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DFT study of the mechanism of alkane hydrogenolysis by transition metal hydrides

1. Interaction of silica-supported zirconium hydrides with methane

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Model reactions of silica-supported zirconium hydrides $(\equiv Si—O—)_3ZrH$ and $(\equiv Si—O—)_2ZrH_2$ with methane, resulting in cleavage of a C—H bond in the methane molecule and the formation of $(\equiv Si—O—)_3ZrCH_3$ and $(\equiv Si—O—)_2Zr(H)CH_3$ as products were studied using the DFT approach with the PBE density functional. The processes proceed as bimolecular reactions without preliminary formation of agostic complexes. According to calculations, zirconium dihydrides $(\equiv Si—O—)_2ZrH_2$ are more reactive toward the methane C—H bonds than zirconium monohydrides $(\equiv Si—O—)_3ZrH$. The calculated activation energies of the reactions with participation of zirconium dihydrides $(\equiv Si—O—)_2ZrH_2$ are in better agreement with the known experimental data for the Yermakov—Basset catalytic system.

Key words: activation of C—H and C—C bonds in alkanes, surface zirconium hydrides, hydrogenolysis of alkanes, nonempirical quantum-chemical calculations, density functional method.

One of the vital problems of petrochemistry is development of catalytic systems for selective cleavage of the C—C bonds in alkanes by the action of hydrogen under mild conditions to improve the efficiency of refining heavy oil fractions.[1] In recent years, considerable interest in this type of catalytic systems increases is due to strong demands for recycling and cost effective utilization of large amounts of polyethylene and polypropylene.[2]

The cleavage of the C—C bonds in alkanes in the reactions with participation of transition metal compounds can be considered as the reversal of alkene polymerization (Scheme 1, stages (2) and (3)) involving an additional stage (1) of activation of the C—H bond in an alkane molecule.

Scheme 1

$$L_mM—R + C_nH_{2n+2} \rightarrow L_mM—C_nH_{2n+1} + RH \qquad (1)$$

$$L_mM—C_nH_{2n+1} \rightarrow L_mM(C_kH_{2k})C_lH_{2l+1} \qquad (2)$$

$$L_mM(C_kH_{2k})C_lH_{2l+1} \rightarrow L_mM—C_lH_{2l+1} + C_kH_{2k} \qquad (3)$$

R = H, Alk; M is metal, and L is ligand;
$l + k = n$; $l = 0, 1, 2, ...$; $k = 2, 3, 4, ...$

Such a process is feasible. However, before putting it to practical use one should find a way for compensating large energy expenditure for cleavage of the C—C bonds and thus make the process thermodynamically favorable.

Detailed theoretical studies of the reactions (1)[3a—c], (2) and (3)[4a—h,5a—c] have been carried out taking the reactions of cationic complexes Cp_2ZrR^+ (R = H, Alk) and systems based on them as examples. Since the stages (2) and (3) are thermodynamically unfavorable in the case of zirconocene catalysts,[4a—h,5a—c] no depolymerisation on these catalysts has been studied so far.

The Yermakov—Basset system known since the early 1970s belongs to a small group of catalytic systems in which all three types of processes (*e.g.*, activation of the alkane C—H bonds and alkene polymerization and depolymerization) were observed experimentally.[6a—f,7a—i] This system was first obtained[6a] by treating the surface of partially or completely dehydroxylated SiO_2 with tetraallylzirconium followed by activation of the "grafted" organozirconium compounds in H_2 atmosphere at 150—200 °C. Pioneering studies[6a—f] revealed that the active species formed behave as zirconium hydrides and exhibit high catalytic activity in ethylene polymerizations. More recently,[7a—i] the surface hydrides of Zr, Ti, Hf, and Ta were prepared and their reactivities toward alkanes in the σ-bond metathesis were investigated.

Scheme 2 presents the mechanism of formation of zirconium hydride groups in the Yermakov—Basset system.[7a—i] The first two stages of this process have been studied by various physicochemical methods and their mechanisms have been established reliably. The most interesting is stage (3), which involves the interaction of highly reactive groups $—ZrH_3$ with the surrounding —Si—O— bonds and can proceed in two stages. The zirconium dihydride groups $(\equiv Si—O)_2ZrH_2$ (**1**) form in stage (3). These groups can interact with the —Si—O— bonds to give the zirconium monohydride groups $(\equiv Si—O)_3ZrH$ (**2**). The nature of the active sites in the Yermakov—Basset system is still unclear. The authors[7h]

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believe that these sites are zirconium monohydrides **2**. According to another pointe of view,[6f] these are zirconium dihydrides **1**. The mechanism of formation of the active sites in the Yermakov—Basset system (see Scheme 2) allows the formation of both types of species, their ratio being mainly determined by the presence of one or two —Si—O— bonds accessible for insertion of the $—ZrH_3$ groups on the silica surface.

Scheme 2

$$\equiv Si—OH + R_4Zr \rightarrow \equiv Si—OZrR_3 + RH \quad (1)$$

$$\equiv Si—OZrR_3 + H_2 \rightarrow \equiv Si—OZrH_3 \quad (2)$$

$$\equiv Si—OZrH_3 + \equiv Si—O—Si\equiv \rightarrow \underset{\mathbf{1}}{(\equiv Si—O)_2ZrH_2} + \equiv SiH \quad (3)$$

$$\underset{\mathbf{1}}{(\equiv Si—O)_2ZrH_2} + \equiv Si—O—Si\equiv \rightarrow \underset{\mathbf{2}}{(\equiv Si—O)_3ZrH} + \equiv SiH \quad (4)$$

$R = CH_2CHCH_2, CH_2CMe_3$

To decide between the species **1** and **2** one should compare their experimentally determined reactivities and the results of calculations. As the first example of such a comparison, in this work we studied the reactions of these groups with the methane molecule. In a recent experimental study[8] of the kinetics of D_2/CH_4 isotope exchange in the Yermakov—Basset system the activation energy of this reaction was estimated at 7±1 kcal mol^{-1}.

Calculation Procedure

All calculations were carried out in the framework of an approach used in our previous studies[3a—c] with the gradient-corrected PBE density functional.[9] An original program[10] uses Gaussian-type basis sets for solving the Kohn—Sham equations and the electron density expansion in an auxiliary basis set. The orbital basis sets had the following contraction patterns: (5s1p)/[3s1p] for H; (11s6p2d)/[6s3p2d] for C, O, and F; (15s11p2d)/[10s7p2d] for Si, and (21s16p12d)/[15s12p7d] for Zr. The auxiliary basis sets were uncontracted sets of Gaussian functions of size (5s1p) for H; (10s3p3d1f) for C, O, and F; (14s7p7d1f1g) for Si, and (21s9p9d8f8g) for Zr. The molecular geometries were optimized without imposing symmetry restrictions. The characters of stationary points located on the potential energy surfaces were determined from analytical calculations of the second derivatives of energy with respect to coordinates.

Results and Discussion

The surface zirconium monohydride groups **2** were modeled by compounds **2a** and **2b** while the models of zirconium dihydrides **1** were compounds **1a** and **1b**. This allowed significant reduction of the computational cost. On the other hand, such a simplification of the real structures seems not to have a strong effect on the results of calculations, since the "cut" fragments of the support structure are built of strong two-center, two-electron O—Si bonds and delocalization effets should be insignificant. Replacement of the skeletal O—Si fragments by fluorine atoms when performing quantum-chemical calculations of the structure of silica-supported compounds was proposed and substantiated earlier.[11] The use of two models for each type of the surface hydrides allowed us to evaluate the effect of skeleton rigidity on the reaction kinetics. We optimized the molecular geometries of model compounds **1a,b** and **2a,b**. Selected geometric parameters of the structures under study are listed in Table 1 and their energies are listed in Table 2.

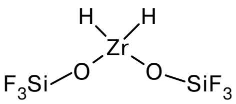
Table 1. Selected interatomic distances (*d*) in transition states **TS1a,b** and **TS2a,b**, model compounds **1a,b** and **2a,b** and products of their reactions with methane molecule

Compound	*d*/Å				
	Zr—H[a]	Zr—H[b]	$Zr—CH_3$[c]	C—H[a]	H—H[c]
1a	1.94	1.94	2.40	1.46	1.05
	(1.86)		(2.21)	(1.10)	(0.75)
1b	1.96	1.96	2.42	1.42	1.09
	(1.87)		(2.21)	(1.10)	(0.75)
2a	2.01	1.97	2.39	1.53	0.97
	(1.85)		(2.21)	(1.10)	(0.75)
2b	2.03	2.00	2.41	1.47	1.03
	(1.88)		(2.24)	(1.10)	(0.75)

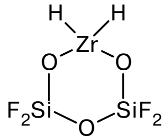
[a] The cleaving bond; the corresponding parameters for isolated reagents ($\equiv Zr—H + CH_4$) are given in parentheses.

[b] The migrating H atom.

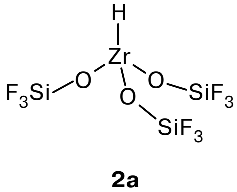
[c] The cleaving bond; the corresponding parameters for isolated products ($\equiv Zr—CH_3 + H_2$) are given in parentheses.



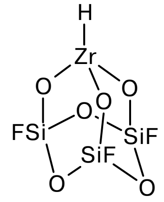
1a



1b



2a



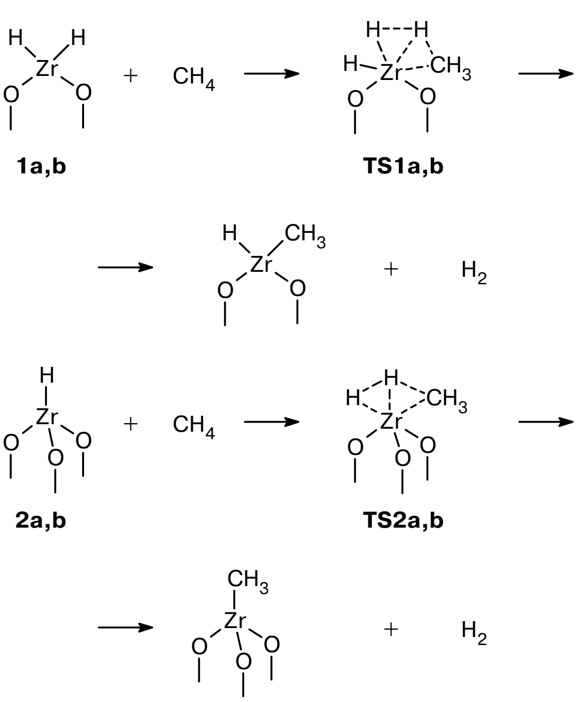
2b

Table 2. Total energies of reagents **1a,b** and **2a,b** and CH_4 calculated without (*E*) and with (H_0) inclusion of zero-point vibrational energy correction

Compound	$-E$	$-H_0$
	au	
1a	4870.28114	4870.24294
1b	4745.84059	4745.80259
2a	5533.94620	5533.89997
2b	5160.59791	5160.55282
CH_4	40.46518	40.42166

Our study of the interaction between methane and hydrides **1a,b** and **2a,b** revealed the absence of local minima corresponding to pre-reaction agostic complexes on the potential energy surfaces of these systems. These complexes are formed in the reactions between alkane molecules and cationic bis(cyclopentadienyl) complexes of Zr and Ti.[3] The reactions of all the four hydrides studied proceed as one-step bimolecular processes *via* four-center transition states **TS1a**, **TS1b**, **TS2a**, and **TS2b** for **1a**, **1b**, **2a**, and **2b**, respectively (Scheme 3).

Scheme 3



The formation of a bond between the Zr atom and the migrating H atom is a salient feature of the geometry of transition states **TS1a,b** and **TS2a,b**. According to calculations, this bond is stronger in zirconium dihydrides **1** than in zirconium monohydrides **2**. Selected geometric parameters of transition states **TS1a,b** and **TS2a,b** are listed in Table 1 and their thermodynamic characteristics calculated with respect to the corresponding parameters for noninteracting reagents are listed in Table 2.

Figure 1 presents the energy profiles of the four reactions studied in this work. The free energy of noninteracting reactants was set to zero. As can be seen in Fig. 1, the energy barriers to the reactions with zirconium monohydrides **2** are much higher than the barriers to the reactions with zirconium dihydrides **1**. The calculated free activation energies $\Delta G^{\neq}$ show that the reactivity of dihydrides **1** toward methane must be higher than that found experimentally in the Yermakov—Basset system. Comparison of the $\Delta H^{\neq}$ values calculated in this work (Table 3) with the experimental estimate[8] (7 kcal mol^{-1}) suggests that our results can be considered as evidence for the dihydride nature of the active sites in the Yermakov—Basset system. Nevertheless, the unambiguous choice of **1** can be made only after comparing the reactivities of zirconium hydrides **1** and **2** in some other experimentally investigated reactions and studying the metal hydride groups that are formed on the silica surface treated with organotitanium and organohafnium compounds.

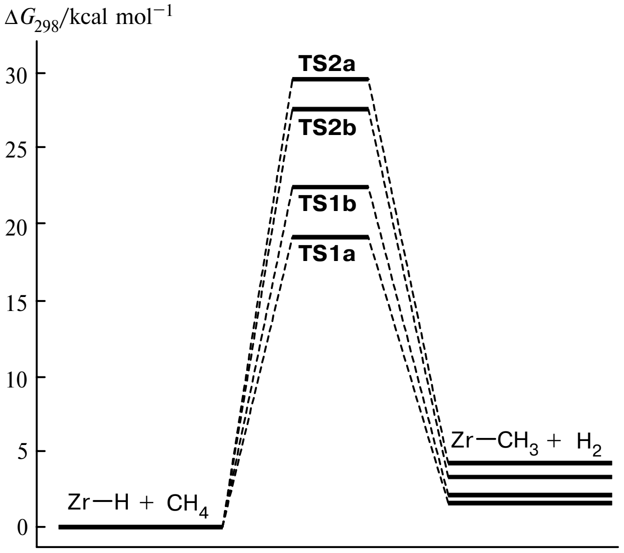


Fig. 1. Energy profiles of the reactions of methane with model compounds **1a,b** and **2a,b**.

The results obtained in this work allowed us to compare the reactions of zirconium hydride groups with methane in homogeneous and heterogeneous systems. Figure 2 presents the energy profiles of two reactions, namely, the reaction we studied earlier[3a,b]

$$Cp_2ZrH^+ + CH_4 \rightarrow Cp_2ZrCH_3^+ + H_2$$

and the reaction of the model system **1a** taken as an example of zirconium hydride with the CH_4 molecule.

Table 3. Thermodynamic characteristics[a] of transition states **TS1a,b** and **TS2a,b** of the reactions of model compounds **1a,b** and **2a,b** with methane molecule

Compound	ν_{imag}[b]	$\Delta E^{\neq}$	$\Delta H_0^{\neq}$	$-\Delta S_{298}^{\neq}$	$\Delta H_{298}^{\neq}$	$\Delta G_{298}^{\neq}$
1a	i901	9.0	8.8	38.9	7.5	19.0
1b	i922	12.4	12.0	37.3	11.2	22.3
2a	i827	21.4	20.6	30.1	20.0	29.0
2b	i958	18.9	17.8	35.4	17.3	27.7

[a] Listed are the energies calculated without ($\Delta E^{\neq}$/kcal mol^{-1}) and with ($\Delta H_0^{\neq}$/kcal mol^{-1}) inclusion of zero-point vibrational energy correction, enthalpies ($\Delta H_{298}^{\neq}$/kcal mol^{-1}), entropies ($\Delta S_{298}^{\neq}$/cal mol^{-1} K^{-1}), and Gibbs free energies ($\Delta G_{298}^{\neq}$/kcal mol^{-1}) given relative to the values of corresponding parameters for noninteracting reagents.

[b] Imaginary vibrational frequency (in cm^{-1}) corrsponding to reaction coordinate.

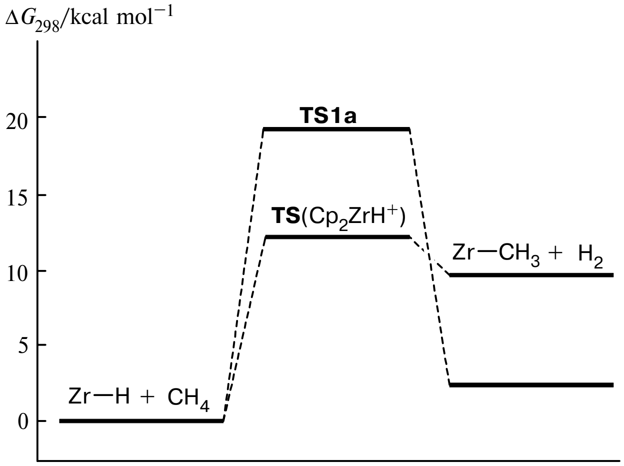


Fig. 2. Energy profiles of the reactions of methane with model compound **1a** and complex Cp_2ZrH^+.

Analysis of the energy profiles presented in Fig. 2 shows that the reaction $Cp_2ZrH^+ + CH_4$ is thermodynamically unfavorable, but has a relatively low energy barrier. On the other hand, the reaction with zirconium hydride does not lead to substantial increase in the free energy of the system; however, the energy barrier to this reaction is much higher than in the former case.

In this connection, development of a new catalytic system to combine the advantages of both systems mentioned above seems to be promising. A possible synthetic route involves immobilization of the cyclopentadienylzirconium complexes $(\eta^5\text{-}C_5H_5)Zr(H)_2O$—support on appropriate surfaces (SiO_2, ZrO_2, Al_2O_3). This type of surface zirconium dihydrides is thought to be more stable, which is of prime importance for practical use. This issue will be addressed in more detail in the forthcoming articles.

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