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A Quantum-Chemical Study of Dissociation of H_2 Molecule on Palladium Clusters

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Abstract—The mechanism of the reaction of Pd_n clusters with an H_2 molecule was suggested on the basis of DFT B3LYP/HW calculations. The catalytic center in an elementary event of the process is one of the vertices of the Pd_n cluster; spillover of hydrogen atoms along the cluster edges results in the formation of a stable Pd_nH_2 complex with a significant energy gain in the case of the singlet reaction channel. In such a mechanism, the cluster size should not significantly affect the reaction up to a certain moment; therefore, when simulating processes involving large clusters, we can restrict ourselves to relatively small sites of their surface.

We have found in [1–3] that colloidal palladium *in situ* has a high catalytic activity in hydrogenation of various organic compounds containing an unsaturated group. The hydrogenation proceeds at room temperature and atmospheric pressure. All the studied reactions are first-order with respect to H_2 concentration and have an induction period during which a palladium cluster (colloidal palladium *in situ*) is formed. The subsequent reaction of dihydrogen and colloidal palladium *in situ* is the rate-determining step of the hydrogenation. The aim of this work was to study by quantum-chemical calculations the similar process in the gas phase as the first step of the hydrogenation mechanism. As the ground state of isolated palladium clusters Pd_n ($n > 2$) is triplet, the first excited state is singlet, and the energies of these states are close, it was necessary to consider the singlet and triplet channels of the reaction.

CHOICE OF THE CALCULATION METHOD AND BASIS SET

Insertion of a palladium atom in C–C, C–H, H–H, and other bonds was extensively studied by quantum-chemical methods of various levels (see, e.g., [4]). This paper is the first in the planned cycle of quantum-chemical studies of reactions catalyzed with palladium clusters; therefore, the methodical part involving the choice of the basis set for the palladium atom and the calculation technique is of special importance here. Palladium clusters Pd_n have stable geometric configurations in both singlet and triplet states at $n > 2$. In this connection, the first requirement to the basis set was to reproduce with a reasonable accuracy the experimental energy difference $\Delta E = E(^3D) - E(^1S)$ in an isolated palladium atom between the first excited (triplet) state and the ground (singlet) state, which lie in the range 0.8–1.25 eV [5] (the average value is ~0.95 eV).

In this work we calculated the electronic structure of the palladium atom by various methods using both effective core potentials in the SBK [6-8] and HW [9] basis sets and in the DZVP full-electron basis set [10]. The results of these calculations (Table 1) show that, when effective core potentials are used, only the density functional method (DFT) gives acceptable

Table 1. Energy difference $\Delta E^a = E(^3D) - E(^1S)$ (eV) between the first excited (triplet) and the ground (singlet) states of palladium atom as calculated by various methods

Basis set	HF	CAS in active space $[4d5s]^{10}$	DFT B3LYP
HW	–0.05	0.09	0.58
SBK	0.17	0.30	0.90
DZVP	0.58	0.67	1.50

[a] Average experimental value 0.95 eV [5].

Table 2. Characteristics of the potential curve of the Pd_2 molecule: equilibrium distances R_e and potential well depth D_e calculated by various methods

Basis	HF + MP2		DFT B3LYP	
	R_e, Å	D_e, eV	R_e, Å	D_e, eV
HW	3.00	0.13	2.79	0.45
SBK	2.98	0.19	2.79	0.51
DZVP	3.19	0.14	2.90	0.31

energy differences ΔE 0.58 (HW) and 0.90 eV (SBK), despite the fact that the calculations of the quintuple-degenerate (at a fixed value of the full spin projection) triplet state D by this method are not quite correct. With the DZVP full-electron basis set, the situation is opposite: The *ab initio* Hartree–Fock (HF) method and the method of multiconfiguration self-consistent field theory in the complete active space (CAS) give the energy difference of 0.58 and 0.67 eV, respectively, whereas the DFT method gives the value of ΔE 1.5 eV which is overestimated as compared to the experimental value. The ΔE value calculated by the *ab initio* methods can be brought closer to the experimental value by going to a wider full-electron basis set. For example, in the WBTS basis [11] the CAS method in the active space $[4d5s]^{10}$ gives the ΔE value of 0.99 eV, which is close to the averaged experimental value. However, this basis is too large for calculations of clusters, as it requires much computer time. Thus, our study has shown that DFT methods with the use of the effective core potential of the metal atom, requiring much less computer time, and *ab initio* methods with the full-electron basis are suitable for the quantum-chemical calculations of the palladium atom.

To describe the structure of isolated Pd_n clusters with a greater reliability, we used in this work both the DFT method with various basis sets and the *ab initio* HF method with the subsequent account for correlation corrections to the total energy. However, the results obtained made us discard the HF + MP2 method (see below).

To study reactions of palladium clusters with an H_2 molecule, we used in this work the B3LYP version of the DFT method [12] with the HW effective core potential ($n_{\text{core}} = 28$) and the corresponding basis of Gaussian functions [13], calculations with which are somewhat less labor-consuming than with the SBK potential. The quantum-chemical calculations were carried out using the GAMESS program complex [14].

CALCULATIONS OF ISOLATED Pd_n CLUSTERS

Pd_2 molecule. Table 2 contains calculated data for the potential curve of the ground state $1^1\Sigma_g^+$ of a diatomic Pd_2 molecule: equilibrium distances (R_e) and potential well depth (D_e). The data obtained show that the choice of a basis within the framework of one method does not play the main role. However, different methods give essentially different values of both the equilibrium distance and the potential well depth. The *ab initio* HF method with corrections to the total energy calculated by the perturbation theory up to the second order (MP2) in the valence and full-electron bases predicts practically repulsive character of the ground-state potential curve for the Pd_2 molecule, whereas the DFT method characterizes this state as weakly bonding. Control calculations in the DZVP basis by the HF + MP4 method and in a rather high-quality WBTS basis by the HF + MP2 method gave the potential well depth of 0.16 and 0.09 eV, respectively, which also proves the repulsive character of the ground state of the Pd_2 molecule. The final answer to this question can be obtained only on the basis of high-precision calculations in a high-quality basis, probably with relativistic corrections. Our calculations also have shown that several low-lying excited states of the Pd_2 molecule are bonding, the first of them being a triplet state.

Pd_3 and Pd_4 clusters. Calculations by the DFT B3LYP method in the HW basis have shown that the Pd_3 cluster has the triplet ground state and the shape of isosceles triangle with the 2.62 Å sides and 2.50 Å base. In the first excited state, which is singlet, this cluster has the shape of a regular triangle with the 2.52 Å side. The energy difference between the states corresponding to the singlet and triplet equilibrium geometries is only ~0.20 eV.

Similar calculations of the geometry of the Pd_4 cluster have shown that its ground state is also triplet with the equilibrium geometry of the C_{3v} symmetry, namely, a trigonal pyramid with the 2.59 Å edges and a regular triangle with the 2.71 Å side in the base. In the first excited (singlet) state, the equilibrium geometry of the Pd_4 cluster has the D_{2d} symmetry and is a trigonal pyramid with isosceles triangles as faces (2.57 Å sides and 2.85 Å base). The lengths of the opposite edges in this pyramid coincide. The difference in energies between the states corresponding to the singlet and triplet equilibrium geometries is in this case ~0.61 eV.

Results of nonempirical HF + MP2 calculations in the DZVP full-electron basis do not agree with DFT results even qualitatively. The HF + MP2 method gives singlet ground states for both the Pd_3 and Pd_4

clusters. To elucidate the causes of such a distinction, we refined the energies of the singlet states using the HF + MP4 method [14]. We found that the second-order perturbation theory strongly overestimates the correlation contribution to the total energy of the singlet state: when corrections up to the fourth order inclusive are taken into account, the total energy of the Pd_4 cluster increases (compared to MP2) by ~0.84 eV. In this connection, using the configuration interaction method, we have carried out check calculations of the electronic structure of the clusters under consideration in the points of the potential energy surface corresponding to the equilibrium DFT geometries. For the Pd_3 cluster, we chose the active space including ten molecular orbitals: three occupied and seven virtual molecular orbitals for the singlet state, and four occupied and six virtual molecular orbitals for the triplet state. For the Pd_4 cluster, the active space of 12 molecular orbitals was chosen, over which 12 electrons were distributed in all possible ways. These calculations have shown that the ground states of the clusters Pd_3 and Pd_4 are triplet.

The whole set of the data obtained allows a conclusion that various versions of DFT and HF methods and of methods with the explicit account for configuration interactions can be used to study isolated palladium clusters. The HF + MP2 method is unsuitable for the description of these systems. We have chosen the DFT method, which is rather simple technically, as the main working method for studying processes involving palladium clusters. Various versions of this method give, as a rule, consistent results.

REACTIONS OF Pd_3 AND Pd_4 CLUSTERS WITH H_2 MOLECULE

We simulated the approach of an H_2 molecule to palladium clusters by scanning the potential energy surface of the system $\{Pd_n + H_2\}$ ($n = 3, 4$) along the straight line connecting the centers of gravity (CG) of the reacting particles with full reoptimization (relaxation) of their geometry at each fixed distance R_{CG} between the centers of gravity. The initial distance between the reacting particles corresponded to R_{CG} 10.00 Å. No additional restrictions were imposed on the choice of a path of approach of the H_2 molecule to the palladium cluster.

As it was noted above, the ground state of isolated palladium clusters is triplet, the first excited state is singlet, and the energies of these states are fairly close. Therefore, a necessity arose to consider two reaction channels: the reactions of a singlet H_2 molecule with palladium clusters in both singlet and triplet states.

According to the results obtained, the singlet and triplet channels of the reactions $Pd_n + H_2$ ($n = 3, 4$) have a common characteristic feature: an H_2 molecule approaches practically without a barrier one of vertices of a palladium cluster, which becomes in fact a catalytic center in the elementary event of the reaction under consideration. This means, in particular, that, up to a certain moment, the size of a cluster should not exert a significant influence on the reaction under consideration and, when simulating processes involving "big" clusters, we can limit ourselves to relatively small sites of their surface.

In all the considered cases, an H_2 molecule approaches one of the cluster vertices to a distance of 1.8–1.6 Å. Closer approach is energetically unfavorable. These results agree with the calculated data available in the literature [15].

As an H_2 molecule approaches a cluster vertex, the length of the H–H bonds increases from 0.74 Å (free H_2 molecule) to 0.81–0.84 Å. The subsequent evolution of the systems under consideration is similar for both clusters and differs only in some geometric details.

Let us briefly consider the reaction of the Pd_3 cluster with a hydrogen molecule and illustrate all details of the process by the example of the addition of the H_2 molecule to the "three-dimensional" Pd_4 cluster. All the calculations were performed using the DFT B3LYP/HW method.

When an H_2 molecule approaches both singlet and triplet Pd_3 cluster, the intermediate species Pd_3H_2 is formed, in which hydrogen atoms are attached to one of the cluster vertices and are located symmetrically on different sides of the Pd_3 plane (C_s symmetry). The difference between the geometries of the singlet and triplet species is insignificant. Cleavage of the H–H bond in the case of the singlet system yields a species containing one hydrogen atom "above" the center of the Pd_3 triangle and the other, "below" one of the Pd–Pd bonds. The total energy gain in the reaction $Pd_3(^1D_{3h}) + H_2 \rightarrow Pd_3H_2$ (singlet channel) is ~164.0 kJ mol^{-1}.

There is another stable geometric configuration of the singlet system Pd_3H_2 in which both hydrogen atoms are located above the center of the Pd_3 triangle, but on its different sides. The energy difference between these two configurations of Pd_3H_2 is insignificant (~9.6 kJ mol^{-1}).

In the case of the triplet system, cleavage of the H–H bond yields a species of the C_2 symmetry in which hydrogen atoms are located above the neighboring Pd–Pd bonds on the different sides of the

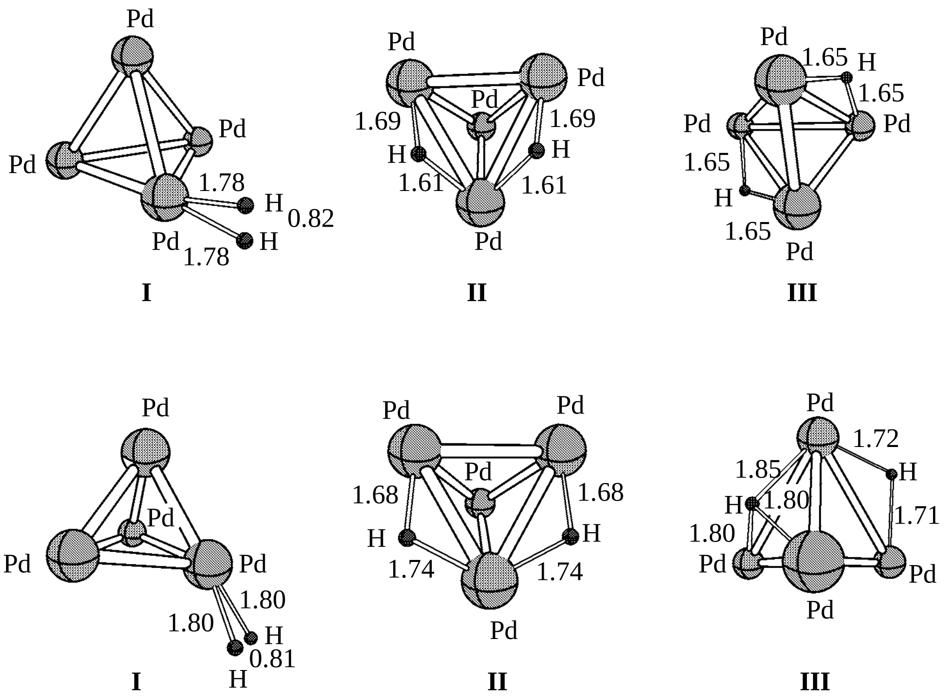

Fig. 1. Geometric structures of (a) singlet and (b) triplet systems Pd_4H_2 corresponding to the local minima on the potential energy surface.

Pd_3 plane. The total energy gain in the reaction $Pd_3(^3C_{2v})$ + H_2 → Pd_3H_2 (triplet channel) is ~67.5 kJ mol^{-1}. We failed to find any other geometric configurations of the triplet species under consideration.

We will consider the attachment of an H_2 molecule to palladium clusters in more detail using Pd_4 as an example. The first step of the reaction of an H_2 molecule with the Pd_4 cluster can be written as follows.

Singlet channel:

$$Pd_4(^1D_{2d}) + H_2 \rightarrow Pd_4H_2\ (\mathbf{I}) + 39.2\ \text{kJ mol}^{-1},$$

Triplet channel:

$$Pd_4(^3C_{3v}) + H_2 \rightarrow Pd_4H_2\ (\mathbf{I}) + 36.7\ \text{kJ mol}^{-1}.$$

Here Pd_4H_2 is stable complex **I** (Fig. 1). To estimate weakening of the H–H bond in this case, we scanned the potential energy surface of the system Pd_4H_2 along the direction corresponding to the elongation of this bond with full reoptimization of the system geometry at each chosen distance *R*(H–H). The potential curve of the H_2 molecule and sections of the potential energy surface of the system Pd_4H_2 for the two reaction channels are shown in Fig. 2. For these sections, the energy scale is shifted so that the energy of the system in the minimal point of the section coincides with the energy of the equilibrium geometry of the H_2 molecule (this energy is shown in Fig. 2 by a dotted line).

In the case of the singlet reaction channel, as *R*(H–H) increases from the minimal point of the potential curve, the energy of the Pd_4H_2 system smoothly increases up to the point corresponding to *R*(H–H) ~2.0 Å (point *A* in Fig. 2), and then it sharply decreases. In this point, the geometry of the whole system undergoes essential reorganization accompanied by the dissociation of the H_2 molecule. Full optimization of the geometry starting from point A results in a “spillover” of hydrogen atoms along the cluster edges with the formation of the stable singlet complex Pd_4H_2 (**II**) (Fig. 1) whose energy is lower than the energy of system Pd_4H_2 (**I**) by ~92.1 kJ mol^{-1}.

A similar pattern was obtained for the triplet reaction channel (Fig. 2). The reorganization of the system geometry with cleavage of the H–H bond occurs at *R*(H–H) ~2.5 Å, which is somewhat longer than in the case of the singlet system. However, the further evolution of the system leads to the triplet complex Pd_4H_2 (**II**) (Fig. 1) whose energy is higher than that of the triplet system Pd_4H_2 (**I**) by ~20.1 kJ mol^{-1}. At the same time, the overall reactions of the starting Pd_4 cluster with the H_2 molecule yielding stable Pd_4H_2

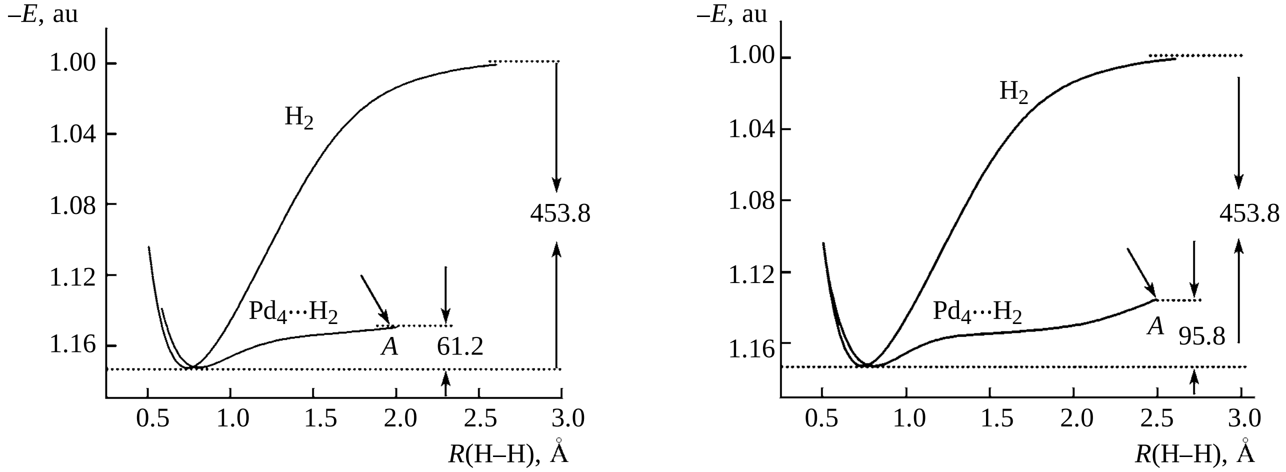

Fig. 2. Section of the potential energy surface of the system Pd_4H_2 (**I**) along the H–H bond [(a) singlet and (b) triplet channels]; (*A*) point of the onset of H_2 dissociation and formation of the complex Pd_4H_2 (**II**).

(**II**) (Fig. 1) are energetically favorable in both singlet and triplet cases.

Singlet channel:

$$Pd_4(^1D_{2d}) + H_2 \rightarrow Pd_4H_2\ (\mathbf{II}) + 131.3\ \text{kJ mol}^{-1},$$

Triplet channel:

$$Pd_4(^3C_{3v}) + H_2 \rightarrow Pd_4H_2\ (\mathbf{II}) + 16.6\ \text{kJ mol}^{-1}.$$

Both singlet and triplet Pd_4H_2 complexes can undergo further intramolecular rearrangement accompanied by a decrease in the total energy of the system. The singlet complex can pass from structure **II** to structure **III** (Fig. 1) with a ~22 kJ mol^{-1} decrease in the energy. In structure **III**, the hydrogen atoms are located above opposite edges of the tetrahedron, whereas in structure **II** they are located above adjacent edges. In the case of the triplet complex, "hanging" of one of the hydrogen atoms above an edge and of the other, above a face of the tetrahedron appears to be more favorable (Fig. 1, structure **III**). The energy gain from such rearrangement is only ~5 kJ mol^{-1}.

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