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## ORGANIC SYNTHESIS AND INDUSTRIAL ORGANIC CHEMISTRY

# Formation and Properties of Hydrogenation Catalysts Based on Palladium Bisacetylacetonate and Sodium Tetrahydroborate

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**Abstract**—Properties of the Pd(acac)$_2$–$n$NaBH$_4$ system in catalysis of the reactions of hydrogenation of alkenes, alkynes, and carbonyl and nitro groups were studied. A number of spectral methods (NMR, UV spectroscopy) and X-ray phase analysis were used to examine the main stages of formation of palladium hydrogenation catalysts produced in the interaction of Pd(acac)$_2$ with sodium tetrahydroborate, and reasons for the bimodal nature of the dependence of the catalytic activity on the B/Pd ratio were considered.

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The recently increased interest in catalytic systems composed of transition metal complexes and alkyl or hydride compounds of nontransition metals is due to the formation of catalytically active nanoparticles of a transition metal in these systems. In the initial stage of studies of these systems, it was believed that the role of nontransition metal compounds consists in the reduction of a transition metal to lower, as a rule, zero oxidation level. However, the effect of the chemical nature of a nontransition metal compound and its derivatives on the formation of catalytically active particles is due not only to its reducing properties and the resulting different dispersities of catalytic systems. It has been found in recent years that this component of catalytic systems may undergo destruction under the action of metal nanoclusters being formed, with their composition changed [1–5], and also plays the decisive role in the stabilization of nanosize particles [6, 7]. Apparently, the stabilizing function should be optimal, because weak stabilization causes loss of the aggregative stability and an increase in the particle size, whereas a too strong stabilization, especially that associated with covalent bonds of the stabilizer with surface bonds of a metal, leads to a decrease in the fraction of metal atoms that are free for catalysis and to full loss of activity. In particular, the decisive effect of the chemical nature of the stabilization of palladium nanoparticles by hydride compounds of nontransition metals and their derivatives on the properties of palladium nanoclusters in the hydrogenation reaction in systems based of palladium bisacetylacetonate and LiAlH$_4$ has been found previously [4, 5].

To continue studies in this area, a task was posed to analyze chemical aspects of formation of hydrogenation catalysts based on palladium bisacetylacetonate and sodium tetrahydroborate. A specific feature of NaBH$_4$ as a reducing agent consists in that, in contrast to LiAlH$_4$, it can exhibit reducing properties not only in organic media, but also in aqueous solutions: in acid, neutral, and alkaline media. This property of sodium tetrahydroborate substantially extends the potential of hydrogenation catalysts for application to syntheses of practically important substances. It is noteworthy that there is no published evidence about catalysts based on palladium and sodium tetrahydroborate: their formation and nature has not been considered and these systems have been analyzed only as regards the hydrogenation of particular substrates, mostly containing unsaturated bonds [8–10].

## EXPERIMENTAL

Solvents (benzene, THF) and substrates were purified by standard methods employed when working with organometallic substances [11]. For deeper dehydration, benzene was subjected to additional distillation over

$LiAlH_4$ in a rectification column and was stored in the atmosphere of argon in sealed ampules over 4A molecular sieves. After removal of peroxides, tetrahydrofuran was successively distilled over metallic sodium, $LiAlH_4$, and benzophenonketyl and stored in the atmosphere of argon in sealed ampules. The concentration of water, determined by the Fisher method [12], was $1.1 \times 10^{-3}$ M in benzene and $1.6 \times 10^{-3}$ M in THF.

Dimethylformamide (DMFA) was shaken with potassium hydroxide to remove admixtures of formic acid, buried under anhydrous copper sulfate for dehydration and removal of admixtures of amines, and kept until a green solution was formed. Then the solution was subjected to double vacuum distillation at a temperature not exceeding 45°C at a residual pressure of 3 mm Hg [13].

Ethanol (rectificate) was boiled with sulfuric acid (8 ml of $H_2SO_4$ per 1 l of ethanol, $\rho = 1.84$ g cm$^{-3}$) to remove unsaturated compounds, distilled over an alkali (5 g of NaOH per liter of the solution) to neutralize the acid, and boiled on a water bath with an alkaline solution of silver oxide (10 g of $AgNO_3$ and 20 g of KOH per liter of the solution) to oxidize aldehydes. On being filtered, ethanol was distilled with a dephlegmator (bp 78°C). To remove trace amounts of water, ethanol was boiled with magnesium shavings with a reflux for 30 min and then was distilled with caution [14].

Palladium bisacetylacetonate was synthesized by the procedure described in [15]. $^1$H NMR spectrum, $\delta$, ppm (solvent $C_6D_6$): 5.04 (s, 1H, CH) and 1.76 (s, 6H, $CH_3$). IR spectrum, $\nu$, cm$^{-1}$ (solvent benzene): $\nu$(C=O) + $\nu$(C=C) 1560, 1516. UV spectrum (solvent benzene): $\varepsilon_{330} = 10\,630$ M$^{-1}$ cm$^{-1}$.

Sodium tetrahydroborate (commercial) [16] was used without preliminary distillation. A weighed portion of $NaBH_4$ was dissolved in ethanol. The resulting solution was filtered through a Schott filter in a neutral atmosphere. The $NaBH_4$ concentration was determined from the amount of hydrogen evolved in hydrolysis with a 50 : 1 mixture of water and sulfuric acid to be 95–98% relative to the theoretical value.

The catalytic hydrogenation was performed in a duck-shaped thermostated glass vessel at 30°C and initial hydrogen pressure of 1 atm in the presence of a catalytic system formed in situ. To a solution of 0.01522 g ($5 \times 10^{-5}$ M) of Pd(acac)$_2$ in DMF, placed in a thermostated vessel, was added dropwise in a flow of hydrogen a $NaBH_4$ solution in ethanol, and the reaction mixture was agitated for 5 min. The B/Pd ratio was varied from 0.25 to 20. The total volume of the solution was 10 ml. To a black-brown mixture was added a substrate whose hydrogenation was carried out under vigorous agitation and an initial hydrogen pressure of 1 atm. The process was monitored volumetrically and by GLC [Khrom-5 chromatograph equipped with a 3.6-m-long packed (Carbowax-20M) column, DIP flame-ionization detector, column temperature 100°C, carrier gas nitrogen].

The interaction between the components of the system was studied at various ratios between the starting compounds in the atmosphere of a dry deoxygenated argon in a thermostated vessel having an internal "pocket," whose design presumes preliminary evacuation and filling with argon. A solution of 0.0761 g ($2.5 \times 10^{-4}$ mol) of Pd(acac)$_2$ in 10 ml of DMF was placed in the thermostated vessel connected to a volumetric system, and a $NaBH_4$ solution in ethanol, in the internal pocket of the vessel. The vessel was closed with a Teflon stopper with a rubber gasket, and the $NaBH_4$ solution was mixed under vigorous agitation with the Pd(acac)$_2$ solution. The evolved hydrogen was determined volumetrically. The solution was analyzed by UV spectroscopy: the absorption band at 330 nm was used to calculate the amount of the reacted Pd(acac)$_2$ ($\varepsilon_{330}$ 10 630 M$^{-1}$ cm$^{-1}$), and the absorption band at 290 nm, to find the concentration of Na(acac) formed [$\varepsilon_{290}$ 20 160 M$^{-1}$ cm$^{-1}$; for Pd(acac)$_2$, $\varepsilon_{290} = 3090$ M$^{-1}$ cm$^{-1}$], $^7$B NMR spectroscopy. After the reaction was complete, the solvent was evaporated in a vacuum (2/3 of the volume), hexane was added, and the resulting precipitate was washed with ethanol and dried in a vacuum (25°C/1 mm Hg). The samples were stored in argon in sealed ampules.

For elemental analysis for the content of Pd, Na, and B, a weighed portion (~0.01 g) of a sample was dissolved in 2 ml of $H_2SO_4$ under boiling and then was diluted with water to 50 ml in a volumetric flask. The concentration of palladium(II) ions was determined by atomic-absorption analysis on a Perkin-Elmer spectrometer in a propane–air flame, the content of boron(III) was found spectrophotometrically with H-resorcinol on an SF-46 spectrophotometer.

The NMR spectra were recorded on a Varian VXR-500S pulsed spectrometer on $^1$H and $^7$B nuclei. The chemical shifts in $^1$H NMR spectra are given relative to tetramethylsilane. The chemical shifts of $^7$B NMR signals were measured relative to boron trifluoride etherate. The

UV spectra were measured with a VSU2-P spectrometer for absorption bands in the range 270–500 nm in an all-welded quartz cuvette with thicknesses of 0.1 and 0.01 cm. Catalyst samples were subjected to an X-ray phase analysis (XPA) on a DRON-3 diffractometer (Cu$K_\alpha$ radiation) [17].

The catalytic properties of the Pd(acac)$_2$–NaBH$_4$ system were studied in hydrogenation of various unsaturated compounds and carbonyl and nitro groups. A search for optimal conditions of fabrication of effective catalytic systems demonstrated that the activity of palladium catalysts depends on the NaBH$_4$/Pd(acac)$_2$ molar ratio, with a double-peak pattern untypical of systems of this kind observed for the first time (Fig. 1). In contrast to Ziegler catalysts [7, 18] and palladium catalysts produced under the action of LiAlH$_4$ [4, 5], in which an extremal behavior was observed for the dependence of the activity on the molar ratio of the reagents, the dependence in the Pd(acac)$_2$–NaBH$_4$ system is bimodal. As the B/Pd molar ratio increases, the catalytic activity first grows (B/Pd = 0–0.25) and then steeply falls at equimolar ratios between the reagents. Further increase in the B/Pd ratio again leads to an increase in the catalytic activity; at B/Pd e” 2.5, the activity falls to zero. It should be noted that, despite the close catalytic activities of palladium catalysts at B/Pd = 0.25 and 2.0, a deactivation was observed for the Pd(acac)2–0.25 NaBH$_4$ system in the course of hydrogenation, accompanied by the formation of a black precipitate and discoloration of the solution. At the same time, at the molar ratio B/Pd = 2.0, the palladium catalyst is comparatively sedimentation-resistant not only in the formation of the catalyst, but also in the course of hydrogenation.

The results obtained in testing the catalytic properties of the Pd(acac)$_2$–2NaBH$_4$ system in hydrogenation of various substrates are listed in Table 1. The palladium catalyst formed in situ exhibits a high activity in the hydrogenation of the double and triple bonds and of the nitro group and surpasses by an order of magnitude the known PdCl$_2$-based palladium catalysts formed under the action of sodium tetraborate [8–10]. Noteworthy is the high selectivity of the palladium catalyst in hydrogenation of unsaturated aldehydes and, in particular, cinnaroic aldehyde [Ph–CH+CH–C(O)H], which was reduced to hydrocinnamaldehyde. It is known that palladium catalysts are the most efficient in selective hydrogenation of α,β-unsaturated aldehydes to saturated aldehydes of aliphatic derivatives. If the double bond C=C is conjugated with a carbonyl group and aromatic ring, as in cinnaroic aldehyde, the carbonyl group is reduced rather easily [19]. For example, hydrogenation of cinnaroic aldehyde in the presence of a Pd-black produced by reduction of PdX$_2$ with hydrogen leads to a mixture of products: hydrocinnamaldehyde (36%), cinnaroic alcohol (Ph–CH=CH–CH2OH) (4%), and phenylpropanol (60%) [10].

With the fact that the double bond is reduced easier than the carbonyl group, it seems, at first glance, that the high selectivity of the Pd(acac)$_2$–NaBH$_4$ catalytic system could be attributed to its deactivation in the course of the catalytic process. However, the inertness of the palladium catalyst formed under the action of sodium tetrahydroborate in hydrogenation of benzaldehyde indicates that the high selectivity in the hydrogenation of the cinnaroic aldehyde is due to the very nature of the catalytically active particles, rather than to deactivation of the catalyst in the course of hydrogenation.

It is known that simple and complex transition metal ions are reduced by the BH$_4$– ion via formation of active complexes with bridge bonds M...H...B (intrasphere mechanism), followed by transfer of a hydrogen atom to the transition metal atom [1]:

$$M^{n+} + BH_4^- \rightarrow [M^{n+} \ldots H^- \ldots BH_3] \xrightarrow[-BH_3]{} [M^{n+} \ldots H^-],$$

$$[M^{n+} - H^-] \rightarrow M^{(n-1)} + 1/2H_2.$$

Therefore, the redox process can be represented, as applied to the catalytic system under consideration, by the following stoichiometric equation:

$$\begin{aligned}&\mathrm{Pd(acac)_2 + 2NaBH_4}\\ &\rightarrow \mathrm{Pd(0) + 2Na(acac) + [BH_3]_2 + H_2}. \qquad (1)\end{aligned}$$

According to Eq. (1), a twofold excess of the reducing agent is necessary for a quantitative reduction of Pd(II). Such a behavior has been, in particular, observed in reduction of nickel salts [2, 3]. A quantitative analysis of UV spectra of the Pd(acac)$_2$–NaBH$_4$ reaction system demonstrated that the fraction of Pd(acac)$_2$ converted under the action of NaBH$_4$ at B/Pd molar ratio < 2 substantially exceeds the value calculated by Eq. (1). For example, 30% of Pd(acac)$_2$ is converted, instead of 12.5%, at B/Pd = 0.25; almost quantitative conversion of Pd(acac)$_2$, rather than 50%, occurs at B/Pd = 1.0 (Table 2).

**Table 1.** Catalytic activity of the $Pd(acac)_2$–$NaBH_4$ in hydrogenation of various substrates $c_{Pd} = 5$ mM, $NaBH_4/Pd = 2.0$, solvent DMF, $T = 30°C$, $P_{H_2} = 1$ atm

| Substrate (mmol) | *W*, (mol $H_2$):(g-at Pd min) | Conversion, % | Products, % (according to GLC) |
|---|---|---|---|
| Styrene, 8.7 | 77 | 100 | Ethylbenzene, 100 |
| Phenylacetylene, 9.1 | 57 (-C=C-) | 96.6 | Ethylbenzene, 96.6 |
| | 68 (-C=C-) | | Styrene, 3.4 |
| Nitrobenzene, 5.7 | 114 | 98 | Aniline, 100 |
| Cinnaroic aldehyde, 10 | 18 | 100 | Hydrocinnamaldehyde, 100 |
| Benzaldehyde, 9.9 | 0 | 0 | |

**Table 2.** Interaction of $Pd(acac)_2$ with sodium tetrahydroborate $c_{Pd} = 5$ mM, $NaBH_4/Pd = 2.0$, solvent DMF, $T = 30°C$

| $NaBH_4/Pd(acac)_2$ mol/mol | Hydrogen formation Hg/Pd, mol/mol | | | Fraction of reduced $Pd(acac)_2$, % | | |
|---|---|---|---|---|---|---|
| | experiment | calculation[a] by equation | | experiment | calculation[a] by equation | |
| | | (1) | (2) | | (1) | (2) |
| 0.25 | 0.48 | 0.125 | 0.25 | 30 | 12.5 | 25.0 |
| 1.0 | 3.09 | 0.50 | 1.00 | 96 | 50 | 100 |
| 2.0 | 3.62 | 1.00 | 1.00 | 100 | 100 | 100 |
| 3.0 | 3.54 | 1.00 | 1.00 | 100 | 100 | 100 |

[a] Calculated by Eqs. (1) and (3) per mole of the starting $Pd(acac)_2$.

In addition, one more fact was established. In the interaction of the components of the $Pd(acac)_2$–$NaBH_4$ reaction system at various molar ratios of the reagents, appearance of a strong absorption band peaked at 290 nm is observed in the UV spectrum, together with a decrease in the intensity of the absorption band at 330 nm ($\pi \rightarrow \pi^*$ electron transitions in chelate complexes of palladium with acac– ligands). The band at 290 nm is characteristic of ligands in Na(acac), whose formation was confirmed by PMR spectroscopy. However, it was found that the experimentally recorded optical density at 290 nm exceeds the value corresponding to formation of Na(acac) at B/Pd < 2.0 (B/Pd 0.25, 0.5, 1.0). Consequently, another reaction product containing an acac-ligand is manifested in this spectral range together with Na(acac). In particular, the peak at 290 nm is also characteristic of $\pi \rightarrow \pi^*$ electron transitions in the acetylacetonate ring of boron derivatives, e.g., $B(acac)Et_2$ [20]. In the Pd(acac)2–$NaBH_4$ reaction mixture, one of reaction products is borane, which also possesses reducing properties:

$$Pd(acac)_2 + 2NaBH_3 \rightarrow Pd(0) + 2BH_2(acac) + H_2. \quad (2)$$

If this fact is taken into account, then, with Eqs. (1) and (2) summed-up, the overall equation of the redox process between $Pd(acac)_2$ and $NaBH_4$ at B/Pd < 2.0 can be represented as

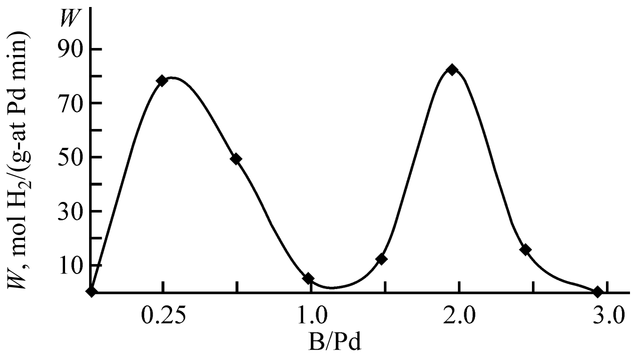


**Fig. 1.** Specific activity W of the $Pd(acac)_2$–$NaBH_4$ catalytic system in hydrogenation of styrene vs. the B/Pd ratio. $c_{Pd} = 5$ mM, $[substrate]/Pd(acac)_2 = 870$, solvent DMF, $T = 30°C$, $P_{H_2} = 1$ atm.

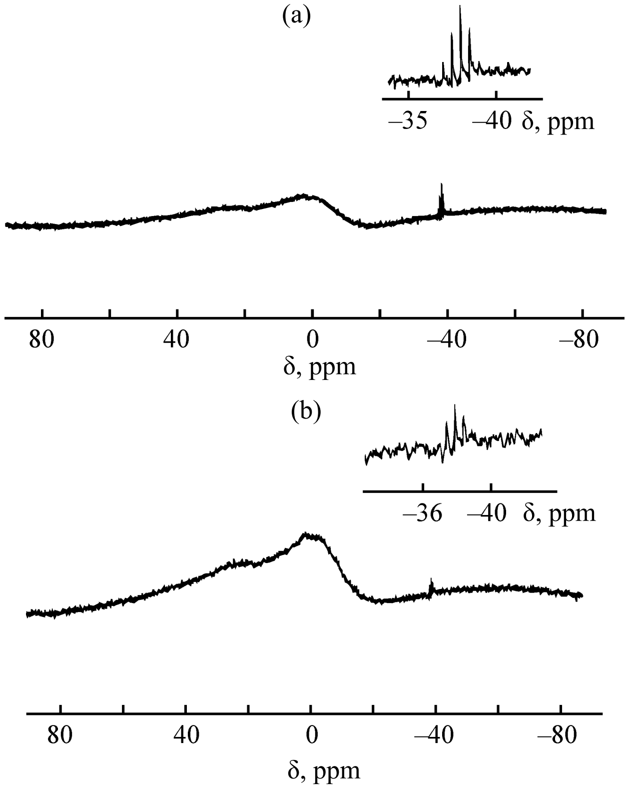


**Fig. 2.** $^{11}B$ NMR spectrum of the $Pd(acac)_2$–$3NaBH_4$ reaction system in (a) 15 min and (b) 3 h. Solvent DMF, $c_{Pd} = 2.5 \times 10^{-2}$ M. (δ) Chemical shift.

$$Pd(acac)_2 + 2NaBH_4 \rightarrow Pd(0) + 2BH_2(acac) + Na(acac) + H_2. \quad (3)$$

According to Eq. (3), $Pd(acac)_2$ reacts with $NaBH_4$ in equimolar amounts at B/Pd < 2.0. This agrees within measurement error with the observed experimental data (Table 2). Thus, it can be assumed that both the starting sodium tetraborate and borane formed in the course of the reaction are involved in the redox process at B/Pd ≥ 2.0.

Molecular hydrogen is also a product formed in the interaction of $Pd(acac)_2$ with sodium tetrahydroborate. An analysis of volumetric data demonstrated that the amount of this hydrogen exceeds not only that following from Eq. (1), but also that found using Eq. (3) (Table 2). It is known that transition metal nanoclusters catalyze both decomposition of borane into elements and hydrolysis of $NaBH_4$ [21]:

$$2BH_3 \rightarrow 2B + 3H_2. \quad (4)$$

$$NaBH_4 + 4H_2O \rightarrow B(OH)_3 + NaOH + 4H_2, \quad (5)$$

where M is Ni, Co, Fe, Pt, Pd, Rh, Au, Ag [1–3].

It should be noted here that palladium possesses a lower catalytic activity in hydrolysis of $NaBH_4$, compared with other metals of the platinum group: Rh > Pt = Ru >> Pd [21]. At the same time, the readily occurring hydrolysis or ethanolysis of borane being formed may substantially contribute to the formation of molecular hydrogen in the system:

$$BH_3 + 3H_2O \rightarrow B(OH)_3 + 3H_2. \quad (6)$$

$$BH_3 + 3C_2H_5OP \rightarrow B(OC_2H_5)_3 + 3H_2. \quad (7)$$

(ethanol was used as a solvent for $NaBH_4$).

As follows from this calculation for B/Pd = 0.5, almost the whole amount of $NaBH_4$ and borane being formed must be consumed for reduction of $Pd(acac)_2$. According to Eq. (3), the volume of hydrogen that can be evolved in the $Pd(acac)_2$–$NaBH_4$ system (B/Pd = 0.25) is 0.25 mol $mol^{-1}$ Pd(0). Consequently the observed difference between the experimental and calculated (0.23 mol $H_2$/mol Pd) is also indicative of the hydrolysis of boron derivatives $BH_2(acac)$:

$$BH_2(acac) + 2H_2O \rightarrow B(OH)_2(acac) + 2H_2.$$

The experimental data on hydrogen evolution at B/Pd ≤ 2 are in good agreement with the values calculated by Eqs. (3), (4), and (6) if the rates at which borane decomposes into elements and is hydrolyzed are assumed to be comparable.

As additional evidence in favor of the hydrolysis of borane and its derivatives can serve $^{11}B$ NMR spectroscopic data. In $^{11}B$ NMR spectra of the $Pd(acac)_2$–$NaBH_4$ reaction system at B/Pd = 0.25, 1.0, and 2.0, there were no resonance signals of $NaBH_4$ ($\delta = -38$ ppm, $J_{B-H} = 82$ Hz) and diborane ($\delta = 16$ ppm, $J_{B-H} = 128$ Hz, and a broad resonance signal attributable to a mixture of polyboric acids was recorded at –30…+30 ppm. The resonance signal from $NaBH_4$ ($\delta = -38$ ppm, quintet, $J_{B-H} = 82$ Hz) was recorded in the $Pd(acac)_2$–$NaBH_4$ system at B/Pd = 3.0, with its intensity gradually decreasing in the course of time (3–5 h) (Fig. 2). These data are consistent with the assumption that the main contribution to the formation of hydrogen in the interaction between the components of the catalytic system at room temperature in the course of 2–5 min is made by the redox process [Eqs. (1) and (3)] and, owing to the kinetic control, by the catalytic decomposition and hydrolysis of borane; the hydrolysis of sodium tetrahydroborate can be neglected.

The composition of the palladium catalysts isolated from the $Pd(acac)_2$–$NaBH_4$ reaction system (B/Pd = 0.25, 1.0, 2.0, 3.0) was studied by XPA and elemental analysis. Broadened diffuse lines were recorded in the X-ray diffraction patterns of all the samples studied at reflection angles 2θ = 40° characteristic of hkl 111 lines of palladium [23]. The coherent-scattering region (CSR) calculated by the Selyakov–Sherrer formula [17] is 3.2, 2.8, 2.6, and 2.0 nm for B/Pd = 0.25, 1.0, 2.0, and 3.0, respectively. Calcination of the samples in an inert atmosphere at 400°C for 4 h leads to crystallization of the substance. Palladium in the crystalline state was identified in all the samples. Reflections from the crystalline phase of an as yet unidentified substance, whose amount decreases as the B/Pd molar ratio increases, were recorded in the diffraction curves (Fig. 3).

According to elemental analysis data, all the palladium catalysts produced by reduction of sodium tetrahydroborate contain boron, whose amount increases with the B/Pd ratio (Table 3). There is no contradiction between the results of X-ray phase and elemental analyses. The boron-containing substance may be in the X-ray-amorphous state and, therefore, is not seen in the X-ray diffraction patterns of the catalysts.

Attention should be given to the following fact. At B/Pd = 1.0, the content of palladium is 96% (Table 3), whereas for systems with B/Pd = 2.0, 3.0, the content of palladium does not exceed 32 wt %, although $Pd(acac)_2$ is quantitatively reduced. Consequently, the precipitate contains boron and products formed in hydrolysis of borane.

The experimental data presented here suggest the following explanation for the double-peak dependence of the specific activity on the reagent ratio. The $Pd(acac)_2$–$NaBH_4$ catalytic system is formed under conditions that are far from equilibrium. The liophobic dispersed systems being formed are thermodynamically unstable and their transition to a more stable state because of a decrease in the excessive free surface energy via aggregation of particles occurs during different intervals of time. According to elemental analysis data, a Pd-black containing 96% palladium is formed at B/Pd = 1.0 and precipitates already in the stage of interaction between the components. The low aggregative stability of the system and the resulting small fraction of surface palladium atoms are the reason why the catalytic activity is low at equimolar amounts of the reagents.

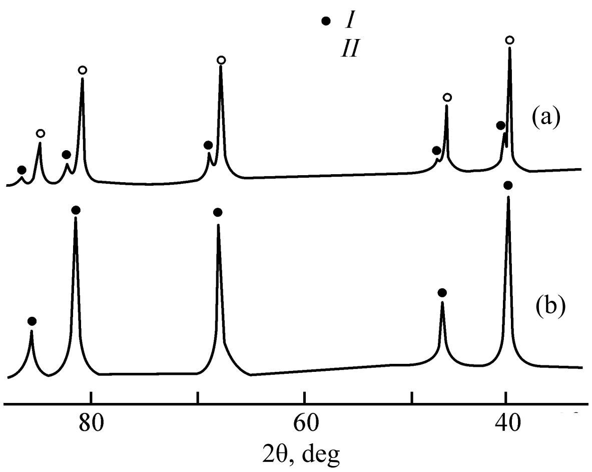


**Fig. 3.** X-ray diffraction patterns of precipitates isolated from the $Pd(acac)_2$–$NaBH_4$ catalytic system at B/Pd = (a) 0.25 and (b) 2.0. (2θ) Bragg angle. (I) Pd and (II) unidentified substance.

As the reagent ratio B/Pd increases, more highly dispersed systems are formed (Table 2), which is quite reasonable for dispersed systems produced by the chemical condensation method. In this case, no precipitation was observed both in the course of formation of the catalytic system and upon completion of the hydrogenation process, i.e., the $Pd(acac)_2$–$nNaBH_4$ catalytic system is comparatively aggregatively stable and sedimentation-resistant at B/Pd ≤ 2.0. A similar behavior was observed in the formation of the $Pd(acac)_2$–$nNaBH_4$ at B/Pd = 0.25. However, a black precipitate was formed in the course of hydrogenation at B/Pd = 0.25, in contrast to systems at B/Pd ≤ 2.0. In the authors' opinion, the reasons for the comparatively high stability of dispersed $Pd(acac)_2$–$NaBH_4$ catalytic systems at small (B/Pd = 0.25) and large (B/Pd ≤ 2.0) ratios between the components in the $Pd(acac)_2$–$nNaBH_4$ systems are different.

At B/Pd = 0.25, about 30% of palladium(II) is

**Table 3.** Characteristics of catalyst samples formed in the $Pd(acac)_2$–$NaBH_4$ system

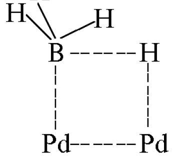
| $NaBH_4$: $Pd(acac)_2$ | Elemental composition of the precipitate, Pd : B | | XPA data (CSR, nm) |
|---|---|---|---|
| | wt% | mol% | |
| 0.25 | 63 : 1.68 | 1 : 0.28 | X-ray-amorphous (3.2) |
| 1.0 | 96 : 2.25 | 1 : 0.26 | X-ray-amorphous (2.8) |
| 2.0 | 32 : 4.16 | 1 : 1.2 | X-ray-amorphous (2.6) |
| 3.0 | 32 : 4.90 | 1 : 1.7 | X-ray-amorphous (2.0) |

reduced. It is the low concentration of metallic particles in solution that is the reason why the stability of the $Pd(acac)_2$–$0.25NaBH_4$ system is comparatively high and, as a consequence, the initial rate of hydrogenation exceeds that for the $Pd(acac)_2$–$NaBH_4$ system at equimolar amounts of the reagents. This suggestion is confirmed by data on reduction of $Pd(acac)_2$ in DMF with hydrogen, when substances capable of stabilizing palladium nanoparticles are absent in the system and are not formed in the course of hydrogenolysis. Indeed, at a $Pd(acac)_2$ concentration of 1 mM, the reduction with hydrogen yielded a black-brown solution containing, according to TEM data, palladium particles 20–30 nm in size and a precipitate was formed in the course of hydrogenation. As a result of the interaction of $Pd(acac)_2$ with $NaBH_4$ at $B/Pd \leq 2.0$, first, smaller particles are formed and, second, a side process, hydrolysis of borane to give polyboric acids acting as stabilizers of palladium particles, occurs to a greater extent.

The inhibiting effect of an excess amount of sodium tetrahydroborate on the catalytic properties of the $Pd(acac)_2$–$nNaBH_4$ system indicates that a sufficient amount of a catalytic poison, which possibly is elementary boron formed in catalytic decomposition of diborane and covering palladium, appears in the reaction system. This assumption is based on recent data on the nature of nickel boride catalysts, according to which the catalysts are composed of nickel nanocrystals "cemented" together by amorphous boron or its compounds [24], rather than being constituted by nickel borides of composition $Ni_2B$, as it has been believed during a number of decades. In addition, it is known that hydrolysis of $NaBH_4$, catalyzed by metal nanoparticles, occurs via stages in which surface compounds are formed:

$$BH_4^- + 2Pd \rightleftarrows BH_3Pd^- + PdH.$$

Therefore, it cannot be ruled out that the catalyst can be poisoned by an excess of $NaBH_4$ as a result of formation of intermediate surface compounds of the type [25]:



Thus, the unconventional double-peak dependence of the catalytic activity of the $Pd(acac)_2$–$NaBH_4$ system on the molar ratio between the reagents is due to different relative stabilities of palladium nanoclusters being formed and to the inhibiting effect of elementary boron and(or) tetrahydroborate anions.

## CONCLUSIONS

(1) A high-efficiency $Pd(acac)_2$–$NaBH_4$ catalyst for hydrogenation of the double and triple bonds, nitro group, and unsaturated aldehydes was suggested.

(2) The main stages of formation of a palladium catalyst for hydrogenation were determined. These stages include reduction of palladium(II) to palladium nanoclusters, catalytic decomposition of borane being formed into elements, and its hydrolysis (or ethanolysis). It is shown that not only $NaBH_4$, but also borane being formed, act as a reducing agent for $Pd(acac)_2$ at small molar ratios between the components ($B/Pd < 2.0$).

(3) It is shown that the double-peak dependence of the catalytic activity of the $Pd(acac)_2$–$NaBH_4$ system on the molar ratio between the reagents is due to the different relative stabilities of palladium nanoclusters and to the inhibiting effect of elementary boron and(or) tetrahydroborate anion.

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