A theoretical study of the mechanism of oxidative dihydrogen addition to palladium clusters

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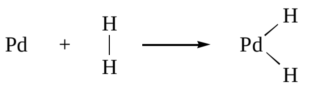
The mechanism of dihydrogen oxidative addition to the simplest palladium cluster has been analysed within the framework of the reaction-path Hamiltonian approximation; a planar dihydride complex has been found to form without the potential energy barrier and intramolecular degenerate exchange of the protons in the complex has been investigated.

The catalytic hydrogenation of unsaturated compounds is one of the most important chemical processes currently used in chemical synthesis and in industry. Its first step involves activation of the dihydrogen molecule. Under the conditions of heterogeneous catalysis the activation is carried out as dissociative dihydrogen chemisorption on the transition metal surface leading to formation of M–H bonds.[1] Under the conditions of homogeneous catalysis, in solution oxidative addition (OA) of the dihydrogen occurs to a transition metal atom within its complex and the oxidation number of the atom increases by two.[2] The OA of dihydrogen to transition metal atoms and small clusters also occurs in the gas phase,[3] according to mass spectrometry and ICR data. Both experimental and theoretical investigations of OA of dihydrogen to transition metal complexes and clusters as well as the dissociative chemisorption on the metal surfaces are of great interest in the development of theoretical models that might govern the creation of new, efficient catalytic systems.[4]

Palladium metal and its compounds are known to be very active hydrogenation catalysts,[5] hence a study of them is especially important.

According to the kinetic data,[6] among small Pd_n (n = 1–5) clusters the simplest Pd_2 cluster shows the highest activity in the dihydrogen OA in the gas phase.

The structures of the intermediates, transition states and products of the H_2 OA to bare palladium atom, reaction (1), were calculated by *ab initio* quantum chemical techniques including both correlation and relativistic effects,[7] as well as spin–orbit coupling.[8]

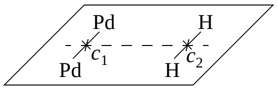


(1)

The geometries and energy values of the precursor complex, transition state and the reaction product (*i.e.*, PdH_2 dihydride) are given in refs. 7 and 8. We have developed the first dynamic model of reaction (1) within the framework of the reaction-path Hamiltonian approximation (RPH).[9]

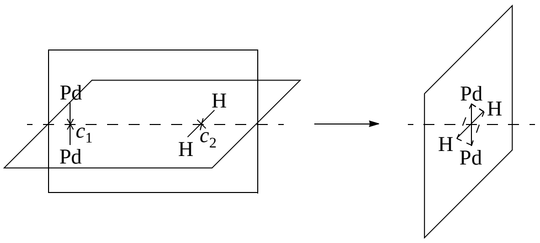
Nakatsuji *et al.* considered the $Pd_2 + H_2$ reaction as the simplest model process simulating the interaction of H_2 with the Pd metal surface.[10] They did not intend to study the entire potential energy surface (PES), but restricted themselves to a study of a tentative model trajectory for reactant approach. Both the molecules were presupposed to be lying in the same plane, while the Pd–Pd distance was fixed at 2.75 Å. The authors showed that the mutually parallel lateral orientation appeared to be the most favourable for the reactants approaching each other. They approach along the c_1–c_2 line (where c_1 and c_2 are the mass centres of the Pd_2 and H_2 fragments).

The calculations of the cross-sections of the PESs were made using the MC SCF formalism. A minimum on the PES was found to be as deep as 15 kcal mol^{-1} (here and below all energies are given with respect to the energy of the separated reactants, SR) for the structure with parameters:



R(Pd–H) = 1.78 Å, $r(c_1$–$c_2)$ = 1.5 Å, and r(H–H) = 0.85 Å. This value of r(H–H) is slightly higher than in an intact H_2 molecule where r(H–H) = 0.74 Å. The authors suggest that this structure is a model of the product of physical dihydrogen adsorption by the palladium metal surface. They showed that the PES in the vicinity of this minimum is essentially flat and within the $r(c_1$–$c_2)$ range 1.4–1.6 Å the energy is almost independent of r(H–H). Cross-sections of the PES for further scission of the H–H bond had been calculated at fixed $r(c_1$–$c_2)$ values and $r(c_1$–$c_2)$ = 1.5 Å appeared to be the optimum value. A second minimum on the model PES was found (E = –17.2 kcal mol^{-1}) at r(H–H) ~ 2.1 Å, and a potential-energy barrier as high as 3.4 kcal mol^{-1} was shown to separate the two minima. This second minimum is related to the structure with R(Pd–H) = 1.53 Å that corresponds exactly to the R(Pd–H) distance in a free PdH molecule.[11] The structure was considered to be a model of the dihydrogen chemisorbed by the palladium surface.

Blomberg *et al.*[12] investigated a different trajectory of H_2 OA to the Pd_2 cluster using the modified coupled-pair functional procedure and extended atomic basis sets. They suggested the H_2 and Pd_2 to approach in perpendicular planes while C_{2v} symmetry was conserved.



This trajectory seemed to lead to a different product without a potential-energy barrier. The product looks like a planar rhombus with bridging hydrogens, and its energy is –35.1 kcal mol^{-1}. They computed only the energies of structures which were presupposed to correspond to the stationary points of the PES, while their geometry parameters were taken from the corresponding structures of the $Pd_2 + CH_4$ reaction.

Castillo *et al.*[13] studied these and other trajectories. They investigated four possible directions of the H_2 OA to each of three lowest electronic states of the Pd_2 cluster using the MC SCF formalism. Potential curves as functions of $r(c_1$–$c_2)$ were calculated with the R(Pd–Pd) distance kept frozen at 2.75 Å (this value had been taken as the experimental distance between the atoms in the crystal lattice of metallic palladium). In particular, as in ref. 12, the deepest minimum (–65 kcal mol^{-1}, *cf.* –35.1 kcal mol^{-1} in ref. 12) for the ${}^1\Sigma_g^+$ term of Pd_2 was found for the product obtained at the mutually perpendicular

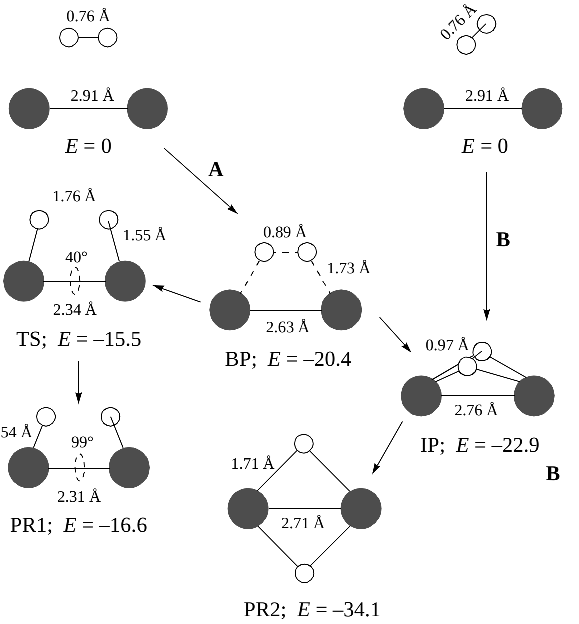


Figure 1 Structures and energies of the PES stationary points and scheme of H_2 OA to Pd_2. The energies are expressed in kcal mol^{-1} and measured with respect to the energy of the SR.

orientation of the approaching reactants, *i.e.* r(H–H) = 1.8 Å. The structure corresponding to the chemisorption complex from ref. 10 was the lowest of those from the planar approach if the four atoms were placed into the same plane, in agreement with ref. 10. Its energy is –37 kcal mol^{-1}, r(H–H) = 1.16 Å, R(Pd–H) = 1.54 Å.

The results cited above show the PES of the $Pd_2 + H_2$ to be of a complicated shape with several local minima, as well as possessing a relatively flat plateau. All calculations in refs. 10, 12 and 13 were carried out with fixed R(Pd–Pd) and the geometry optimisation was incomplete.

In order to obtain more detailed information on the PESs and dynamical behaviour of the molecular system (MS), we have studied the mechanism of the $Pd_2 + H_2$ reaction in terms of the RPH approximation.[14] The PESs were calculated using the CNDO/S^2 semiempirical technique developed specially to treat systems containing transition metals.[15] CNDO/S^2 was parametrised on the base of either experimental data or *ab initio* high-level calculations and proved to be a very suitable tool for study of methane and ethane OA to Pd atom and Pd_2 cluster.[9,16–18]

As a result of construction of the RPHs two trajectories (**A** and **B**) were discovered (Figure 1) and a connection between them was made. We have computed using the software in ref. 19 for both paths **A** and **B**:

– the $V_0(s)$ potentials along the minimum-energy path (MEP), *i.e.* reaction path (RP), where s is the intrinsic reaction coordinate (IRC);

– vibrational frequencies $\omega_i(s)$ of the modes orthogonal to the RP;

– $[B_{1j}(s)]$ functions of dynamic coupling between the motion along the RP and jth orthogonal vibrational mode, which determine the RP curvature.

We have found the following stationary points on the PES (Figure 1):

1. *Bifurcation point* (BP). The MS is of C_{2v} symmetry. We referred it to as ‘BP’ since there are two different vectors leading to the different products (*i.e.*, to the minima of the PES) of the OA, namely to either PR1 or PR2. $E_{BP} = -20.4$ kcal mol^{-1}, and r(H–H) = 0.89 Å, which is consistent with those of the adsorption complex in ref. 10. However, the Hessian matrix for BP has a negative eigenvalue ω^2_{RP} ($\omega_{RP} = 113i$ cm^{-1}) corresponding to rotation of the H_2 and Pd_2 fragments about the c_1–c_2 axis. This rotation transfers the MS from trajectory **A** to **B**.
2. *Transition state* (TS) *of C_2 symmetry.* $E_{TS} = -15.5$ kcal mol^{-1}, $\omega_{RP} = 271i$ cm^{-1}. The vector corresponding to the negative Hessian eigenvalue is of the χ^{PdH}_{PdH} type.
3. *Vicinal product* (PR1) *of C_2 symmetry.* $E_{PR1} = -16.6$ kcal mol^{-1}.
4. *Product of D_{2h} symmetry* (*i.e.*, planar rhombic product PR2). $E_{PR2} = -34.1$ kcal mol^{-1}.

As the MS moves along the IRC from the SR toward PR2, the potential energy falls monotonously, and C_{2V} symmetry is conserved. We have found a plateau on the PES where the norm of the energy gradient is least. The plateau contains an inflection point (IP, $\omega_{RP} \to 0$) that must be distinguished because it lies between two other inflection points and the two RPs (**A**) and (**B**) converge smoothly at this point. $E_{IP} = -22.9$ kcal mol^{-1}.

The whole mechanism of the reaction may be represented by three processes. Plots of the energy and the vibrational frequencies *vs.* the IRC for the three stages are shown in Figures 2–4.

The first step is the formation of a BP structure from the SR (Figure 2) along the **A** trajectory. In the region between SR and BP ($s < -3$) the vector corresponding to the IRC depends mainly on the variation in r(Pd–H). The modes other than stretching ones Q(Pd–Pd) ($\omega \approx 120$ cm^{-1}) and q(H–H) ($\omega \approx 4400$ cm^{-1}) are negligible.

In the vicinity of BP six non-zero modes arise owing to the interaction between Pd_2 and H_2. $\omega_4 \sim 1000$ cm^{-1} corresponds to the IRC (that is the approach of the H_2 and Pd_2 fragments). $\omega_5 \sim 1500$ cm^{-1} is related to the q^-(Pd–H) mode. $\omega_6 \sim 2660$ cm^{-1} is related to the q(H–H) mode, while $\omega_3 \sim 200$ cm^{-1} corresponds to the β-(Pd–Pd–H) mode. $\omega_2 \sim 140$ cm^{-1} is related to the vector containing mainly the variation in R(Pd–Pd). The frequency $\omega_1 = 113i$ cm^{-1} is related to the χ^{PdH}_{PdH} mode.

The second step, *i.e.*, formation of PR1 from BP *via* TS

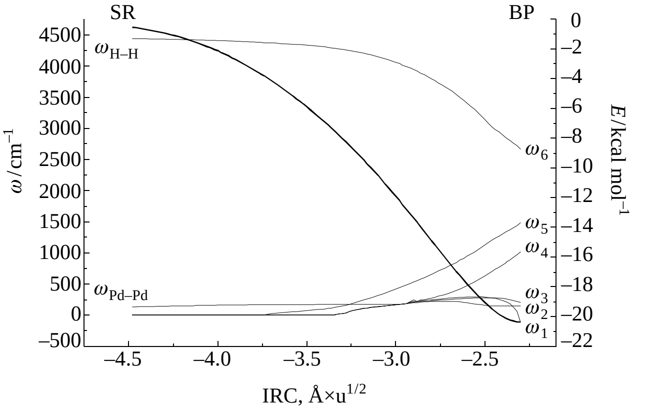


Figure 2 The potential (thick line) and the frequencies of the normal vibrations (thin lines) along the MEP of $Pd_2 + H_2$ leading from the SR to BP.

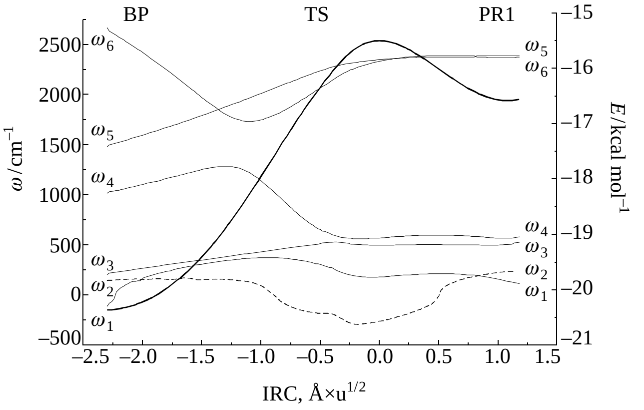


Figure 3 The potential (thick line) and the frequencies of the normal vibrations (thin lines) along the MEP of $Pd_2 + H_2$ leading from BP to PR1. The dashed line corresponds to the IRC.

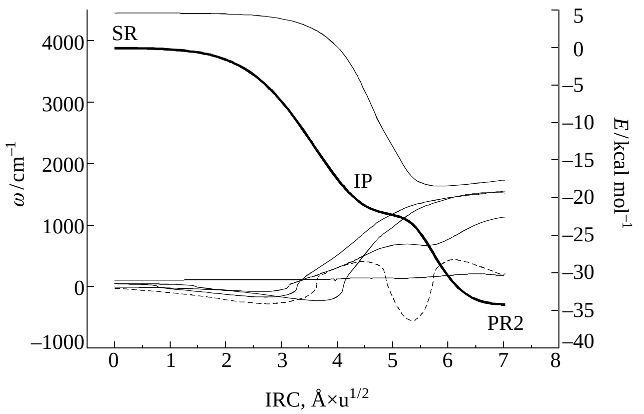


Figure 4 The potential (thick line) and the frequencies of the normal vibrations (thin lines) along the MEP of $Pd_2 + H_2$ leading from the SR to PR2. The dashed line corresponds to the IRC.

(Figure 3) is related to the changes in all the vectors and frequencies. Near BP the RP vector is of Q(Pd–Pd) shape. In the region between TS and BP the RP vector transforms to the $\chi^{\mathrm{PdH}}_{\mathrm{PdH}}$ mode with $\omega_2 = 270i$ cm^{-1} at TS, whereas the vector of $\chi^{\mathrm{HH}}_{\mathrm{PdPd}}$ shape at BP turns into the Q(Pd–Pd) mode with $\omega_1 = 270i$ cm^{-1}. The vector with ω_4 frequency (*i.e.*, the RP of the previous trajectory) becomes the β^+(Pd–Pd–H) mode.

In going from BP to TS the q(H–H) vector gradually turns into the q^+(Pd–H) mode. Thus, in the TS–BP region the frequencies of both stretching vibrations $\omega_6[q^+$(Pd–H)], and $\omega_5[q^-$(Pd–H)] (*ca.* 2300 cm^{-1}), as well as the frequencies of both the bending ones $\omega_4[\beta^+$(Pd–Pd–H)], and $\omega_3[\beta^-$(Pd–Pd–H)] (*ca.* 500 cm^{-1}) become closer to one another.

The other trajectory (**B**) is a composition of PR2 from SR *via* IP (Figure 4). In going from SR to IP six non-zero vibrational frequencies appear. ω_3–ω_6 correspond to four vibrations of complex shape and A_1, A_2, B_1, B_2 symmetry, respectively. The totally symmetric q(H–H) mode takes A_1 symmetry and becomes the q^+(Pd–H) mode. Near PR2 $\omega_6(A_1) \approx 1700$ cm^{-1}, $\omega_5(B_2) \approx 1550$ cm^{-1}, $\omega_4(A_2) \approx 1520$ cm^{-1}, and $\omega_3(B_1) \approx 1130$ cm^{-1}. ω_2 of Q(Pd–Pd) mode increases to 200 cm^{-1} near PR2.

In going from SR to IP the displacements in α(Pd–Pd–H) internals contribute mainly to the RP vector. In the vicinity of IP $\omega_1 \approx 500i$ cm^{-1}. In the region $s < 0$ the RP vector is represented by the $\chi^{\mathrm{PdH}}_{\mathrm{PdH}}$ mode. On the whole RP (**B**) C_{2v} symmetry is conserved.

In addition, we have investigated the process of permutation of the bridging hydrogens in PR2 (PR2 → IP → BP → IP → PR2). The MEP corresponding to the permutation is depicted in Figure 5. When the vibrational problem for this potential was solved, the PR2 was revealed to be of a non-classical structure. The half-width of the Boltzmann distribution function (BDF) *versus* θ(H–Pd–Pd–H) is *ca.* 70° at $T = 298$ K. The use of the PES for SR → IP → PR2 → IP → SR for the vibrational problem gives similar results.

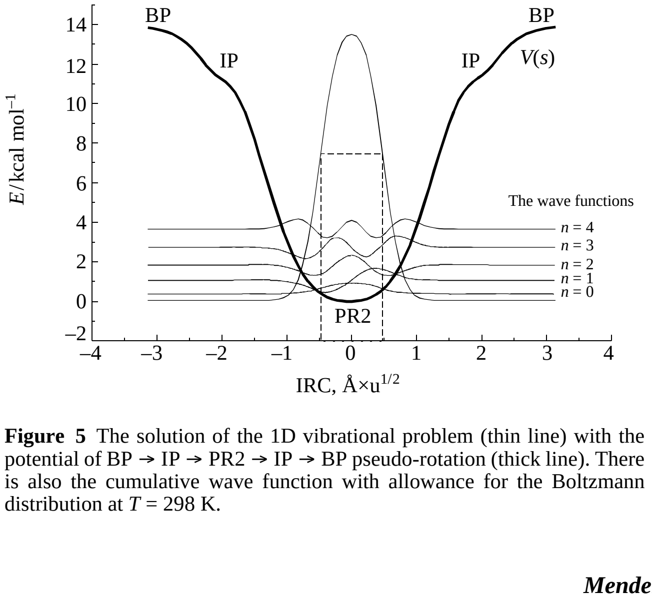
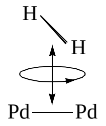


Figure 5 The solution of the 1D vibrational problem (thin line) with the potential of BP → IP → PR2 → IP → BP pseudo-rotation (thick line). There is also the cumulative wave function with allowance for the Boltzmann distribution at $T = 298$ K.

In order to estimate the dynamic effects in the reaction of H_2 OA to Pd_2 we have computed the dependence of the energy of the MS against two internals: $r(c_1–c_2)$ and the dihedral angle γ between the Pd–c_1–c_2 and H–c_1–c_2 planes. All internals other than $r(c_1–c_2)$ and γ were optimized in the course of calculation of the PES.



It appeared that when $r(c_1–c_2) > 1.5$ Å the rotation about the c_1–c_2 axis had little affect on the energy of the MS (the energy changed little more than 0.4 kcal mol^{-1}), which was evidence for free rotation of the H_2 over the Pd_2.

Additionally, the PES of the RR2 → IP → BP → IP → PR2 was analysed with fixed R(Pd–Pd) in the range 2.3–2.9 Å depending on $r(c_1–c_2)$ while r(H–H) was optimized. The results of the solution of the vibrational problem show that the half-width of the BDF for PR2 is governed by the R(Pd–Pd) bond length at $T = 298$ K. At R(Pd–Pd) = 2.7 Å the half-width of the BDF is equal to 0.8 Å. If R(Pd–Pd) shortens by *ca.* 0.2 Å the half-width of the BDF increases to 1.4 Å, and the H–H bond remains broken, since within such a range of the half-width of the BDF r(H–H) is close to 2 Å.

Probably, variation of the ligand environment in dimer complexes of Pd(0), and Pd(I), leading to change in the Pd–Pd bond length, may well be an important factor governing the half-width of the BDF in the products of the H_2 OA to such complexes and open up an opportunity to create efficient catalytic systems based on these complexes.

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