

Spin effects in activation of hydrocarbons The role of triplet states in catalysis

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Abstract

A simple valence bond (VB) method is used in order to stress the role of triplet excited state of hydrocarbons in spin-uncoupling mechanism of their activation by transition metal center. The nature of activation barriers in bimolecular reactions is determined by exchange repulsion between closed shell molecules; a catalyst can diminish the barrier assisting the change of spin-coupling schemes in molecules. Involvement of the triplet excited state of activated molecule with participation of open-shell electrons of the catalyst in configuration interaction scheme is a general requirement for VB interpretation of catalysis. A well-known “donation and back-donation” scheme of molecular orbital description is also compatible with the spin-uncoupling mechanism. Both, the high-spin and low-spin states of a catalyst, are important in CI mixing, but only the low-spin state is reactive. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Catalytic transition-metal (TM) reactions attracted great interest for their industrial applications [1,2]. The TM-centered reactions consist of one or more elementary steps such as oxidative addition, reductive elimination, migratory insertion, etc. [1]. They accelerate transformations of hydrocarbons by opening a lower activation-energy pathways, often one that was symmetry forbidden [2]. It is well-known that the activation barrier in chemical reactions, forbidden by orbital symmetry, arises from the avoided crossing of the ground state and a doubly excited state [3].

Before consideration of spin effects in catalysis one has to consider some general features of chemical reactions between stable diamagnetic substances. The nature of activation barriers in bimolecular reactions is determined by exchange repulsion between closed shell molecules. It can be explained by higher weight

of the intermolecular triplet spin pairing (Fig. 1). Spins are singlet-coupled inside the ground state molecules AB and CD, but intermolecular pairing is arbitrary: all possible pairing schemes are equally probable. Just from statistics there are three triplets and one singlet state for pair of non-correlated electrons. In a framework of VB method the intermolecular interaction between two closed-shell systems (Fig. 1) can be described by exchange integrals for two singlet-paired states and six triplet-paired states. The singlet pairs are stabilized by exchange integrals, the triplets are much stronger destabilized [3]. The total balance of the exchange intermolecular interaction is repulsion, which produces a barrier. In order to solve a question “how to diminish the barrier?” one has to note that the repulsion will be changed by strong intermolecular attraction when the triplet excited covalent states in each molecule are involved. In addition to intermolecular attraction a cleavage of each bond occurs and new

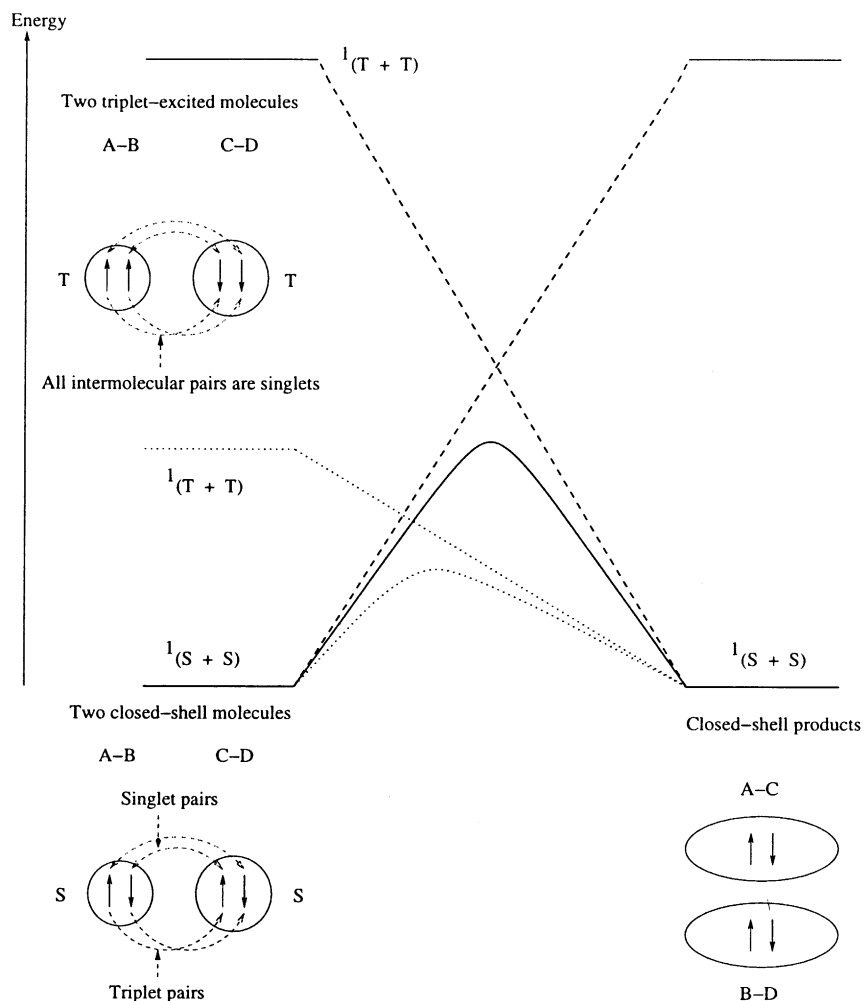


Fig. 1. Exchange repulsion between two closed-shell molecules (triplet pairing prevails) and dependence of the activation barrier on the “double-triplet” excited state coupled to the singlet. The lower the “double-triplet” state the lower activation barrier (dashed lines).

cyclization (or insertion) products AC + BD will be formed. It does not matter what kind of products are considered (it should be also cyclization or insertion); exchange repulsion between closed shell reagents is determined by the fact, that new intermolecular overlaps growing along the reaction path, trends to destabilize spin-pairing inside molecules [4]. Two excited triplet states are coupled into the total singlet state; the avoided crossing between two singlet states produces the activation barrier. These are the ground singlet state and the “double-triplet” singlet excited state; their diabatic behavior is shown by dashed lines

in Fig. 1. The height of the barrier, the reaction path and the heat of reaction are determined mostly by the properties of the triplet states. The thermal chemical reactivity is often coded by the triplet excited states of the diamagnetic reagents [5,6]. Thus, the triplet excited states involvement is a useful way of understanding of the nature of barrier and chemical reactivity. It does not mean that the triplet excited states participate in thermal chemical reaction as kinetic intermediates. This is only a correlation diagram of VB method, which indicates that at the transition state region there is a strong mixing of two singlet states

with different spin-coupling patterns. The avoided crossing realizes the spin-uncoupling process during reaction. If the energy of one (or both) triplet states in the reagents is lowered in some way, the activation barrier would be diminished (dotted lines in Fig. 1). This is what a catalyst really does in chemical activation. In the following some elementary steps of catalytic reactions of hydrocarbons are presented in order to support and illustrate this general statement.

An important part of a number of catalytic processes is the oxidative addition of hydrocarbons to a transition-metal center [1]. The C–H bond activation is a crucial step in any catalytic cycle designed to convert alkanes (methane first of all) into useful products. That is why the activation of C–H bonds in alkanes by TM compounds (metallorganics and bare TM atoms) has attracted considerable attention. Reactions have been studied in solvents, gas phase and in molecular beams; the oxidative addition mechanism has been definitely discovered [7–10]. *Ab initio* studies on the oxidative addition of hydrocarbons to the second-row TM atoms and complexes [10–17] have revealed some trends in the electronic structure factors, mostly the connections between spectra of the TM-catalyst and its activity. But spectroscopic properties of hydrocarbons have not been explored so far in qualitative analysis. An interesting trend in activation of hydrocarbons has been stressed: the stronger C–H bond is easier to activate than the weaker C–H bond [17]. Jones and Feher [18] concluded that it is metal–carbon bond strengths of the product that dominate in the determination of the position of the hydrocarbon activation equilibria, not the reactant C–H bond strengths. Siegbahn [17] has calculated metal–carbon (M–C) bond strengths for a number of $M-C_nH_m$ compounds, where M is the second-row TM atom, and found that *sp*-hybridized carbon atom forms much stronger M–C bond than *sp*²-hybridized carbon atom and the bond formed by *sp*³-hybridized carbon atom is still weaker. Siegbahn [17] has explained all trends of M–C bond strengths by ionic and steric contributions. Similar explanation has been applied for the trend in activation barriers with additional account of promotion energy and exchange energy loss in TM atom [10].

In the following the idea of spin-uncoupling in catalytic processes [4,19–21] is implemented in explanation of covalent chemical bond activation by TM compounds, including bare TM atoms. A clear

chemical understanding of these fundamental reactions is obviously of interest. Spin pairing is the main feature of chemical bonding: the change of spin pairing schemes, their alternation during bond cleavage and new bond formation, should be mediated by exchange (and magnetic) interactions with spins of the catalyst. Though the numerous DFT calculations of reactions of the transition metal compounds with hydrocarbons provide unique structural and thermo-chemical information of great importance, the general features of C–H bond activation are not outlined yet. In this work the valence bond method with simple approximations [22] is used in order to stress the importance of triplet excited state of the activating molecule in catalysis by TM atoms and complexes. Activation of the C–H bond in methane and in other alkanes and alkenes is used as the most important example illustrating essential features of catalysis. Well-studied reactions of hydrocarbons with the second-row TM atoms [10] are used for illustration of new features which have not been taken into account before in the explicit way. The important findings from previous studies [10,23,24] are compatible with the new spin-uncoupling concept.

2. Typical examples of spin-uncoupling

The simplest example of bimolecular chemical interaction provides the $H_2 + H_2$ pair as an electronic model for the isotope exchange process. Gerhartz et al. [6] have calculated by VB method a number of excited states in the trapezoidal H_4 system. It follows from their results that the doubly excited singlet state, which correlates with two H_2 molecules being excited to the triplet state $^3\Sigma_u^+$, is responsible for the avoided crossing with ground state energy curve when two parallel molecules approach each other and the system reaches the square transition state. This corresponds to a conceivable concerted reaction $H_2 + D_2 = 2HD$. (The real isotope exchange reaction lies outside the trapezoidal subspace.) The activation barrier at the square transition state is formed by the avoided crossing of these singlet states, as it is depicted in the general case (Fig. 1). Similar results have been obtained in other concerted chemical reactions forbidden by orbital symmetry in the Woodward–Hoffmann classification [3]: in disrotatory electrocyclic reactions of

polyenes [25], in norbornadiene–quadricyclene transformation [6] and in the singlet oxygen cycloaddition to polyenes [26–28].

Interesting spin-uncoupling process which is similar to some catalytic reaction can be illustrated by the singlet oxygen $O_2(^1\Delta_g)$ cycloaddition to butadiene

[29]. The correlation diagram for *cis*-butadiene reaction with molecular oxygen is shown in Fig. 2. The first triplet excited state of *cis*-butadiene, 3B_2 , combines with the ground triplet state of O_2 molecule, $^3\Sigma_g^-$. This combination creates a singlet coupled excited term (called “double-triplet”), which finally

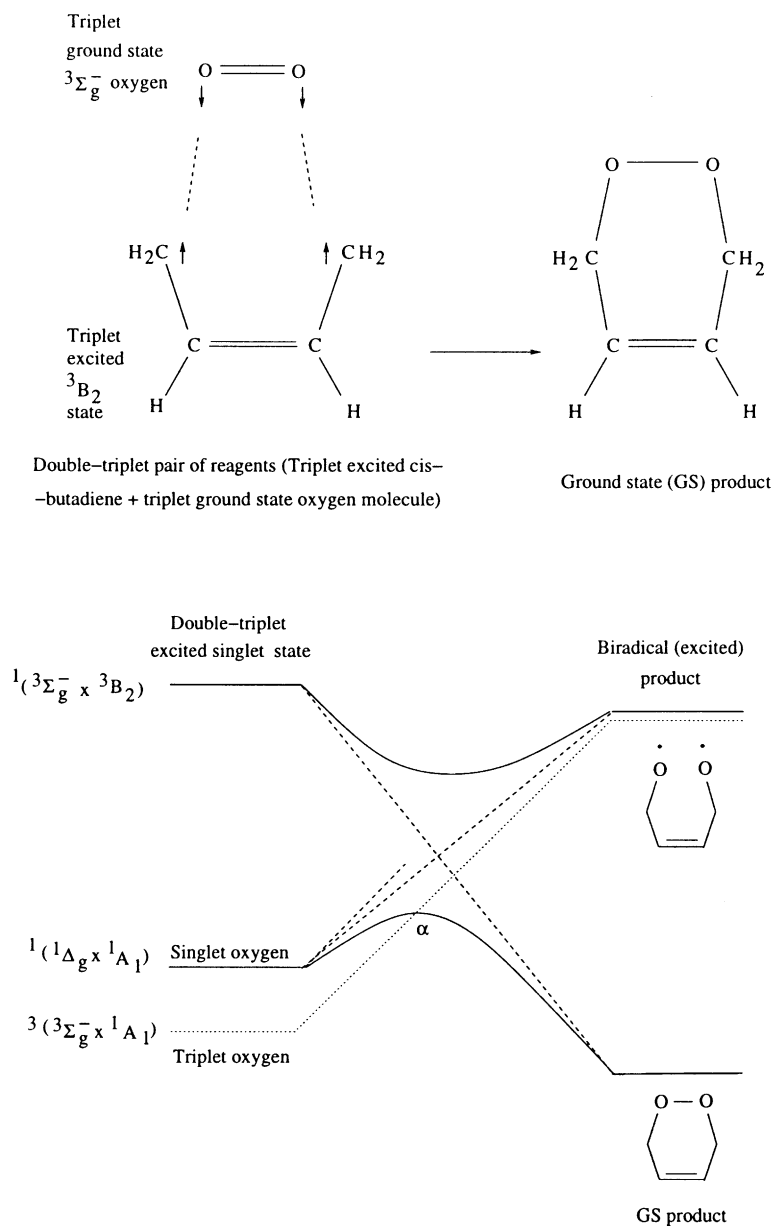


Fig. 2. Correlation diagram for the singlet molecular oxygen cycloaddition to *cis*-butadiene.

influences the reactivity of the singlet oxygen $O_2(^1\Delta_g)$ molecule by an avoiding crossing (dashed lines in Fig. 2). It is obvious that the “double-triplet” singlet state correlates with the ground state of the cyclization product and produces an avoiding crossing with the ground singlet state of reactants which correlates with the excited biradical. Fig. 2 makes clear why the singlet oxygen $O_2(^1\Delta_g)$ cycloaddition to dienes has smaller barrier than the Diels–Alder cycloaddition [29]; the oxygen molecule has a triplet ground state while alkenes have to be excited to the triplet state of high energy, thus the “double-triplet” singlet reactants and the crossing point in correlation diagram for the Diels–Alder cycloaddition should be much higher.

An obvious conclusion follows from Fig. 2: the ground triplet state oxygen molecule has to produce a spin flip at the singlet–triplet (S–T) crossing point α in order to react with diamagnetic species. The spin flip can be induced by spin–orbit coupling (SOC) matrix element between the S and T states. For concerted reaction presented in Fig. 2 the SOC at the crossing point α is forbidden. If the S–T crossing occurs at the beginning of the reaction (point α is close to the reactants) the spin–orbit coupling is forbidden since it comes to SOC matrix element between the $^3\Sigma_g^-$ and $^1\Delta_g$ states, which is zero by symmetry [30]. If the S–T crossing occurs at the right side from the barrier, the SOC is zero since it comes to the matrix element between the S and T states of the diene [27,31]. At the intermediate case both factors combine and produce a negligible SOC matrix element.¹ Similar arguments for spin flip probability can be applied in catalytic reactions [21].

The conrotatory and disrotatory closure of dienes are classical examples of the orbital symmetry selection rules and states correlation in chemistry [3,32]. In photochemical disrotatory closure of dienes the reacting singlet excited state is known to be produced by double excitations [32]. This is a well-known “dark” (or “hidden”) 2^1A_1 state of butadiene and of higher dienes, which is connected with the problem of “sudden

polarization” and mechanisms of vision (in retinales) [3]. For example, in *cis*-butadiene the second 2^1A_1 totally symmetric singlet excited “hidden” state (Fig. 3a) can be presented as consisting of two triplet excitations localized at each CH–CH₂ moiety (covered by dashed contours in Fig. 3a)² which are coupled to the total zero spin (singlet state) [25,31]. This “hidden” 2^1A_1 excited state is actually prepared for the disrotatory electrocyclic photoreaction; it correlates with the ground state cyclobutene product because the spin pairing scheme is useful for the cyclization (dotted lines in Fig. 3a).

The avoided crossing between the ground state and the “double-triplet” singlet excited state is the reason for activation barrier in disrotatory cyclization reaction (Fig. 3a). The process occurs as a photochemical reaction, but not as a thermal one [3,25]. The disrotatory closure of *cis*-butadiene is symmetry forbidden in the ground state and has a big barrier. When the reaction is perturbed by a TM-complex with a low lying triplet state (like $RhH(NH_3)$ [16]) the barrier should be diminished drastically: now the “double-triplet” singlet state, which produces an avoided crossing with the ground PES, includes the first excited triplet states in the activated molecule and in the catalyst. This can be illustrated by analogy with Fig. 2, where the singlet oxygen $O_2(^1\Delta_g)$ cycloaddition to *cis*-butadiene is presented. Let us imagine that instead of O_2 molecule we have the catalyst $RhH(NH_3)$. The low-lying triplet excited state of the catalyst can be used instead of the ground triplet state of molecular oxygen in the correlation diagram of the type presented in Fig. 2. The TM-center can bind two CH₂ moieties of *cis*-butadiene in a disrotatory manner; the barrier for such addition reaction would be low and reaction can be completed by disrotatory closure of *cis*-butadiene, when the catalyst will go away. The departure of the catalyst would not cost much energy since the catalyst has to be released in the singlet ground state: when the spin-uncoupling is completed after the barrier passage the two closed-shell species simply repel each other.

The situation is illustrated further in Fig. 3b. The reaction starts in the ground states of two closed shell species. The highest doubly occupied orbitals are ψ_2 and $5s^2$ in butadiene and catalyst, respectively. One spin in each orbital, shown by dashed (and lowered)

¹ This is an oversimplification for the triplet oxygen reaction. The triplet state reaction coordinate is not concerted; it goes to non-symmetric diradical [26,27]. There are also two different channels of reactivity in the singlet $O_2(^1\Delta_g)$ states [26,27]. One channel leads to diradical intermediate, were the S–T crossing occurs; spin–orbit coupling in this diradical is also forbidden.

² These are double C–C bonds in the ground state butadiene.

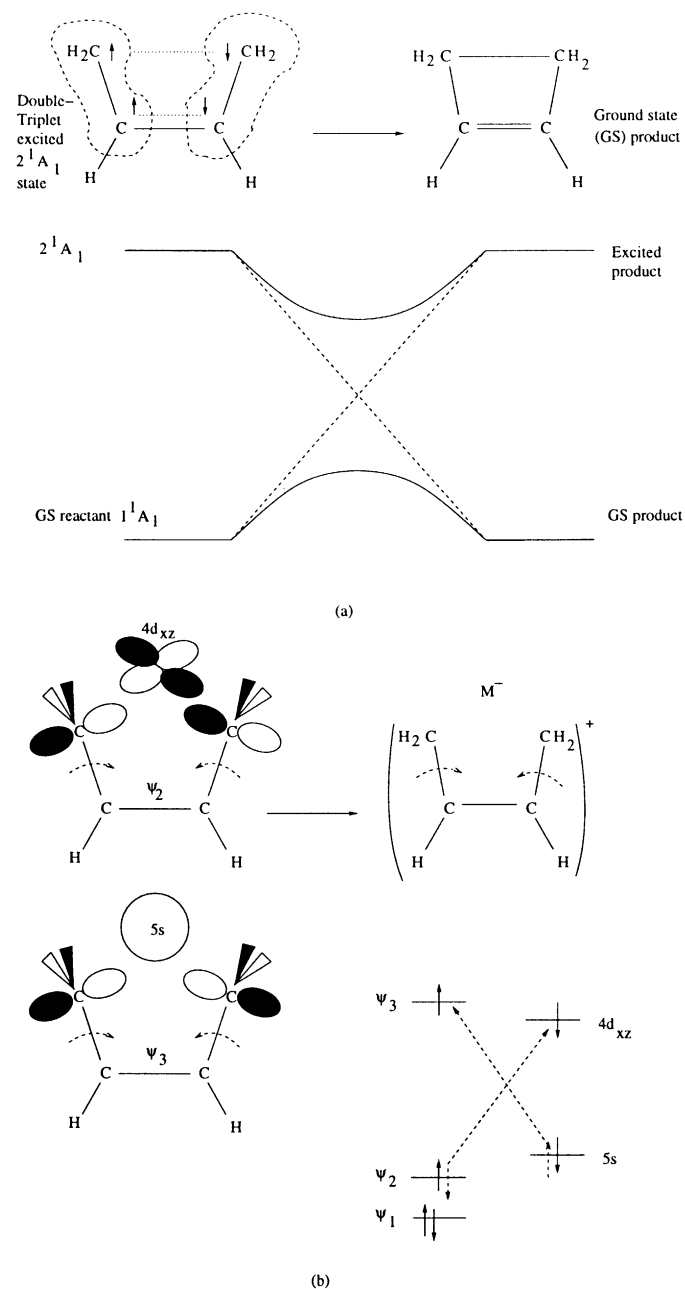


Fig. 3. Correlation diagram for disrotatory closure of *cis*-butadiene.

arrow, can participate in donation $\psi_2 \rightarrow 4d_{xz}$ and back-donation $5s \rightarrow \psi_3$ process. Since both electron transfer processes occur simultaneously without spin flip, they produce the “double-triplet” singlet state

(Fig. 3b). The “donation and back-donation” mechanism is well-known in TM complexes and in catalysis [1,2,46]. One can see that it is compatible with the spin-uncoupling scheme [19].

This rather artificial example of conceivable stereo-selective catalytic process is presented here in order to illustrate the importance of relative position of the high-spin and low-spin states of the catalyst. In the case of oxygen cycloaddition to dienes (Fig. 2) the ground (high-spin) state is non-reactive. Reaction has to be sensibilized by dye excitation and by energy transfer in order to produce the reactive (low-spin) singlet oxygen $O_2(^1\Delta_g)$ [26,27]. Similar optical pumping experiment has been performed for methane activation by molybdenum atom in crossed beams studies of high-spin (7S) and low-spin (5S) Mo atoms collisions with CH_4 [33]. This crossed beam experiment supported a general rule obtained from the spin-uncoupling scheme [19,21]: only the low-spin state is reactive in catalysis.

Very often the catalyst (unsaturated TM complex) has a low-spin ground state with a high-spin state being very close in energy [4,21,34]. This situation is very useful for catalysis; it is not necessary to produce a spin flip and a low barrier can be achieved at the low-spin potential energy surface (PES). The metal surface is an ideal catalyst in this sense: a high-spin multiplicity can be realized at the local site of the surface, perturbed in the course of chemisorption process: a finite metal cluster which simulates the surface in the course of chemisorption process has a number of quasi-degenerate state with different spin-multiplicities [35]. The crucial role of electron spin and exchange interaction in the control of the reaction channels in the region of the activation complex is easily inferred from the general principles of chemical bonding in the framework of VB method. The radical-like (or diradical-like) moieties appear in the transition state wave functions of many chemical reactions including catalysis [4]. This is illustrated by the following simple models which indicate how the TM species can help an organic molecule to cleave the C–H bond.

3. Activation of hydrocarbons by second-row transition-metal atoms

We first consider a simple oxidative addition of second-row transition-metal atoms to methane:



This process is well-studied by ab initio calculations [10], which indicate that Y, Zr, Nb, Ru and Rh atoms produce very stable insertion products $H-M-CH_3$ in the reaction (1) with small activation barrier ($E_a \sim 4-20$ kcal/mol). The reactions simulate catalysis since the barrier is much lower than the C–H bond dissociation energy (103 kcal/mol). Some metals (Nb, Ru, Rh) have to change spin multiplicity [10] in the course of the reaction (1). This spin-effect is a rather general feature of catalysis and will be considered latter.

3.1. Y atom insertion into methane

Let us start with the yttrium atom oxidative addition to methane: the reaction presented by Eq. (1) for $M = Y$. The transition state (TS) of this reaction has been optimized by the restricted open shell Hartree–Fock (ROHF) method [3] with a 3-21 G basis set [36] using the GAMESS code [37]. The structure of the TS is found similar to those presented in [13]. The intrinsic reaction coordinates (IRC) and the configuration interaction (CI) [38] at a few points along the IRC have been also calculated. The high-spin excited states wave functions are quite similar in both approaches at the TS region [19], but spin-uncoupling pattern cannot be seen on the Hartree–Fock level, since the molecular orbitals are mixed.

The Y atom has a doublet ground state (2D , $4d^15s^2$). In a simple VB consideration only one d -AO can be taken into account as the first approach. (The orbitals of the activated C–H bond, the sp^4 -hybrid and the $1s$ -AO on hydrogen atom, will be denoted as c and h , respectively.) The canonic structure of the ground state of the reactants in the VB method [3] is represented by the doublet state wave function

$$\Psi_{1r} = 2^{-1/2}(|c\bar{h}d| + |h\bar{c}d|). \quad (2)$$

The bar here denotes a beta spin-orbit and the usual notation of determinants [3] is used. The zero differential approximation [3] is applied in the following simple analysis.

This diabatic state represents the ground state of the reactants with singlet spin pairing in the covalent C–H bond when the third electron on the catalyst is decoupled from this pair. When the system moves along

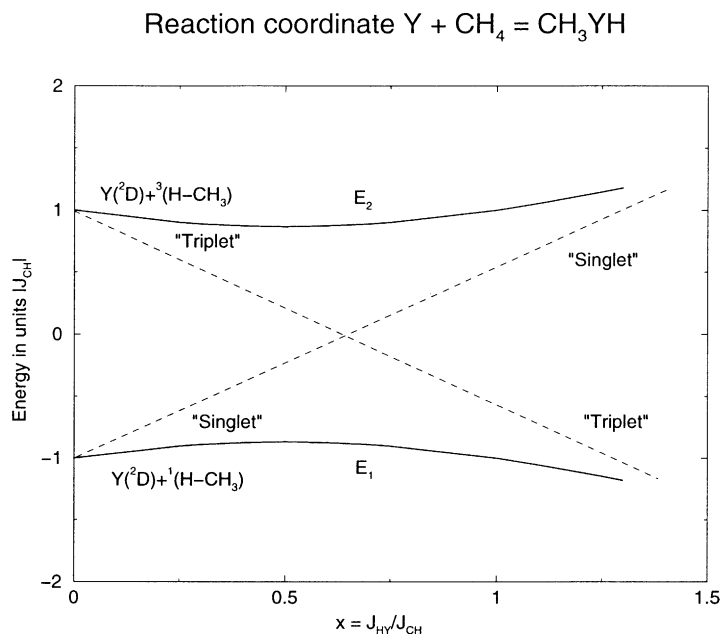


Fig. 4. Potential energy curves for two doublet states in Y atom insertion into C–H bond of methane obtained by a simple VB approximation ($y \simeq 0$). The dashed lines correspond to the diabatic states correlation: the notions “singlet” and “triplet” are associated with spin pairing at the activated C–H bond.

the reaction path the repulsive exchange interaction between the single electron of the catalyst and the covalent electron pair will grow for the reactant state, Eq. (2). This is because the triplet coupling (three repulsive states) will suppress the singlet pairing (one attractive state) between the respective spins of the catalyst and catalysant [39]. The exchange repulsion will predominate in the Y+CH interaction (one singlet and one triplet coupling) and increase while the system moves to the transition state; prolongation of the C–H bond will also destabilize the system. This diabatic ground state of the reactants, Eq. (2), correlates with the excited state of the product (Fig. 4). The energy increase of the ground state reactants is shown by dashed line in Fig. 4. Besides the ground state reactants, Eq. (2), the second doublet covalent structure exists, Eq. (3) [3]:

$$\Psi_{2r} = 6^{-1/2}(|c\bar{h}d| - |h\bar{c}d| + 2|c\bar{d}h|). \quad (3)$$

This is the triplet excited state localized on the activated C–H bond with a repulsive exchange interaction. The shorter distance between Y atom and

methane will strengthen the growing Y–C or Y–H bonds; simultaneous prolongation of the C–H bond will stabilize this type of valence bond structure. Such VB diabatic state correlates with the ground state insertion product (Fig. 4).

A general analysis of the three-center, three-electron problem, have been presented in [22]. The authors have obtained the energy of two VB structures (Eqs. (2) and (3)) neglecting the overlap S_{ij} in comparison with one-electron core integral [3], and neglecting S_{ij}^2 in comparison with the exchange integral J_{ij} ,

$$J_{ij} = S_{ij}[2h_{ij} + S_{ij}h_{kk} + 2(ij|kk)] + (ij|ji), \quad (4)$$

where

$$(ij|kl) = \left\langle i(1)j(1) \left| \frac{e^2}{r_{12}} \right| k(2)l(2) \right\rangle, \quad (5)$$

indexes i, j, k, l denote the atomic centers, C, H, Y in our case, and run from 1 to 3. With these approximations the following formula for the energy of two

VB structures, Eqs. (2) and (3), has been obtained [22,40]:

$$E_{1,2} = Q \pm \sqrt{0.5[(J_{CH} - J_{CY})^2 + (J_{CH} - J_{HY})^2 + (J_{CY} - J_{HY})^2]}. \quad (6)$$

In this expression “+” corresponds to the excited potential curve which correlates with the triplet methane valence bond structure in the reactants (Eq. (3)) and “-” corresponds to the ground state potential curve which correlates with the singlet C–H pairing in the reactants. Q is the Coulomb term [3]. This expression, Eq. (6), corresponds to the well-known London’s formula of three atoms, which has been widely used in Eyring–Polanyi theory of classical reaction $H_2 + H$ [41]. An avoided crossing of the ground state and the triplet excited state of the H_2 moiety has to be obtained for this reaction, but in chemical kinetics attention has been concentrated only on the lower surface [41].

Let us consider the insertion reaction, Eq. (1), for $M = Y$ with the transition state structure optimized by ROHF method. In this case the Y–H distance is much longer than the C–H separation and both are shorter than the Y–C distance [40]. One can introduce the useful ratios [22,40]:

$$x = \frac{J_{HY}}{J_{CH}}, \quad y = \frac{J_{CY}}{J_{CH}}. \quad (7)$$

Account of these notations allows to express the energy formula of London’s type, Eq. (6), in a useful form which has been implemented before in radical reactions [22]:

$$E_{1,2} = Q \pm |J_{CH}| \times \sqrt{0.5[(1-x)^2 + (1-y)^2 + (x-y)^2]}. \quad (8)$$

At the beginning of the reaction $x = y = 0$; the upper and lower states have energies $E_2 = Q + |J_{CH}|$ and $E_1 = Q - |J_{CH}|$, respectively. This corresponds to the catalyst at infinite distance from methane in the triplet and singlet state, respectively. IRC calculation from the transition state indicates that a weak precursor complex formation occurs first in the beginning of the reaction. The precursor complex is stabilized by electrostatic interactions; this is van der Waals complex with a very weak exchange stabilization. Thus, $y \sim x \sim 0$ at this stage. Movement along IRC from the precursor complex to the transition state is determined by growing of the Y–H bond and a rise of the x

ratio. At the same time the C–Y distance is kept long and fixed; the C–Y bond is still electrostatic along this IRC-movement. The ratio y is much smaller than the ratio x . One can use until the transition state is reached $y \simeq 0$,

when x is growing. By account of Eq. (9), the basic energy expression, Eq. (8), is simplified to:

$$E_{1,2} = Q \pm |J_{CH}|(1-x+x^2)^{1/2}. \quad (10)$$

These two potential energy curves are shown by solid lines in Fig. 4; they indicate a strong avoided crossing between the diabatic terms, which correlate with the singlet and triplet states of methane (shown by dashed lines in Fig. 4). It reproduces the most essential part of a more general picture, where ionic and other excited states are accounted [40]. The simple approximation, Eq. (9), has meaning until $x < 0.6$. After the point of the transition state ($x = 0.5$) the J_{CH} exchange integral starts to decrease and Eq. (9) is not valid any more. In spite of a very crude approximations involved, the potential energy curves, Eq. (10), reproduce essential features of CI calculations. For the lower potential curve, shown in Fig. 4 by solid line and presented by the “-” sign in Eq. (10), the activation barrier at the point of TS, $x = 0.5$, is equal to

$$E_a = |J_{CH}| \left(1 - \frac{1}{2}\sqrt{3}\right). \quad (11)$$

This analysis of three-electron catalytic system is similar to previous works [39,40,42] and to the theory of radical reactions [22]. The results of CI calculations of the C–H bond dissociation reaction in methane with the 6-311++G(2d,2p) basis set [36] are presented in Fig. 5. The complete active space for 8 electrons in 8 orbitals is accounted. Calculation predicts that the vertical S–T excitation energy in methane is 11.4 eV. Following the above approximation it is equal $2|J_{CH}|$. From Eq. (11) the activation energy for the yttrium atom oxidative addition to methane should be 17.6 kcal/mol. This simple estimation is in a reasonable agreement with very accurate ab initio calculations of Carroll et al., $E_a = 20.7$ kcal/mol [10].

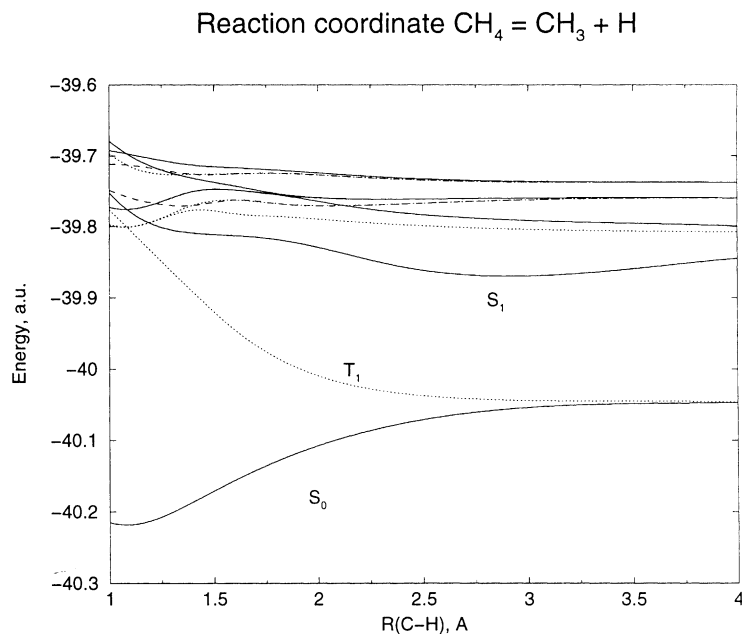


Fig. 5. Potential energy curves for C–H bond dissociation in methane. CAS CI, 6-311++(2d,2p).

The non-equality of exchange interactions $|J_{CY}| \ll |J_{HY}|$ near the transition state is important for the efficiency of the “S–T” avoiding crossing. If $x = y$, one obtains from Eq. (8) the following result:

$$E_{1,2} = Q \pm |J_{CH}|(1 - x), \quad (12)$$

in the whole range of the reaction. It means that a direct “S–T” crossing (not avoided) occurs at the point $x = 1$; at this point $E_{1,2} = Q$ and the activation energy for the lower curve is extremely high: $E_a = |J_{CH}|$. Thus, the activation energy is just a half of the S–T excitation; for methane activation the E_a would be more than the dissociation energy (103 kcal/mol). The addition reactions of free radicals to olefins with a symmetric triangular approach ($x = y$) have been called “exchange forbidden” [22]. This extreme case can though not be realized in catalysis. Account of 5s-electrons and additional excited states in TM-species will remove the “exchange forbidden” character of the simple VB approach even in a symmetric reaction like Pd addition to ethylene [19]. Thus, the catalyst promotion energy is an additional factor which determines the activation barrier [10]. An important further complication

is connected with the exchange energy loss upon metal atom excitation and bond formation [11,23,43].

The ground 2D state of the Y atom is five-fold degenerate. The degeneracy is lifted by interaction with methane and there are a number of low lying excited states of different symmetries. At the beginning of the reaction the ground state is $\sigma_{\text{CH}}^2 5s^2 4d_{xy}^1$. A number of low lying excited states of the $5s \rightarrow 5p$ and $4d \rightarrow 5p$ type occurs below 3 eV with the $5s^1 5d^1 5p_z^1$ being the lowest one (1.5 eV); z is π -axis perpendicular to the symmetry plane (CHY). The VB method provides mixing of all relevant states of proper symmetry. A number of ionic states, including a few $\text{CH}_4^+ \text{Y}^-$, $\text{CH}_3^+ \text{YH}^-$ structures, participate in the CI mixing and contribute to the barrier height lowering. The charge-transfer configurations reach particularly low energies at the transition state geometry. Coulomb attraction between the ions reaches maximum before they begin to participate in covalent bonding. The “S–T” avoided crossing just characterizes the TS system where exchange bonding is quenched: C–H bond is broken and the new bonds, Y–C and Y–H, start to grow. At this point the ionic contributions and local excitations in TM atom are admixed to the VB

wave function. The excited states produced by promotion (${}^2D \rightarrow {}^4F[4d^25s^1]$) in the metal were also accounted; they contribute to spin uncoupling and participate in additional avoided crossing between the Ψ_{1r} , Ψ_{2r} states and the charge-transfer excitations. Thus, the simple VB scheme, Eqs. (2)–(12), is supported by more sophisticated method.

A similar approach can be applied for the Y atom insertion into the C–H bond of other alkanes and alkenes. For alkenes the S–T excitation energy is in the range 3–4 eV [44]. This is the $\pi\pi^*$ excitation which transforms to the $\sigma\sigma^*$ excitation localized on the activated bond when the system moves along the reaction path of TM-atom insertion into C–H bond of alkene [19]. The C–H bond dissociation in ethylene has been calculated by CI method in 6-311++G(2d,2p) basis set with complete active space for 10 electrons on 9 orbitals. The lowest ${}^3(\pi\pi^*)$ state in the course of C–H bond cleavage transforms to the ${}^3(\sigma\sigma^*)$ state by the T–T avoided crossing near the point $R_{CH} = 1.65 \text{ \AA}$. The calculated barrier on the T_1 potential energy surface is getting smaller in the course of Y atom insertion into C–H bond of ethylene. The π – σ mixing in this reaction is very efficient because of strong interaction with the 4d-AO's of TM-atom. Estimations by previous formulas, Eqs. (10) and (11), give $E_a \sim 4$ –6 kcal/mol for Y atom insertion into alkenes; this is in a reasonable agreement with ab initio results for Y and Zr atoms ($E_a \sim 2$ kcal/mol) insertion into the C–H bond of ethene [10]. All the second-row TM atoms (except Ag) react with linear alkenes of sufficient size [10].

The yttrium atom at room temperature does not react with methane but reacts slowly with cyclopropane [10]. The calculated barrier to the C–H bond insertion is 11 kcal/mol. The C–H bond in cyclopropane is stronger than in methane (calculated 108 versus 103 kcal/mol) [10]. Nevertheless, for all second-row TM atoms the barriers to C–H insertion are lower in cyclopropane than in methane. This was explained by a larger ionicity of the C–H bond in cyclopropane compared to the C–H bond in methane [10]. Behind this factor the new important argument follows from the above discussion and the VB correlation diagram; the triplet excited state in cyclopropane is lower than in methane (calculated 221 versus 262 kcal/mol by the CI method in 6-311++G(2d,2p) basis set in comparable complete active spaces). The delocalized and degenerate triplet

excited state in cyclopropane and methane easily transforms to the local C–H excitation during the insertion reaction of the Y atom. The quantitative curve-crossing diagram, Fig. 4, where the transition state occurs by avoided crossing of the “singlet”- and “triplet”-coupled C–H valence bond structures is very useful not only to understand C–H bond activation by Y atoms but, in fact, to understand all catalytic processes with participation of TM species [40]. At the same time the above-described picture is not complete. An important additional complication is connected with the metal atom excitation and exchange energy loss [11,23,43]. This is getting clear when one starts to consider methane activation by other TM atoms.

3.2. Zr atom insertion into methane

The odd number of electrons at the catalyst center is not of principal importance, as it follows from the simple three-electron picture, Eqs. (2)–(11). The presence of low lying multiplets with nonzero total spin is the essential requirement for catalysis. The open shell state of the catalyst (3F ground state of Zr atom) can mix the singlet and triplet states of the activating bond since all states are triplets, so providing the spin uncoupling which is necessary for chemical activation. Before the barrier is achieved and C–H bond starts to break the double-triplet state of the upper curve starts to interact with the lower triplet curve, thus CH_4 prepares for the bonding towards Zr atom. In this region the intermolecular interaction between methane and Zr is repulsive; the system is described mostly by the reactant state wave function

$${}^3\Psi_1 = 2^{-1/2}(|d_1d_2c\bar{h}| + |d_1d_2h\bar{c}|), \quad (13)$$

where d_1 , d_2 are d_{xz} , $d_{x^2-y^2}$ in our choice of axis. This is the triplet 3F state of Zr atom being in contact with the spin-paired C–H bond. The s^2 couple of the ground state of Zr atom 3F , d^2s^2 [45] is omitted for simplicity for the first approach. The repulsion is changed by a strong attraction in an excited triplet states of reactants:

$${}^3\Psi_2 = \left(\frac{1}{2}\right)(|d_1d_2(c\bar{h} - h\bar{c})| - |ch(d_1\bar{d}_2 - d_2\bar{d}_1)|). \quad (14)$$

This is “out-of-phase” combination of two triplet states which has the total spin $S = 1$. The energy of this

structure is higher than the ground state reactants, Eq. (13), by the S–T excitation energy in methane, but in TS region both states are mixed; their avoided crossing produces the barrier. The system of four electrons on four orbitals has the third possible triplet state VB structure [44]:

$${}^3\Psi_3 = 2^{-1/2}(|chd_1\bar{d}_2| + |chd_2\bar{d}_1|). \quad (15)$$

The energy of this canonic covalent structure involves the triplet excitation of methane and the promotion energy (${}^3F \rightarrow {}^1D$) of the metal. This configuration is also admixed to the TS wave function; thus the promotion energy of the metal is important for the barrier height in this case. Before the barrier the Zr–CH₄ interaction is repulsive and the metal adopts the state which is least repulsive.

Calculations show that account of 5s-electron pair is getting important to the left from the barrier. The 5s-electrons are the most diffuse in the metal [46]. The highly excited b^3F state ($4d^35s^1$) with excitation energy 1.5 eV [45] is getting important in the region from the precursor complex till TS: its admixture to the ground triplet state gives the lower repulsion. Blomberg et al. [46] have noted that $4d^{n+1}5s^1$ configuration is important for all second-row TM atoms in oxidative addition to methane, because in that case the repulsion can be reduced by the formation of two *sd*-hybrids, one pointing toward the C–H bond and the other in perpendicular direction. By placing two electrons in the latter of these the repulsion is significantly decreased [46]. For both Y and Zr atoms the ground state configuration is $4d^n5s^2$, thus the admixture of $4d^{n+1}5s^1$ configuration reduces repulsion. Addition of 5s-pair to the previous simple analysis, Eqs. (2)–(15), indicates the importance of 5s-excitations, but does not change the main conclusion about the “S–T” avoided crossing at the transition state. Instead of three exchange integrals in a simple treatment, Eq. (6), a large number of intra- and inter-atomic $J_{i,j}$ parameters occurs for Zr and Y atoms insertion into methane. One should remind that the intratomic exchange integrals, Eq. (4), are positive; $S_{ij} = 0$ for orthogonal AO at the same center and only inter-electronic repulsion enter the integral equation (4). The inter-atomic exchange integrals are negative because the core attraction ($h_{ij} < 0$) prevails. There are many complicated details connected with account of promotion energy and the intratomic exchange energy loss. However, because of

cancellation of some inter-atomic and intratomic exchange integrals the most important factor determining the activation energy is the “singlet”–“triplet” avoided crossing, which depends on the S–T splitting of activated bond. An electronic promotion energy from the ground triplet state ${}^3F_2(4d^25s^2)$ to the quintet state ${}^5F(4d^35s^1)$ of the Zr atom has to be taken into account [43,45] in order to produce the ground triplet state (${}^3A''$) insertion product HZrCH₃. For Zr and Y atom insertion into methane the calculated activation energies are 16.9 and 20.7 kcal/mol [10]. The lower barrier for Zr insertion in comparison with the Y atom reaction can be explained by the smaller excitation energy from the ground triplet state to the excited quintet ${}^5F(4d^35s^1)$ term. This promotion energy for the Zr atom is 0.6 eV, while for the Y atom the promotion (${}^2D \rightarrow {}^4F$) energy is 1.36 eV [45]. The difference between these two values cannot be compared with the difference between activation barriers for the two reactions since the promotion energy is only a minor factor in a barrier formation. To a great extent the barrier is determined by the S–T energy gap in methane as follows from a simple VB consideration, Eq. (11).

For Zr and Nb atom insertion into methane the calculated activation energies are 16.9 and 15.6 kcal/mol [10], which are also in good agreement with a simple estimation obtained from Eq. (11): $E_a = 17.6$ kcal/mol. These atoms have four and five valence electrons and different ground state configurations, $4d^25s^2$ and $4d^45s^1$, respectively. The more detailed analysis indicates [40] that the number of valence electrons (at least for $n = 3$ –5) in catalysts is not important for estimation of the barrier, Eq. (11). All three atoms, Y, Zr and Nb, have non-zero spin in the ground state, which is sufficient in order to produce mixing and avoided crossing between the singlet and triplet states of the C–H bond; geometrical structure of the transition state is quite similar for all three atoms [13,46]. However, some important peculiarity of Nb atom reaction with methane has to be considered.

3.3. Nb atom insertion into methane and cyclopropane

For Nb, Mo, Ru and Rh atoms there is a spin flip during the insertion reaction; the spin multiplicity has to be changed along the lowest energy reaction path [10]. The ground state of Nb atom is sextet ${}^6D_{1/2}(4d^45s^1)$ and the low lying excited state is a low-spin quartet

$^4F_{3/2}(4d^35s^2)$; the multiplet averaged excitation energy is only 0.2 eV (for the lowest J sublevels it is 0.14 eV) [45]. The ground state configuration is reversed from $4d^n5s^2$ (like in Y and Zr) to the $4d^{n+1}5s^1$ in Nb (the last configuration produces the high-spin sextet 6D ground state which is lower than the 4D quartet by 1 eV [45]). Exchange integral $J_{4d,5s}$ in Nb is higher than in Y and Zr atoms. A small promotion energy ($^6D \rightarrow ^4F$) contributes to a smaller barrier for Nb insertion reaction into methane. Valence bond structure produced by combination of the ground sextet state of Nb atom (6D) with the triplet excited $T(\sigma\sigma^*)$ state of methane, when two pairs of spins from each moiety compensate each other, generates a quartet state; this low-spin state is prepared for the insertion reaction. In the VB approach this state interacts with the other low-spin quartet state: Nb (4F) + ground singlet state of methane (S_0). Avoided crossing between these two quartet VB structures produces an activation barrier.

The ground sextet state reactants in order to react and to produce the quartet insertion product have to carry out the sextet–quartet transition at the crossing point. This spin flip can be induced by spin–orbit coupling (SOC). Simple rules, based on one-center approximation for SOC analysis in chemical reactions [27,47,48], can be easily applied for TM catalysis [4,21,49]. If the crossing occurs before the barrier just at the beginning of the reaction coordinate the SOC matrix element will be dominated by pure atomic SOC integral between the 6D and 4F states of the Nb atom. This SOC integral is pretty large (220 cm^{-1} for $J = 3/2$) and can provide the sextet–quartet transition. The calculated barrier for Nb atom insertion into methane is still high ($E_a = 15.6 \text{ kcal/mol}$), so the reaction has not been detected at 300 K [10]. But for Nb atom insertion into cyclopropane with spin flip the activation energy is only 4.3 kcal/mol [10] and such a reaction has been observed with a high rate constant ($3 \times 10^{-12} \text{ cm}^3/\text{s}$ [10]). For Zr reaction with cyclopropane the barrier is higher ($E_a = 7 \text{ kcal/mol}$ [10]). The reaction proceeds without spin flip, but still with the lower rate constant ($0.66 \times 10^{-12} \text{ cm}^3/\text{s}$ [10]). It seems that Nb atom insertion into cyclopropane with spin flip is effectively allowed by a strong one-center SOC perturbation. The Mo atom reactions with hydrocarbons present examples of the opposite type.

3.4. Conceivable Mo atom insertion into methane and cyclopropane

The Mo atom has the high-spin ground state $^7S(4d^55s^1)$ [45]. The large insertion barrier for Mo reaction with methane is determined by very high excitation energy (1.6 eV) to the low-spin state $^5S(4d^55s^1)$ [45]. The $4d5s$ -spin pairing upon transition determines the loss of exchange energy in the Mo atom [24]. Later it leads to the loss of exchange energy upon bond formation and to low-spin coupling of $4d$ -electrons [24,46,50]. One should stress that the low-spin coupling is involved because of interaction of two valence bond structures of the type, presented by Eqs. (2) and (3), with the singlet and triplet spin pairing inside methane moiety. The “S–T” avoided crossing for the corresponding spin states still determines the barrier for the low-spin quintet state PES. The importance of the low-spin state in reaction of Mo atom with methane has been proved recently in crossed beams studies of Mo(a^7S) and Mo(a^5S) collisions with methane and ethane [33]. For collisions of the ground state Mo(7S) atom with methane no reactive signal was observed [33]. For collisions of the metastable low-spin state Mo(5S) atom with methane, the dehydrogenation product MoCH₂, was observed at all collision energies studied [33]. The insertion product, H–Mo–CH₃, with lower energy is kinetically unstable in this beam experiment; the energy flow in the hot intermediate, H–Mo–CH₃, between vibrational modes leads finally to the dissociation product MoCH₂ + H₂ with higher energy. The crossed beams experiment [33] is a direct verification of the VB correlation diagram with the “S–T” avoided crossing for two low-spin quintet states Mo(a^5S) + CH₄(S_0) and Mo(a^7S) + CH₄($T_{\sigma\sigma^*}$). This is optically induced spin-catalysis when the spin forbiddenness of the catalytic process is overcome by optical pumping.

The ground state Mo atom does not interact neither with methane nor with cyclopropane at 300 K [10]. Since both reactions proceed with a spin flip, the additional reason for absence of reactivity is connected with a strong spin prohibition: there is no SOC mixing between high-spin (a^7S) and low-spin (b^5S) states. The orbital angular momentum change does not occur at the septet–quintet crossing point during the reaction.

3.5. Rh atom insertion into methane and ethane with a spin flip

Only Rh and Pd atoms react with linear alkanes at 300 K [10]. Insertion of Rh atom into C–H bond of methane and ethane has no barrier, but includes a spin flip from the high-spin ground state $^4F(4d^85s^1)$ reactant to the low-spin state $^2D(4d^9)$ reactive PES. The reason for the low-spin state reactivity is obvious from the spin-uncoupling scheme: the doublet state combination of the ground state $^4F(4d^85s^1)$ with the triplet excited state of hydrocarbon is reactive and produces an avoided crossing with the $a^2D(4d^9) + S_0$ reactants. The quartet–doublet spin flip occurs in the beginning of the reaction and is effectively allowed by a strong one-center SOC mixing between 4F and 2D states.

3.6. Pd atom insertion into methane and ethane

The singlet ground state palladium atom ($^1S, d^{10}$) can also insert into the C–H bond of methane with a low activation barrier, $E_a = 3.6$ kcal/mol [10], because the excitation energy to the triplet ($^3D, d^9s^1$) state is only 0.81 eV [45]. This energy is very small in comparison with the S–T excitation in methane (11.37 eV), so the “double-triplet” ($^1(^3\sigma\sigma^*, ^3D)$) singlet state can interact with the ground singlet state in the reaction Pd + CH₄. This situation is very general for many bond activation processes by TM species. The general spin-uncoupling scheme, which includes also the Pd atom insertion into C–H bond of methane and ethane, is shown in Fig. 6. The general scheme (Fig. 6) can be applied to Pd atom addition to the

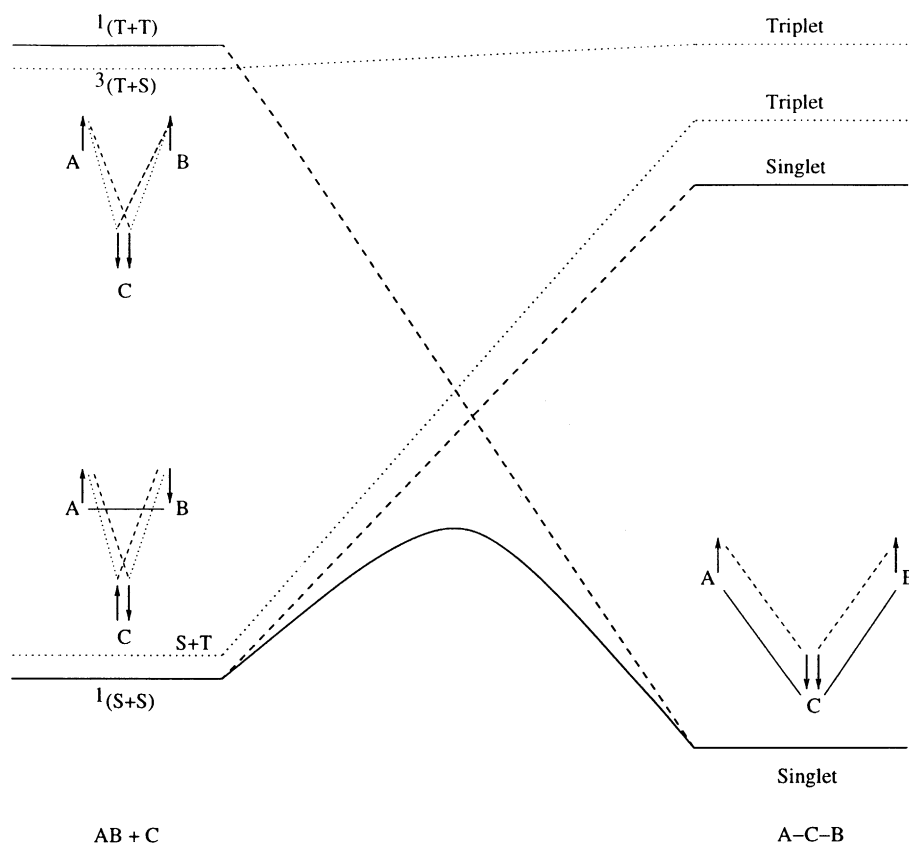


Fig. 6. Correlation VB diagram for a diamagnetic catalyst insertion into A–B bond. The catalyst has a low lying triplet excited state. The triplet states correlation is shown by dotted lines. (Intermolecular singlet spin pairing in the “A – B + C” covalent structures is shown by dashed lines.)

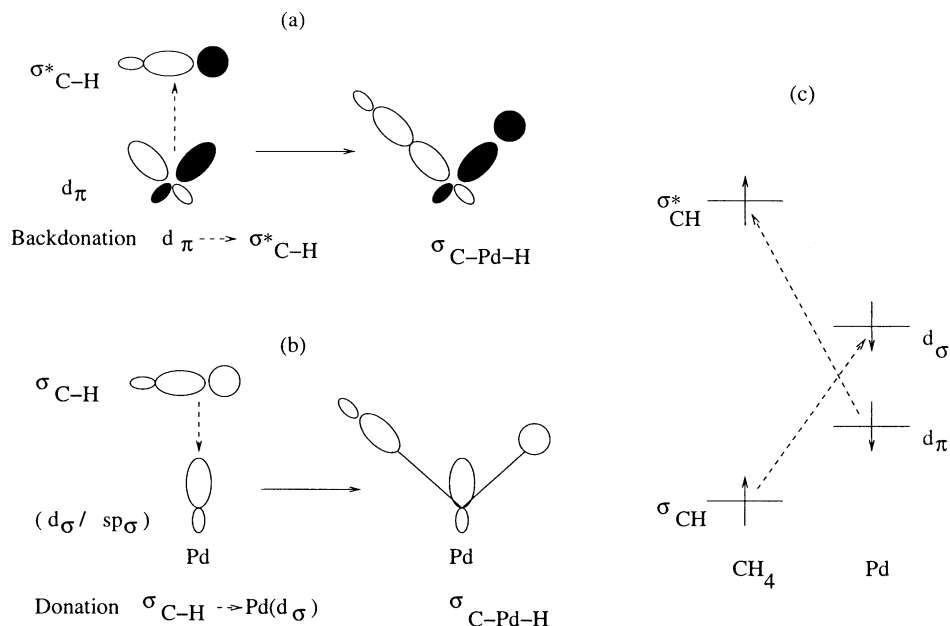


Fig. 7. MO description of spin uncoupling for Pd atom insertion into C–H bond of methane. The $\sigma \rightarrow d_\sigma$ donation (b) and $\sigma^* \leftarrow d_\pi$ backdonation (a) lead to the spin polarization of the “double-triplet” type (c).

double bond of ethene [19] and to many catalytic processes with ligated TM complexes [1,2,16].

It is difficult to see such spin uncoupling in molecular orbital (MO) description with CI method. Mixing of orbitals is so strong at the Hartree–Fock level that only one closed-shell determinant dominates in the CI expansion of the ground state for Pd atom reaction with methane. But a well-known “donation–backdonation” scheme [2], which is revealed by charge distribution [1,16,19] in many oxidative addition reactions, can be understood in terms of the “double-triplet” singlet state occurrence [19]. Spin uncoupling for Pd atom insertion into C–H bond of methane, obtained by MO description, is presented in Fig. 7. The $\sigma \rightarrow d_\sigma$ donation (Fig. 7b) and $\sigma^* \leftarrow d_\pi$ backdonation (Fig. 7a) [2] leads to the spin polarization of the “double-triplet” type (Fig. 7c). It is important to stress that only such “donation–backdonation” scheme with spin polarization is essential. If the “donation–backdonation” process would proceed without such spin polarization and produce the “double-singlet” state, this configuration will not contribute to the reaction activation. The reason is not only determined by a high energy of such configuration (the

triplet states in each species are lower in energy than the singlet excited counterparts). From Fig. 5 one can see that the singlet excited state (S_1) in methane does not lead to the C–H bond dissociation. It produces a weakly bound CH_3^*H excimer. Involvement of such structure in the VB configuration mixing will not produce lowering of activation barrier. Only the triplet (T_1) state (Fig. 5) is important for catalysis of the C–H bond cleavage. One can stress that both states, S_1 and T_1 , have the same orbital configuration and orbital symmetry. From the orbital symmetry selection rules [3] it is impossible to distinguish the “double-singlet” state formed by the “donation–backdonation” scheme and the “double-triplet” structure presented in Fig. 7. This shortcoming reduces the importance of the orbital symmetry selection rules in catalysis.

4. Oxidative addition of methane to TM complexes with ligands

Ligands effects on the reactivity of TM complexes are divided into essentially two different classes: those which have a steric origin and ligand effects

that are of electronic origin [15,34,51]. Steric effects are best handled by molecular mechanics methods and only electronic effects are considered in the present analysis. Experimental [7,33,52] and theoretical [1,16,34] studies on the oxidative addition reactions between TM complexes and methane have given recently considerable detailed insight into the mechanism of this important process of the C–H activation.

4.1. Spin uncoupling

Activation of alkanes by organometallic complexes is well-known now [7–9]; it also occurs on metal surface [1]. Saturated TM complexes are usually unreactive with alkanes [33]. Besides a simple chemical reason, additional explanation is getting obvious from the presented valence bond method: the S–T gap is too high in such saturated TM complexes. The coordinatively unsaturated TM centers, in some cases insert into the C–H bonds of alkanes [7–9,34]. Siegbahn and Svensson [16] have calculated rhodium complexes with two ligands, RhLL' ($L, L' = \text{Cl, H, CO, NH}_3$), and their reactions with methane. The authors of [16] have compared formation energy for the molecular precursor complex and for the transition state of the oxidative addition reaction and have stressed different requirements imposed upon the metal-complexes by these two processes. Siegbahn and Svensson [16] have found that a ground singlet state is required for the formation of a strongly bound molecular precursor complex. At the same time a ground triplet state is required for a low transition state barrier. (The low-lying singlet and triplet state, respectively, have also a great advantage). According to [16] this means that the barrier is not expected to be characteristic for the methane dissociation reaction, but is dependent on the S–T splitting of the TM complexes being different for the different ligands combinations. It is obvious that the triplet state of the TM complex itself cannot influence chemical reactivity of the singlet spin channel: only the singlet transition state and products of the singlet spin channel have been studied in Ref.[16]. Thus, the T state of the TM complex can be involved in chemical reactivity only in combination with the T state of the second reactant, methane. Only a singlet coupled combination of two triplet states from both reactants, which quench each other, can influence chemical

reactivity on the singlet potential energy surface. This is a direct support of the VB correlation diagram (Fig. 6) discussed above.

Both $\text{RhCl}(\text{CO})$ and RuH_2 complexes, which are ground state triplets (with the S–T energy gap about 13–20 kcal/mol [16]), thus have low barriers for the methane oxidative addition. (The transition state is lower than the singlet state asymptote by about 7 kcal/mol.) For $\text{RhH}(\text{NH}_3)$ complex, which is a ground state singlet, but has a very low excitation energy (1 kcal/mol) to the triplet state, the transition state is even lower (–15 kcal/mol). The $\text{RhH}(\text{CO})$ complex has a ground state singlet with a high adiabatic excitation energy (13 kcal/mol) to the triplet. For this complex the transition state barrier in methane activation is the highest of the systems studied [16].

The molecular precursor complex is a strongly bound van-der-Waals system. Its formation does not need any bond cleavage: the precursor complex occurs between two closed shell species as a result of electrostatic polarization. Its binding energy does not depend on the S–T splitting neither in methane, nor in metallorganic complex. According to the presented spin-uncoupling scheme the transition state barrier depends on the “double-triplet” state energy of two reactants. The S–T energy gap in methane is constant and the barrier of the oxidative addition reactions between transition-metal complexes and methane depends on the S–T energy gap in the transition metal compound. The lower triplet state of the TM complex, the lower activation barrier. Thus, the spin-uncoupling scheme can easily explain the important findings of spin dependence from [16].

4.2. Spin flip

Bergman et al. have found that the complex $\text{C}_5(\text{CH}_3)_5\text{RhCO}$, generated by photolysis, inserts spontaneously into many alkanes [7–9]. This and other complexes of general formula MCpL ($L = \text{CO, PR}_3$) or MCIL_2 ($L = \text{PPh}_3$) have been found to activate C–H bond [7,8,52]. The common feature of all these TM complexes ($M = \text{Rh, Ir}$) is a very low S–T energy gap;³ the involvement of the

³ For Rh-complex CpRhCO the triplet state is slightly below the singlet. This is not important in present context since both states are in thermal equilibrium. Catalysis proceeds in the singlet state.

high-spin (triplet) state is necessary for combination with the triplet excited state of the C–H bond in order to produce the “double-triplet” singlet reactive state.

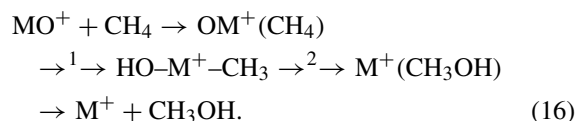
Only rhodium and iridium complexes were found to activate C–H bond of alkanes. Contrary to this activity, the cobalt complexes were found to be inert, which was surprising for TM belonging to the same group [34]. Siegbahn has explained this puzzle: it is due to the triplet ground state of the CpCo(CO) complex, which is much lower than the singlet (contrary to the Rh, Ir complexes) [34]. As usual, the insertion product, CpCo(CO)HCH₃, has a singlet ground state. Thus, the triplet ground state cobalt complex has to change spin during the reaction. Siegbahn has shown that the S–T crossing point reproduces a high activation barrier and this has been considered as the reason why the insertion does not occur [34].

The addition of CO molecule to the CpCo(CO) complex also needs to overcome spin prohibition, since the product is singlet. Siegbahn has shown that the S–T crossing point in this reaction is lower in energy than the reactant triplet state [34]. The S–T crossing does not need activation barrier: by this reason the CO addition proceeds very fast [34]. It was shown recently that SOC at the region of the S–T crossing seam is negligible in the CpCo(CO) complex insertion into the C–H bond [21]. The T–S transition occurs mostly on the C–H moiety and does not involve any orbital rotation. (Such rotation or orbital angular momentum change during the T–S transition is necessary in order to produce effective one-center SOC contribution [26].) At the same time in the CO addition to the CpCo(CO) complex it is not necessary to cleave the bond and the triplet excitation in the CO moiety is not involved in the reaction process. The T and S states differ by the orbital rotation between 3*d*-manifold on Co atom; thus the SOC matrix element is comparatively large [21]. The spin flip is effectively allowed during this reaction.

4.2.1. Methane–methanol conversion by TM-oxide cations

Yoshizawa et al. [53] have calculated by DFT method the conversion of methane to methanol by the transition-metal-oxide cations, MO⁺ + CH₄ → M⁺ + CH₃OH, where M = Mn, Fe and Co. They have shown that the reaction proceeds in such a

way [53]:



The double arrow →¹→ means overcoming the first transition state (TS1). Yoshizawa et al. [53] have shown that a crossing between high-spin (the ground state of all TM-oxide cations) and low-spin state occurs on the lowest potential energy reaction path. The spin crossing occurs twice (both at the entrance channel and at the exit channel) for FeO⁺ and CoO⁺, but it occurs only once near TS2 for MnO⁺.

The activation energy at TS1 for MO⁺ insertion into C–H bond of methane plays a central role in this reaction. It is 9 kcal/mol for MnO⁺ being much smaller than 22 and 31 kcal/mol for FeO⁺ and CoO⁺ [53]. The activation energy from the insertion intermediate to M⁺(CH₃OH) via TS2 is computed to be 25, 29 and 36 kcal/mol for M = Co, Fe and Mn, respectively. Calculations of Yoshizawa et al. [53] explain experimental data [54,55] on reactions efficiency (low for CoO⁺ and intermediate for FeO⁺) and the methanol-branching ratio; it is 100% for CoO⁺, 41 % for FeO⁺ and almost zero for MnO⁺. Yoshizawa et al. [53] have to postulate that the intersystem crossing between high-spin and low-spin potential energy surfaces greatly contributes for the reactivity of FeO⁺ and CoO⁺ in order to decrease activation barrier at the TS1 stage.

Spin selectivity in reaction of FeO⁺ with methane can be explained by the general scheme [40,55]. The ground sextet state of the reactant complex OFe⁺–CH₄ has to be combined with the triplet excited state of methane in order to produce more reactive quartet state with intermolecular spin pairing between the O–H and Fe–C growing bonds and the simultaneous C–H bond cleavage. That is why the quartet state of the reactant complex has smaller activation barrier and the reaction involves the sextet–quartet spin flip.

Yoshizawa et al. [53] have referred to SOC calculations presented by Danovich and Shaik [56] for a similar reaction FeO⁺(⁶Σ⁺) + H₂ → H₂O + Fe⁺(⁶D). This process also involves two spin-inversion junctions between the sextet and quartet PES near the entrance channel and at the exit channel [56]. The author have reproduced some important intermedi-

ate structures published by Yoshizawa et al. [53] for $M = \text{Fe}$ in reaction (16) and calculated SOC matrix elements by the MRCI (TZV) method with effective nuclear charges and GAMESS code like in [56]. The results are quite similar to the SOC integrals presented by Danovich and Shaik [56] for hydrogen oxidation. The only important difference is connected with the quartet–sextet SOC matrix elements at the exit channel. The authors of [56] have obtained a relatively very small SOC integral at the second quartet–sextet crossing which occurs just before the C_p stage ($\text{Fe}^+ - \text{OH}_2$ complex at the exit channel). Contrary to the FeO^+ reaction with hydrogen [56] the quartet–sextet crossing at the exit channel of the methanol production occurs *after* the C_p stage (the product cluster $\text{Fe}^+ - (\text{CH}_3\text{OH})$ formation) [53].

The quartet product cluster is more stable and has a shorter $\text{Fe}^+ - \text{O}$ bond (1.96 Å) than the sextet cluster (2.07 Å) [53]. Vibration of this bond (reaction coordinate for the exit channel) induces the quartet \rightarrow sextet nonadiabatic transition by energy flow to a new $\text{Fe}^+ - \text{O}$ oscillator with the shifted equilibrium. The driving force for such transition is spin–vibronic coupling [27]. The calculated derivative of the SOC integral in respect to the nuclear displacement is 0.045 eV/Å. The Franck–Condon factor and density of states are also relatively large, which provides finally a competitive rate constant for the quartet \rightarrow sextet transition.

5. Conclusions

An important advantage of the VB approach to catalysis is that it relates the excited triplet state and spin–uncoupling scheme to the traditional way in which chemists rationalize chemical structure and reactivity [3,5,22]. In order to construct diabatic electronic states representing specific resonance structures of a catalytic system one has to include the triplet excited state of activated chemical bond. A simple three-electron VB scheme, Eqs. (2)–(8), and its generalization to many-electron catalytic systems illustrate, first of all, the crucial importance of the triplet excited state of activated molecule. In the VB method an account of this state includes also involvement of some excited states of the catalyst, which is in line with previous findings [10,11,24]. Then it is

easy to understand that only the low-spin state of the catalyst is reactive and the small energy gap between high-spin and low-spin states is the main electronic factor of catalytic activity.

It is known that the ionic contributions are very important in the transition state region [10,19]. In general considerations of the three-center problem by the VB approach it was shown that ionic structures produce considerable lowering of the barrier even in the case of a symmetric triangular approach of the free radical to olefins [22]. The “S–T” crossing still occurs, but at lower energy. In present work an account of the ionic structures is also found as an important additional factor of catalytic activity.

The presence of a low-lying $4d^{n+2}5s^0$ state was found before [43] to be of key importance for a low activation barrier. This excited state should enter the qualitative analysis of all results, since this is possible reacting state, being analogous of the Ψ_{1r} (Eq. (2)) reactant valence bond structure, which can participate in the “S–T” avoided crossing with the “triplet” counterpart valence bond structure Ψ_{2r} (Eq. (3)).

This is remarkable for spin uncoupling scheme that metal surfaces are known as important catalysts. Any desirable spin state can be easily achieved in a large metal cluster, which simulate the adsorption site on the surface. Some models of hydrocarbons adsorption on copper surfaces illustrate the spin–uncoupling features [35]. Geometry optimization of the adsorbed unsaturated hydrocarbons indicates that their structure and energy are very close to the excited triplet states characteristics of the gas-phase molecules [35]. The copper clusters simulate the local site on the surface perturbed by adsorption. The Cu(1 1 0) and Cu(1 0 0) clusters consisting of 14 atoms have been chosen [35] in order to simulate the surfaces prepared for adsorption; these clusters have the triplet ground state. Combination with the triplet excited state of hydrocarbon can be accounted in the VB correlation diagram; it illustrates the involvement of the triplet excited hydrocarbon in the adsorption process. Direct DFT calculations of adsorbate [35] are in excellent agreement with the spin uncoupling scheme. Thus, the involvement of the triplet state of hydrocarbon is a common feature of spin uncoupling in catalysis by TM species.

The role of the triplet state in thermal chemistry is hidden, since this is a virtual and unstable state for a localized covalent bond. (It is seen in

photodissociation experiments; for conjugated molecules the triplet state is often stable and its manifestations are well-known in photochemistry and phosphorescence [44].) The triplet state is not important for many chemical properties of stable diamagnetic molecules (without heavy atoms). But it is getting important for analysis of reactivity of such molecules in respect to radicals [22]. Since the nature of TM catalysis is connected with spin-uncoupling and is determined by the high-spin and low-spin energy gap, as well as by other spin-effects in the TM catalyst, the role of the triplet state of diamagnetic reagents is coming to the first place. The presented VB scheme is probably too simple, but it illustrates the importance of the triplet state, which is not so obvious in a conventional MO treatment.

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