

CHEMICAL KINETICS
AND CATALYSIS

**Kinetics of the Hydrogenation of a Mixture of Nitrobenzene
and Azoxybenzene on Skeletal Nickel
in an Aqueous Solution of Propan-2-ol**

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Received December 18, 2014

Abstract—The sequence of the reduction of nitro and azoxy groups in the combined hydrogenation of nitrobenzene and azoxybenzene on skeletal nickel in an aqueous azeotropic solution of propan-2-ol is considered. The time dependences of the rates and concentrations of the initial compound and reaction product for the hydrogenation of individual compounds (nitrobenzene and azoxybenzene) in the solvent of the indicated composition are discussed for comparative analysis. In all cases, the reactions proceed selectively to aniline without accumulating side products. The reduction of the nitro and azoxy groups involves hydrogen bound by the active sites of the catalyst surface. The competitive character of adsorption between the initial compounds and formed aniline is observed. Nitrobenzene is characterized by the highest adsorbability, whereas azoxybenzene and aniline are less adsorbable.

Keywords: nitrobenzene, azoxybenzene, aniline, hydrogen, skeletal nickel, aqueous solution of propan-2-ol.

DOI: 10.1134/S0036024415100222

INTRODUCTION

It is known that nitrobenzene hydrogenation on skeletal nickel proceeds via a multipath scheme to form a whole series of side and intermediate compounds, one of which is azoxybenzene [1–3]. For nitrobenzene hydrogenation, the azoxybenzene concentration can be rather high. Its high concentration and high reactivity compared to other intermediates of nitro group reduction can be determining factors for the selectivity of the reaction to amine [4–6]. It has been established experimentally that the reaction rates had the same order and were equal to 110 ± 5 and $41 \pm 2 \text{ s}^{-1}$ for the hydrogenation of nitrobenzene and azoxybenzene, respectively, on skeletal nickel in an aqueous azeotropic solution of propan-2-ol at low concentrations of the hydrogenated compounds (not higher than 1.35×10^{-5} and $0.6 \times 10^{-5} \text{ mol/cm}^3$ for nitrobenzene and azoxybenzene, respectively) [7, 8]. The selectivity of the hydrogenation of these compounds to the final amines can depend on both the conversion rate of the nitro and azoxy groups and the adsorbability of the organic compound. However, there are few data in the literature for the comparative estimation of the adsorbability of nitrobenzene and azoxybenzene.

The aim of this work was to reveal the sequence of the reduction of nitrobenzene (NB) and azoxybenzene (AB) on skeletal nickel for their combined presence in

aqueous solutions of propan-2-ol of different compositions.

EXPERIMENTAL

Skeletal nickel was used as the catalyst and was prepared by treating nickel–aluminum alloy (Ni : Al : Fe = 47.5 : 50.2 : 0.3 wt %, average particle radius 4.5–4.8 μm) with an aqueous solution of sodium hydroxide using the familiar procedure in [9]. The active catalyst had a specific surface and porosity equal to $90 \pm 2 \text{ m}^2/\text{g}$ and $0.5 \pm 0.06 \text{ cm}^3/(\text{cm}^3 \text{ of Ni})$, respectively [9]. An azeotropic ($x_2 = 0.68$ molar fractions) aqueous solution of propan-2-ol was used as a solvent, the amount of the catalyst was $0.500 \pm 0.005 \text{ g}$, and the amounts of NB and AB in the reactor were 1.34 ± 0.02 and $0.60 \pm 0.01 \text{ mmol}$, respectively.

The kinetic characteristics of hydrogenation on skeletal nickel were studied via the static method in a closed reactor with vigorous stirring of the liquid phase under atmospheric pressure with hydrogen at $295 \pm 1 \text{ K}$ using the procedure in [9]. The experimental conditions excluded the effects of external mass transfer on the reaction rate.

The volumes of absorbed hydrogen were measured volumetrically during each experiment. The concentrations of the initial compounds and aniline (A) as the reaction product were monitored via high-performance liquid chromatography and spectrophotome-

Ratios of the amounts of NB, AB, A, and hydrogen for the hydrogenation of a mixture of NB and AB on skeletal nickel in an aqueous solution of propan-2-ol

t, s	$n_R, \text{ mol}$			$n_{H_2}^{\text{nec}}, \text{ mmol}$		$n_{H_2}^{\text{abs}}, \text{ mmol}$	$n_{H_2}^{\text{nec}} - n_{H_2}^{\text{abs}}, \text{ mmol}$	$n_R, \text{ mmol}$ $A = \Sigma_{\text{NB} + \text{AB}}$
	NB	AB	A	NB	AB			
0	1.34	0.60	0.00	0.00	0.00	0.00	0.00	0.00
15	0.05	0.50	Not determined	3.87	0.15	0.70	-3.32	1.49
60	0.00	0.48	1.50	4.02	0.18	2.50	-1.70	1.58
127	0.00	0.38	1.78	4.02	0.33	4.00	-0.35	1.78
240	0.00	0.32	1.89	4.02	0.42	5.10	0.66	1.90
300	0.00	0.17	1.49	4.02	0.65	5.39	0.72	2.20
420	0.00	0.00	1.28	4.02	0.90	5.90	0.98	2.54
540	0.00	0.00	1.08	4.02	0.90	6.16	1.24	2.54
600	0.00	0.00	1.00	4.02	0.90	6.16	1.24	2.54
720	0.00	0.00	1.00	4.02	0.90	6.16	1.24	2.54

$n_{H_2}^{\text{nec}}$ is the amount of hydrogen necessary for the conversion of NB and AB to A; $n_{H_2}^{\text{abs}}$ is the amount of hydrogen absorbed in the reaction to the given time moment; and t is the reaction time.

try. A Shimadzu chromatograph was used to analyze NB, and AB and A were analyzed on a LEKI SS 2110 UV scanning spectrophotometer. Chromatography was performed according to the procedure described in [7].

The wavelengths of the absorption maxima for NB, AB, and A in propan-2-ol were 260 ($\epsilon = 14325 \pm 612$), 323 ($\epsilon = 13724 \pm 586$), and 280 ($\epsilon = 2808 \pm 280$) nm, respectively. The absorption spectra for NB, AB, A, and their mixtures are presented in Fig. 1. The sensitivity of the employed methods was no lower than 10^{-2} mmol.

The initial rates of hydrogen uptake $r_{H_2}^0$ were used as a kinetic characteristic. Static analysis of the experimental results showed that the errors of rate determi-

nation did not exceed 10%. The error of determination for the current concentrations of NB, AB, and A did not exceed 5% of the measured value. Each experiment was repeated at least three times to obtain convergent results.

RESULTS AND DISCUSSION

Figure 2 shows the time dependences characterizing the change in the rates of hydrogen uptake for the reduction of individual compounds (NB and AB) and their mixture at the same initial amounts. As follows from the presented dependences, the initial reduction rate of the mixture corresponds (within the error of determination) to the rate of hydrogen uptake during

Absorbance, rel. units

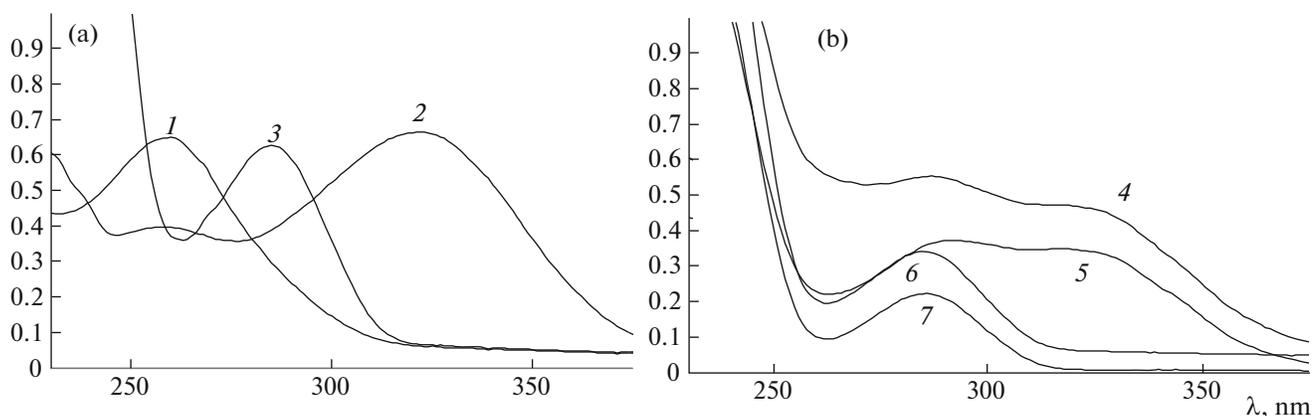


Fig. 1. Absorption spectra of (a) individual compounds: (1) NB, (2) AB, and (3) A; (b) absorption spectra of the hydrogenation products samples taken at different moments of the reaction: at $\tau =$ (4) 15, (5) 120, (6) 360, and (7) 480 s. Solvent, propan-2-ol.

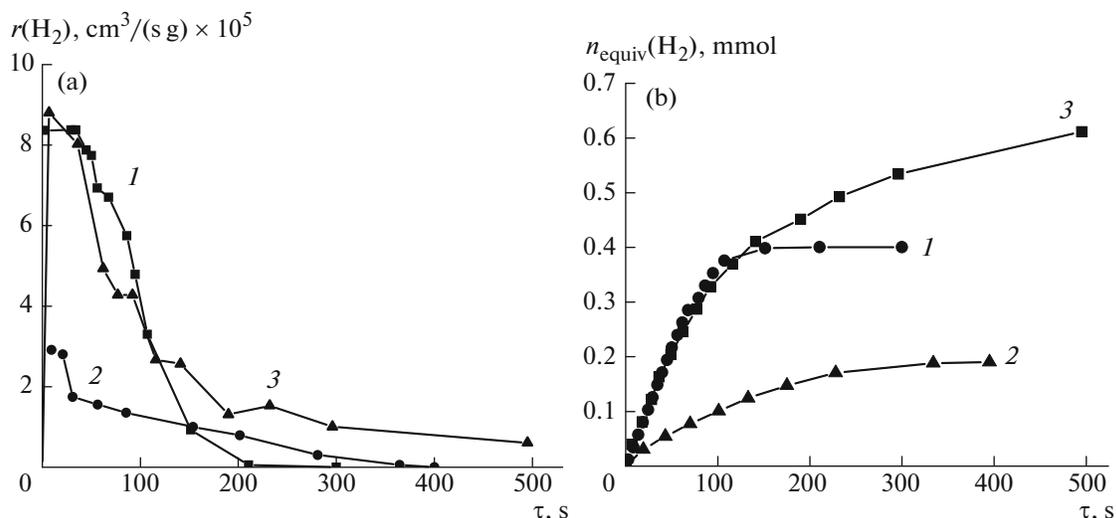


Fig. 2. Time dependences of the (a) rate and (b) total amount of absorbed hydrogen in the hydrogenation of (1) NB, (2) AB, and (3) their mixture on the skeletal nickel catalyst in an aqueous solution of propan-2-ol ($x_2 = 0.68$) under atmospheric pressure with hydrogen at $T_{\text{exp}} = 295 \pm 1$ K, $m_{\text{cat}} = 0.500 \pm 0.005$ g, and a liquid phase volume of 100 cm^3 : (1) $n_{\text{NB}} = 1.34 \pm 0.02$ mmol, (2) $n_{\text{AB}} = 0.60 \pm 0.01$ mmol, and (3) a mixture of NB (1.34 ± 0.02 mmol) and AB (0.600 ± 0.01 mmol) in the reactor.

NB hydrogenation. The rate of hydrogen uptake falls rapidly and becomes equal to the initial rate of pure AB reduction at NB conversions lower than 0.8. We may thus say that NB and AB are reduced consecutively during the reduction of a mixture of these compounds. The primary reduction of NB indicates that its adsorbability is higher than that of AB. This agrees with the opinion advanced in [6], where the adsorbabilities of the intermediate products of NB reduction were comparatively estimated from the anodic potential shift of the catalyst.

For a series of other mixtures, e.g., a mixture of 4-nitroaniline (4NA) with 4-aminoazobenzene (4AAB), the nitro compound was first reduced, confirming the high adsorbability of nitrobenzenes, compared to the compounds containing nitrogen–nitrogen double bonds. It is characteristic that the initial rate of hydrogen uptake corresponded to the rate of individual 4NA reduction for the hydrogenation of a mixture of 4NA and 4AAB. At a degree of reaction completion equal to 0.8, a reduction in the rate of hydrogen uptake was observed in the kinetic curve. For this conversion of 3NA, the rate of hydrogen uptake became equal to the initial rate of 4AAB hydrogenation and then fell smoothly to the complete conversion of 4AAB. The data from chromatographic analysis of the hydrogenation products samples confirmed the sequence of the transformation of 4NA and then 4AAB.

The time dependences of the changes in the concentrations of NB, AB, and A during the reduction of a mixture of NB and AB are presented in Fig. 3. The points in the kinetic curves correspond to the averaged measured values. Our results suggest a higher reactivity for NB, which is entirely consistent with the values of

the rate constants presented above. The presented kinetic curves are also characterized by a notable reduction in the amount of A at high conversions of AB.

The data on material balances for hydrogen and the analyzed substances during the hydrogenation of a mixture of NB and AB are based on the results from volumetric measurements and chromatographic and

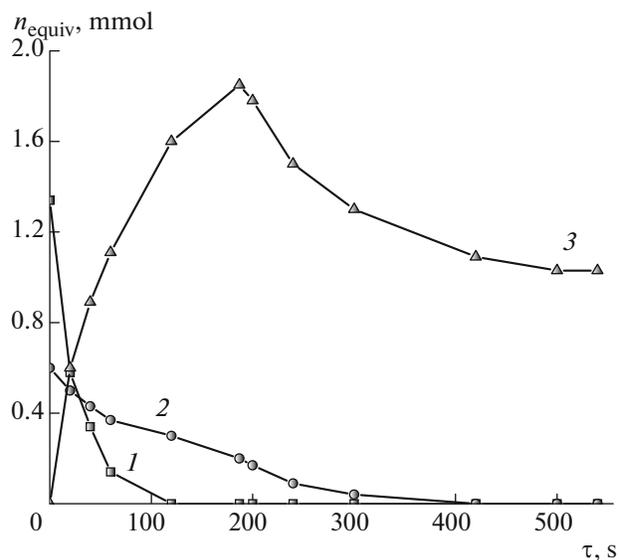


Fig. 3. Time dependences of the changes in the amounts of (1) NB, (2) AB, and (3) A during the hydrogenation of the mixture on the skeletal nickel catalyst in an aqueous solution of propan-2-ol ($x_2 = 0.68$) under atmospheric pressure with hydrogen at $T_{\text{exp}} = 295 \pm 1$ K, $m_{\text{cat}} = 0.500 \pm 0.005$ g, and a liquid phase volume of 100 cm^3 ; $n_{\text{NB}} = 1.34 \pm 0.02$ mmol and $n_{\text{AB}} = 0.60 \pm 0.01$ mmol in the reactor.

spectrophotometric analyses and are given in the table. As follows from the data in the table, before the maximum content of A is attained in the solution volume, the amount of hydrogen absorbed from the gas phase ($n_{\text{H}_2}^{\text{abs}}$) is smaller than the one necessary for the conversion of NB and AB to A ($n_{\text{H}_2}^{\text{neq}}$).

The maximum divergence of these values ($n_{\text{H}_2}^{\text{neq}} - n_{\text{H}_2}^{\text{abs}}$) corresponds to the initial moment in time. This difference diminishes rapidly upon moving from negative to positive values in attaining the complete conversion of NB and at the conversion of AB higher than 0.5.

As follows from the data in Fig. 3, the time dependence of the amount of A passes through a maximum. A drop in the amount of A at high conversions was also observed for the hydrogenation of phenylhydroxylamine [10] and azobenzene [11]. We may assume that the adsorbabilities of NB, AB, phenylhydroxylamine, and azobenzene are higher than those of A. The recovery of hydrogen on the surface begins simultaneously with a reduction in the amount of A in the solution volume (table). This could be experimental proof that hydrogen and organic compounds are adsorbed independently of each other and do not compete for active sites on the catalyst's surface.

The drop in the amount of A from the solution to the completion of the reaction was 0.89 mmol or 1.78 mmol/g. It was established from the data of adsorption measurements and processing the obtained isotherms in different model approximations that the experimental data is best described by the Dubinin–Radushkevich equation [10]. The authors conclude that the adsorption of A on skeletal nickel in aqueous solutions of propan-2-ol can be described using the theory of the volume filling of micropores (TVFM), and the amounts adsorbed of A ranged from 0.45 ± 0.05 to 12.7 ± 0.10 mmol/(g of catalyst). The data from our kinetic and adsorption measurements are consistent and do not contradict the literature data.

Prior to the moment when the maximum amount of A is attained in the solution volume, the hydrogen uptake in the reaction is lower than the theoretically necessary amount, even if we allow for the adsorption of the hydrogenated compound (see table). The excessive amounts of adsorbed NB and AB in an aqueous azeotropic solution of propan-2-ol on skeletal nickel at the chosen amount of the initial NB cannot exceed 0.40 ± 0.05 mmol/(g of catalyst) [8]. We may therefore assume that the azoxy and especially nitro groups are reduced under hydrogen deficient conditions in the initial reaction phase at high degrees of filling of the porous space of the catalyst with an organic compound. This was mentioned earlier when analyzing the

kinetic regularities of the hydrogenation of individual oxygen-containing compounds on the skeletal nickel catalyst in [12]. As the process finishes, the actual amount of hydrogen absorbed in the reaction is even somewhat greater than the one necessary for the transformation of NB and AB. The overabsorption of hydrogen is due to the saturation of the catalyst surface as a result of its removal in the initial reaction phase, and possibly to the reduction of the partially oxidized surface catalyst.

The close values of the analytically determined amounts of A in the phase volume and the values calculated from the reduction in NB and AB (see table) indicate that at the chosen ratio of the amounts of catalyst NB and AB, the latter are selectively reduced to A, there is no accumulation of intermediate products in the phase volume, and the irreversible oxidation of the catalyst surface is prevented.

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Translated by E. Yablonskaya