A theoretical study of the catalytic cycle of ethylene hydrogenation by a bipalladium cluster

Viktor M. Mamaev,*[a] Igor P. Gloriozov,[a] Dmitrii A. Lemenovskii[a] and Yurii V. Babin[b]

[a] *Department of Chemistry, M. V. Lomonosov Moscow State University, 119899 Moscow, Russian Federation.*
Fax: +7 095 938 8846; e-mail: vmam@nmr.chem.msu.su
[b] *Far Eastern State Academy of Economics and Management, 690091 Vladivostok, Russian Federation. Fax: +7 4232 40 6634*

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In terms of the reaction-path Hamiltonian formalism, the catalytic cycle of ethylene hydrogenation by the Pd_2 cluster has been found to involve 5 reactions with 10 stationary points on the potential-energy surface.

In the last 20 years, a great body of data concerning quantum-chemical studies of catalytic reactions with the participation of organometallic compounds were published. Among these reactions, which are important steps in the catalytic cycles of hydrocarbon conversion, are olefin addition,[1] oxidative addition and reductive elimination involving the activation of H–H, C–H and C–C bonds.[2–7] Recently, two reviews concerning the theoretical studies of catalytic reactions were issued.[8] However, a study of the full catalytic cycle involving a series of elementary reactions remains to be difficult to perform. Morokuma and co-workers performed theoretical studies of the full cycles of homogeneous olefin hydrogenation,[9] hydroboration[10] and hydroformylation[11] with a Rh^I complex catalyst. They also theoretically examined alkyne and alkene diboration with diphosphine complexes of Pd and Pt.[12] The reasons for the inactivity of C_2H_4 (a high barrier in the insertion of the hydrocarbon into a Pt–B bond and an endothermic effect) and of the palladium complex in alkyne diboration [the impossibility of the oxidative addition of a B–B bond to $Pd(PH_3)_2$ because of an endothermic effect and a very low barrier of 0.1 kcal mol^{-1} for a reverse process] were found. Albert *et al.*[13] examined a catalytic cycle of ethylene addition to phenyl bromide with the participation of a palladium complex with two diaminocarbene ligands. It was found that ethylene insertion into the Pd–Ph bond and β-hydride elimination (barriers from 8.3 to 11.5 kcal mol^{-1}) are the key steps of the catalytic cycle. The above studies involved calculations of the stationary points of elementary steps using *ab initio* and density functional theory (DFT) methods; based on these calculations, the potential-energy profile of the full catalytic cycle was chosen.

The aim of this work was to study theoretically the catalytic cycle of ethylene hydrogenation with the Pd_2 cluster. Previously,[14] we used the reaction-path Hamiltonian (RPH) approximation[15] for studying in detail the oxidative addition of the H_2 molecule to the Pd_2 cluster. We found that the potential-energy surface of this reaction exhibits a complex shape with several valleys and stationary points. A pseudo-square-planar complex with the energy of –34 kcal mol^{-1} with respect to separated reactants corresponds to the global minimum. A reaction path (RP) with no barrier leads to this complex. Another RP, *via* a bifurcation point and a transition state (TS), leads to the *trans*-product with the energy higher by 18 kcal mol^{-1}. In this work, we supplemented this reaction to the catalytic cycle of ethane formation from ethylene:

$$Pd_2 + H_2 \longrightarrow Pd_2H_2, \tag{1}$$

$$Pd_2H_2 + C_2H_4 \longrightarrow Pd_2 + C_2H_6. \tag{2}$$

The CNDO/S^2 semiempirical technique[16] was used for quantum-chemical calculations of PESs for complex molecular systems (MSs) including transition metal atoms on the basis of the RPH approach. The technique was parametrised on the basis of both experimental data and *ab initio* high-level calculations. We repeatedly used the above technique for studying the activation of H–H and C–H bonds by the Pd atom and the Pd_2 cluster.[7,14] Additional calculations were performed for the main stationary points of the PES using the DFT method in two approximations for exchange correlation energy (DFT-BLYP[17] and DFT-PBE[18]), which were implemented in the program.[19]

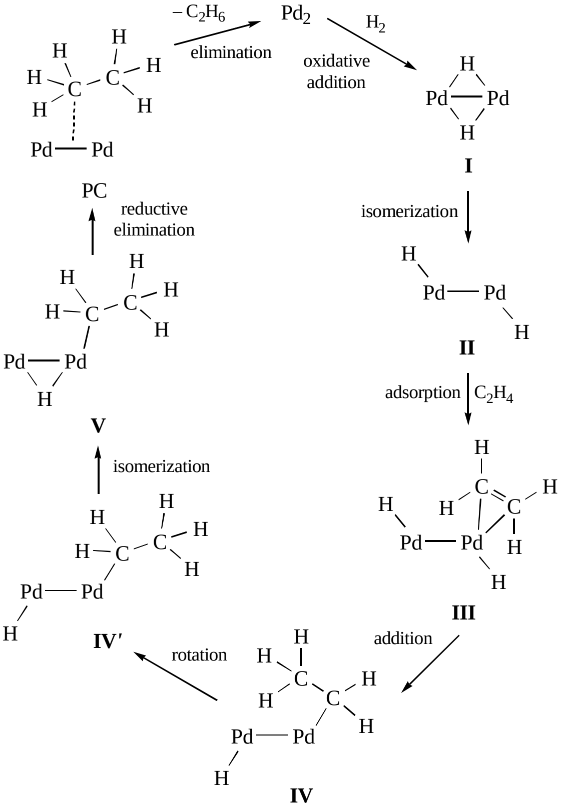

Figure 1 Schematic diagram of the catalytic cycle of ethylene hydrogenation by the Pd_2 cluster.

A detailed study of the PESs of reactions (1) and (2) by the CNDO/S^2 technique based on the RPH approach allowed us to separate five interrelated RPs (RP_1, RP_2, RP_3, RP_4 and RP_5), elementary steps of the full catalytic cycle. Figure 1 shows the schematic diagram of the cycle, Figure 2 — the potential-energy profile, and Figure 3 demonstrates the structures of the stationary points.

As mentioned above, RP_1 with no barrier from the separated reactants (SR) H_2 and Pd_2 leads to bridged pseudo-square-planar complex Pd_2H_2 **I** (Figure 3). The RPs are represented as the normal coordinate s with dimensions of Å $u^{1/2}$ (*i.e.*, the mass of proton is taken as unity). Reaction (1) was studied in detail elsewhere.[14] In further studies, we found that species **I** cannot add an ethylene molecule with hydrogen atom transfer, and it forms only an adsorption complex. *trans*-Form **II** was found to be active in the propagation of the catalytic cycle. The calculations of product **I** by the DFT-BLYP method are consistent with the CNDO/S^2 calculations, whereas DFT-PBE results in a lower energy, which can be explained by overestimated exchange and correlation contributions in the bridged structure (Figure 3).

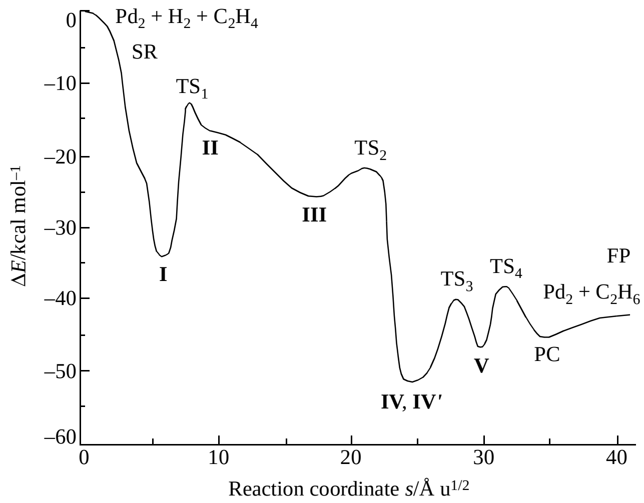

Figure 2 Potential-energy profile along the normal coordinate (s) of the catalytic cycle of ethylene hydrogenation by the Pd_2 cluster.

RP_2 corresponds to a change from pseudo-square-planar complex **I** to *trans*-reactant **II** in the separated reactants Pd_2H_2 and C_2H_4. The RP_2 vector involves a shortening in the Pd–Pd distance and an increase in the Pd–Pd–H plane angles. The energy of the system increased by 17.3 kcal mol^{-1} with a barrier of 21.5 kcal mol^{-1} (TS_1). The TS_1 saddle point exhibits the second imaginary frequency (ω_2), which corresponds to the rotational vibration of Pd–H bonds with respect to the Pd–Pd bond. The motion along the reaction path that corresponds to the rotational vibration leads to the *cis*-product which is higher than the *trans*-product in terms of energy.[14] The DFT calculations also gave similar results for the structures of stationary points (Figure 2). Note that they also gave two imaginary frequencies in TS_1. At the same time, for the planar *trans*-product, the DFT-BLYP method gave no minimum, and the potential barrier was 19.7 kcal mol^{-1}. On going to the DFT-PBE method, the potential barrier increased up to 28.2 kcal mol^{-1} with a decrease in the energy in product **II** by 1.3 kcal mol^{-1}. Note that a frequency (~50i cm^{-1}) corresponding to the RP_3 vector (approach of Pd_2H_2 and C_2H_4) was present in all stationary points calculated by the CNDO/S[2] and DFT methods. RP_3 consists of two portions: a gentle portion (coordination of an ethylene molecule to a palladium atom with the formation of intermediate **III**) with a decrease in energy (by 9.1, 9.3 or 10.8 kcal mol^{-1} according to the CNDO/S[2], DFT-BLYP or DFT-PBE method, respectively) at a long segment of 9 Å u$^{1/2}$ and a steep portion associated with synchronous rupture of the Pd–H bond, formation of a new C–H bond and transfer of the second H atom from a Pd atom to the other. The second region of RP_3 includes the transition state (TS_2) with a barrier of 4.3, 6.5 or 5.8 kcal mol^{-1} according to the CNDO/S[2], DFT-BLYP or DFT-PBE method, respectively. Next, the energy dramatically decreased to product **IV** (by 30.0, 20.9 or 18.6 kcal mol^{-1} ac-

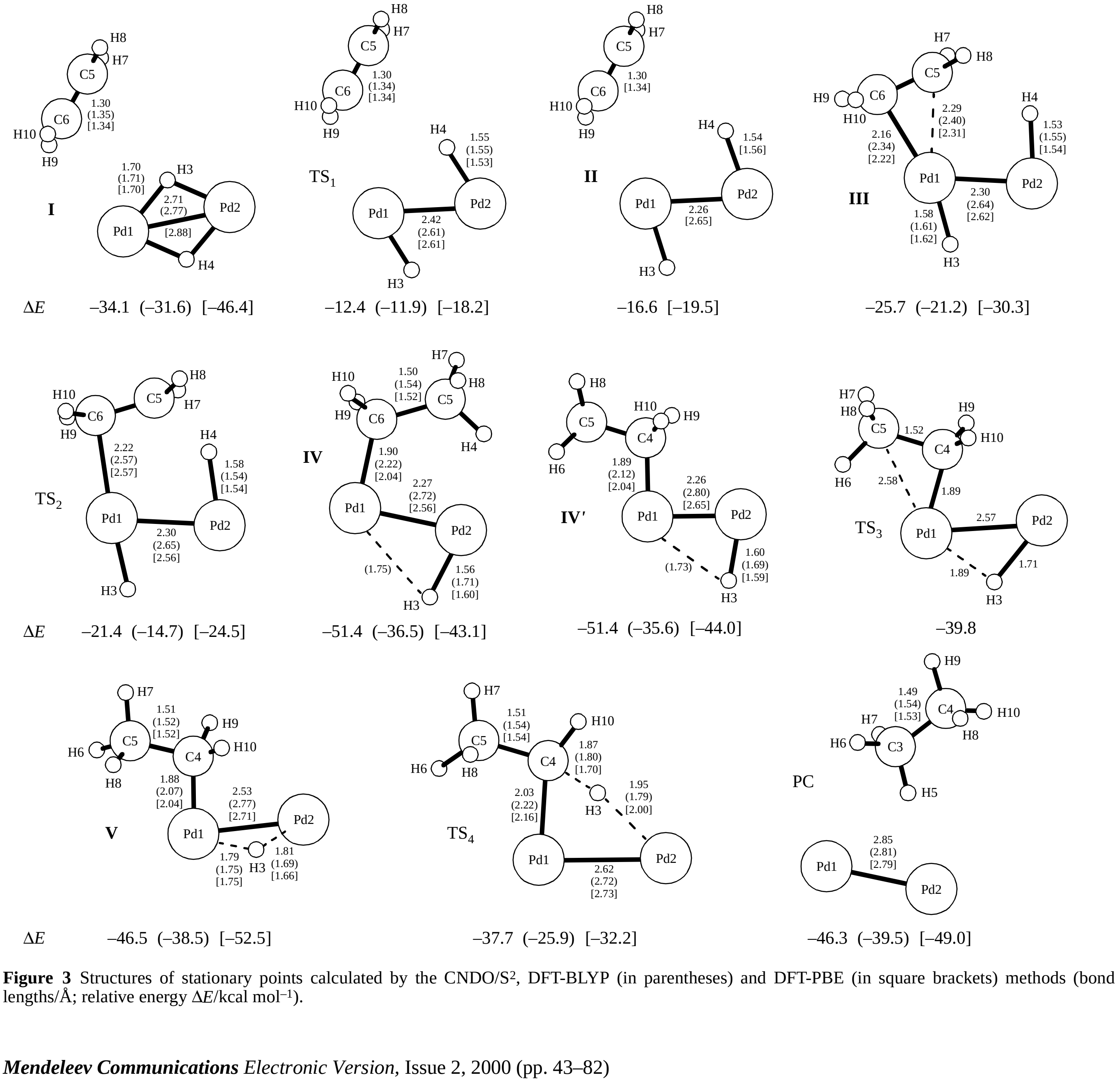

Figure 3 Structures of stationary points calculated by the CNDO/S[2], DFT-BLYP (in parentheses) and DFT-PBE (in square brackets) methods (bond lengths/Å; relative energy ΔE/kcal mol^{-1}).

cording to the CNDO/S^2, DFT-BLYP or DFT-PBE method, respectively). This latter is the *trans*-product of C–H bond activation in ethane (the CNDO/S^2 and DFT-PBE methods) or a bridged product (DFT-BLYP). The next portion of the catalytic cycle PES is associated with the vibrational mode analogous to RP$_1$.

The vector corresponding to RP$_4$ rearranges *trans*-product **IV′** (formed from **IV** by almost barrierless rotation about the Pd–C bond) to product **V** with the bridging bond Pd–H–Pd turned through 90° with respect to the C–Pd–Pd plane (Figure 3). As calculated by the CNDO/S^2 method, product **V** is higher than the *trans*-product by 4.7 kcal mol^{-1} in terms of energy; the barrier towards it (TS$_3$) is 11.6 kcal mol^{-1}, and the width is about 4 Å u$^{1/2}$. This barrier is an artefact of calculations by the CNDO/S^2 method, which overestimated the stability of products **IV** and **IV′** (according to DFT calculations, a barrier was absent in this process). However, even the potential barrier TS$_3 \approx 10$ kcal mol^{-1} obtained using the CNDO/S^2 method is no restriction for proceeding the catalytic cycle. Product **V** exhibit a vibrational mode that results in the final step of the catalytic cycle, reductive elimination of ethane.

The RP$_5$ vector involves an approach of the H$_3$ proton to the C$_4$ atom by rotation about the Pd–Pd bond from product **V** to the saddle point (TS$_4$) with an increase in energy by 9.4 kcal mol^{-1} (Figure 3). Next, from TS$_4$, the rupture of the bridging Pd–H–Pd bond and the formation of a new C–H bond occur synchronously to result in the pre-reaction complex (PC) of separated Pd$_2$ and C_2H_6 molecules (FP) with the energy higher than that in **V** by 0.4 kcal mol^{-1}.

The total positive energy effect of reactions of the catalytic cycle is 42.6 kcal mol^{-1}.

In conclusion, note that the results obtained by calculations using the CNDO/S^2 and DFT methods are in good agreement. Moreover, according to our data, the ethylene conversion into ethane proceeds only after the formation of *trans*-product **II** from pseudo-square-planar complex **I** (see RP$_2$). In this case, ethylene can initially interact only with one activated hydrogen atom (see RP$_3$). This fact is consistent with the experimental data[20] that hydrogen atoms escaped from Ni(111) bulk metal to the surface easily hydrogenate ethylene adsorbed on the surface to ethane. At the same time, according to experimental data, surface boundary hydrogen atoms do not exhibit hydrogenating activity; this is consistent with our conclusion on the inactivity of pseudo-square-planar complex **I**.

It is believed that bimetallic complexes that easily produce a *trans*-form by adding H$_2$ will be the most effective catalysts. The new catalytic system[21] based on the coordination of bimetallic transition metal clusters on metal porphyrins exhibits this property.

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