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**CATALYSIS** =

## Origin of the Activity of Hydrogenation Catalysts Based on Palladium Complexes and Primary Phosphines

L. B. Belykh, T. V. Goremyka, and F. K. Shmidt

Irkutsk State University, Irkutsk, Russia

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Abstract—The activity of the catalytic system based on palladium bisacetylacetonate and phenylphosphine in hydrogenation catalysis was studied.

The unique capability of transition metals to catalyze hydrogenation of unsaturated organic molecules with gaseous hydrogen is known for a long time and is used in numerous industrial processes [1-3]. Among Group VIII transition metals, much attention is given to palladium-based catalysts. Modification of palladium with nitrogen-containing compounds (quinoline, ethylenediamine, alkaloids) allows preparation of highly selective catalysts for hydrogenation of alkynes, chemoselective hydrogenation of unsaturated aldehydes and ketones, enantioselective hydrogenation of derivatives of  $\alpha$ ,  $\beta$ -unsaturated acids, etc. [1, 2]. Along with studies of heterogeneous supported palladium catalysts, active efforts have been made in the past three decades to elucidate factors responsible for the activity of palladium complexes with phosphine ligands as hydrogenation catalysts. Whereas the modifying effect of tertiary [4-7] and secondary [8] phosphines on the properties of palladium complexes as hydrogenation catalysts has been studied in detail, primary phosphines have not yet been used in hydrogenation catalysis. Interest in these systems is due to the fact that primary phosphines exhibit simultaneously the properties of Lewis bases and Brønsted acids. Furthermore, primary phosphines, like other threecoordinate phosphorus compounds, are reductants.

The goal of this work was to gain insight into the promoting effect of  $PH_2Ph$  in a microheterogeneous hydrogenation catalyst based on  $Pd(acac)_2$ .

## EXPERIMENTAL

The solvents were purified by standard procedures used in organometallic chemistry [9].

Palladium bisacetylacetonate was prepared according to [10].

Phenylphosphine was prepared by reaction of phenylchlorophosphine with lithium aluminum hydride [11] and isolated by vacuum distillation (38°C/5 mm Hg). <sup>31</sup>P NMR:  $\delta$  –122 ppm (<sup>1</sup>J<sub>PH</sub> 200 Hz). The compound was stored in a sealed ampule under argon.

The catalyst based on Pd(acac)<sub>2</sub> and PH<sub>2</sub>Ph was prepared as follows. To a solution of 0.00304 g  $(1 \times 10^{-5} \text{ mol})$  of Pd(acac)<sub>2</sub> in DMF, prepared in a duck-shaped vessel that had been evacuated and filled with hydrogen, 1 ml of a phenylphosphine solution was added; the P/Pd ratio was 0.1–2.0. The lemonyellow reaction mixture was stirred in a hydrogen atmosphere at 80°C for 5–15 min. The resulting black-brown "solution" was cooled to 30°C, and a substrate to be hydrogenated was introduced with a syringe. Hydrogenation was performed with vigorous stirring at the initial hydrogen pressure of 1 atm. The reaction progress was monitored volumetrically and by GLC.

Acetylacetone and benzene in the catalyzate were determined by GLC, after evaporation–condensation of the solution in a vacuum unit  $(20^{\circ}C/1 \times 10^{-3} \text{ mm} \text{Hg})$ , on a Chrom-5 chromatograph equipped with a 3.6-m packed column (stationary phase SE-30) and flame ionization detector. The column temperature was 100°C, and the carrier gas was nitrogen. The error in determination of acetylacetone and benzene did not exceed 10%.

The UV spectra were recorded on a Specord UV VIS spectrometer in an all-sealed cell. The concentration of Pd(acac)<sub>2</sub> was calculated from the absorption band at 330 nm ( $\epsilon_{330} = 10\,630\,1\,\text{mol}^{-1}\,\text{cm}^{-1}$ ), and that of acetylacetone, from the band at 290 nm [for Hacac,  $\epsilon_{290} = 5000$ , and for Pd(acac)<sub>2</sub>, 3090 1 mol<sup>-1</sup> cm<sup>-1</sup>].

X-ray phase analysis of the catalyst samples was performed on a DRON-3M diffractometer,  $CuK_{\alpha}$ 

radiation. The procedure for determination of Pd(0) was described in [12].

We showed previously that palladium bisacetylacetonate, like palladium(II) acetate [13], is not reduced with hydrogen in aprotic solvents (benzene, toluene) below 80°C in the absence of water. We found that water breaks down the oligomeric species  $[Pd(acac)_2]_n$ preserved upon dissolution in benzene and facilitates heterolytic cleavage of the hydrogen molecule. The hydrogenolysis of Pd(acac)<sub>2</sub> in DMF occurs under milder conditions. At 30°C, it takes no less than 2 h, whereas at 80°C it is complete in 5–15 min depending on the Pd(II) concentration.

The initial rate of styrene hydrogenation in the presence of the thus generated Pd black is relatively low, and the maximal specific activity W does not exceed 19 mol of styrene per mole of Pd per minute. At low initial concentrations of Pd(acac)<sub>2</sub>, the catalyst undergoes rapid deactivation in the course of hydrogenation (Table 1). Introduction of water enhances the performance of Pd black.

To obtain a more effective catalytic system, we used PH<sub>2</sub>Ph as modifier. Catalytic hydrogenation of styrene in the presence of the system based on Pd(acac)<sub>2</sub> + *n*PH<sub>2</sub>Ph (P/Pd = 0.3, 1.0, 2.0) at 30°C in DMF is characterized by a long induction period (40 min) and low reaction rate. The catalyst that is the most active in hydrogenation is formed after preliminary reaction of the system components, Pd(acac)<sub>2</sub> + *n*PH<sub>2</sub>Ph, with H<sub>2</sub> in DMF at 80°C for 5–15 min. The catalytic system exhibits the highest performance at the PH<sub>2</sub>Ph : Pd(acac)<sub>2</sub> ratio of 0.3 (Fig. 1).

The specific activity of the system  $Pd(acac)_2 + 0.3PH_2Ph$  does not change upon hydrogenation of no less than 3000 mol of styrene per mole of Pd, after which the activity gradually decreases with formation of a precipitate. The reaction rate as a function of the catalyst concentration nonlinearly grows in the range 0.5–2 mM and starts to decrease at  $c_{Pd} > 1.4$  mM (Fig. 2).

In hydrogenation of other unsaturated hydrocarbons and of carbonyl and nitro compounds, the system under consideration also shows high activity and selectivity (Table 2).

In reduction of benzaldehyde on palladium catalysts (Pd/C), the C–O bond in the forming benzyl alcohol usually undergoes further hydrogenolysis, with the rates of both steps being comparable [2]. At the same time, the selectivity of the system  $Pd(acac)_2 + 0.3PH_2Ph$  in benzaldehyde hydrogenation reaches 92%. Nitrobenzene is usually selectively reduced to **Table 1.** Hydrogenation of styrene in the presence of Pd black formed from Pd(acac)<sub>2</sub>. Solvent DMF, 30°C,  $P_{\rm H_2} = 1$  atm, substrate concentration  $c_{\rm sub} = 8.7 \times 10^{-3}$  M<sup>2</sup>

Pd(Acac) <sub>2</sub> ,* mM	mol H <sub>2</sub> /(r	W, nol Pd min)	Styrene con- version, %	
0.45	2	11**	3	29**
0.90	6	19**	25	61**
2.27	12	16**	62	100**
4.54	9	12**	100	100**

\* Reduction of  $Pd(acac)_2$  with hydrogen was performed at  $80^{\circ}C$ .

\*\* Reduction of Pd(acac)<sub>2</sub> was performed with addition of 1 wt % H<sub>2</sub>O to the solvent.

aniline on palladium catalysts. The advantage of our catalyst is the high reaction rate. The specific activity of our catalyst in reduction of the nitro group exceeds by a factor of 3.5 that of Pd nanoparticles immobilized on the styrene–divinylbenzene copolymer [14] but is lower than that of the Pd catalyst with diphenylphosphine [8].

To gain insight into the promoting effect of  $PH_2Ph$ , we studied in more detail the system with P/Pd = 0.3.



**Fig. 1.** Hydrogenation of styrene in the presence of the catalytic system Pd(acac)<sub>2</sub> +  $nPH_2Ph$ . (W) Specific activity and (P/Pd) ratio of the starting reactants. Solvent DMF,  $c_{Pd} = 0.9$  mM, 30°C,  $P_{H_2} = 1$  atm.



**Fig. 2.** Rate of styrene hydrogenation W in the presence of the catalytic system  $Pd(acac)_2 + 0.3PH_2Ph$  as a function of the  $Pd(acac)_2$  concentration c. Solvent DMF, 30°C,  $P_{H_2} = 1$  atm,  $c_{sub} = 8.7 \times 10^{-3}$  M.

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Substrate	W, mol H <sub>2</sub> /(mol Pd min)	Conversion, %	Products, %
PhC=CH	104 (-C≡C-), 112 (-C=C-)	100	Ethylbenzene 85, styrene 15
PhC=CPh	113 (-C=C-), 21 (-C=C-)	100	Diphenylethane 69, <i>cis</i> -stilbene 24, <i>trans</i> -stilbene 7
PhCH=CH <sub>2</sub>	260	100	Ethylbenzene 100
PhC(O)H*	10	70	Benzyl alcohol 92, toluene 8
PhNO <sub>2</sub> *	48	97	Aniline 100

**Table 2.** Catalytic properties of the system  $Pd(acac)_2 + 0.3PH_2Ph$  in hydrogenation. Solvent DMF,  $c_{Pd} = 0.9$  mM, 30°C,  $P_{H_2} = 1$  atm,  $c_{sub}/c_{Pd} = 870$ 

\*  $c_{\text{Pd}} = 5 \text{ mM}.$ 

**Table 3.** Conversion of the catalytic system  $Pd(acac)_2 + nPH_2Ph$  in hydrogen, according to UV and GLC data. Solvent DMF, 80°C,  $c_{Pd} = 5 \text{ mM}$ 

PH <sub>2</sub> Ph/Pd(Acac) <sub>2</sub>	Reaction time, min	Concentra		
		Pd(Acac) <sub>2</sub>	HAcac	$C_6H_6/PH_2Ph$
0.3	5	2	99	0.26
0.3	15	0	98	0.50
0.3	40	0	99	0.51
0.5	15	2	87	0.46
0.5	40	0	93	0.45
1.0	15	24	79	0.13
1.0	40	12	83	0.19
1.0	60	-	113	0.20

Phenylphosphine, in contrast to tertiary phosphines, exhibits both base and acid properties. The previous study of the reaction of  $Pd(acac)_2$  with  $PH_2Ph$  in benzene and DMF in an inert atmosphere [15] showed that the reaction went beyond simple complexation and was accompanied by fast exchange of acetylacetonate ligands for organophoshorus groups, yielding acetylacetone and polynuclear palladium complexes containing  $\mu_3$ -PPh,  $\mu_2$ -PHPh, and coordinated PH<sub>2</sub>Ph ligands, and also *O*,*O*-chelate acetylacetonate ligands, like





The reaction is complete in 2-3 min. At the P/Pd

ratio of 0.3, upon ligand exchange, about 15% of Pd appears in the form of polynuclear complexes, and 85%, in the form of Pd(acac)<sub>2</sub>. The degree of conversion of Pd(acac)<sub>2</sub> to the reaction products grew with an increase in the P/Pd ratio. Quantitative formation of acetylacetone was observed at P/Pd > 2.

Additional treatment of the system  $Pd(acac)_2$  + *n*PH<sub>2</sub>Ph with hydrogen results in quantitative formation of acetylacetone (Table 3), i.e., not only  $Pd(acac)_2$ but also acetylacetonate ligands incorporated in polynuclear Pd complexes are subject to hydrogenolysis. The catalyzate from the reaction with  $H_2$  contained not only acetylacetone but also benzene originating from decomposition of the organophosphorus ligands. The amount of benzene formed per mole of PH<sub>2</sub>Ph grows as the P/Pd ratio is decreased. The content of  $Pd(acac)_2$  grows in the same direction. Similar trends were observed with triphenylphosphine [5]. The observed dephenylation is consistent with the previously proposed mechanism according to which degradation of organophosphorus ligands occurs in the coordination sphere of Pd(0) [8]; therefore, the mechanism of benzene formation in the system can be tentatively presented as follows.



 $Pd(acac)_2$  is readily reduced with hydrogen in DMF at 80°C to Pd(0). The Pd(0) atoms arising from hydrogenolysis of  $Pd(acac)_2$  can both aggregate to form palladium clusters and react with phenylphosphinylidene ligands in polynuclear palladium complexes. Oxidative addition of Pd(0) to these complexes with hydrogenolysis of the P–C bond yield benzene and, probably, palladium phosphides:

$$\begin{bmatrix} PPh \\ Pd & Pd \end{bmatrix} + Pd(0) \xrightarrow{+1/2H_2} Pd_x P.$$

Elemental analysis of the black precipitate (sample 1) isolated from the reaction system  $Pd(acac)_2$  +  $0.3PH_2Ph + H_2$  corresponds to the empirical formula  $Pd_8P_1C_1H_1$ , and the content of Pd(0) determined chemically does not exceed 28%. According to X-ray phase analysis, sample 1 is elemental palladium in the dispersed state; the size of its coherent scattering domain, as estimated from the shape of the Pd line hkl 111, is 2 nm. We believe that the results of X-ray phase and elemental analyses do not contradict each other. Sample 1 may contain higher palladium phosphides in the X-ray amorphous state for which the main reflections are observed in the same region as for elemental palladium and overlap with the broadened Pd(111) line. It should be noted that the products formed by the components of the catalytic system in an inert atmosphere, associates of polynuclear palladium complexes, were X-ray amorphous, giving a diffuse maximum (halo) at d/n = 13.556 Å; the size of coherent scattering domains was 2.7 nm. The absence of an amorphous halo at small diffraction angles  $(2\theta = 5^{\circ} - 40^{\circ})$  in the diffraction pattern of sample 1 indicates that the structure of polynuclear palladium complexes is broken down upon treatment of the catalytic system with hydrogen.

It was shown previously that the catalytic activity of the system  $Pd(acac)_2 + nPPh_3$  in hydrogenation of phenylacetylene was maximal at the P/Pd ratio of 0.3 also [16], and the solid reaction products identified were palladium phosphide  $Pd_3P$  and crystalline Pd. However, whereas formation of the system with triphenylphosphine took no less than 24 h, with phenylphosphine the formation time was as short as 5 min.

Our results suggest that, in the course of formation of the catalytic system based on  $Pd(acac)_2$  at P/Pd =0.3, phenylphosphine acts as a structural promoter. Its effect can be described as follows. The reaction of  $PH_2Ph$  with  $Pd(acac)_2$  yields nanosized associates of polynuclear palladium complexes with organophosphorus ligands. The associates of the polynuclear palladium complexes and palladium phosphides formed in an H<sub>2</sub> atmosphere by decomposition of organophosphorus ligands act as crystallization centers for immobilization and growth of Pd(0) clusters. At higher P/Pd ratios, the content of Pd(I) and Pd(II) complexes with phosphorus-containing ligands increases relative to Pd(0), and the catalytic activity of the system decreases.

## **CONCLUSIONS**

(1) A new high-performance catalyst based on  $Pd(acac)_2$  and  $PH_2Ph$  was suggested for hydrogenation of unsaturated bonds and of carbonyl and nitro groups.

(2) Transformations of the catalytic system  $Pd(acac)_2 + nPH_2Ph$  in hydrogen yield nanosized particles (2 nm) containing elemental palladium and, probably, palladium phosphides. Associates of polynuclear palladium complexes and palladium phosphides are crystallization centers for immobilization and growth of Pd(0) clusters. Phenylphosphine acts as a structural promoter.

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