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Tunnelling effects in the oxidative addition of a dihydrogen molecule to the palladium ethylenediphosphine complexes $[H_2P(CH_2)_2PH_2]Pd$ and $[H_2P(CH_2)_2PH_2]Pd_2$

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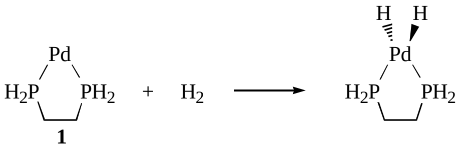
In terms of the reaction-path Hamiltonian formalism, the ligand environment has been found to have almost no effect on the activation barrier in the oxidative addition of H_2 to the title complexes (the under-barrier tunnelling in the reaction was predominant at $T < 230$ K).

The currently available technologies of oil and gas processing are based on high-temperature catalytic processes and result in high energy consumption. Therefore, it is important to develop new ways of activation of small molecules by transition metal complexes. Theoretical studies devoted to the activation of unsaturated bonds are few in number. As a rule, a static quantum-chemical model is used, which describes the reaction kinetics and mechanism only in terms of energy and geometry of the structures corresponding to the stationary points of potential energy surfaces (PES). Nevertheless, the oxidative addition of dihydrogen implies a substantial contribution of tunnelling to the overall kinetics of the reaction. This contribution can be estimated only by a dynamic model developed using the reaction-path Hamiltonian (RPH)[1] formalism, which includes an analysis of dynamic structures of stationary points on PES.

We report here a quantum-chemical study of the oxidative addition of the hydrogen molecule to $[H_2P(CH_2)_2PH_2]Pd$ complex **1** taking into account a contribution of tunnelling to the overall reaction rate constant:



(I)

Complex **1** can be used as a model of an unsaturated 14-electron palladium complex with bis(diphenylphosphino)ethane, whose active participation in the activation of small molecules was found experimentally.[2]

The oxidative addition of hydrogen and methane molecules to transition metal atoms, clusters and complexes was not examined by *ab initio* methods in the RPH approximation taking into account a tunnelling contribution to the thermal rate constant. With the use of high-level *ab initio* methods, the consideration was usually restricted by calculations of stationary points or a unidimensional potential depending on the interior coordinate.[3] Note that, even in the calculation of PES stationary points of the activation of H–H and C–H bonds by transition metals and their complexes, the results of the calculations significantly depended on the *ab initio* method used. The reaction energies for the activation of a C–H bond by Pd and Ni atoms (E) were compared in ref. 4. The energies were calculated by *ab initio* methods of two levels, which were different in the size of the basis and in the consideration for the electron correlation (Large: IC-ACPF, large basis, CH-correlation. Standard: CCI + Q, standard basis, no CH-correlation). In the case of Pd, E = 9.1 kcal mol^{-1} (Large) and 17.6 kcal mol^{-1} (Standard); in the case of Ni, E = = –3.3 kcal mol^{-1} (Large) and 4.3 kcal mol^{-1} (Standard). Hence it follows that, with the use of *ab initio* methods, it is also difficult to calculate the most accurate values of relative energies for stationary points. As for the applicability of the density functional theory (DFT), which significantly shortens the calculation time and is a good alternative to the *ab initio* method with correlation corrections, it gives a minimum in the Pd + H_2 system only for the pre-reaction complex with the H–Pd–H angle 28° and the distance R(H–H) = 0.85 Å. This is in contradiction with the most accurate calculations.[5] We obtained a similar result by calculating the molecular system under discussion using the DFT method.

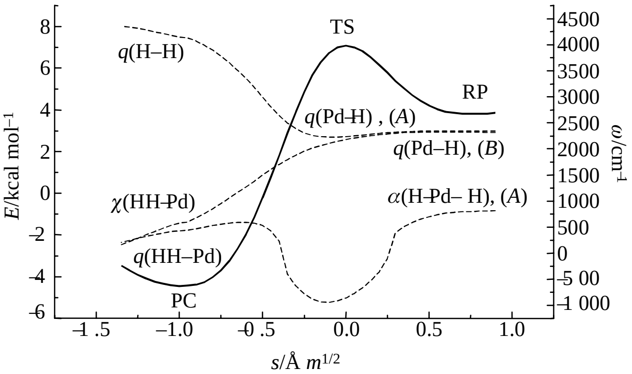


Figure 1 Potential $V_0(s)$ of the $[H_2P(CH_2)_2PH_2]Pd + H_2$ reaction (thick solid line) and frequencies of the most important normals against the reaction coordinate s (m is the proton mass).

The calculations of PES were performed by the CNDO/S^2 method.[6] This semiempirical method was specially developed for calculating PES of molecular systems containing transition metals. The method was parametrised on the basis of both experimental data and high-level *ab initio* calculations. It was reliable in a study of the activation of H–H and C–H bonds by the Pd atom and Pd_2 cluster.[7] Relative energies and geometry parameters of the stationary points were also calculated by the *ab initio* Hartree–Fock (HF) and MP2 methods from the GAMESS program package[8] in the 6-31G(d) basis set with the SBK pseudo-potential[9] on the palladium atom (Table 1). For comparison, Table 1 also includes data[10] on the high-level calculations (MP4) of methane

Table 1 Relative energies and geometry parameters (bond lengths in Å) of stationary points on PES in reaction (I).

	Method	E/kcal mol^{-1}	r(H–H)	r(Pd–H)	∠H–Pd–H	r(Pd–P)
PC	CNDO/S^2	−5.3	0.82	2.19	21°	2.72
	HF	−1.5	0.75	2.07	21°	2.47
	MP2	−1.5	0.82	1.85	25°	2.29
	MP4[10]	−5.1	—	—	—	2.32
TS	CNDO/S^2	6.2	1.31	1.60	48°	2.66
	HF	13.3	1.32	1.59	49°	2.52
	MP2	5.0	1.39	1.65	50°	2.34
	MP4[10]	—	—	1.56	—	2.38 2.46
RP	CNDO/S^2	3.0	1.95	1.55	78°	2.54
	HF	10.1	1.93	1.57	76°	2.50
	MP2	4.0	1.89	1.62	71°	2.33
	MP4[10]	—	—	1.55	—	2.39 2.45

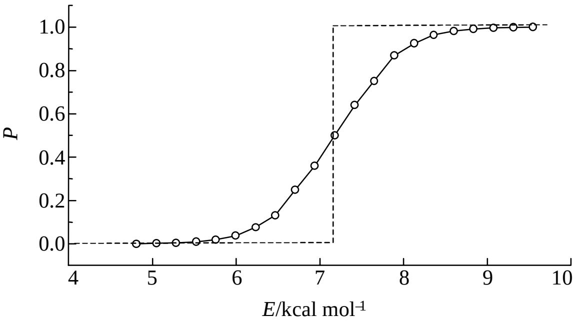


Figure 2 Reaction probability $P(E)$ for the reactions of $[H_2P(CH_2)_2PH_2]Pd$ with dihydrogen. The Heaviside function is designated by a dotted line.

C–H bond activation by complex **1**.

It can be seen in Table 1 that the stationary points found by different methods are rather close in geometry (except for Pd–P bond lengths, which were overestimated by the CNDO/S2 method as well as by *ab initio* calculations without considering the correlation energy) and comparable in energy; this fact confirms the reliability of our results. Note that, for stationary points of the Pd + H_2 reaction, the results of the CNDO/S2 calculations[11] are consistent with the *ab initio* calculations by Low and Goddard.[5(*a*)] We plotted the RPH for the oxidative addition of H_2 to complex **1** and calculated the $V_0(s)$ potential along the reaction path (RP) and the vibration frequencies $\omega_i(s)$ of modes orthogonal to RP, where s is the reaction coordinate expressed in weighted Cartesian coordinates. We found that the reaction path passes through three stationary points on PES: pre-reaction complex (PC), transition state (TS), and reaction product (RP). The molecular system retained the axis of symmetry C_2. The dependence of the energy and vibration frequencies orthogonal to RP on the reaction coordinate s for reaction (I) is presented in Figure 1 (vibration frequencies that change insignificantly during the reaction are not presented; the region in which the frequency exhibits imaginary values is represented by the negative semi-axis).

In the PC region, the reaction coordinate is the vibration with the frequency $\omega_{q(Pd–H\ H)} = 206\ cm^{-1}$ corresponding to the motion of H_2 to the Pd complex. The vibration frequency of H–H is close to that in the dihydrogen molecule [q(H–H) = 4390 cm^{-1}]. The third vibration with a low frequency [ω_χ(HH–Pd) = 200 cm^{-1}] corresponds to the rotation of hydrogen about the line connecting the palladium atom with the centre of the H–H bond. The geometry of the complex in the PC region remains almost unchanged as compared to the separated structure. The Pd–H bond length indicates a weak interaction of the dihydrogen molecule and the Pd atom: the Pd–H bond order is less than 0.1.

An analysis of the RP vector shows that, in the TS region at $s > -0.5$, the change in the system geometry is mainly determined by a change in one internal coordinate, namely, $\alpha_{(H–Pd–H)}$ [in TS, $\omega_{\alpha(H–Pd–H)} = 944i\ cm^{-1}$).

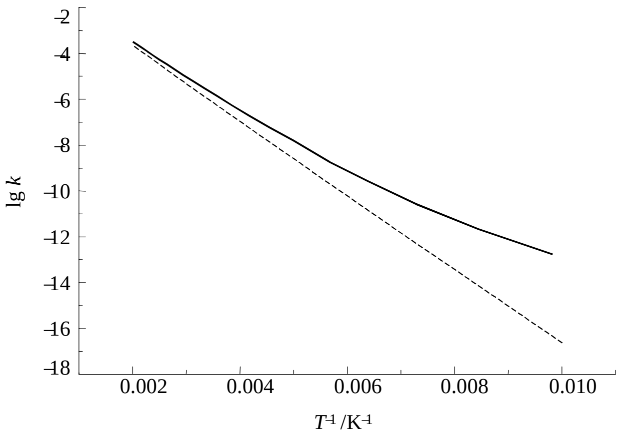


Figure 3 Temperature dependence of the logarithms of the overall quantum (solid) and classic (dotted) rate constants for the $[H_2P(CH_2)_2PH_2]Pd + H_2$ reaction.

During the motion along RP, the q(H–H) vibration of the H_2 molecule is transformed into the stretching vibration q^+(Pd–H) (symmetry A), and the free rotation of the H_2 molecule about the axis perpendicular to the C_∞(H–H) axis (whose frequency is equal to zero in the separated reactants) is transformed into the stretching vibration q^-(Pd–H) (symmetry B). In the region from PC to TS, a considerable decrease in the vibration frequency of the H–H bond q(H–H) exceeds an increase in the rotation frequency of the dihydrogen molecule χ(H–H). As the result, taking account of the frequencies [see equation (2)] leads to a decrease in the reaction barrier (unlike that in the Pd + H_2 reaction[11]).

In the TS and RP regions, the Pd–H bond length in the complex structure changes especially strongly. In the PC region, the bond has the distinct *s*-character, and *d*-orbitals do almost not participate in the bond formation, while the Pd–H distance decreases due to *sd*-hybridization in the TS and RP regions.

The overall thermal rate constants of the bimolecular reactions were calculated in terms of the transition state theory with tunnelling correction:[12,13]

$$k(n,T) = \frac{1}{\sqrt{2\pi\mu k_B T}} \int_E^\infty P(n,E)\exp\left(-\frac{E}{k_B T}\right)dE \qquad (1)$$

where μ is the effective mass of motion of the molecular system (MS) along RP, k_B is the Boltzmann constant, E is the energy of collisions of particles and $P_n(E)$ is the probability of the reaction in the case when reactants considered as MS exist in the nth vibrational state ($n = \{n_1, n_2, ..., n_{3N-7}\}$ is the vector of quantum numbers, and N is the number of atoms of MS).

The probability of the reaction $P_n(E)$ was calculated in the quasi-classic approximation[12] with vibration-adiabatic functions $V(n,s)$:

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

Plotting RPH makes it possible to calculate the dependence of the frequencies of transversal vibrations on the reaction coordinate. Taking account of these frequencies can change substantially both the height and the shape of the energy barrier. Moreover, the effect of selective vibrational excitation on the shape of the potential curve and, hence, on the kinetics of reactions can be analysed.

Note that, in the reaction at temperatures below 500 K, the population of vibrational levels is insignificant (< 1%), except for the ground state. Therefore, all data presented below are related to the ground vibrational level ($n = 0$).

Figure 2 illustrates the results of calculations of the probabilities $P(E)$ for reaction (I). As in the case of the reaction of the palladium atom with the dihydrogen molecule, tunnelling and repulsion from the barrier make a great contribution to the reaction probability. Therefore, these quantum effects should be taken into account in the calculation of the thermal rate constant. The account of them results in the deviation from the linear dependence of the logarithm of the overall thermal rate constant on the inverse temperature (Figure 3).

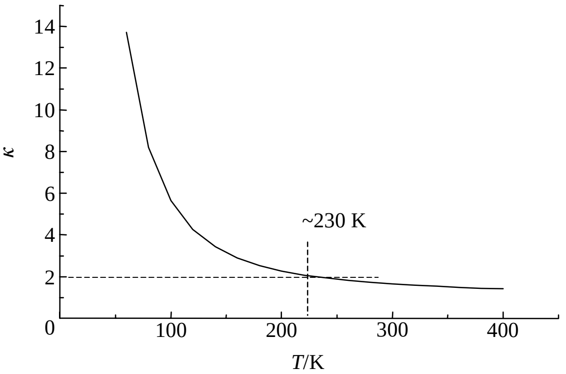


Figure 4 Temperature dependence of the transmission coefficient for the $[H_2P(CH_2)_2PH_2]Pd + H_2$ reaction.

The integral in the expression for the rate constant [equation (1)] can be presented as the sum:

$$\int_0^{\infty} P(0,E)\exp(-\frac{E}{k_{\mathrm{B}}T})\mathrm{d}E = \int_0^{V_{\max}} P(0,E)\exp(-\frac{E}{k_{\mathrm{B}}T})\mathrm{d}E + $$

$$+ \int_{V_{\max}}^{2V_{\max}} P(0,E)\exp(-\frac{E}{k_{\mathrm{B}}T})\mathrm{d}E + \int_{2V_{\max}}^{\infty} \exp(-\frac{E}{k_{\mathrm{B}}T})\mathrm{d}E \qquad (3)$$

where $V_{\max}$ is the potential barrier.

The first term corresponds to the under-barrier particle flow, and the latter two terms correspond to the over-barrier particle flow through the barrier. This makes it possible to estimate separately the under-barrier (tunnelling) and over-barrier (activation) contributions to the rate constant. It was accepted that $P(E) = 1$ at $E > 2V_{\max}$.

The temperature dependence of the transmission coefficient was calculated for the quantitative estimation of the tunnelling contribution to the total rate constant (Figure 4).

$$\kappa(T) = k^{\mathrm{total}}(T)/k^{\mathrm{activation}}(T) \qquad (4)$$

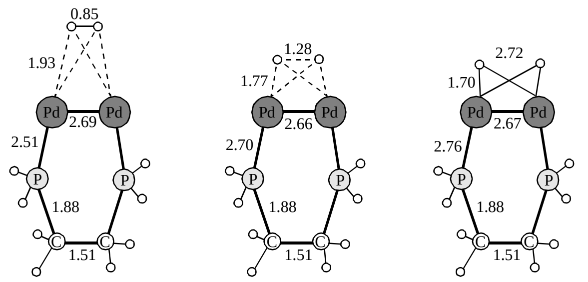
It is evident that at $\kappa > 2$ the tunnelling contribution to the rate constant is higher than the activation contribution. Thus, PES in the RPH approximation and the kinetics of reaction (I) with account of tunnelling have been completely analysed for the first time.

An analysis of the mechanism of activation of the H–H bond shows that the $[H_2P(CH_2)_2PH_2]Pd + H_2$ reaction is similar to the $Pd + H_2$ reaction in both the geometry of stationary points and the activation barriers, except for the fact that the account of vibration frequencies results in a decrease in the barrier of reaction (I), unlike that of the $Pd + H_2$ reaction.[11] The kinetic behaviours of these reactions are also similar. For example, tunnelling also predominates in reaction (I) at temperatures below 230 K. At room temperature, the contribution of tunnelling to the reaction rate constant is about 25%.

It is well known that the ligand environment at the Pd atom increases the activation barrier of oxidative addition of small molecules as, for example, in the $Pd(PH_3)_2$ and $PdCl_2(PH_3)_2$ complexes.[14] In this case, the use of $H_2P(CH_2)_2PH_2$ as the ligand did almost not affect the potential barrier as compared to that in the activation of H_2 by the Pd atom. Fayet *et al.*[15] experimentally examined the activation of small molecules by Pd_n clusters (n = = 1–25). Neutral palladium clusters were found to be much more active than atomic palladium. Maximum activities were observed for Pd_2 and $Pd_{n>5}$. Earlier,[7] we also theoretically studied the activation of a dihydrogen molecule by the Pd_2 cluster and found that its activity is higher than that of the Pd atom. The next step was a study on the oxidative addition of a dihydrogen molecule to the hypothetical complex $[H_2P(CH_2)_2PH_2]Pd_2$ **2**. The RPH was constructed, and the stationary points were found. A rather deep potential well (E_{PC} = –8. 6 kcal mol^{-1}) corresponds to the optimised PC structure (C_2 symmetry). The dihydrogen molecule is perpendicular to the plane of the complex, and r(H–H) = 0.85 Å. The TS and RP exhibit the same symmetry (Figure 5). The energies of all optimised structures on the PES are lower than the energy of the separated reactants (SR); that is, the reaction is formally barrierless and exothermic. However, we suggested that the formation of RP from TS is the rate-limiting step and performed corresponding calculations for this step. Taking into account the frequencies of vibrations transverse with respect to the reaction path results in a significant decrease in the barrier height (from 5.1 to 3.8 kcal mol^{-1}). Tunnelling was found to be predominant below 100 K, whereas at high temperatures the reaction mainly proceeds by an activation mechanism.

In conclusion, activation of the H–H bond by the binuclear palladium complex with ethylenediphosphine significantly lowers the barrier for oxidative addition of a dihydrogen molecule as compared with the mononuclear complex. In this case, the energy of the TS becomes lower than that of the SR.

Thus, catalytic systems designed on the basis of binuclear cyclic complexes of transition metals (palladium) will exhibit higher activation ability, as compared with the corresponding mononuclear complexes.



PC TS RP

Figure 5 Structures of the stationary points of the reaction $[H_2P(CH_2)_2–PH_2]Pd_2 + H_2$ (bond lengths in Å).

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