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A theoretical study of the mechanism of oxidative methane addition to the palladium ethylenediphosphine complex $[H_2P(CH_2)_2PH_2]Pd$ with consideration for tunnelling

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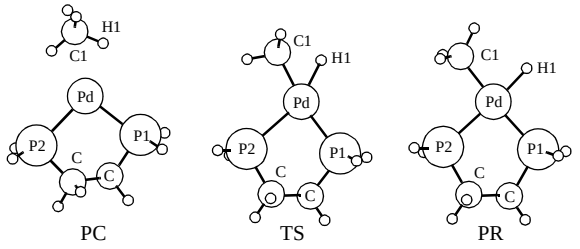
In terms of the reaction-path Hamiltonian formalism, tunnelling has been found to make the major contribution to the rate constant of methane activation by the title complex at $T < 270$ K.

Previously,[1] we found that tunnelling was predominant in the reaction of hydrogen molecule activation by ethylenediphosphine complex $[H_2P(CH_2)_2PH_2]Pd$ **1** at temperatures below 230 K, and the energy parameters of stationary points are similar to those of the activation by the palladium atom. Recently,[2] the geometries and energies of structures at the stationary points of the potential energy surface (PES) of oxidative addition of methane to complex **1** were calculated using the MP4 method. Separated reactants (SR), the prereaction complex (PC), the transition state (TS), and the reaction product (PR) are related to the stationary points.



In this work, we used the reaction-path Hamiltonian (RPH) formalism[3] based on the CNDO/S[2] semiempirical technique.[4] This semiempirical technique was specially developed for calculating the PESs of molecular systems (MSs) containing transition metals. The technique was parametrised on the basis of both experimental data and *ab initio* high-level calculations and proved to be reliable in studies of the activation of H–H and C–H bonds by Pd atoms and Pd_2 clusters.[5] Additional calculations were performed for the stationary points using the DFT method in two approximations for exchange correlation energy (DFT-BLYP[6] and DFT-PBE[7]), which were implemented in the program.[8] Table 1 summarises the results of calculations of the geometry parameters and relative energies of stationary points using different techniques. It can be seen that semiempirical and nonempirical calculations gave consistent results.

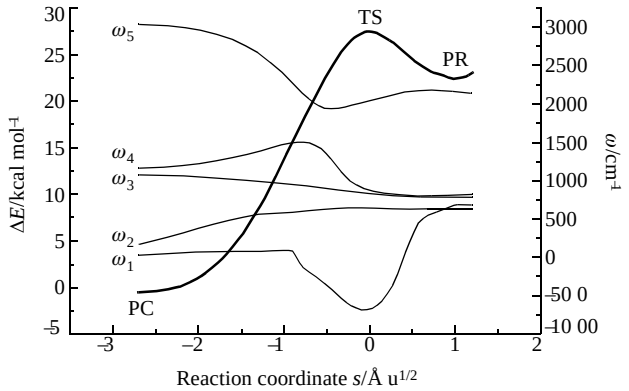


Figure 1 Potential (thick solid line) and frequencies normal vibrations (thin lines) along the minimum-energy path of the $[H_2P(CH_2)_2PH_2]Pd + CH_4$ reaction.

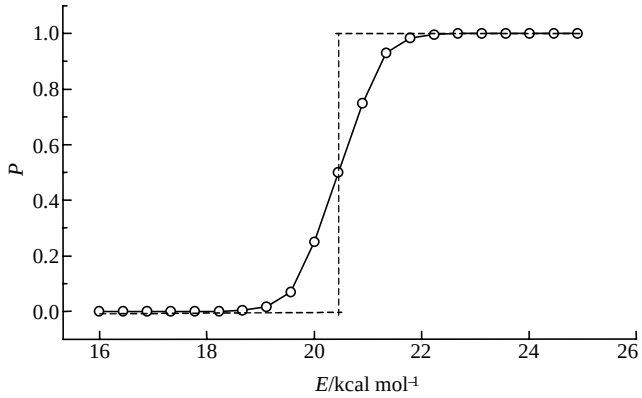


Figure 2 Reaction probability $P(E)$ for the reactions of $[H_2P(CH_2)_2PH_2)Pd$ with methane (open circles). The Heaviside function is designated by a dotted line.

Using the RPH approximation, we calculated the $V_0(s)$ potential along the reaction path (RP), represented as the normal coordinate s with dimensions of Å u$^{1/2}$ (*i.e.*, the mass of proton is taken as unity), and the vibrational frequencies $\omega_i(s)$ of modes orthogonal to the RP for the oxidative addition of CH_4 to complex **1**. Figure 1 shows the energy and frequencies of vibrations orthogonal to the RP *versus* the reaction coordinate s (imaginary values are arbitrarily shown as negative values). The frequencies of vibrations transverse to the RP in the PC region are very similar to the vibrational frequencies of the methane molecule and the skeleton of the complex. The vector corresponding to the reaction coordinate Q(Pd–C H) with the frequency ω_1 is responsible for the approach of the methane molecule to complex **1**. In the PR region, the vibration that corresponded to the q(C–H) vi bration in the PC region becomes the stretching vibration q(Pd–H) with the frequency $\omega_5 \sim 2500$ cm^{-1} . Two bending vibrations (with the frequencies ω_3 and ω_4) that correspond to the vibrations α(H–C–H) in methane turned into the bending vibrations β(Pd–C–H). The torsional vibrations of a methyl group (they are not given in Figure 1) exhibit a low frequency of 100 cm^{-1} along the entire RP. Skeleton vibrations, which did not undergo dramatic changes, are also not shown. The ratio between the contributions from shifts of various internals to the RP vector on moving along the RP considerably changed, as in the case of the Pd + CH_4 reaction. In the PC region, shortening of the R(Pd–C) and R(Pd–H) distances, which describe the approach of the Pd atom and the CH_4 molecule as a whole, primarily contribute to the RP, whereas the CH_4 geometry changes insignificantly. In the TS and PR regions, a change in the α(H–P d–C) angle gave the major contribution to the reaction coordinate.

The overall thermal rate constants of the bimolecular reactions were calculated in terms of the transition state theory with tunnelling correction:[9,10]

Table 1 Relative energies (ΔE) and geometry parameters of stationary points in the reaction of methane C–H bond activation by the palladium complex $[H_2P(CH_2)_2PH_2]Pd$.

Method	MS	ΔE/kcal mol^{-1}	$R_{C1\text{-}P\,d}$/Å	$R_{H1\text{-}P\,d}$/Å	$R_{C1\text{-}H\,1}$/Å	$R_{Pd\text{-}P\,1}$/Å	$R_{Pd\text{-}P\,2}$/Å	$R_{P1\text{-}P\,2}$/Å	$\alpha_{C1\text{–}Pd\text{-}H\,1}$/°
CNDO/S[2]	PC	–0.7	3.134	2.676	1.104	2.470	2.470	3.616	
	TS	27.5	1.975	1.675	1.592	2.347	2.596	3.382	50.9
	PR	22.3	1.932	1.631	2.342	2.281	2.396	3.314	81.6
DFT-PBE	PC	–3.4	2.713	2.290	1.106	2.335	2.335	3.352	
	TS	21.6	2.161	1.597	1.875	2.369	2.438	3.202	58.5
	PR	20.1	2.123	1.606	2.140	2.365	2.409	3.181	79.1
DFT-BLYP	PC	–0.9	2.962	2.347	1.104	2.379	2.379	3.436	
	TS	26.4	2.200	1.605	1.847	2.428	2.512	3.283	55.4
	PR	24.3	2.148	1.609	2.423	2.424	2.481	3.249	78.8
MP4SDQ	PC	–5.1	2.700			2.319	2.319	3.310	
	TS	26.7	2.142	1.559	1.730	2.377	2.464	3.231	53.3
	PR	19.8	2.090	1.547		2.390	2.446	3.218	74.4

$$k(n,T) = \frac{1}{\sqrt{2\pi\mu k_B T}} \int_0^\infty P(n,E)\exp(-\frac{E}{k_B T})\mathrm{d}E \qquad (1)$$

where μ is the effective mass of motion of the MS along the 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 the MS exist in the nth vibrational state ($n = \{n_1, n_2, \ldots n_{3N-7}\}$ is the vector of quantum numbers, and N is the number of particles in the MS).

The probability of the reaction $P(n,E)$ was calculated in the quasi-classic approximation[10] with the vibration-adiabatic potential functions $V(n,s)$:

$$V(n,s) = V_0(s) + \hbar \sum_{j=1}^{3N-7} (n + 0.5)\omega_j(s) \qquad (2)$$

Note that, in the reaction at temperatures below 500 K, the total population of excited vibrational levels is no higher than 3%. Therefore, no consideration has been given to vibrationally excited states, and all data presented below are related to the ground vibrational level ($n = 0$). Taking into account the energies of zero vibrations affects the potential function, so that the reaction barrier decreases by 1.2 kcal mol^{-1}.

Figure 2 demonstrates the results of calculations of the reaction probabilities $P(0,E)$. It can be seen that $P(0,E)$ is considerably different from the Heaviside function. Thus, tunnelling and reflecting from the barrier considerably contribute to the reaction probability.[9] Taking into account the quantum effects results in a deviation of the logarithm of the overall thermal rate constant as a function of inverse temperature from linearity (Figure 3).

The integral in equation (1) can be presented as the sum:

$$\int_0^\infty P(0,E)\exp(-\frac{E}{k_B T})\mathrm{d}E = \int_0^{V_{max}} P(0,E)\exp(-\frac{E}{k_B T})\mathrm{d}E + \int_{V_{max}}^{2V_{max}} P(0,E)\exp(-\frac{E}{k_B T})\mathrm{d}E + \int_{2V_{max}}^\infty \exp(-\frac{E}{k_B T})\mathrm{d}E \qquad (3)$$

where V_{max} is the potential barrier.

The first term corresponds to the under-barrier particle flow, and the other two terms correspond to the over-barrier particle flow. This makes it possible to estimate separately the under-barrier (tunnelling) and over-barrier (activation) contributions to the rate constant: $k(T) = k^{act}(T) + k^{tun}(T)$.

To evaluate quantitatively the tunnelling contribution to the rate constant, we calculated the temperature dependence of the transmission coefficient $\kappa(T) = k(T)/k^{act}(T)$ (Figure 4). It is evident that at $\kappa > 2$ the tunnelling contribution to the rate constant is higher than the activation contribution. Thus, tunnelling predominates in the reaction with the complex at temperatures below 270 K, whereas at high temperatures the reaction mainly proceeds by an activation mechanism.

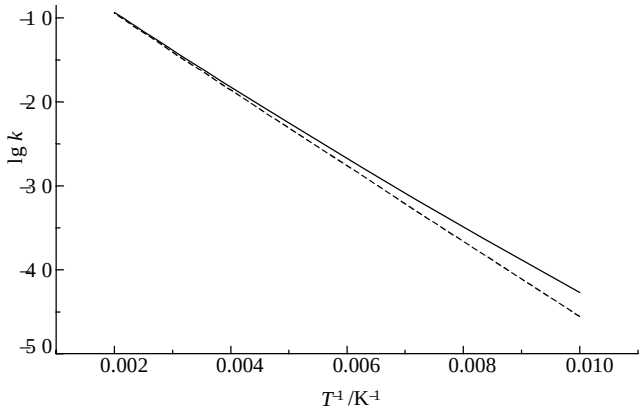


Figure 3 Temperature dependence of the logarithms of the overall quantum (solid line) and classic (dotted line) reaction rate constants.

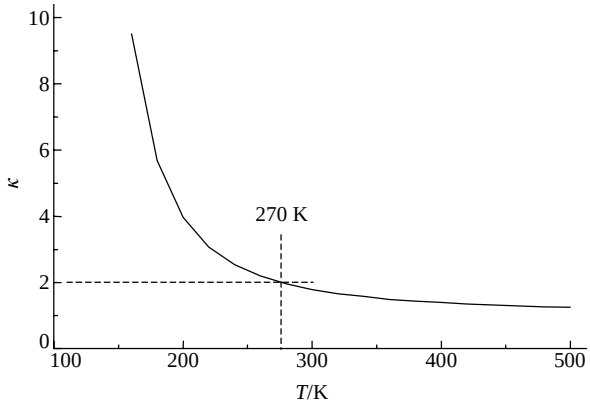


Figure 4 Temperature dependence of the transmission coefficient κ for the $[H_2P(CH_2)_2PH_2]Pd + CH_4$ reaction.

The evidence for a difference between the tunnelling effects of the reactions of oxidative methane addition to the ethylene-diphosphine complex and of hydrogen addition to the same complex[1] is a considerable difference between the heights of potential barriers of these reactions and between the effective masses of the molecular systems. As a rule, an increase in the height of a potential barrier primarily decreases the activation contribution to the rate constant, which results in an increased tunnelling contribution as compared with the activation contribution. At the same time, an increase in the effective mass decreases the tunnelling contribution.

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