

Hydrogenation Catalysts Based on Polynuclear Palladium Complexes with Organophosphorus Ligands

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Abstract—A new procedure is proposed for the preparation of hydrogenation catalysts. This procedure includes the synthesis of cyclic tetranuclear palladium complexes with bridging diphenylphosphide ligands followed by a reaction with $\text{Pd}(\text{CH}_3\text{COO})_2$ in the presence of hydrogen to form nanosized particles. In the test catalysts, the ensembles of palladium atoms (or palladium hydrides) immobilized on supramolecular structures formed by the association of phosphinidene and phosphide complexes of palladium are responsible for the catalytic activity.

INTRODUCTION

The determination of the nature of catalytically active species is one of the main problems of catalysis. This problem for is debatable hydrogenation catalysts based on the phosphine complexes of palladium(II), although great bodies of data have been published.

Previously, we found that the transformation of bis(acetylacetonato)(triphenylphosphine)palladium(II) under the action of various reducing agents (hydrogen [1] and sodium hypophosphite [2]) resulted in the formation of microheterogeneous systems with the average particle size of the dispersed phase equal to 3–5 nm. In this case, depending on the nature of the reducing agent, two models for the structure of nanosized particles were proposed [3]. Nanosized particles formed in the reduction of the phosphine complexes of palladium(II) with sodium hypophosphite consisted of a metal nucleus stabilized with organophosphorus ligands. If hydrogen was used as a reducing agent, the degradation of organophosphorus ligands resulted in the formation of polynuclear palladium complexes with phosphide and phosphinidene ligands. The associates of these complexes formed a nucleus at the surface of which $\text{Pd}(0)$ clusters were immobilized.

It is well known [4, 5] that polynuclear palladium complexes with diaryl- or dialkylphosphide ligands can be prepared by reactions of palladium(II) compounds with secondary phosphines or alkali metal phosphides. The composition and structure of the reaction products depend on the nature of the organophosphorus compounds and on the ratio between P and Pd at the stage of catalyst preparation. We considered a system based on bis(acetylacetonato)palladium and diphenylphosphine for the preparation of polynuclear palladium complexes with diphenylphosphide ligands, for the determination of the role of these complexes in hydro-

genation, and for their later use in the synthesis of highly active and selective hydrogenation catalysts.

EXPERIMENTAL

The solvents were purified in accordance with standard procedures used in operations with organometallic compounds [6].

Diphenylphosphine. Diphenylphosphine was prepared according to Stuede *et al.* [7]; $T_b = 152^\circ\text{C}$ at 13 Torr (^{31}P NMR: $\delta = -41$ ppm, $J_{\text{P-H}} = 210$ Hz).

The reaction between bis(acetylacetonato)palladium and diphenylphosphine was performed in an oxygen-free dry argon atmosphere in a special finger-type vessel, which can be preevacuated and filled with argon. A 2-ml portion of a diphenylphosphine solution (0.75 mmol) from a Schlenk vessel was added drop by drop to a solution of 0.0913 g (0.3 mmol) of $\text{Pd}(\text{acac})_2$ in 8 ml of benzene, and the mixture was stirred at room temperature for 24 h. The resulting cherry red solution was passed through a Schott filter in an argon atmosphere; next, the solvent was distilled to decrease its volume by 1/3 (20°C , 1 Torr) and hexane was added until a precipitate began to form. The resulting dark cherry precipitate was filtered off and dried in a vacuum (20°C , 1 Torr). Yield: 0.14 g. For $[\text{Pd}_3(\text{PPh}_2)_4(\text{HPPH}_2)_2\text{C}_6\text{H}_6]$, anal. calcd. (%): Pd, 21.18; P, 12.34; C, 62.10; H, 4.38. Found (%): Pd, 20.18; P, 11.17; C, 59.02; H, 3.80.

Preparation of a Catalyst Based on $[\text{Pd}_3(\text{PPh}_2)_4(\text{HPPH}_2)_2\text{C}_6\text{H}_6]$ and $\text{Pd}(\text{OAc})_2$

The palladium complex $[\text{Pd}_3(\text{PPh}_2)_4(\text{HPPH}_2)_2\text{C}_6\text{H}_6]$ (0.026 g, 4×10^{-5} mol), which was prepared by the reaction of $\text{Pd}(\text{acac})_2$ and HPPH_2 , was placed in a preevacuated long-necked flask filled with hydrogen, and 7.5 ml of dimethylformamide (DMF) and a certain amount of palladium acetate (10–200% based on the

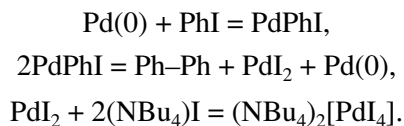
Table 1. ^{31}P NMR-spectroscopic parameters: chemical shifts (δ , ppm) and spin–spin coupling constants (J , Hz)

System	$\mu\text{-PPh}_2$ (1, 3)	$\mu\text{-PPh}_2$ (2)	PPh_2 (4)	PPh_2H (5)	$\text{PPh}_2\text{-PPh}_2$
Complex I	$\delta = 147.5$ ppm (d) $^1J = 159$	$\delta = 144$ ppm (dd) $^1J_{\text{AM}} = 147, ^1J_{\text{BM}} = 165$	$\delta = 63$ (s)	$\delta = -1$ $^1J_{\text{PH}} = 302$	$\delta = -16$
Complex I +0.20Pd(OAc) $_2$	$\delta = 151.5$ ppm (d) $^1J = 169$	$\delta = 145$ ppm (dd) $^1J_{\text{AM}} = 158, ^1J_{\text{BM}} = 176$	$\delta = 69$ (s)	$\delta = -1, -1.3$ $^1J_{\text{PH}} = 316$	$\delta = -16$

parent complex) were added. The reaction mixture was stirred in a hydrogen atmosphere at 80°C for 40 min. The concentration of benzene formed in the reaction system and the composition of the products of catalysts were determined by GLC (a Chrom-5 chromatograph with a 3.6-m packed column with SE-30 as a stationary phase and a flame-ionization detector were used; the analysis temperature was 120°C, and nitrogen was the carrier gas).

Determination Procedure for Pd(0) [8]

A solution containing 2×10^{-5} mol of Pd in 10 ml of DMF was placed in a preevacuated thermostatted vessel filled with argon, and 0.1477 g (0.4 mmol) of NBu_4I and 0.109 ml (1 mmol) of iodobenzene were added. The reaction mixture was stirred at 80°C with the use of a magnetic stirrer until the concentration of the PdI_4^{2-} anion became constant. This anion resulted from the following reactions:



The concentration of PdI_4^{2-} was determined by spectrophotometry on a VSU2-P spectrometer from an absorption band at 340 nm ($\epsilon_{340} = 23750 \text{ l cm mol}^{-1}$) using a sealed quartz cell with an optical path length of 0.1 cm. Biphenyl was simultaneously determined on a chromatograph.

The NMR spectra were measured on a VXR-500S pulse spectrometer (Varian). The chemical shifts of ^{31}P are given with reference to 85% phosphoric acid. Positive values correspond to downfield shifts. The IR spectra of samples in mineral oil were measured in the region 4000–400 cm^{-1} on a Specord IR-75 instrument.

The X-ray diffraction analysis of catalyst samples was performed on a DRON-3M diffractometer using CuK_α radiation.

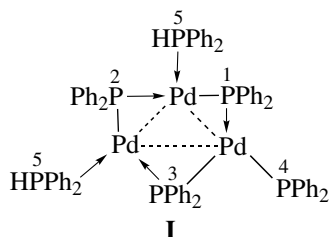
RESULTS AND DISCUSSION

Previously, we found that the reaction of bis(acetylacetonato)palladium with diphenylphosphine did not

stop at the step of complexation [9]. At an equimolar ratio between the reactants, the exchange of an acetylacetonate ligand for a diphenylphosphide fragment occurred with the formation of free acetylacetonate molecules and the following two palladium complexes with bridging PPh_2 and chelating acetylacetonate ligands: $[\text{Pd}(\text{acac})\text{PPh}_2]_2$ and $[\text{Pd}_3(\text{acac})_2(\text{PPh}_2)_4]_2$. According to IR-spectroscopic data, the action of an excess of PPh_2H with respect to $\text{Pd}(\text{acac})_2$ ($\text{P/Pd} = 2.3$) resulted in the quantitative formation of acetylacetonate. Tetra-phenyldiphosphyl and a new palladium complex (tentatively denoted as complex I) containing ^{31}P ligands and coordinated diphenylphosphine molecules were detected in the reaction mixture by ^{31}P NMR spectroscopy. This complex was characterized by the following ^{31}P NMR-spectroscopic parameters: $\delta = 144$ ppm (dd, $^1J_{\text{AM}} = 147$ Hz, $^1J_{\text{BM}} = 165$ Hz) and $\delta = 147.5$ ppm (d, $^1J = 159$ ppm); $\delta = 63$ ppm (br s), and $\delta = -2$ ppm (br s). The resonance signals with $\delta = 144$ ppm (dd, $^1J_{\text{AM}} = 147$ Hz, $^1J_{\text{BM}} = 165$ Hz) and $\delta = 147.5$ ppm (d, $^1J = 159$ ppm) (integrated intensity ratio of 1 : 2) belong to three magnetically nonequivalent bridging PPh_2 ligands in a cyclic palladium complex with a metal–metal bond [4, 10]; the signal with $\delta = 63$ ppm (s) belongs to a terminal PPh_2 ligand [11]; the signal with $\delta = -2$ ppm (s) belongs to coordinated diphenylphosphine molecules ($^1J_{\text{PH}} = 302$ Hz) (Table 1). The ratio between the integrated intensities of resonance signals at 147.5, 144, 63, and -2 ppm was 2 : 1 : 1 : 2. Unfortunately, we failed to measure the spectrum at a completely hindered exchange.

The UV spectrum of a solution of complex I exhibited a broad absorption band with a maximum at 420–430 nm, which is characteristic of trinuclear palladium clusters with bridging diphenylphosphide ligands [10] and alkali metal phosphides $\text{M}^+\text{-PPh}_2^-$, in which the phosphorus atom bears a negative charge [12]. An analysis of the ^{31}P NMR-spectroscopic parameters in accordance with IR- and UV-spectroscopic data and elemen-

tal analysis allowed us to propose the following structure for the palladium complex:



Elemental analysis and GLC data suggest that complex **I**, which was isolated from the $\text{Pd}(\text{acac})_2 + 2.3\text{HPPH}_2$ reaction system, contains a solvent (benzene) molecule.

Complex **I** is inactive in the catalysis of hydrogenation reactions, and it does not undergo dephenylation in an atmosphere of hydrogen. The treatment of complex **I** with hydrogen at 80°C in the presence of palladium acetate resulted in the formation of a catalyst that exhibited high activity in both the hydrogenation of unsaturated bonds and the reduction of the nitro group (Table 2).

Note that the specific activity of palladium black, which was formed under the same conditions by the reduction of palladium acetate, was no higher than $15 \text{ mol styrene (g-atom Pd)}^{-1} \text{ min}^{-1}$, whereas the turnover frequency of the **I** + $x\text{Pd}(\text{OAc})_2$ system was as high as 140 min^{-1} based on the total palladium amount depending on the ratio between the initial components (Fig. 1).

The fact that the hydrogenation of unsaturated compounds was accompanied by an induction period, the duration of which decreased with the $\text{Pd}(\text{OAc})_2/\text{I}$ ratio, has engaged our attention (Fig. 2).

The occurrence of an induction period in styrene hydrogenation suggests that catalytically active palladium species were absent from the **I** + $x\text{Pd}(\text{OAc})_2$ system even after treatment with hydrogen. The presence of both hydrogen and a hydrogenated substrate is required for the formation of these species. To explain the behavior observed, we considered the transformations of the initial components in either argon or hydrogen.

The interaction of palladium acetate with complex **I** in argon is characterized by the small downfield shifts of signals due to phosphorus nuclei in bridging (1, 3) and terminal (4) diphenylphosphide ligands of complex **I** in the ^{31}P NMR spectrum. Moreover, the coordinated diphenylphosphine molecules become magnetically nonequivalent (see Table 1). These data suggest that the donor-acceptor interaction between palladium acetate and the terminal diphenylphosphide ligand of complex **I** occurs at the first step;

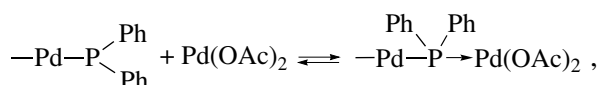


Table 2. Hydrogenation in the presence of the complex **I** + $0.25\text{Pd}(\text{OAc})_2 + \text{H}_2$ catalytic system

Substrate	Maximum activity of the catalytic system, $(\text{mol H}_2) (\text{g-atom Pd})^{-1} \text{ min}^{-1}$	
	on a $\text{Pd}(\text{OAc})_2$ basis	on a total Pd basis
Styrene	662	140
Phenylacetylene	179	36
Tolan	405	81
1-Hexene	490	98
Nitrobenzene	420	84

Note: $[\text{I}] = 1 \text{ mmol/l}$; $[\text{Pd}(\text{OAc})_2] = 0.25 \text{ mmol/l}$; $T = 30^\circ\text{C}$; $P_{\text{H}_2} = 1 \text{ atm}$; solvent, DMF; $V_{\text{substrate}} = 1 \text{ ml}$.

where $-\text{Pd}-\text{PPh}_2$ is a fragment of complex **I**.

The transformation of the complex **I** + $0.20\text{Pd}(\text{OAc})_2$ catalytic system in hydrogen is characterized by the formation of acetic acid (^1H NMR spectrum of CH_3COOH : $\delta = 11.60 \text{ ppm}$ (s, H, OH); $\delta = 1.98 \text{ ppm}$ (s, 3H, CH_3)) as a result of $\text{Pd}(\text{OAc})_2$ hydrogenolysis and by the degradation of diphenylphosphide ligands.

The ^{31}P NMR monitoring of the complex **I** + $0.20\text{Pd}(\text{OAc})_2 + \text{H}_2$ system indicated the complete conversion of complex **I**. Although the concentration of

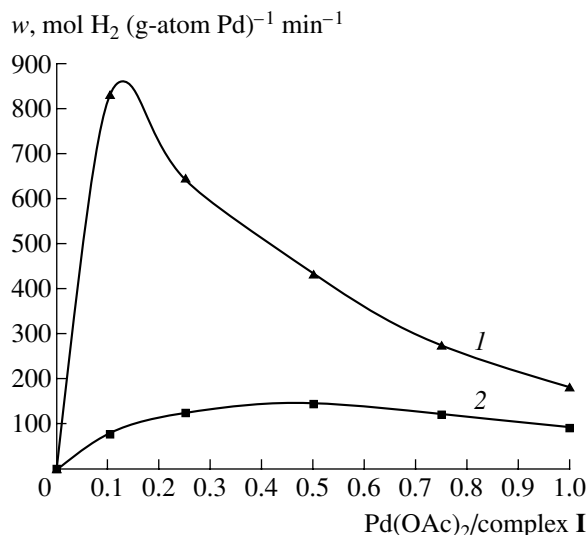


Fig. 1. Dependence of the catalytic activity of the complex **I** + $x\text{Pd}(\text{OAc})_2$ system on the ratio between the initial components: (1) on a $\text{Pd}(\text{OAc})_2$ basis and (2) on a total palladium basis. $[\text{I}] = 1 \text{ mmol/l}$; $T = 30^\circ\text{C}$, $P_{\text{H}_2} = 2 \text{ atm}$; $v_{\text{styrene}} = 9 \text{ mmol}$; solvent, DMF.

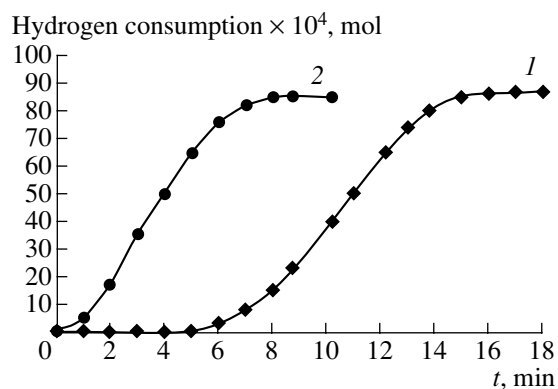


Fig. 2. Kinetic curves of styrene hydrogenation in the presence of the complex **I** + $x\text{Pd}(\text{OAc})_2 + \text{H}_2$ catalytic system at various ratios of initial components. $x = (1) 0.25$ or $(2) 1$. $[\text{I}] = 1 \text{ mmol/l}$; $T = 30^\circ\text{C}$; $P_{\text{H}_2} = 1 \text{ atm}$; $v_{\text{styrene}} = 9 \text{ mmol}$; solvent, DMF.

solution was high and the accumulation was long, only weak resonance signals due to the partial oxidation products of diphenylphosphine were detected in the ^{31}P NMR spectrum: $(\text{PhO})_2\text{P}(\text{O})\text{H}$ ($\delta = 1.4 \text{ ppm}$, $^1J_{\text{PH}} = 605 \text{ Hz}$ [13]); 11.7 and 18.3 ppm. This fact suggests that the substances produced in the course of catalyst formation occurred in a colloidal dispersed state, and their relaxation time was much shorter than the relaxation time of true solutions.

In our opinion, the formation of a disperse system at low concentrations of palladium acetate is related to the degradation of diphenylphosphide ligands, and the degree of this degradation depends on the ratio between the initial components (Fig. 3). According to GLC data, the maximum amount of benzene corresponds to the removal of one phenyl group. The ability of the phosphinidene ligand (PPh) to form bonds with three or even four metal atoms is responsible for the appearance of the nuclei of a new phase.

Previously [1], it was hypothesized that the degradation of organophosphorus ligands results from the oxidative addition of PR_x to $\text{Pd}(0)$ followed by the hydrogenolysis of the $\text{Pd}-\text{C}$ bond. If these processes occur in the catalytic system under discussion, $\text{Pd}(0)$ formed by the reduction of $\text{Pd}(\text{OAc})_2$ with hydrogen is converted into an oxidized state because of the degradation of PPh_2 ligands:

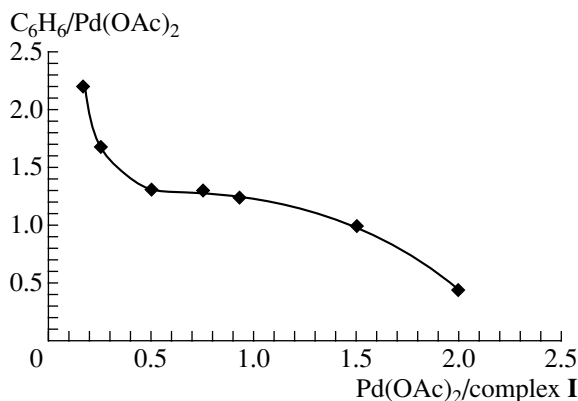
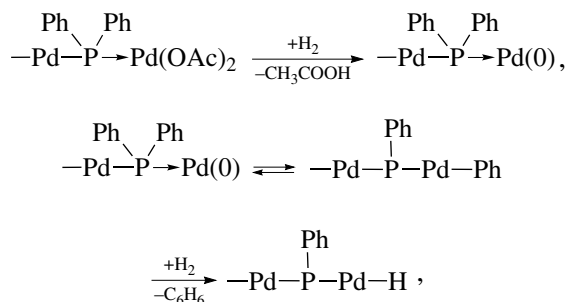
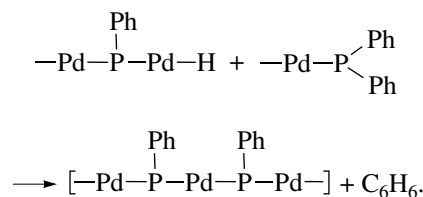


Fig. 3. Degradation of organophosphorus ligands in the complex **I** + $x\text{Pd}(\text{OAc})_2$ system. $[\text{I}] = 5 \text{ mmol/l}$; $T = 80^\circ\text{C}$, $P_{\text{H}_2} = 1 \text{ atm}$.



The conversion of $\text{Pd}(0)$ into an oxidized state with the formation of palladium complexes with phosphinidene ligands is responsible for an induction period in the hydrogenation of styrene. To test the above hypothesis, we determined the fraction of reduced palladium in the complex **I** + $x\text{Pd}(\text{OAc})_2$ catalytic system at different stages of its formation.

It is well known [8] that $\text{Pd}(0)$, which occurs as palladium black or is supported on a carrier, goes into solution as $(\text{NBu}_4)_2[\text{PdI}_4]$ under the action of iodobenzene and tetrabutylammonium iodide. The $[\text{PdI}_4]^{2-}$ anion can easily be determined by UV spectrophotometry using an absorption band at 340 nm. We performed preliminary experiments without iodobenzene in order to provide support for the fact that $(\text{NBu}_4)_2[\text{PdI}_4]$ was formed in the reaction systems as a result of the oxidative addition of iodobenzene followed by the reaction with tetrabutylammonium iodide rather than via exchange reactions with $\text{Pd}(\text{II})$ compounds. In these cases, an absorption band at 340 nm was absent from the UV spectra. This fact supported the reliability of the determination of $\text{Pd}(0)$.

The concentration of $\text{Pd}(0)$ in the complex **I** + $x\text{Pd}(\text{OAc})_2 + \text{H}_2$ system, where $x = 0.1$ or 0.2 , after treatment with hydrogen was low, whereas at $x = 0.7$ $\text{Pd}(0)$ occurred in a considerable amount in the catalytic system even before hydrogenation (Table 3).

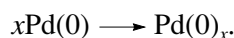
This fact indicates that at $x > 0.2$ palladium acetate incompletely reacted with complex **I** in accordance with the above reaction scheme, while a portion was

Table 3. Concentration of Pd(0) in the **I** + $x\text{Pd}(\text{OAc})_2$ system before and after the hydrogenation of styrene

Entry	$\frac{\text{Pd}(\text{OAc})_2}{\text{complex I}}$	Fraction of $\text{Pd}(\text{OAc})_2^*$, %	Concentration of Pd(0), %	
			before hydrogenation	after hydrogenation
1	0	0	0	—
2	0.1	9.1	2.5	19.7
3	0.2	16.6	3.7	24.9
4	0.7	41.2	38.8	44.2

* Based on the total palladium content of the system.

reduced by hydrogen to Pd(0), which underwent aggregation:

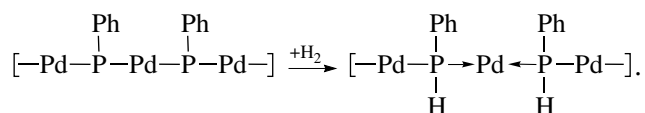


However, even at $x = 0.7$, a sample separated from the reaction system was an X-ray amorphous substance free of palladium in a crystalline state. The diffraction pattern exhibited an amorphous halo in the diffraction angle range $2\theta = 36^\circ\text{--}50^\circ$. The coherent-scattering region of this sample was 2.4 nm, as calculated using the Selyakov–Scherrer formula [14].

The concentration of Pd(0) in all of the above catalytic systems increased after the hydrogenation of styrene, and it was higher than the fraction of $\text{Pd}(\text{OAc})_2$. Consequently, not only palladium added as palladium acetate but also, in part, palladium from the initial trinuclear palladium complex was converted into a reduced form.

It is well known [15] that the M-PR_x bond ($x = 1$ or 2) can be sufficiently labile depending on the nature of the metal and the anionic ligands and on the coordinative unsaturation of the metal. Thus, for example, the Hf-PR_x bond was cleaved under the action of H_2 , CO, or C_2H_4 at room temperature with the formation of phosphine (or diphosphine) and $[\text{Hf}(\text{H})_2]$, $[\text{Hf}(\text{CO})_2]$, or $[\text{Hf}(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2)]$. On the other hand, it is well known that, in the hydrophosphorylation catalyzed by platinum and palladium complexes, a coordinated olefin is inserted into the M-P bond for Pt and Pd and into the M-H bond for Pd [16]. The subsequent step of reductive elimination resulted in the reaction products of hydrophosphorylation and $\text{M}(0)$ regeneration. A quantitative analysis of the ^1H NMR spectrum of the complex **I** + $0.20\text{Pd}(\text{OAc})_2 + \text{H}_2$ system after degassing and mixing with an equimolar amount of styrene in an argon atmosphere at room temperature demonstrated that the concentration of styrene remained unchanged. Consequently, the insertion of styrene into the Pd-P bond did not occur under these conditions. Therefore, we assume that an increase in the concentration of

Pd(0) in the course of styrene hydrogenation was due to the hydrogenolysis of the Pd-PPh bond



It is our opinion that the role of styrene can be associated with the dissociation of polynuclear palladium complexes on the coordination of styrene and with the facile activation of the hydrogen molecule.

According to the reaction scheme proposed, individual Pd(0) atoms can be active in hydrogenation, or an active center can be formed in the course of catalyst formation. This active center contains the $[\text{Pd}(0)]_n$ ensemble of palladium atoms, which are immobilized on supramolecular structures formed by the association of phosphinidene and phosphide complexes of palladium. The formation of hydride clusters containing palladium hydrides $[\text{Pd}_x\text{H}_y]_n$ under conditions of hydrogenation catalysis cannot be excluded.

A linear relationship between the rate of styrene hydrogenation and the concentration of Pd(0) at small amounts of Pd(0) (Fig. 4) is direct evidence for the fact that Pd(0) or $[\text{Pd}_x\text{H}_y]_n$, which is formed from Pd(0), acts as a species that is catalytically active in hydrogenation in the system under consideration.

The catalytic system under discussion is sufficiently labile, and it is transformed in the course of catalysis. This is due to the fact that organophosphorus ligands undergo degradation not only on the formation of the catalytic system in hydrogen but also in the course of hydrogenation (Table 4). In this case, in the hydrogenation of styrene, the concentration of benzene remained unchanged during the induction period; this fact is consistent with the above reaction scheme proposed for the degradation of organophosphorus ligands in the coordination sphere of Pd(0).

Thus, in the course of operation of the complex **I** + $x\text{Pd}(\text{OAc})_2 + \text{H}_2$ catalytic system, the hydrogenation of both styrene and organophosphorus ligands takes place resulting in repeated redox processes. The polynuclear complexes of palladium with organophosphorus

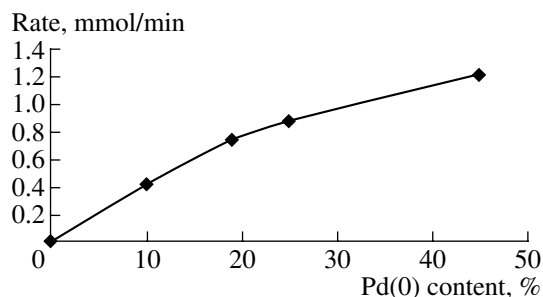


Fig. 4. Dependence of the rate of styrene hydrogenation on the Pd(0) content. $[\text{Pd}]_{\Sigma} = 1 \text{ mmol/l}$; $T = 30^{\circ}\text{C}$; solvent, DMF.

ligands actively participate in the formation, operation, and deactivation of the catalyst. On the one hand, the degradation of diphenylphosphide ligands results in the conversion of Pd(0) into an oxidized state to poison the catalyst. On the other hand, the resulting palladium complexes with phenylphosphinidene ligands regenerate Pd(0), probably as a result of the hydrogenolysis of the Pd–P bond. The deeper degradation of organophosphorus ligands results in the visually observed heterogenization of the system. In our opinion, this is the main reason for catalyst deactivation.

Table 4. Degradation of organophosphorus ligands in the course of styrene hydrogenation in the **I** + $0.25\text{Pd}(\text{OAc})_2$ system

Styrene portion number	Benzene amount $\times 10^5$, mol	
	before hydrogenation	after hydrogenation
1	1.10	2.76
2	2.76	3.20
3	3.22	3.46
4	3.45	3.54
5	3.54	3.55

Note: $[\text{I}] = 6 \text{ mmol/l}$; $[\text{Pd}(\text{OAc})_2] = 1.5 \text{ mmol/l}$; $T = 30^{\circ}\text{C}$; $P_{\text{H}_2} = 1 \text{ atm}$; solvent, DMF; $v_{\text{styrene}} = 9 \text{ mmol}$ (in a single portion).

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REFERENCES

1. Shmidt, F.K., Belykh, L.B., and Cherenkova, T.V., *Kinet. Katal.*, 2001, vol. 42, no. 2, p. 182.
2. Shmidt, F.K., Belykh, L.B., Umanets, V.A., Cherenkova, T.V., and Belonogova, L.N., *Kinet. Katal.*, 1999, vol. 40, no. 3, p. 466.
3. Goremyka, T.V., *Cand. Sci. (Chem.) Dissertation*, Irkutsk: Irkutsk State Univ., 2002.
4. Leoni, P., Marchetti, F., Papucci, S., and Pasquali, M., *J. Organomet. Chem.*, 2000, vols. 593–594, p. 12.
5. Zhuravel, M.A., Moncarz, J.R., and Glueck, D.S., Lam, K.-C., and Reingold, A.L., *Organometallics*, 2000, vol. 19, p. 3447.
6. Gordon, A.J. and Ford, R.A., *The Chemist's Companion: A Handbook of Practical Data, Techniques and References*, New York: Wiley, 1972.
7. Stuede, C., Lesuer, W.M., and Norman, G.R., *J. Am. Chem. Soc.*, 1955, vol. 47, p. 3526.
8. Shmidt, A.F. and Mametova, L.V., *Kinet. Katal.*, 1996, vol. 37, no. 3, p. 431.
9. Shmidt, A.F., Belykh, L.B., and Goremyka, T.V., *Koord. Khim.*, 2002, vol. 28, no. 2, p. 98.
10. Cartwright, S.J., Dixon, K., and Rattray, A., *Inorg. Chem.*, 1980, vol. 19, no. 5, p. 1120.
11. Hou, Z., Breen, T.L., and Stephan, D., *Organometallics*, 1993, no. 12, p. 3158.
12. Schumann, H., *Angew. Chem.*, 1969, no. 23, p. 970.
13. Nifant'ev, E.E. and Vasyanina, L.K., *Spektroskopiya YaMR ^{31}P* (^{31}P NMR Spectroscopy), Moscow: Moscow State Pedagogical Inst., 1986.
14. Kitaigorodskii, A.I., *Rentgenostrukturnyi analiz* (X-Ray Structural Analysis), Moscow: Izd. Tekhn. Teoret. Lit., 1950.
15. Stephan, D.W., *Angew. Chem., Int. Ed. Engl.*, 2000, vol. 39, p. 314.
16. Wicht, D.K., Kourkine, J.V., Lew, B.N., *et al.*, *J. Am. Chem. Soc.*, 1997, vol. 119, p. 5039.