

Catalytic hydrogenation of acetylenic alcohols using palladium complex of fullerene C₆₀

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Abstract

Catalytic properties of Pd–fullerene complex $\eta^2\text{-C}_{60}\text{Pd}(\text{PPh}_3)_2$ have been studied in the hydrogenation of acetylenic alcohols. The kinetics of the homogeneous hydrogenation has been investigated under static conditions. The catalyst quantity and the initial concentration of acetylenic alcohol have been varied. Physico-chemical properties of Pd–fullerene complex have been studied using methods of ¹H NMR, IR- and UV-spectroscopies. Using experimental results and physico-chemical investigations, the mathematical model of the process and the reaction mechanism have been offered. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

During the last decades the problem of selectivity became one of the most important problems in catalysis. With decreasing selectivity, accessory substances are formed, thus the quality of final product deteriorates.

The methods for syntheses of fragrant substances and vitamins E and A used in industry now include the stage of selective hydrogenation of acetylene compound dehydrolinalool (3,7-dimethyl-octaene-6-yne-1-ol-3, DHL) to linalool (3,7-dimethyl-octadiene-1,6-ol-3, LN) using different Pd-containing catalysts.

A number of catalytic systems for selective hydrogenation of acetylene compounds to olefins have been described elsewhere [1,2]. Among them there are homogeneous catalysts containing complexes of VIII Group metals (mostly, Pd, Pt, Rh, Ni) with different ligands.

The use of fullerene complexes as ligands is perspective branch of new catalytic systems creating. A great number of chemical reactions with fullerenes were described and a great number of them can be predicted [3–9]. As is known from the literature, the catalysts for different chemical processes can be created on the basis of fullerenes. Thus, fullerene-based materials are active catalysts for the processes of methane dehydrogenation to pyrolytic carbon and its aromatization to benzene, toluene, phenanthrene [10]. Fullerene and fullerene soot were used as

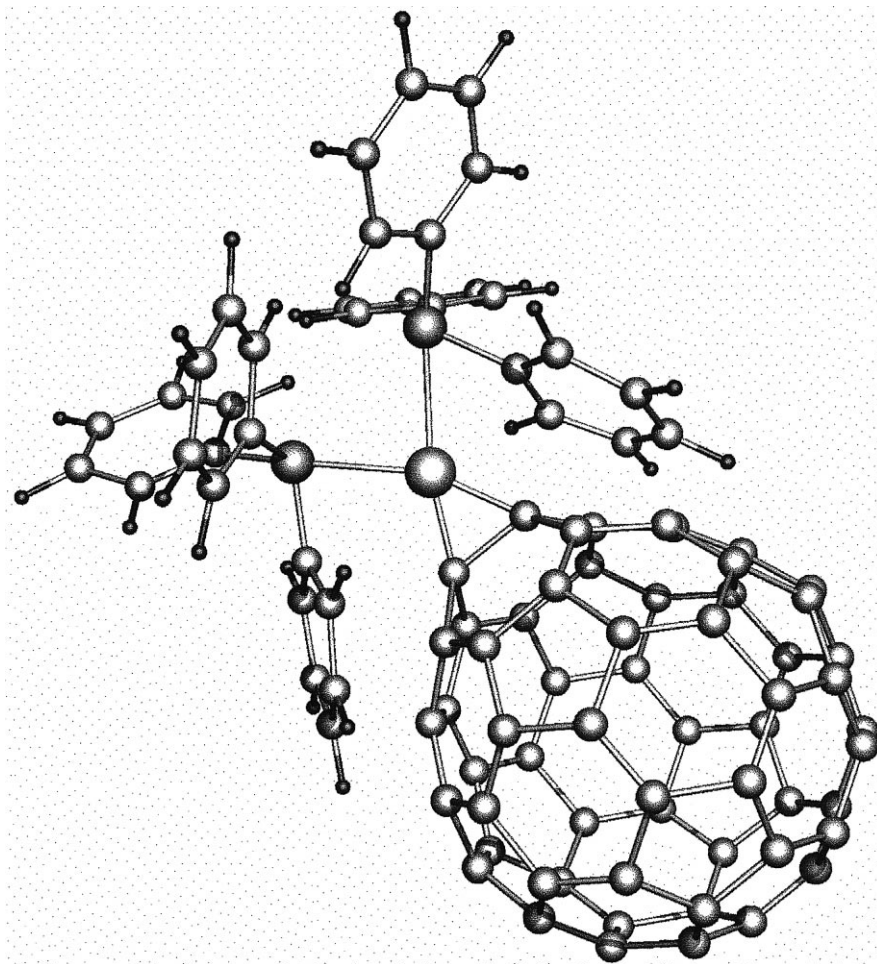
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the catalyst supports in the propylene polymerization [11]. Fullerene complexes are also known as catalysts of hydrogenation. The effect of fullerenes on the catalytic properties of Ru was investigated [12]. Fullerene-based ruthenium catalyst was studied in low-temperature CO hydrogenation and liquid phase hydrogenation of 2-cyclohexenone.

Catalytic hydrogenation properties of palladium supported on C_{60} were observed [13]. One mole percent of the complex $C_{60}[Pd(OAc)_2(PPh_3)]_3$ promoted 100% conversion of diphenylacetylene, phenylacetylene, cyclohexene and hex-1-ene to 1,2-diphenylethane, phen-

ylethane, cyclohexane and hexane, respectively. Similar hydrogenations over a Pd/active charcoal catalyst gave similar yields but took longer.

In this paper, the catalytic properties of the fullerene–Pd–phosphine complex $\eta^2-C_{60}Pd(PPh_3)_2$ (complex **1**, Scheme 1) are investigated in selective hydrogenation of DHL to LN. The reaction is presented in Scheme 2. When hydrogenation goes on non-selectively, LN transforms into dihydrolinalool (DiHL, 2,6-dimethylocten-2-ol-6), which is a possible side product of this reaction. The selectivity to be achieved using complex **1** as the catalyst is 99%.

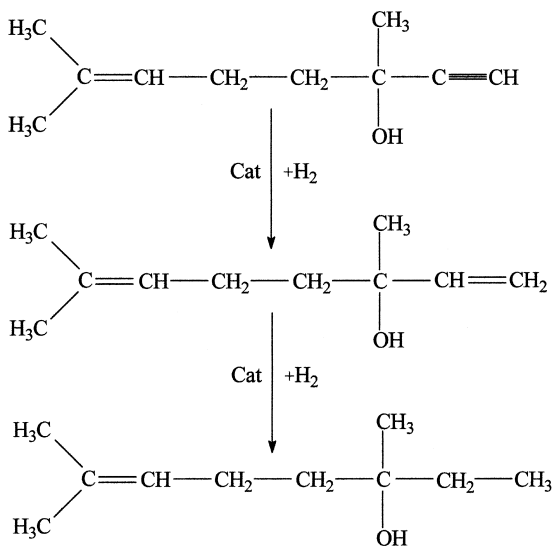


Scheme 1. Complex **1**: $(Ph_3P)_2Pd(\eta^2-C_{60})$.

2. Experimental

2.1. Reactor

The experiments on investigation of Pd–fullerene complexes catalytic properties were carried out under static conditions. The catalytic reactions were carried out in a glass batch isothermal reactor installed in a shaker and connected to a gasometric burette [14]. The reactor was equipped with two inlets: for catalyst, solvent, and substrate loading and for hydrogen feeding. Before the substrate was charged into the reactor, the catalyst was pretreated with H_2 for 60 min. The process of hydrogenation was carried out under conditions providing the absence of diffusion limitations. Previously, it was found that stirring intensity less than 900 shakings/min provided diffusion limitations (the process rate was determined by the rate of reagents diffusion to the catalyst surface) [15]. Thus, by the process kinetics study it is necessary to stir the reaction mixture with the intensity more than 900 shakings/min. Then the process rate will be limited by the rate of the reaction itself.



Scheme 2. Hydrogenation of DHL.

2.2. Analysis

2.2.1. Chromatography

Analysis of reaction mixture was carried out by gas chromatography (GC) using chromatograph “CHROM-5” with FID and glass column 3 m/3 mm. The column was filled with solid phase: “Chromaton N” (0.215–0.315 mm) saturated with “Apiezon L” (15% of liquid phase to support weight). Before analysis the column was conditioned with nitrogen under conditions: temperature: from 50 to 220°C, heating rate: 1°C/min, duration: 3–5 h. The temperature of the evaporator was 200°C, of the detector – 180°C. Supporting gas was nitrogen. Outlet velocity of nitrogen was 80 ml/min and of hydrogen – 35 ml/min. The analysis duration was approximately 10 min.

2.2.2. Spectroscopy

IR-spectra were recorded at room temperature at the spectrophotometer “Specord-M80” (Carl Zeiss, Jena) in the interval of 400–4000 cm^{-1} . Cuvettes and windows from KBr were used. The spectra were calculated as described elsewhere [16].

UV-spectra were recorded at room temperature at the spectrophotometer SP-26 in the interval of 186–1100 nm.

2.3. Catalyst

Synthesis of complex **1** is described in Ref. [16]. Buckminsterfullerene, C_{60} , reacts with $\text{Pd}(\text{PPh}_3)_4$ in solution to give in high yield complex **1**, in which fullerene is ligated in a η^2 -fashion. The molecular structure of this compound was established by the X-ray study of a single crystal. Its characteristics coincide with those previously described in literature [17]. Fullerene complex is very sensitive to light and air oxygen influence. So, the ampoule with crystalline complex **1** was sealed and kept under conditions providing the absence of light.

The homogeneous catalyst was prepared in inert media from complex **1** crystals and toluene (1 mg of complex **1**, 1 ml of toluene). Toluene is one of the organic solvents suitable both for dissolving of complex **1** and for DHL hydrogenation.

3. Results and discussion

Catalytic properties of the homogeneous catalyst created on the basis of complex **1** were investigated in the process of DHL selective hydrogenation according to the methods above described. The effect of the catalyst quantity was studied at constant concentration of acetylene alcohol $C_o = 0.22$ mol/l and solvent quantity of 30 ml by complex **1** quantity C_c varying from 0.05 to 0.3 g/l. The results obtained are presented in Table 1 (m_{DHL} is DHL quantity, t_h is the hydrogenation temperature).

According to the results obtained, maximum relative rate is observed in the presence of 3 mg quantity of complex **1**. Subsequent increase of the catalyst quantity does not influence on the hydrogenation rate.

Following kinetic study was carried out with optimal homogeneous catalyst quantity $C_c = 0.1$ g/l by DHL quantity varying C_o from 8.3 to 33.3 g/l. For all the data obtained the dependence ‘‘DHL conversion, θ ’’ was determined.

Table 1

The influence of the catalyst (complex **1**) quantity on its activity in the process of homogeneous hydrogenation of DHL (solvent: toluene, m_{DHL} : 1 g, t_h : 60°C, liquid phase volume: 30×10^{-6} m³, P_{H_2} : 0.1 MPa, shakings: 960/min)

Number	Catalyst quantity (mg)	Relative rate $r \times 10^2$ (m ³ H ₂)/(g Pd mol DHL s) ^a
1	1.5	0.7
2	2.0	1.1
3	3.0	1.5
4	9.0	1.4

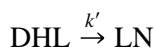
^aAt 20% hydrogen uptake.

Relative rate θ was calculated according to equation:

$$\theta = \tau/q^n. \quad (1)$$

Here τ is the reaction time, $q = C_o/C_c$, n is the degree index. To determine n the dependence of $\ln \tau_{0.5}$ on $\ln q$ was graphically presented (Fig. 1). One can see that DHL half-conversion time $\tau_{0.5}$ depends little on q . n is the tangent of the angle of line $\tau_{0.5} = q^n$: $n = 0$ [13]. According to Eq. (1), the relative time θ is equal to the reaction time τ . The dependence ‘‘DHL conversion, θ ’’ is presented in Fig. 2 ($C_c = \text{const}$).

The reaction scheme was used for the experimental data description:



where k' is the rate constant.

According to this scheme some kinetic models were offered using mathematical treatment and the kinetic data obtained. Substrate adsorption was not considered (the catalyst was homogeneous). The best results were obtained for the model described by the following equation:

$$W' = - \frac{dx_i}{d\tau} = k, \quad (2)$$

where W' is the relative hydrogenation rate, k is the kinetic parameter of the reaction, $x_i = C_i/C_o$, where C_i is the DHL concentration by the moment τ .

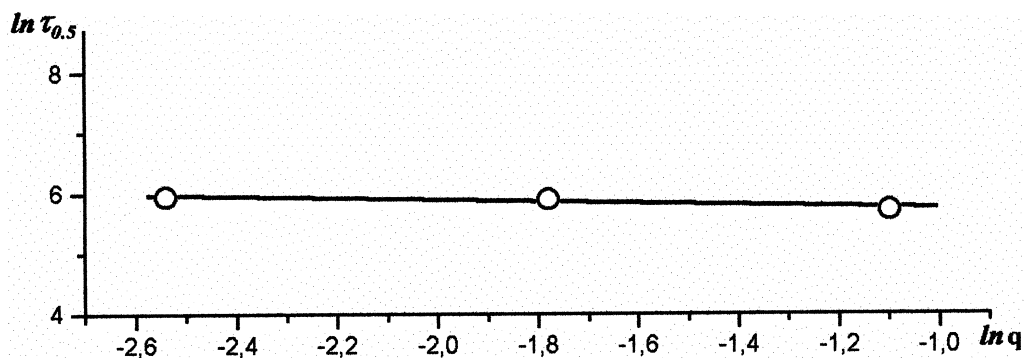
The calculated curves agree well with experimental points (Fig. 2).

By concentration expressing in mol/l (instead of mol/mol) Eq. (2) transforms into:

$$W = - \frac{dC_i}{d\tau} = kC_o. \quad (3)$$

However, Eq. (2) is not applicable for the beginning of the hydrogenation (induction period) which is well described by the most complicate dependence.

The presence of induction period is probably related to additional processes leading to the

Fig. 1. The dependence of $\ln \tau_{0.5}$ on $\ln q$.

reactive complex formation. The rate increasing in this period confirms the supposition.

UV-spectroscopy was used to study the stability of the homogeneous catalyst after hydrogenation. The initial Pd–fullerene complex has UV-spectra band ~ 450 nm, which is present after hydrogenation, too. Thus, complex **1** was not destroyed during the process investigated.

The analysis of IR-spectra of toluene solution of complex **1** showed that the absorption band

of the bond P–C (ν_{P-C}) moved from 665 cm^{-1} for coordinated DHL to 648 cm^{-1} for uncoordinated DHL. Also it was observed that the absorption band $\nu_{C=C}$ moves to bigger frequencies on 20 cm^{-1} in comparison with uncoordinated DHL.

Interaction is likely to take place between DHL and complex **1**. It is due to the transition of electronic density from phosphorus to palladium and then to the triple bond, that matches

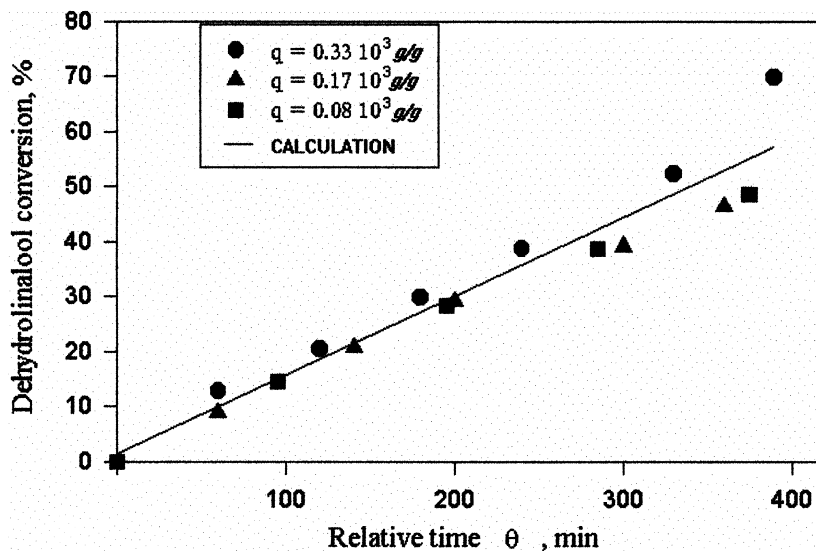
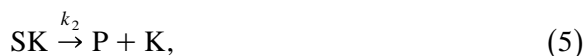
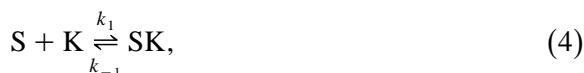


Fig. 2. The dependence of dehydrolinalool conversion on relative time.

the literature data [16]. Thus, IR-spectra confirm the possibility of the reactive complex “substrate–catalyst” formation.

The complication of metal–fullerene molecules permits to establish a close relationship between catalysis in the presence of such complexes and fermentative catalysis. As in the case of fermentative catalysis the simplest scheme of the process studied can be offered:



where S is the substrate, K is the catalyst, SK is the reactive complex “substrate–catalyst”, P is the product.

If the stage of the product formation is supposed to be the slowest one and the equilibrium of the process (4) displaces to the reverse reaction, then the rate of hydrogenation is directly proportional to the initial substrate concentration.

Then, the kinetics of catalytic reactions can be described by Michaelis–Menten equation (the main equation of fermentative catalysis theory) when the catalyst concentration is constant [17]:

$$W = \frac{V[S]_0}{K_M + [S]_0}, \quad (6)$$

where W is the rate of fermentative process, $V = k_2[K]_0$, $[S]_0$ is the initial substrate concentration, K_M is the Michaelis’ constant ($K_M = [k_{-1} + k_2]/k_1$).

If $[S]_0 \ll K_M$ then

$$W = k'[S]_0, \quad (7)$$

where $k' = V/K_M$.

Thus, one can see a match between Eqs. (3) and (7).

4. Conclusion

(1) The catalytic properties of the [60] fullerene–Pd–phosphine complex $\eta^2\text{-C}_{60}\text{Pd}(\text{PPh}_3)_2$ were firstly investigated in selective hydrogenation of the dehydrolinalool triple bond to a linalool double one.

(2) The kinetics of the process was studied, catalyzed by the homogeneous catalyst created on the basis of this complex. The kinetic model was proposed on the basis of the data obtained. The catalytic properties of the homogeneous catalyst were supposed to be like those of enzymes. So, the mechanism of the hydrogenation was proposed.

(3) The study on the mechanism of the catalytic activity of palladium–phosphine complex and its physico-chemical properties is carried out now using methods of quantum chemical modelling. The electron structure of the active site is calculated.

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