Kinetic isotope effects in the activation of H–H bonds by palladium clusters

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The mechanism of oxidative dihydrogen addition to palladium clusters has been analysed in terms of the reaction-path Hamiltonian approximation, and the abnormal H/D kinetic isotope effect has been explained.

The oxidative addition of alkanes and dihydrogen molecules to atoms, clusters and complexes of transition metals are the key steps of catalytic cycles of alkane functionalization under mild conditions.[1] Theoretical studies of H–H and C–H bond activation, as a rule, are restricted to structures corresponding to the stationary points of potential-energy surfaces (PESs) [*i.e.*, to precursor complexes (PC), transition states (TS), intermediates and products (PR) of reactions] for model reactions with the use of various *ab initio* methods.[2]

Experimental studies of H–H and C–H bond activation by transition metal clusters in a gas phase[3–5] demonstrated that neutral palladium clusters were more active than palladium atoms. A clearly defined relationship between the reactivity of the clusters and the number of metal atoms was found. For Pd_n clusters ($n = 1$–5), the maximum reactivity was observed for Pd_2.[3] Fayet *et al.*[3] have detected an inverse H/D kinetic isotope effect (KIE) (*i.e.*, $k_H/k_D < 1$) for the reaction $Pd_2 + H_2$. They have suggested that this effect is due to a higher rate of the reverse reaction of reductive H_2 elimination from the product of addition in comparison with the deuterated analogues.

Some model trajectories of the oxidative dihydrogen addition to Pd_2 cluster were studied by MC SCF[6,7] and MCPF[8] techniques using relativistic effective core potentials for the Pd atom. Because different atomic basis sets and different *ab initio* techniques were used, and a constrained geometry optimization was performed, the energies and geometry parameters of the structures of the stationary points of PESs are in only qualitative agreement.

Mamaev *et al.*[9] analysed the PES of the oxidative H_2 addition to the Pd_2 cluster within the reaction-path Hamiltonian (RPH) approximation[10] on the basis of the semiempirical CNDO/S^2 method.[11] The H_2 addition to the Pd_2 cluster is known to occur without a potential-energy barrier.[6–9]

It was found[9,12] that the results of CNDO/S^2 calculations of the structures of the stationary points of the PESs of the H–H bond activation by both the Pd atom and the Pd_2 cluster are in a good agreement with the data of *ab initio* calculations that took into account correlation and relativistic effects. According to our CNDO/S^2 calculations for the $^1\Sigma_g^+$ state of a Pd_2 cluster, the equilibrium Pd–Pd distance is equal to 2.93 Å; $\omega_{Q(Pd–Pd)} = 103$ cm^{-1}; the dissociation energy $D_0 = 16.7$ kJ mol^{-1}. These results agree with the MC SCF data[14] (where $R_e = 2.87$ Å; $\omega_{Q(Pd–Pd)} = 121$ cm^{-1}; $D_0 = 29.3$ kJ mol^{-1}).

However, the calculations of the stationary points of the PES of the $Pd_2 + H_2$ oxidative addition by *ab initio* methods[6–8] cannot explain the abnormal KIE in this reaction. For this purpose, the reaction probabilities and rate constants for molecular systems (MSs) in the ground electronic state and without vibrational excitation should be computed at least at a semiclassical approximation. The use of rigorous *ab initio* schemes to compute the PES of this reaction is impossible because these calculations (complex calculations of Coulomb correlations of *d*-electrons and relativistic effects for motion of the inner electrons in transition metal atoms) are very labour intensive. Therefore, we employed the semiempirical SCF CNDO/S^2 method specially developed to study MSs containing palladium and nickel atoms and clusters.[11] According to the RPH formalism, the PES of the reaction is computed on normal coordinates.

To calculate the semiclassical rate constants, we used the transition state theory (TST) with tunnel corrections.[15] In terms of the TST, the cumulative thermal rate constant k^{CUM} of a bimolecular reaction of MS transfer from the left unbound state to the right bound state is computed as follows:

$$k^{CUM}(T) = \frac{1}{\Theta}\int_0^\infty P(E)\exp\left(-\frac{E_A}{k_BT}\right)dE, \tag{1}$$

where Θ is the translational partial function of the reactants, E_A is the activation barrier and $P(E)$ is the reaction probability. The quasiclassical function $P(E)$ is calculated[15] by solving the time-dependent Schrödinger equation. In the case of a parabolic barrier (*i.e.*, near the saddle point):

$$P(E) = \frac{1}{1 + \exp[2\theta(E)]}, \tag{2}$$

where $\theta(E)$ is the quasiclassical tunnel integral

$$\theta(E) = \frac{1}{\hbar}\int_{s<}^{s>}\sqrt{[2\mu\{V^G(s) - E\}]}ds, \tag{3}$$

where $V^G(s)$ is the vibrationally adiabatic potential function, μ is the reduced mass of the molecular system, s is the intrinsic reaction coordinate, and $s<$ and $s>$ are the points of the turns.

The transmission factor $\chi(T)$ is introduced to evaluate the quantity of the tunnel effect in the reaction. $\chi(T)$ is equal to the ratio of the cumulative rate constant to the over-the-barrier constant k^{ACT} found from the Arrhenius equation:

$$\chi(T) = \frac{\sum_n f_n(T)k^{CUM}(n,T)}{k^{ACT}(T)}.$$

The $f_n(T)$ functions represent the contributions from the separate vibrational states of the reactants to the rate constants; $k^{ACT}(n,T)$ may be computed by equation (1) if $P(n,E)$ is replaced with the Heaviside step function.[15] Mamaev *et al.*[12] proposed the use of quasiclassical reaction probability (2) instead of the

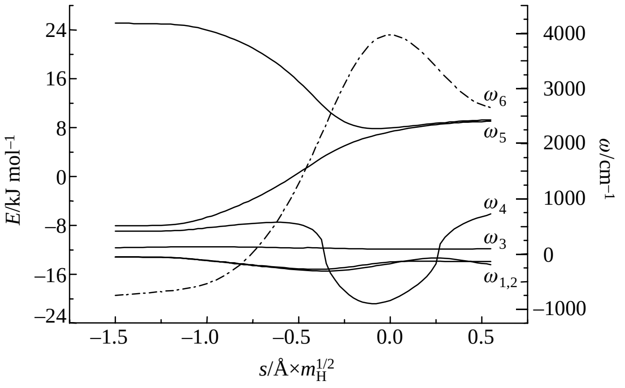


Figure 1 The $V_0(s)$ potential function for reaction (I) along the minimum-energy path (dashed line): ω_1–ω_6 are the frequencies of the normal vibrations; s is the intrinsic reaction coordinate; $\omega < 0$ reflect an imaginary frequency.

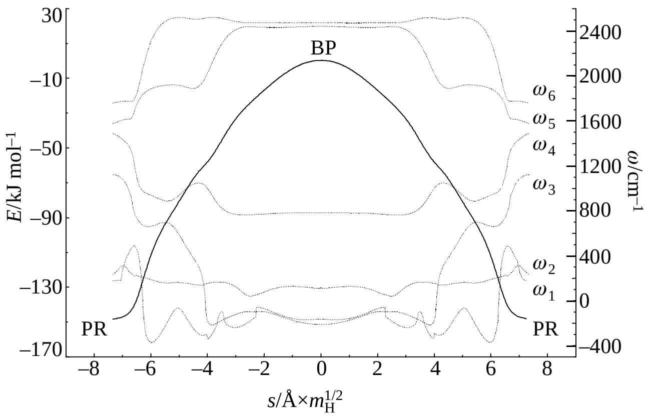
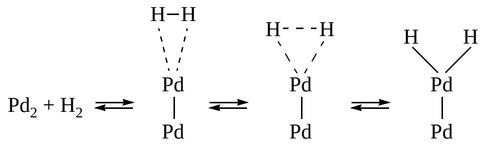


Figure 2 The $V_0(s)$ potential function (solid line) and the $\omega(s)$ functions (dashed lines) for reaction (IIIA). The vibrations are enumerated at the PR point.

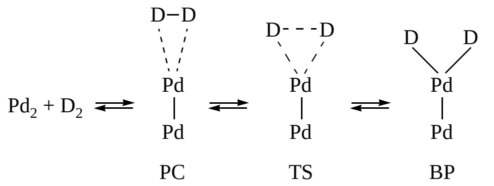
classical one for calculations of k^{ACT}, because it allows us to take into account the effect of the over-the-barrier reflection of the MS. If the over-the-barrier reflection is neglected, then the values of χ may be less than 1; this is inconsistent with the definition of χ.[12]

Thus, the values $\chi \geq 2$ show that the reaction occurs mainly by a tunnel mechanism at the given temperature.

Here, we have studied the mechanism of the H–H and D–D bond activation by the Pd_2 cluster in terms of the RPH approximation:



(I)



(II)

We have obtained three stationary points in the PES, namely, PC, TS and a product corresponding to a bifurcation point (BP) [its Hessian has two negative eigenvalues of ω_1^2 and ω_2^2 (Figure 1)].

Along the entire reaction path (RP), the MS conserves the C_{2v} symmetry. There are six vibrational modes of the following symmetry types: $\Gamma = 3A_1 + B_1 + 2B_2$. An analysis of the eigenvector of the Hessian directed tangentially to the RP (the RP vector) showed that for $s > -0.5$ Å×$m_H^{1/2}$ (m_H is the proton mass, equal to 1834 amu) displacements of the atoms, corresponding to this vector, are mainly defined by a variation in one internal coordinate, namely, the α(H–Pd–H) angle.

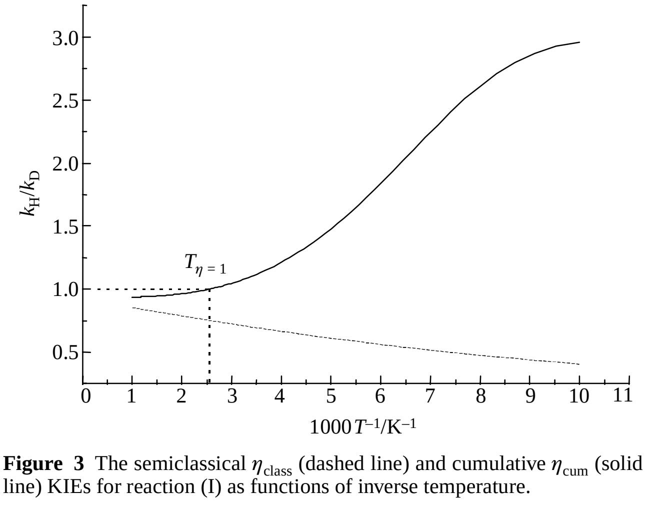
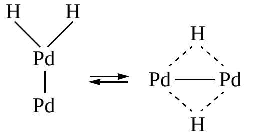


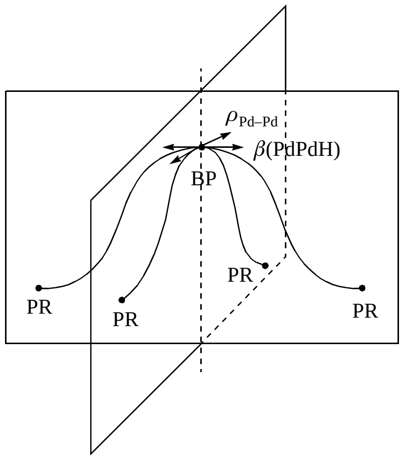
Figure 3 The semiclassical η_{class} (dashed line) and cumulative η_{cum} (solid line) KIEs for reaction (I) as functions of inverse temperature.

The modes whose frequencies ω_1, ω_2, ω_5 are zero in the dissociation limit turn to the β(PdPdH), $\rho_{\mathrm{Pd-Pd}}$ and q^-(Pd–H) modes of B_2, B_2 and B_1 symmetry, respectively. As the MS moves along the RP, the q(H–H) vibration of the dihydrogen molecule transforms to the stretching q^+(Pd–H) mode (ω_6, A_1 symmetry). The frequency ω_3 of the totally symmetric Q(Pd–Pd) vibration changes slightly along the entire RP.

In the BP, the values of ω_1 and ω_2 are equal to 213i and 167i cm^{-1}, respectively, *i.e.*, the eigenvectors of the Hessian of the β(PdPdH) and $\rho_{\mathrm{Pd-Pd}}$ shapes point at directions of descent into two different minima on the PES (processes IIIA and IIIB, respectively). We have constructed the RPHs for both of these processes and found the two descents to lead to the structures corresponding to the true PR:



(III)



A rhombic structure of the D_{2d} symmetry with bridging protons[7,8] corresponds to the global PR minimum. Its six normal vibrations belong to the following symmetry subspaces: $\Gamma = A_{2u} + 2A_{1g} + A_{2g} + 2B_{2u}$. The $\chi_{\mathrm{PdH}}^{\mathrm{PdH}}$ vibration of the A_{2u} symmetry has the frequency $\omega_1 = 179$ cm^{-1}; the Q(Pd–Pd) vibration of the A_{1g} symmetry has the frequency $\omega_2 = 225$ cm^{-1}. The shapes of ω_3–ω_6 modes are synchronous and asynchronous motions of the protons along the Pd–Pd and H–H axes, respectively.

In going from BP to PR, the rearrangement of the protons occurs by path IIIA asynchronously, and the RP vector represented in the basis of displacements of the internals changes significantly along the entire RP (Figure 2).

Since the potential functions of processes IIIA and IIIB are even, we trace the variation in the shape of the RP vector on the positive s semi-axis. In the region from $s = 0$ to $s \approx 4$ the bridging Pd–H–Pd bond is formed, whereas the other proton is fixed at the Pd–Pd axis [in Figure 2, this is seen as the behaviour of $\omega_5(s)$ and $\omega_6(s)$ functions]. Near $s \approx 4$, the first bridging bond is completely formed, and $\omega_5(s)$ is quickly dropped by 600 cm^{-1}, while the frequency of the vibration of the other proton, $\omega_6(s)$, bonded by an ordinary bond to a palladium atom, does not change. In the region of a small plateau at $s \approx 4$, the shape of the RP vector changes abruptly: the first proton stands between the palladium atoms, and the other proton moves back to form the second bridging bond.

Unlike to path IIIA, the motion of protons *via* path IIIB is synchronous, because the MS conserves the σ_V-plane of symmetry, which is perpendicular to the plane of the molecule in BP, and the RP vector is of the A' symmetry along the entire RP.

The RP vector is of the $\rho_{\mathrm{Pd-Pd}}$ shape at the BP ($s = 0$). In the region from $s << 1.5$ to $s >> 4$, variations in the α(H–Pd–H) angles contribute significantly to the RP vector (up to 50%). In the vicinity of both minima, the RP vector corresponds to the $\chi^{\mathrm{PdH}}_{\mathrm{PdH}}$ vibration. Vibrations with the frequencies ω_3–ω_6 become α(H–Pd–H), β(PdPdH), q^-(Pd–H) and q^+(Pd–H) vibrations in the BP.

According to refs. 6 and 7, the H_2 addition to Pd_2 clusters by trajectories without the formation of the BP structure occurs with no barrier. Thus, the formation of the BP structure from the separated reactants with an activation barrier of 22.2 kJ mol^{-1} is the rate-limiting step of reaction (I), and consequently, the abnormal H/D KIE of reaction (I)[3] can be assessed by construction of the RPH for reaction (II).

In the framework of our dynamic model, the KIE appears by three reasons. First, at the stage of composing the vibrationally adiabatic potential functions, the barrier heights for R–H and R–D bond activation become different because of differences in the values of corresponding $\omega_i(s)$ functions for MSs containing protons and deuterons (*i.e.*, a so-called semiclassical KIE appears). Second, because of employing mass-weighted Cartesians in the computation of the RP H/D substitution causes $V_0(s)$ functions to expand in the ratio of the effective masses of the reactive MSs. Third, as the protons are replaced with deuterons, the RP curvature diminishes, leading to a decrease in the tunnel contribution to the cumulative rate constant.

At the stage of the formation of the vibrationally adiabatic function $V(s)$ of the H–H bond activation, an abnormal difference in the energies of the stationary points of the PESs of reactions (I) and (II) appears. The unique peculiarity of the H–H bond activation in comparison with C–H and C–C bond activation is that the addition of the zero point vibrational energy to the $V_0(s)$ causes the energies of BP and TS to raise by 3.3 kJ mol^{-1} for reaction (I). This fact was first detected in the course of construction of the dynamic model of the reaction $Pd + H_2$.[12] Finally, the heights of the barriers of H–H and D–D bond activation differ by 0.6 kJ mol^{-1}.

Note that, for $Pd + CH_4$, the H/D substitution leads to an increase in the energies of TS and PR.[16]

For reaction (I), the shape of the $k^{\mathrm{CUM}}(1/T)$ function is typical of tunnel chemical processes. If the RP curvature is taken into account in the computation of the reaction probability, k^{CUM} grows by a factor of 1.5 at $T = 150$ K or by 10% at 300 K. The temperature dependence of the transmission factor shows that the tunnel mechanism dominates in reaction (I) at $T < 400$ K. For instance, at 200 K, the tunnel contribution to the rate constant exceeds the activation barrier by a factor of 8; at 280 K, the former is three times greater than the latter. For reaction (II), the tunnel contribution to k^{CUM} exceeds the activation barrier at $T < 280$ K.

The H/D substitution lowers the height of the potential barrier by 0.6 kJ mol^{-1}, *i.e.*, the k^{ACT} component in the rate constant grows. This leads to the appearance of the inverse semiclassical KIE (η_{class}) of reaction (I), which was observed in practice[3] (Figure 3). However, the ratio between the cumulative rate constants of reactions (I) and (II) (η_{cum}) exhibits a KIE of the normal sign at $T < 400$ K, *i.e.*, where $\chi > 2$ for reaction (I). An inverse KIE is observed only in the temperature region where the activation mechanism of the oxidative addition prevails.

Thus, the reactions of H–H bond activation can exist, for which the H/D substitution increases the thermal rate constant because of the influence of the frequencies of vibrations transverse to the RP by the height of the potential barrier.

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