions of aqueous solutions of alcohols, the relationship between the ratio of the hydrogenation rates 4NA/4AAB and the dielectric constant of the solvent was maintained – Table 1 (the dielectric constant of the water-alcohol solvent was calculated as an additive value).

The content of the weakly bound form of adsorbed hydrogen was most noticeable when mixed solvents were used – when changing from an aqueous solution of alcohol containing an acid with a low pH to a solution containing sodium hydroxide – pH = 12-14 [1-6, 12].

When 4NAB is hydrogenated, the transition to a solvent with the addition of sodium hydroxide leads to a sharp decrease in 4HA yield, which indicates an increase in the rate of reduction of the nitro group. Indeed, in the presence of a base, the rate of reduction of the nitro group upon hydrogenation of 4NA increases, while the observed rate of hydrogenation of the azo group in 4AAB decreases sharply. Experimental data illustrating this position is shown in Table 2.

Table 2

The ratio of the rates of conversion of 4HA / 4AAB [13], the maximum amounts of 4HA and 4AAB produced by hydrogenation of 4NAB, and the yield of products containing the benzotriazole cycle [14] formed by hydrogenation of 2NAB on skeletal nickel in mixed solvents

Таблица 2. Соотношение скоростей превращения 4HA/4AAB [13], максимальных количеств 4HA и 4AAB, образующихся при гидрогенизации 4NAB, и выход продуктов, содержащих бензотриазольный цикл [14], образующихся при гидрогенизации 2NAB на скелетном никеле в смешанных растворителях

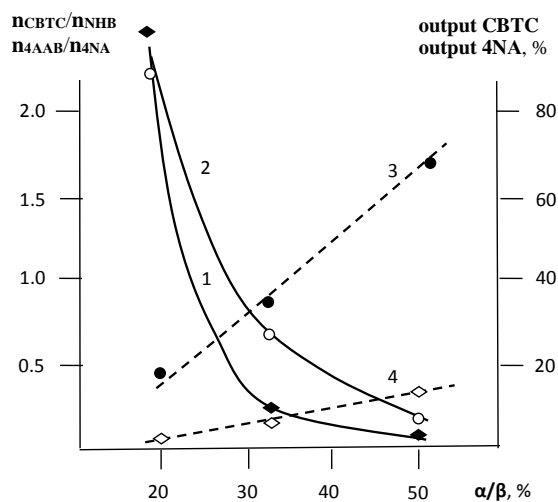
Solvent	$\Gamma_{4NA}/\Gamma_{4AAB}$	$n_{4NA}/n_{4AAB}$	output CBTC, %
2-propanol-water ( $x_2 = 0.68$ )-CH <sub>3</sub> COOH	$0.30 \pm 0.15$	10	$20 \pm 2$
2-propanol-water ( $x_2 = 0.68$ )	$0.70 \pm 0.20$	5	$35 \pm 2$
2-propanol-water ( $x_2 = 0.68$ )-NaOH	$1.70 \pm 0.25$	0.4	$70 \pm 2$

Fig. 2 shows the dependences illustrating the relationship between the ratios of the maximum amounts of 4AAB/4HA and CBTC/NHB and the amounts of weakly bound and strongly bound forms of hydrogen –  $\alpha/\beta$  for aqueous solutions of 2-propanol with the addition of acid and base, calculated according to [1, 3, 6].

Curve 1, shown in Fig. 2, confirms the fact that an increase in the content of strongly bonded forms of hydrogen, favorably affecting the interaction of hydrogen with a nitro group, leads to an increase in the ratio of maximum amounts of  $n_{4AAB}/n_{4NA}$  and an increase in the selectivity of hydrogenation of 4NAB with respect to 4AAB – curve 4.

In the case of 2NAB, this ensures an increase in the selectivity of hydrogenation with respect to products containing the benzotriazole cycle – curve 3 and, accordingly, to an increase in the ratio of quantities  $n_{CBTC}/n_{NHB}$  – curve 2 as the ratio  $\alpha/\beta$  decreases.

It can be argued that the dependences of changes in the ratio of the amounts of  $n_{4AAB}/n_{4HA}$  and  $n_{CBTC}/n_{NHB}$  on the ratio of active forms of hydrogen are of the same type. The nature of the dependences is preserved in the case of taking into account the amount



2-propanol-water ( $x_2=0.68$ )-NaOH (0.01 M)    2-propanol-water ( $x_2=0.68$ ) (0.01 M)    2-propanol-water ( $x_2=0.68$ )-CH<sub>3</sub>COOH (0.01 M)

Fig. 2. Dependence of the ratio of the maximum amounts of 4AAB/4HA – 1, CBTC/NHB – 2, formed during hydrogenation of 4NAB and 2NAB, and also the outputs of CBTC – 3 and 4NA – 4 on the ratio of the amounts of weakly bound and strongly bonded forms of hydrogen –  $\alpha/\beta$

Рис. 2. Зависимость соотношения максимальных количеств 4AAB/4HA – 1, ПБТЦ/НГБ – 2, образующихся при гидрогенизации 4NAB и 2NAB, а также выходов ПБТЦ – 3 и 4NA – 4 от соотношения количеств слабосвязанной и прочносвязанной форм водорода –  $\alpha/\beta$

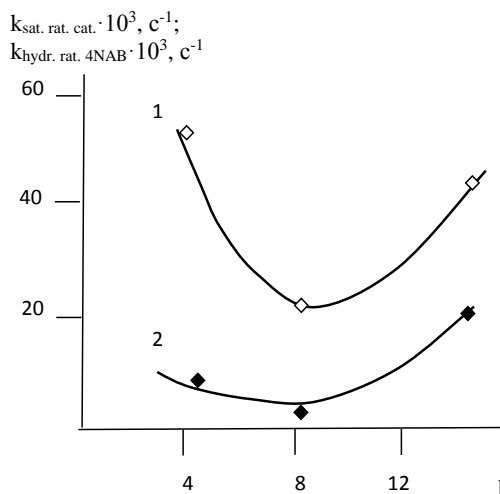


Fig. 3. Dependence of the rate constant of catalyst saturation with hydrogen – 1 [17, 18] and the rate constant of hydrogenation of 4NAB – 2 on skeletal nickel on the pH of aqueous solutions of 2-propanol with the addition of acid and base

Рис. 3. Зависимость константы скорости насыщения катализатора водородом – 1 [20, 21] и константы скорости гидрогенизации 4NAB – 2 на скелетном никеле от pH водных растворов 2-пропанола с добавками кислоты и основания

of a strongly bonded atomic non-ionized  $\gamma$ -form of adsorbed hydrogen, that is, using the ratio  $\alpha/(\beta + \gamma)$  instead of  $\alpha/\beta$ .

It should be noted that in all studied compositions of the solvent, the transformation of the starting

compounds proceeded by the hydrogenation mechanism, i.e. in the absence of diffusional drag on hydrogen [12]. This is evidenced by the same type of change in the rate constants of saturation of the catalyst surface with hydrogen [17, 18] and the conversion of 4NAB from the pH of an aqueous solution of 2-propanol – Fig. 3. Moreover, the rate constant for saturation of the catalyst surface with hydrogen is 2.5-5 times higher than the conversion rate constant of 4NAB.

Hydrogenation of 2NAB in an aqueous solution of 2-propanol with the addition of acid, despite the fact that the rate of hydrogenation of the azo group increases, as evidenced by the increase in the ratio  $n_{4NA}/n_{4AAB}$  – Table 1. The selectivity of the reaction by CBTC is maintained at 20%. This suggests that the formation of a benzotriazole cycle in the adsorption layer is possible as a result of the reorganiza-

tion of bonds in the complex of the associative type “2NAB-hydrogen” while simultaneously attacking the nitro group and the nitrogen-nitrogen bond of the azo group with hydrogen.

According to the results of quantum-chemical calculations, only in this case a water molecule can be separated from the complex of the associative type. The charges on the oxygen atoms of the nitro group and the  $\alpha$ -nitrogen atom of the nitrogen group in the 2NAB molecule, corresponding to the *trans*-isomer and the preservation of the intramolecular hydrogen bond with the  $\beta$ -nitrogen atom [11, 19], have positive values. It can be assumed that the most active in this case will be tightly bound, ionized atomic forms of adsorbed hydrogen, in particular,  $H^{\delta}$ , the content of which, as noted above, increases when there is a base in the solvent.

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Поступила в редакцию 14.05.2019  
Принята к опубликованию 22.04.2020

Received 14.05.2019  
Accepted 22.04.2020