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Tunneling in the Oxidative Addition Reaction of Methane to a Bare Palladium Atom

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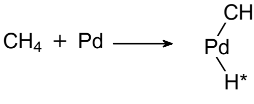
Quantum rate constant evaluations and kinetic isotope effects for the oxidative addition of CH_4 (and CD_4) to a bare Pd atom, calculated in terms of the Reaction Path Hamiltonian approximation, show quantum tunneling to play a very important role in the process when $T < 200$ K.

Activation of C–H bonds in alkanes for their functionalization under mild conditions is one of the most challenging problems of modern hydrocarbon chemistry. The oxidative addition of alkanes to bare transition metal atoms in the gas phase[1,2] and to their complexes in solution,[3–7] as well as dissociative chemisorption of alkanes on metal surfaces,[8–10] is the most general method for such activation. Oxidative addition reactions possess some interesting peculiarities which were observed experimentally. In particular, these are:

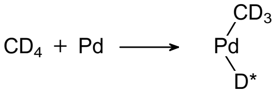
- Unusually high H/D kinetic isotope effects exceeding the usual semiclassical values.
- Effective activation energy decreasing with reduction in temperature for surface reactions.[7–10]

The existence of these peculiarities allows one to conclude that tunneling brings a considerable contribution to the rate constants of oxidative addition. An evaluation of this contribution could be performed only within the dynamic model framework.[11] In this paper we have solved such a problem for reactions (I) and (II) within the Reaction Path Hamiltonian (RPH) approximation.[12] We used the computer program for RPH construction written earlier[13] on the basis of the semiempirical LCAO MO CNDO/S^2 technique. The CNDO/S^2 method was developed by Filatov *et al.*[14] specially for the potential energy surface (PES) calculations of catalytic reactions with transition metals.



$$\mathrm{CH_4 + Pd} \longrightarrow \overset{CH_3}{\underset{H^*}{\mathrm{Pd}}}$$

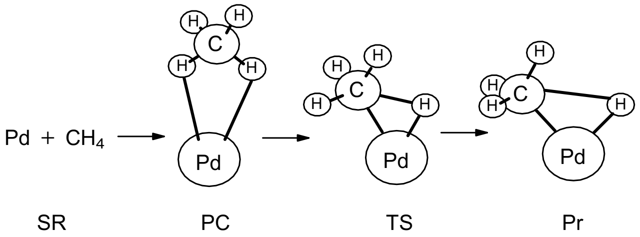
(I)



$$\mathrm{CD_4 + Pd} \longrightarrow \overset{CD_3}{\underset{D^*}{\mathrm{Pd}}}$$

(II)

Our CNDO/S^2 calculation results are in a good agreement with those obtained by an *ab initio* technique, including correlation and relativistic corrections[15–16] for the structures corresponding to the PES stationary points of reaction (I), where SR, PC, TS and Pr are the structures corresponding to the well-spaced reactants, pre-reaction complex, transition state and reaction product, respectively.



We have computed, using the software in ref. 13, the following for reactions (I) and (II):

- The $V_0(s)$ potential along the minimal energy path [*i.e.* reaction path (RP)], leading from the reactants to the products *via* the transition state (TS) (where s is the intrinsic reaction coordinate expressed in terms of mass-weighted Cartesian coordinates).
- Vibration frequencies orthogonal to the RP.
- Coefficients of dynamic coupling between motion along the RP and orthogonal vibrational modes, which determine the RP curvature.

Thermal rate constants $k(T)$ were calculated within the quasiclassical approximation through the reaction probabilities, $P(E)$, depending on the translational energy E for the ground state of the reactants.[17–18]

$P(E)$ values were computed with the vibrational-adiabatic potential functions $V(s)$,[17] equation (1):

$$V_n(s) = V_0(s) + \sum_{i=2}^{3N-6}(\vec{n} + \frac{1}{2})\hbar\omega_i(s) \tag{1}$$

where N is the number of atoms of reactive molecular system (MS) and $\vec{n}$ is the vector of vibrational quantum numbers.

According to our results, the RP curvatures of reactions (I) and (II) are negligible (curvature values are not more than 1 Å^{-1}). Thus, the vibrationally-adiabatic approximation proves correct.

Evaluation of the transmission coefficient $\chi(T)$ (*i.e.* ratio of the cumulative thermal rate constant to the activation one, k^{act}), equation (2):

$$\chi = \frac{k(T)}{k^{\mathrm{act}}(T)} \tag{2}$$

was performed in order to estimate the tunnel contribution in the rate constant $k(T)$. We evaluated the k^{act} value involving the effect of reflection from the potential energy barrier.[18] Transmission coefficient χ values are represented in Fig. 1.

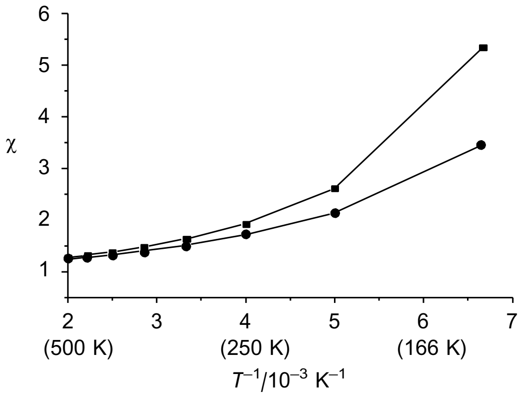


Fig. 1 Transmission coefficient χ dependencies on temperature (T) for the reactions Pd + CH_4 (■) and Pd + CD_4 (●).

When $\chi > 2$ the tunnel contribution in the rate constant exceeds its activation counterpart. One may see that for the reaction Pd + CH_4 tunneling proves dominant at $T < 200$ K, while for Pd + CD_4 it is dominant at $T \leqslant 150$ K.

From Fig. 1, as temperature diminishes, the transmission coefficient χ values grow rapidly. This effect seems to be a reason for the lowering of effective activation energy in dissociative methane chemisorption on transition metal surfaces, which was observed in practice.[8,9] In Table 1 the calculated H/D kinetic isotope effect (η) values of reactions (I) and (II) at various temperatures are given. The observed trend in the $k_{\mathrm{H}}/k_{\mathrm{D}}$ variation with respect to temperature is reported to be typical for tunnel chemical processes. In the region of 200 K the H/D kinetic isotope effect values are similar to those found experimentally for oxidative addition of $C_6H_{12}|C_6D_{12}$ to a 16-electron rhodium complex in solution.[5]

These results confirm those obtained earlier by working in terms of a more rough approximation.[19]

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Table 1 Kinetic isotope effect $\eta = k_{\mathrm{H}}/k_{\mathrm{D}}$ for Pd + CH_4/CD_4 → Pd(H)Me/Pd(D)CD_3 value dependence on temperature according to calculation data.

T/K	η_{class}	η_{tunn}	η_{total}
100	153.5	7.05	1081.8
120	66.3	3.5	230.2
160	23.2	1.9	43.1
200	12.4	1.4	17.9
220	9.9	1.3	13.3
260	6.9	1.25	8.7
300	5.4	1.2	6.6

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