Theoretical study of oxidative methane addition to palladium clusters

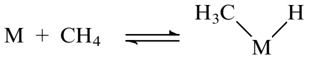
Victor M. Mamaev,* Igor P. Gloriozov, Vahan V. Simonyan, Andrew V. Prisyajnyuk and Yury A. Ustynyuk

Department of Chemistry, M. V. Lomonosov Moscow State University, 119899 Moscow, Russian Federation. Fax: + 7 095 932 8846; e-mail: vmam@nmr.chem.msu.su

The mechanism of oxidative addition of methane to palladium clusters has been analysed whithin the framework of the reaction-path Hamiltonian approximation, and the higher catalytic activity of the cluster compared to a bare Pd atom has been elucidated.

Activation of C–H bonds in alkanes is an essential and important step in their catalytic functionalization. One of the most challenging problems in modern hydrocarbon chemistry is to find chemical processes which allow this conversion to be carried out under conditions as mild and selective as biochemical ones.[1]

Oxidative addition (OA) of alkanes to either bare atoms or clusters of transition metals is one of the most promising methods of C–H bond activation.[2] Model reactions of this type have been studied by both theoretical and experimental methods. High level *ab initio* calculations have been performed for the structures corresponding to the most important stationary points on potential-energy surfaces (PES) for the simplest OA of methane to the first- and second-row transition metal bare atoms,[3–5] reaction (1). The results obtained opened up an opportunity to compare the catalytic activities of different transition metals. We have developed the first quantum dynamic model for reaction (1) (M = Pd)[6] within the framework of the reaction-path Hamiltonian (RPH) approximation.

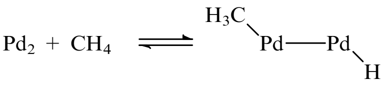

(1)

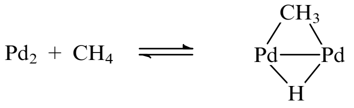
We have shown in ref. 6 that tunneling contributes mainly to the thermal rate constant at low temperatures.

A kinetic study of both methane and ethane OA to a bare Pd atom and Pd$_n$ clusters in the gas phase has shown the simplest Pd$_2$ cluster to be much more active than the Pd atom.[7] Blomberg *et al.*[8] have performed a theoretical investigation of methane OA to the Pd$_2$ cluster within the *ab initio* framework using extended bases (augmented with the f-AOs on Pd) and electron correlation. They showed that an isolated Pd$_2$ cluster had a triplet term 7 kcal mol^{-1} lower in energy than the singlet one. In contrast, for the reactive system the triplet state proves to be less stable than the latter. According to ref. 8, a planar pseudo-square complex (PR3)HPd$_2$Me corresponds to the global PES minimum. The corresponding precursor complex (PC3) and transition state (TS3) lie 8.8 and 12.9 kcal mol^{-1} higher in energy, respectively. The most interesting fact is that the saddle point (TS3) on the singlet PES is 0.8 kcal mol^{-1} *lower* in energy than the separated reactants. The *cis*-product and the *trans*-product (*cis*-PR2, *trans*-PR2) energies both calculated in the same bases proved 10.7 and 5.1 kcal mol^{-1}, respectively, higher than that of PR3. However, none of these structures was completely optimized, and an additional study is needed to conclude finally on the trajectory of the methane OA to the Pd$_2$ cluster. More recent calculations by Blomberg showed that due to a geometry optimization the energy of *trans*-PR2 fell below that of the PR3.[9] In general, the data from ref. 8 show good consistency with the experimental data in ref. 7.

In this communication we report a detailed study of the mechanism of reactions (2) and (3) in the RPH approximation.

The general approach developed in ref. 6, and the computer program for RPH construction written earlier[10] based on the semiempirical SCF CNDO/S^2 scheme[11] were employed in this study. The CNDO/S^2 formalism was developed specially to compute the PESs of reactions catalysed by transition metals.


(2)


(3)

We showed earlier that for reaction (1) the CNDO/S^2 scheme reproduces quantitatively both the barrier heights and the PES stationary point structures acquired from *ab initio* high level calculations.[3–5]

We assumed the Pd$_2$ cluster to be in the $^1\sum_g^+$ term. Preliminary test CNDO/S^2 calculations on the interatomic distance in the naked cluster have found an equilibrium at 2.91 A. The frequency of $Q_{\mathrm{Pd-Pd}}$ was found at 111 cm^{-1}. These results are consistent with *ab initio* data obtained with both relativistic and correlation corrections ($R_{\mathrm{Pd-Pd}}$ = 2.87 A, $\omega_{Q_{\mathrm{Pd-Pd}}}$ = 121 cm^{-1}).[12] Thus, the CNDO/S^2 scheme may well be used for our goals.

We have computed, using the software in ref. 10, for both reaction (2) and (3):

– the $V_0(s)$ potentials along the minimum energy path (MEP), *i.e.*, reaction path (RP), leading from the reactants to the products *via* a transition state (TS), where s is the intrinsic reaction coordinate IRC expressed in terms of mass-weighted Cartesian coordinates $[\mathrm{A}\times(\mathrm{amu})^{1/2}]$;

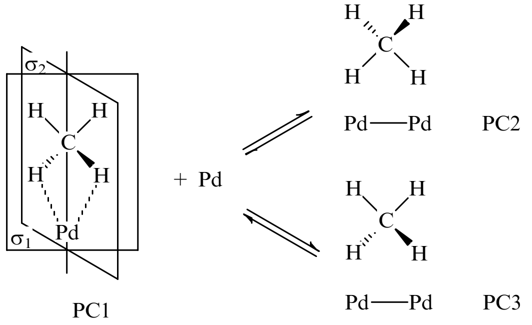
– vibration frequencies $\omega_i(s)$ of the modes orthogonal to the RP;

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

We have obtained the structures and reactive energies of both *cis*-PR2 and *trans*-PR2 quite similar to those in ref. 8, while the energies of PR3 and TS3 are by *ca.* 10 kcal mol^{-1} higher than those in reaction (2) (see Figure 1). Here we will discuss the reaction (2) data in more detail.

According to our results, the RP passes through the PES stationary points in the following order: precursor complex PC2, transition state TS2, intermediate *pseudo*-product *cis*-PR2, and the ultimate product *trans*-PR2. The structures of the stationary points are given in Figure 1, while Figure 2 displays their relative positions upon the RP. Note that the four structures are of C$_s$ symmetry. As with PC2 the two Pd atoms bind to the methane, so the PC2 minimum is three times deeper than that in reaction (1) (PC1, M = Pd; see Figure 1). In a special additional study we have found that in the course of approach of PC1, in the presence an extra bare Pd atom, either PC2 or PC3 may be formed, depending on which σ_v plane of the PC1 the Pd moves in.

Rotation of the methane about axes perpendicular to the Pd–Pd bond in PC2 and PC3 does not change the energy of the molecular systems (MSs) by more than 1 kcal mol^{-1}. Therefore, the geometry of the MSs is determined by



distribution functions derived from the Schrödinger equation for the internal rotation. As those functions are rather diffuse, so both PC2 and PC3 are stereochemically non-rigid structures.

In TS2 both the Pd atoms participate effectively in elongation and weakening of the C–H* bond. Therefore, TS2 appears earlier than does that in reaction (1) (TS1). In TS2 r(C–H*) is equal to 1.3 A, whereas in TS1 it is 1.5 A, the latter being closer to that in the alkylhydride complex MePdH PR1. In TS2 the frequency of q(C–H*) is less by a half than the methane q(C–H) A_1 vibration frequency (ω_{12}, see Figure 2), while in TS1 it diminishes only by 30%.[6] The potential-barrier height [without allowance for $\omega_i(s)$] falls by one order of magnitude in going from reaction (1) to reaction (2) (see Figure 1 and ref. 6). We have evaluated the RP curvature to be fairly small (< 1 A^{-1}), which allows us to use the vibrationally-adiabatic approximation to estimate the effect of the frequencies ω_i on the $V(s)$ potential along the RP, where N is the number of degrees of freedom of a reactive MS, $\hbar$ is the vector of the vibrational quantum numbers. As seen in Figure 3, the potential barrier of reaction (2) (all $n_i = 0$) reduces to zero, when the correction for the orthogonal vibration modes have been made, equation (1).

$$V(s) = V_0(s) + \sum_{j=2}^{3N-6} \left(\vec{n} + \frac{1}{2}\right)\hbar\omega_j(s) \qquad (1)$$

The motion of the MS along the RP from PC2 to *trans*-PR2 is followed by an essential shortening of R(Pd$^{(1)}$–Pd$^{(2)}$) (by *ca.* 0.5 A) with simultaneous migration of the H* atom toward the second Pd atom. Such shortening is typical of a transfer reaction for a light particle between heavy ones.[13]

The ω_1^2 eigenvalue corresponds to the VC1 Hessian eigenvector directed tangentially to the RP in the first stage of reaction (2). Since in the region of TS2 $\omega_1^2 < 0$, the ω_1 negative values optionally represent the imaginary frequency in Figure 1.

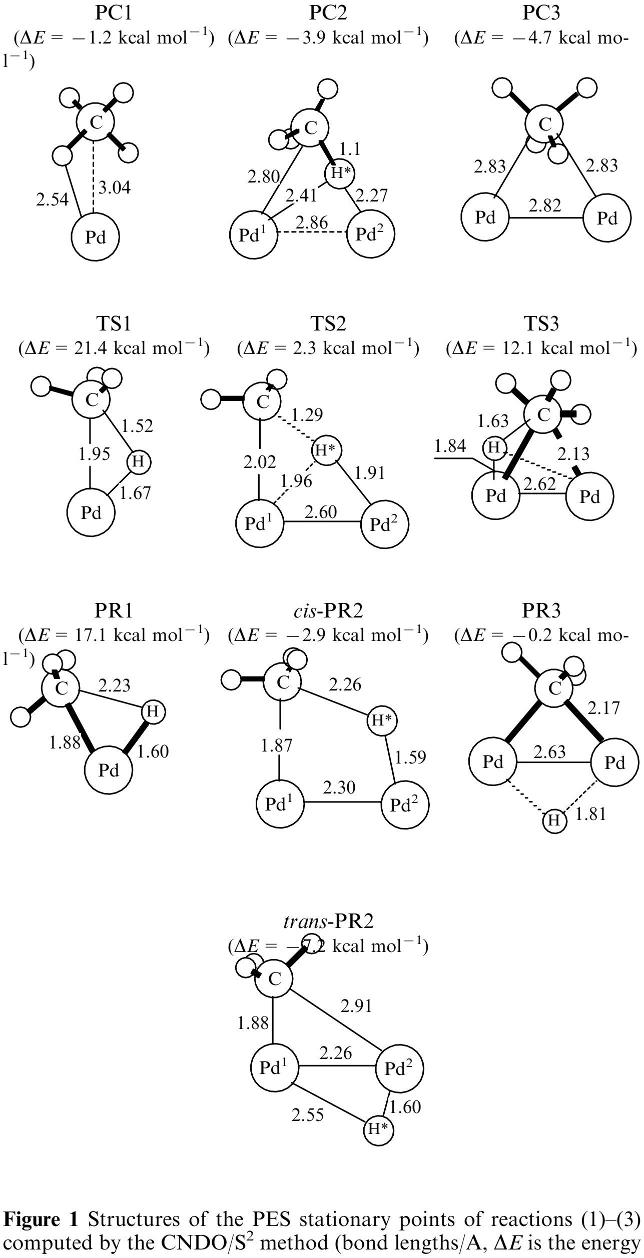


Figure 1 Structures of the PES stationary points of reactions (1)–(3) computed by the CNDO/S^2 method (bond lengths/A, ΔE is the energy with respect to the separated reactants).

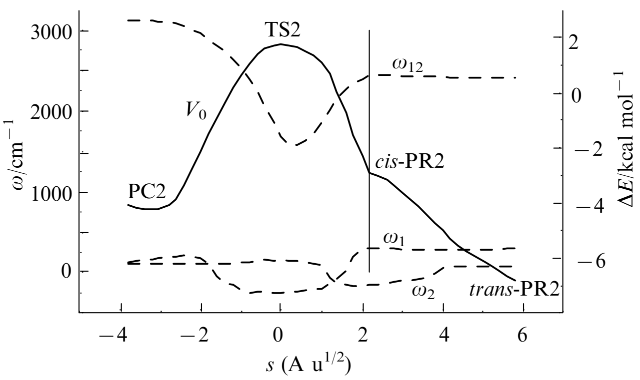


Figure 2 The $V_0(s)$ potential along the MEP (solid line) and the frequencies of the transverse vibrations (dashed lines). Shown are ω_{12} of most significant variation, and ω_1, ω_2 that correspond to the VC1 and VC2 vectors for the two stages of reaction (2).

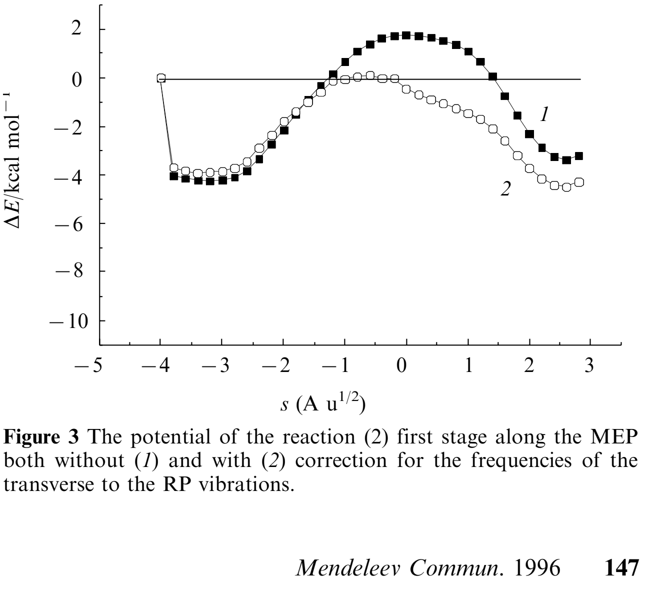


Figure 3 The potential of the reaction (2) first stage along the MEP both without (*1*) and with (*2*) correction for the frequencies of the transverse to the RP vibrations.

An analysis of the VC1 components shows that variations of r(C–H*) [or, β(C–Pd$^{(1)}$–H*)] and R(Pd$^{(1)}$–Pd$^{(2)}$) internal coordinates contribute predominantly to it. As the reactive molecular system (MS) moves from TS2 in the VC1 direction, $V_0(s)$ passes through a minimum near $s \sim 2.2$ (see Figure 2) which is referred to as *cis*-PR2. On the other hand, the stationary point is a saddle point with respect to the VC2 eigenvector (which is of the type $\chi^{\mathrm{PdH}}_{\mathrm{PdCH_3}}$; the ω_2^2 eigenvalue becomes negative). In fact, if the MS takes the VC2 direction (*i.e.* orthogonal to VC1) at this saddle point, the potential energy will further decrease leading to *trans*-PR2. One can see that during this internal rotation the potential energy diminishes by *ca.* 4 kcal mol^{-1} while the modes transverse to the RP remain unaffected.

After the Schrödinger equation for the potential function of $\chi^{\mathrm{PdH}}_{\mathrm{PdCH_3}}$ had been solved, *trans*-PR2 was revealed to be a non-classical stereochemically non-rigid structure. The half-width of the spatial distribution function of *trans*-PR2 reaches $\sim 120°$ at $T = 300$ K.

As mentioned above, shortening of R(Pd$^{(1)}$–Pd$^{(2)}$) in moving from PC2 (2.86 A) to TS2 (2.60 A), and further, to *trans*-PR2 (2.26 A) is a peculiar feature of reaction (2).

We are grateful to Professor M. R. A. Blomberg for her very stimulating remarks and information on the latest results of *ab initio* calculations for the $\mathrm{Pd_2 + CH_4}$ system, offered before publication. This study was supported by both the International Soros Science Foundation (grant no. MFC300) and the Russian Foundation for Basic Research (grant no. 94-03-09863).

References

1 *Activation and Functionalization of Alkanes*, ed. C. L. Nill, Wiley, New York, 1989.
2 A. E. Shilov, *The Activation of Saturated Hydrocarbons by Transition Metal Complexes*, Riedel, Dordrecht, 1984.
3 M. A. Blomberg, P. E. M. Siegbahn and M. Svensson, *J. Am. Chem. Soc.*, 1992, **114**, 6095.
4 J. J. Low and W. A. Goddard III, *Organometallics*, 1986, **5**, 609.
5 M. R. A. Blomberg, P. E. M. Siegbahn, V. Nagashima and J. Wennerberg, *J. Am. Chem. Soc.*, 1991, **113**, 424.
6 V. M. Mamaev, I. P. Gloriozov, S. Ya. Ishchenko, V. V. Simonyan, E. M. Myshakin, A. V. Prisyajnyuk and Yu. A. Ustynyuk, *J. Chem. Soc., Faraday Trans.*, 1995, **91**, 3779.
7 P. Fayet, D. M. Kaldor and J. Cox, *J. Chem. Phys.*, 1990, **92**, 254.
8 M. R. A. Blomberg, P. E. M. Siegbahn and M. Svensson, *J. Phys. Chem.*, 1992, **96**, 5783.
9 M. R. A. Blomberg, *private communication.*
10 V. V. Rusanov, I. P. Gloriozov and V. M. Mamaev, *Zh. Strukt. Khim.*, 1993, **34**, 170 [*J. Struct. Chem.* (*Engl. Transl.*), 1993, **34**, 326].
11 M. J. Filatov, O. V. Gritsenko and G. M. Zhidomirov, *J. Mol. Catal.*, 1989, **54**, 462.
12 K. Balasubramaniam, *J. Chem. Phys.*, 1988, **89**, 6310.
13 I. Yu. Skorynin, V. M. Mamaev and S. Ya. Ischenko, *Dokl. Akad. Nauk*, 1992, **325**, 329 [*Dokl. Chem.* (*Engl. Transl.*), 1992, **325**, 326].

Received: Moscow, 28th November 1995
Cambridge, 4th March 1996; Com. 5/07961F