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Mechanism of the Solvent Effect on the Rate of the Cyclohexene Hydroxymethoxycarbonylation Catalyzed by Bis(triphenylphosphine)palladium

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Abstract—Kinetic data of the cyclohexene hydroxymethoxycarbonylation catalyzed by bis(triphenylphosphine)palladium $Pd(PPh_3)_2$ were processed and considered on the basis of the quantum-chemical calculations. By the method of density functional DFT PBE/3z we found that among the possible catalyst moleculs based on the tetrakis(triphenylphosphine)palladium the most stable is $Pd(PPh_3)_2$ with the coordination number of palladium equal 2. The interaction energy of $Pd(PPh_3)_2$ with acetone, acetonitrile, dichloroethane, 1,4-dioxane, nitromethane, and tetrahydrofuran calculated by PM3 method was found to correlate linearly with the reaction rate logarithm. The mechanism of the solvent effect on the reaction rate consists in a specific complexation with the catalyst depending on the molecule rigidity and the creation of energetic and steric constraints for the substrate to access the catalyst.

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Among the catalytic systems used in the alkene hydroxymethoxycarbonylation reactions [1, 2] a special attention with respect to the reactants conversion degree, selectivity, mildness of conditions, and the catalyst stability attract the systems based on the palladium phosphine complexes [3–8]. The possibility of performing such reactions with a high rate and sufficient selectivity required the knowledge of the mechanism of catalytic action and the nature of the involvement of the solvent molecules [9]. The theoretical data on the structure and properties of these palladium complexes are needed to elucidate how the solvent molecules influence the reaction mechanism and to predict application of other suitable catalysts and solvents. With this purpose, in this work we solve a problem of determining the features of the spatial and electronic structure of the bis(triphenylphosphine) palladium $[Pd(PPh_3)_2]$ complexes with the molecules of different solvents in the model reaction of cyclohexene hydroxymethoxycarbonylation.

The objects and methods of investigation. The values of the rate of catalytic cyclohexene hydroxymethoxycarbonylation in different environments at varied volume fraction of solvent in the reaction mixture, presented in [9], give a quantitative basis for discussing the influence of solvent nature on the reaction rate. In order to adapt these data for the fulfillment of the task of this work we recalculated them to get the data for the same molar concentration of the solvent. To do this, we calculated their relative molar concentration in the reaction mixture in accordance with the expression $C_r = \varphi \cdot M/M_a$, where φ is the volume fraction of solvent, M is the molar mass of a particular solvent, M_a is the molar mass of the acetonitrile solvent, assuming that the solvents have approximately the same specific density. Then, graphically in the coordinates $r - C_r$ reaction rates in the medum of each solvents at $C_r = 40$ were determined, related to the values of φ from 15 to 30 vol %. The values of the reaction rates, together with the other data (see below) are listed in Table 1.

For the interpretation of our kinetic data the geometric structure, electronic structure, and thermodynamic properties of the palladium complexes

Table 1. Experimental values of the reaction rate of cyclohexene hydroxymethoxycarbonylation (r) at C_r = 40, and changes in the total (ΔE) and Gibbs (ΔG) energies for the complexation of solvent molecules (X) and $Pd(PPh_3)_2$ with the formation of the complex $Pd(PPh_3)_2X$ calculated by the PM3 method

X	r, 10^{-3} mol $l^{-1}s^{-1}$	ΔE, kJ mol^{-1}	ΔG, kJ mol^{-1}
Cyclohexane	1.35	–9.7	43.3
1,2-Dichloroethane	0.90	–5.4	38.0
Acetone	0.11	–41.1	16.5
1,4-Dioxane	0.05	–56.7	0.9
Nitromethane	0.025	–67.9	–20.2
Tetrahydrofuran	0.025	–66.1	–12.2
Acetonitrile	–	–52.9	–3.0

$Pd(PPh_3)_n$, n = 2, 3, and 4, were calculated quantum-chemically,and also those of the solvent molecules X (Table 1) and the complexes of composition $Pd(PPh_3)_2X$ and $Pd(PPh_3)_2X_2$.

The quantum-chemical calculations were performed by semiempirical PM3 method using HYPERCHEM 8.0.8 package [10] and by the method of density functional in a PBE/3z approximation using the program PRIRODA [11, 12].

In the first stage we considered the precursor molecules of the catalytic palladium complexes, $Pd(PPh_3)_n$ where n = 2, 3, and 4. The commercial product tetrakis(triphenylphosphine)palladium Pd $(PPh_3)_4$ is often used as a catalyst for many reactions [13]. Therefore it was important to determine the most probable form of its occurrence in the reactions. Some results of calculation of optimal geometric structure of the $Pd(PPh_3)_2$, tris(triphenylphosphine)palladium, and tetrakis(triphenylphosphine)palladium molecules are listed in Table 2.

Both used methods describe qualitatively similarly the geometric structure of tris- and tetrakis(triphenylphosphine)palladium. The PM3 method underestimates, while PBE/3z overstates the Pd–P bond length compared to the crystallographic data (231.6 pm for n = 3 [14] and 245.0 for n = 4 [15]).

It was found that in the crystal structure of the tris (triphenylphosphine)palladium the short intramolecular contacts Pd···H (about 282–303 pm) of the hydrogen atoms in the *ortho*-positions of phenyl rings are located above and below the P_3 plane, blocking the axial positions of the palladium [14] . Such contacts were found also by quantum-chemical calculations. However, these distances (Pd···H in Table. 2) obtained by PM3 method are significantly underestimated, while the method PBE/3z shows that they fall in the experimentally determined interval.

We have considered two types of spatial structure of $Pd(PPh_3)_2$ [16]. The first corresponds to the coordination unsaturation of palladium having a coordination number (CN) equal two. The second relates to the structure of palladium with CN = 4 (Fig. 1).

Table 2. Calculated geometric parameters and effective atomic charges of the poly(triphenylphosphine)palladium $Pd(PPh_3)_n$ molecules

n	2		3		4	
Method	PM3	PBE/3z	PM3	PBE/3z	PM3	PBE/3z
Group	Structure of the group					
PdP_n	angular	practically linear	flat distorted trigonal		slightly distorted tetrahedral	
Bond length, pm						
Pd–P	223.1	234.8	~229.7	241.1	231.3	~254
C–H (···Pd)	258.6	109.3	115.8	109.2	110.5	109.0
Shortest distance, pm						
Pd···H	168.7	315.0	246.3	295.6	259.3	332.8
Pd···C_{ortho}	205.9	373.1	340.1	362.2	402.0	394.1
Effective atomic charge, au						
Pd	–0.32	–0.32	–0.47	–0.30	–0.61	–0.34
P	1.65	0.25	1.35	0.24	1.38	0.24
H (···Pd)	–0.13	0.04	0.16	0.04	0.15	0.03

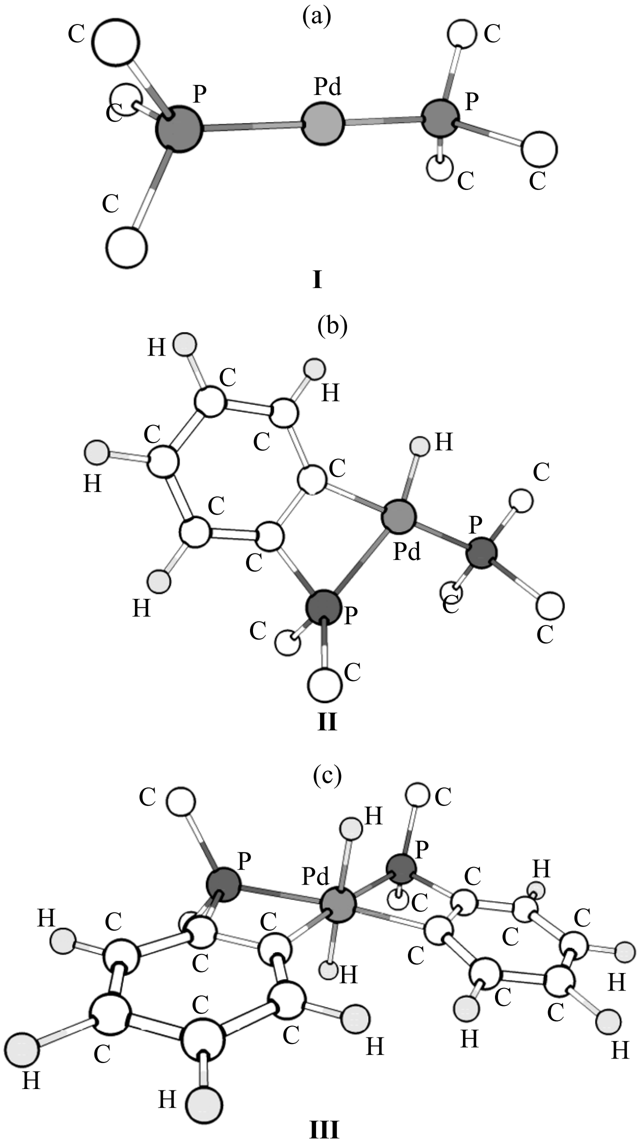

Fig. 1. Location of ligands in the coordination sphere of palladium in the $Pd(PPh_3)_2$ molecules: (a) *CN* = 2, (b) *CN* = 4, and (c) *CN* = 6 (*CN* is coordination number). To simplify the figure, the phenyl groups not forming coordination bonds with palladium are not shown but only their carbon atoms in the Pd–C bonds are shown.

It turns out that semiempirical quantum-chemical PM3 method predicts as the most stable the third structure **III** (Fig. 1c), with two hydrogen atoms in the *ortho*-positions of the two phenyl groups shifted to palladium and vacant carbon valences filled by palladium. The resulting *CN* of palladium becomes equal to six and the ligands are located at the vertices of distorted octahedron. Palladium gets a negative effective charge (–0.32 au), and on the phosphorus atoms the positive charge increases compared to triphenylphosphine (from 0.68 to 1.65 au). The hydrogen atoms connected with Pd, like the palladium itself, have negative effective charges (–0.13) and, thus, are of hydride type, while the remaining hydrogen atoms carry a positive charge. The carbon atoms of the phenyl radicals coordinated with palladium bear positive effective charge (0.13 au), while the remaining carbon atoms bear negative charge. Such a charge distribution is a result of combining the polar covalent and donor–acceptor chemical bonds with the participation of palladium. Highest occupied molecular orbital (HOMO) of $Pd(PPh_3)_2$ has energy –7.82 eV and includes mainly the antiphase contributions of atomic orbitals of both hydride hydrogen atoms. Next occupied molecular orbital (–8.51 eV) contains the contribution of the π-orbitals of phenyl rings. Lowest unoccupied molecular orbital (LUMO) contains the contributions of antibonding π-orbitals of phenyl rings.

The method of density functional PBE/3z, on the contrary, predicted as the most stable structure **I** in which the palladium is surrounded by only two phosphorus atoms. The hydrogen atoms remain bound to carbon atoms and are not involved in the coordination interaction with the palladium. As a result, their effective charges are small positive. It should be noted that the PM3 method fails to obtain the structure **I**. The PBE/3z method revealed all three listed structures. Structure **I** by PBE/3z at 298.15 K is predicted to be by ~129 and ~ 340 kJ mol^{-1} more stable than the structures **II** and **III**, respectively. This preference for the structure **I** is consistent with the experimental data [16].

The thermodynamic measure of the stability of these molecules is their Gibbs formation energies from the atomic palladium and the molecular triphenylphosphine, in accordance with the equation:

$$Pd + n\,PPh_3 = Pd(PPh_3)_n. \qquad (1)$$

As seen from Table 2 and Fig. 2, qualitatively the used methods of calculation lead to the same result: increase in the number of triphenylphosphine groups in the palladium coordination sphere increased the Pd–P bond length and the Gibbs energy. This indicates a decrease in the stability of the molecule. The increase in the temperature also acts in the same direction.

However, in quantitative terms, only the calculation by the PBE/3z method agree with the experimentally observed decrease in the stability of tetrakis(triphenylphosphine)palladium at the loss of triphenyl-

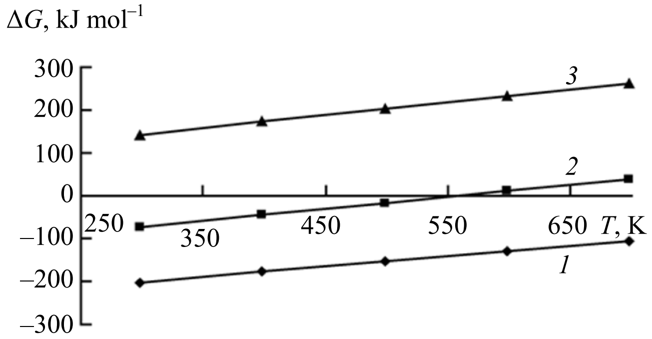

Fig. 2. The change of the Gibbs energy vs. temperature in the reaction (1) calculated by PBE/3z method: (*1*) $n = 2$, (*2*) $n = 3$, (*3*) $n = 4$.

phosphine molecules and the formation of the derivatives of compounds with lower coordination number of palladium (see references in [15]). Indeed, according to the PBE/3z method, the Gibbs formation energy of tetrakis(triphenylphosphine)palladium is larger than zero and this compound is expected to be unstable. At the same time, according to the PM3 method this energy is negative, indicating a high thermodynamic stability of this compound. It follows that, in the quantitative terms, the PBE/3z calculations are in better agreement with the experimental data on the structure and properties of poly(triphenylphosphine)palladium molecules. The most stable of the considered palladium compounds is $Pd(PPh_3)_2$.

It should be noted that the key role of coordination-unsaturated particles in the formation of active forms of phosphine–palladium catalysts in the interpretation of the reaction mechanism of hydrocarboxylation and hydroalkoxycarbonylation has been validated kinetically [4, 5, 9, 17–19]. Nevertheless, the material balance of all forms of the catalyst in these systems suggests that contribution of these particles in its initial concentration is negligible [17, 20]. This is confirmed by the *in situ* spectroscopic studies of these reaction systems: the method of IR spectroscopy was not sensitive enough to detect $Pd(PPh_3)_2$ [20], and ^{31}P NMR spectra evidence only indirectly the existence of consecutive reversible reactions [21]:

$$Pd(PPh_3)_4 \xrightleftharpoons{-PPh_3} Pd(PPh_3)_3 \xrightleftharpoons{-PPh_3} Pd(PPh_3)_2. \quad (2)$$

This contradiction is easily solvable in terms of the existence of more favorable equilibrium between the coordination-unsaturated phosphine-palladium particles and the reaction components including the source of hydride, solvent and reactants. This causes transformation of most of these particles into phosphine-palladium complexes involved in the catalytic cycle. Thus, the key role of $Pd(PPh_3)_2$ particles in the formation of active forms of the catalyst agree completely with the coordination unsaturation of these particles, and their low concentrations seems explicable in the framework of a complex equilibrium involving the formation of $Pd(PPh_3)_2$ and its interaction with the reaction components. In this regard, the $Pd(PPh_3)_2$ particles were chosen to simulate the interaction of palladium complexes with the solvent.

In the quantum-chemical calculations the $Pd(PPh_3)_2$ interaction with the solvent was simulated by the formation of [1+1] and [1+2] complexes from the respective molecules. The calculations were performed only by PM3 method for several reasons. Because of the large number of reaction centers at the intermolecular interaction the potential energy surface of even [1+1] complex has numerous local minima. In a non-empirical quantum chemical method this fact and the large size of the complex require significant computational resources to find the global minimum. This was shown in our PBE/3z test calculations. The problem becomes even more significant because simultaneously it is necessary to account for the error of the basis set superposition at the calculation of the complex formation energy. Therefore, although the application of the individual non-empirical quantum-chemical calculations seems to be more correct, it is very likely that the selection of the most stable conformation of the intermolecular complex in this case would be incorrect. A semiempirical calculation due to its high rate allows the consideration of a sufficiently large number of conformations of the complex. The absolute error of the method in this case can be leveled by considering the relative energies of the complex formation.

The calculations showed that there are two types of preferred conformations of the [1+1] complexes. The first type of complex structure is such that the solvent molecules are introduced into the palladium coordination sphere. For example, a molecule of nitromethane is coordinated by its methyl group with palladium to form hydride hydrogen in the Pd–H bond and the C–Pd bonds. Such intermolecular complexes of the first type of coordination are formed preferably by the molecules of the following solvents: dichloroethane, acetone and nitromethane.

When a solvent of the group cyclohexane, 1,4-dioxane, tetrahydrofuran, and acetonitrile is taken, a complex with the coordination of the second type becomes preferable. The complex is formed by the intermolecular interaction of hydrocarbon sites of Pd $(PPh_3)_2$ molecule and a molecule of the solvent. The solvent molecule is located away from the palladium. Geometric parameters of the nearest coordination environment of palladium and its electronic distribution in this case coincide with those in the original $Pd(PPh_3)_2$.

The cause of the first and the second type of coordination of solvent molecules must obviously correspond to the peculiarities of their electronic structures. Among various characteristics of the electronic structure of molecules of the examined solvents, there is one which clearly differs for the solvent coordinated by the first and the second type: the difference in the HOMO and LUMO energies. This difference is known to determine the hardness, an index of reactivity of molecule: $\eta = \varepsilon_{\mathrm{LUMO}} - \varepsilon_{\mathrm{HOMO}}$. The calculated hardness of the molecules from the group with the 1st type of coordination, dichloroethane, acetone, and nitromethane (11.21, 11.54 and 12.15 eV, respectively) is smaller than for the solvent of the 2-nd type of coordination, cyclohexane, 1,4-dioxane, tetrahydrofuran and acetonitrile (14.77, 13.29, 13.57, and 13.73 eV, respectively). The hardness of $Pd(PPh_3)_2$ is 7.79 eV, it is closer to that of the solvents of type 1 coordination. The $Pd(PPh_3)_2$ molecule includes two sites differing by hardness: the central (low hardness, that comprises palladium and phosphorus atoms) and peripheral (high hardness, contain phenyl groups). In this regard, the existence of two types of coordination of solvent molecules with $Pd(PPh_3)_2$ is in accordance with the rule that the hard reagents easily coordinated and react with the hard ones and soft with the soft ones [22].

It was found that the calculated changes of the total energy (ΔE) and Gibbs energy (ΔG) at the complexation of a solvent molecule (X) with $Pd(PPh_3)_2$ in the reaction (3) are consistent with the experimental kinetic data (Table 1):

$$Pd(PPh_3)_2 + X = Pd(PPh_3)_2X. \qquad (3)$$

Figure 3 shows the corresponding dependence of the function of the natural logarithm of reaction rate on the values of ΔE_s and ΔG_s.

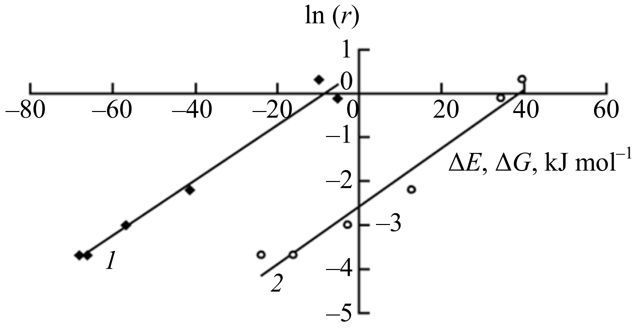

Fig. 3. Changes of ln (r) vs. changes in the total energy (*1*, ΔE, $R^2 = 0.98$) and the Gibbs energy (*2*, ΔE, $R^2 = 0.96$) in the reaction (3) of formation of monosolvated $Pd(PPh_3)_2X$ complexes: (*1*) total energy, ΔE, $R^2 = 0.98$ and (*2*) Gibbs energy, ΔG, $R^2 = 0.96$.

The obtained linear dependence suggests that the energy of the complex formation between the solvent and $Pd(PPh_3)_2$ affects the activation parameters of the reaction reducing the reaction rate and increasing the strength of binding the solvent to the complex. The results indicate that the solvent plays an important role in defining the structure of the transition state as an agent hampering the access of substrate to the catalytic complex. The specific feature of the solvent in this case lies in the fact that some of the solvents preferably interact with the palladium in the complex, and others with the ligands. As far as there is a correlation between the experimental and theoretical data (Fig. 3), we can expect that both the complex forming agent and the ligands of the complex are involved into the transition state of the studied reactions.

The consideration of the energy characteristics of double solvated complexes in accordance with the Eq. (4) also showed the presence of linear correlations, such as shown in Fig. 3. However, the reliability of a linear correlation in the second case (0.73) is low. This fact together with more positive values of the change in the formation free energy of bi-solvated complexes indicates a lower probability of their formation compared with mono-solvated complexes.

$$Pd[Pd(PPh_3)_2 + 2X = Pd(PPh_3)_2X_2. \qquad (4)$$

Thus, the quantum-chemical calculations of the molecules of poly(triphenylphosphine)palladium show a decrease in their stability with an increase in the number of triphenylphosphine groups. The most stable state of the molecule corresponds to the $Pd(PPh_3)_2$ structure with the palladium coordination number equal two. Molecules of less hard solvents may be introduced into the coordination sphere of palladium, and the molecules of harder solvents are located in the area distant from palladium and interact with the phenyl groups of $Pd(PPh_3)_2$. The formation of the mono-solvated $Pd(PPh_3)_2$ complexes is more probable compared to bi-solvated. The transition state of the catalyzed reaction should be considered as including molecules of the solvent.

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