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Molecular models of active sites of C_1 and C_2 hydrocarbon activation

G.M. Zhidomirov, V.I. Avdeev, N.U. Zhanpeisov, I.I. Zakharov, I.V. Yudanov

Boreskov Institute of Catalysis, Novosibirsk 630090, Russia

Abstract

A short review of the quantum chemical approach to the problem of alkane activation is presented. The results of ab initio calculations of oxidative addition of methane molecules to the transition metal (TM) atoms and complexes are discussed, as well as some questions of methane dissociation on TM surfaces. Both homolytic and heterolytic mechanisms of methane activation on oxide systems are considered.

1. Introduction

The high chemical stability of alkanes can be easily explained by their electronic structure. An essential feature of this structure is that the number of valence electrons in alkanes is equal to the number of valence orbitals [1] and that there are no lone pairs and empty orbitals, which are important for heightened reactivity. Among the factors decreasing the activity of alkanes can also be mentioned a low polarity of the C–H bond and a relatively high binding energy (ca. 100 kcal/mol) together with the tetrahedral arrangement of bonds which imposes steric hindrance for the attack of the carbon atom. Thus, the problem of searching for chemical species capable of alkane activation is very interesting both from experimental and theoretical points of view. A number of such chemical systems were found to date, for example, transition metals, various transition metal complexes, basic oxides, strong acids. The success of experimental investigations initiated quantum chemical studies in this field. In the present review we are mainly concerned with theoretical problems of alkane activation by transition metal compounds and basic oxides.

2. Methane activation by transition metal complexes and metals

The first attempts at a quantum chemical investigation of alkane activation by TM complexes used semi-empirical approaches. The coordination of CH_4 by square-planar chlorine and aquachlorine Pt(II) complexes were studied with the CNDO/2 method in ref. [2]. It was shown that the coordination interaction results in weakening and polarization of C–H bonds accompanied by redistribution of electron density between ligands and the central ion. The binuclear complexes, with CH_4 coordinated to TM ion and the oxygen atom of the ligand simultaneously, appeared to be the most efficient in the activation process. It was also found that a certain optimal correlation of donor–acceptor and dative interactions is required for real CH_4 activation.

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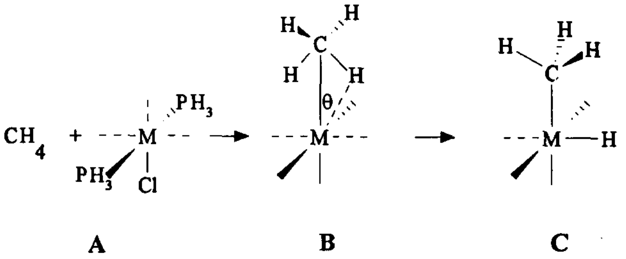

Fig. 1. Reaction scheme of methane addition to $MCl(PH_3)_2$.

Another promising method for methane catalytic activation by TM complexes is the process of oxidative addition. A comprehensive analysis of this reaction using the EHT method was provided in ref. [3]. The importance of the coordinative desaturation of the TM ion in the complex was emphasized and the conclusion was reached that $\sigma_{CH4} \rightarrow$ M electron transfer dominates the first stage of the reaction. At the same time an electron transfer from M to σ^*_{CH4} is required for the complete form of oxidative addition.

The concept of two directions of electron transfer ensuring different stages of methane activation reaction was actively discussed in subsequent theoretical work. Several investigations were devoted to calculating the oxidative addition of methane to naked neutral TM atoms [4] or to naked TM cations [5]. The calculations were provided by non-empirical methods taking into account both electron correlation and relativistic effects. It was found that the barrier for C–C insertion is 14–20 kcal/mol higher than that for C–H insertion. The activation barriers in general are considerably lower for second transition row atoms than for the first row ones. As for reactions with cations, the activation energy decreases for ions in the beginning and in the middle of the transition row but increases for ions from the end of the row. This effect cannot be explained by the differences in the energy of products, because insertion products are less stable for cations. The explanation proposed in ref. [5] associates the differences in activation energies with different occupations of s orbitals of TM which influence on repulsion between the metal electrons and the electrons of methane. For the case of cations the charge induced dipole interaction provides the stabilization of molecular complex precursor at the initial stage of the reaction.

The formation of stable methane adducts of TM complexes on the first stage of methane activation was reported from results of non-empirical calculations by several authors [6–8]. The calculations showed a significant covalent contribution to the stabilization of the adducts.

The role of TM ion electronic state and the nature of ligands are the most important questions of methane activation. A number of studies were devoted to these problems [6,7,9–11]. As calculations showed the mechanism of the ligand influence on the reaction is rather intricate. Nevertheless it is possible to distinguish the most important aspects of this influence. One of them is associated with controlling the direction of the electron density transfer mentioned above. As an example let us consider the model quantum chemical studies of one of the most efficient systems of methane activation which was found by Periana and Bergman [12].

The model complex was considered for ab initio investigations [6] of the process:

$$CH_4 + RhCl(PH_3)_2 \rightarrow H^{\cdot}RhCl(PH_3)_2^{\cdot}(CH_3) \quad (1)$$

It was shown that reaction (1) proceeds through a bifurcated η^2-CH_4 complex (intermediate structure B in Fig. 1). On the basis of this model we have calculated ab initio the reaction path for M = Pt,Ir,Os. To compare our results with those previously obtained [6] we have also performed calculations of the Rh complex. The calculations

Table 1.
Main energetic characteristics of reaction (1) potential curve (kcal/mol) calculated at Hartree-Fock (HF) level and using second order Møller-Plesset (MP2) perturbation theory.

M	reactants	transition state		product	
		HF	MP2	HF	MP2
Pt	0	54	40	51	34
Ir	0	18	-2	-5	-24
Os	0	14	-2	6	-10
Rh	0	26	1.5	14	-24

were performed with a GAUSSIAN 92 package of programs [13] using effective core potentials to replace the inner shell electrons of P, Cl, Pt, Ir, Os and Rh atoms [14]. Both the minimal basis set (MB) and the valence split basis set (DZ) were used for light atoms and valence electrons of heavy atoms.

Calculations of the reaction path were performed in two stages. At first the geometry of CH_4–$MCl(PH_3)_2$ complex was optimized with MB basis for certain points of reaction path corresponding to $\theta=30$–$90°$ (Fig. 1). Then the calculations were repeated with DZ basis and taking into account the electron correlation on the level of second order Møller–Plesset perturbation theory using the geometries obtained at the first stage. The calculated relative energies of reactants (Fig. 1A), intermediate complex (Fig. 1B) and product (Fig. 1C) are given in Table 1. The analysis of changes of electron density distribution along the reaction path showed that acceptor Cl ligand forms a positive charge on M promoting an attack of the trans-vacancy in the complex by CH_4 molecule. In turn, donor PH_3 ligands control the ability of the complex to form a M–H bond. One of the ways of regulating the strength of the influence of the ligand on the electron transfer flows along the reaction path is by changing the bond length M–L (M–Cl and M–PH_3).

The strong dependence of the activation energy on occupation of d-orbitals in neutral atoms should be mentioned. In the case of Pt(d^9s^1), the energy barrier is so high that one could hardly expect significant activation of the C–H bond by the Pt complex. At the same time, in the case of isoelectronic Rh and Ir (d^7s^1) atoms, the calculations predict high activity of $IrCl(PH_3)_2$ and $RhCl(PH_3)_2$ complexes in reaction of oxidative addition of CH_4.

It is interesting that the mechanism of methane activation on the metal surfaces is qualitatively similar to that for TM complexes discussed above. In our recent work [15] we have calculated the reaction path of the dissociative adsorption of methane over the Ni(100) surface.

$$CH_4 \rightarrow CH_3(s) + H(s) \qquad (2)$$

We have used cluster approximation and the Hartree-Fock method (RHF for closed shells and ROHF for open shells). According to our calculations the most important peculiarity of methane decomposition is the formation of local centres on the metal surface due to the high lability of electron density. It is evident from an analysis of the reaction path that two types of active centres are required for C–H bond activation. First an acceptor ability favourable to Ni–CH_3 bond nucleation occurs on the adsorption centre. However, adsorption centres with an electron density excess are also required for Ni–H bond formation. According to calculations these centres appear during the reaction but they are remote from the centre of the Ni–CH_3 bond nucleation. Thus the metal surface should display strong acceptor properties at the first steps of the reaction path and donor properties at the final steps.

Let us summarize now the results of the quantum chemical study of methane activation by the metal surface and metal complexes. Two active centres remote from each other are formed on the metal surface. These centres control the rupture of the C–H bond and the formation of new M–CH_3 and M–H bonds. Two ligands with opposite properties in the $MCl(PH_3)_2$ complex play in fact the same role on a single metal centre.

3. Methane activation by solid oxides

Two alternative mechanisms of methane activation by basic oxides are usually discussed. According to one of them activation proceeds through heterolytic dissociation of methane on the surface. Surface defect structures containing low-coordinated (LC) ions must be particularly active in the process. The other mechanism suggests preliminary formation of active oxygen species (O^-, O_2^-, O_3^-, O_2^{2-} etc.) which can abstract H from CH_4 with elimination of CH_3 into the gas phase. Both of these mechanisms were the subject of quantum chemical investigations.

We have studied the heterolytic dissociative chemisorption of the methane molecule on MgO and Li/MgO surfaces with the semi-empirical MINDO/3 method [16]. The specially parameterized MINDO/3 gives reliable geometric and energetic characteristics of various surface structures and permits to perform calculations of molecular clusters large enough to reproduce the properties of real crystal active sites [17,18]. The magnesium oxide surface was modelled by Mg_9O_9 and $Mg_{12}O_{12}$ clusters. These models allowed us to analyze the role of all the types of low-coordinated (three-, four- and five-coordinated) Mg_{LC}^{2+} and O_{LC}^{2-} ions in the chemisorption of methane. The heterolytic mechanism implies dissociation of the methane molecule into H^+ and CH_3- ions which are stabilized by O_{LC}^{2-} and Mg_{LC}^{2+} low-coordinated ions, respectively. According to calculations, adsorption on the pair of O_{3C}^{2-} and Mg_{3C}^{2+} three-coordinated ions is the only stable state with energy gain of 15 kcal/mol. This result is in good agreement with ab initio calculations of Ito et al. [19]. Adsorption on the statistically preferable O_{3C}^{2-}–Mg_{4C}^{2+} and O_{4C}^{2-}–Mg_{3C}^{2+} ion pairs is energetically less profitable, although these centres may participate at relatively high temperature. Investigating the Li/MgO system we used clusters of the same size as for pure MgO with Li_{LC}^{+} ion substituted for one of Mg_{LC}^{2+}. The negative charge arising from this substitution was compensated by attaching a proton to the O_{3C}^{2-} ion. We found that Li–CH_3/O–H and Li–H/O–CH_3 adsorption complexes which include Li_{LC}^{+} ion are energetically unprofitable. On the other hand, adsorption on the O_{3C}^{2-}–Mg_{4C}^{2+} and O_{4C}^{2-}–Mg_{3C}^{2+} ion pairs proceeds with an essential gain in energy on the Li/MgO surface in contrast to pure MgO. The concentration of four-coordinated ions is evidently much higher than of three-coordinated ones, therefore the number of active sites available for dissociative adsorption of methane is much larger on the Li-promoted MgO surface than on the pure one. This result should be taken into account when discussing the mechanisms of methane activation.

We have also studied with the MINDO/3 method the activation of methane on the ZnO surface. Parameterization of the method was extended for calculations of Zn-containing compounds [21]. The structures with the lowest energy are produced by heterolytic dissociative adsorption of methane on the pairs of low-coordinated ions Zn_{2C}^{2+}–O_{2C}^{2-} and Zn_{2C}^{2+}–O_{3C}^{2-} with energy gain 23.6 and 2.8 kcal/mol, respectively.

The dissociative adsorption of CH_4 on Al_2O_3 was calculated in ref. [22] by the non-empirical method. The structure $Al(OH)_3$ was considered as a model of a Lewis acid site on an alumina surface.

Various cluster models have been proposed in the literature for active oxygen containing centres of homolytic dissociation of CH_4. Much attention has been paid to molecular models of O^- on oxide surfaces [23–28]. The structure of such a centre can be presented, for example, for Li-doped MgO as $[Li^+O^-]$. The simplest model of this structure used for calculations in refs. [23,24] is diatomic lithium oxide molecule. One of the first cluster models of the O^- centre on MgO was suggested in ref. [25], where the 3-layer $Mg_{21}O_{20}^{2+}$ cluster was considered and the process of CH_4 dissociation was calculated by the semi-empirical ASED method. Cluster models of smaller size were proposed for ab initio calculations of Li-doped MgO in refs. [26–28].

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5. References

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