Activation of ethane in the metathesis reaction on silica-supported tantalum hydride: a quantum-chemical study

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The structures of the $(H_4Si_2O_5)O_2TaR$ and $(H_4Si_2O_5)O_2TaRH_2$ clusters (R = H, Me, or Et), which model the main structural units of the catalytic cycle of the ethane metathesis on silica-supported tantalum hydride, were studied using the density functional theory at the B3LYP level. Even at high temperatures, activation of ethane cannot proceed *via* a two-step mechanism involving the oxidative addition of ethane and reductive elimination of hydrogen to form pentavalent tantalum compounds.

Key words: alkane metathesis, activation of C—H bonds, tantalum surface complexes.

Activation of alkanes is still one of the most important problems in catalytic chemistry. In a number of studies,[1—17] it was found that silica-supported hydrides of different metals (Ti, Zr, Hf, or Ta) can activate the C—C and C—H bonds of alkanes under mild conditions. In particular, silica-supported tantalum hydride exhibits activity in alkane metathesis[9,12,14,16] giving rise to the reversible cleavage of the C—C and C—H bonds at moderate temperatures (25—200 °C) followed by the formation of higher and lower alkane homologs.

It was demonstrated[10,11] that the formation of tantalum hydride on the SiO_2 surface proceeds in two steps. The first step involves the interaction of the organometallic compound $TaNpenNp_3$ (Npen = $CHCMe_3$, Np = CH_2CMe_3) with OH groups of partially dehydroxylated silica gel at ~20 °C to form tantalum-containing surface compounds.

$$x \equiv SiOH + TaNpenNp_3 \longrightarrow (\equiv SiO)_xTaNpenNp_{3-x} + x\ NpH$$
$$x = 1, 2$$

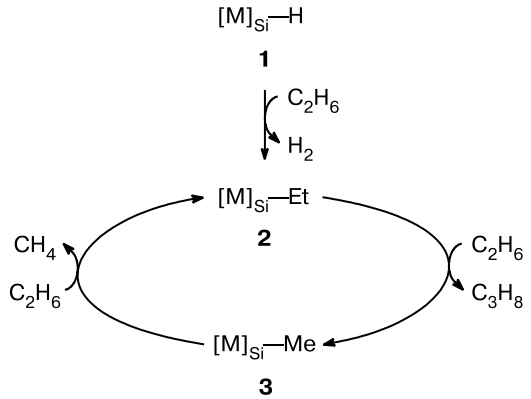
In the second step, the resulting complexes react with hydrogen.

$$(\equiv SiO)_2TaNpenNp + 2\ H_2 \longrightarrow (\equiv SiO)_2TaH + 2\ NpH$$

$$(\equiv SiO)TaNpenNp_2 + 3\ H_2 + \equiv SiOSi\equiv \longrightarrow (\equiv SiO)_2TaH + 3\ NpH + \equiv SiH$$

Metathesis of ethane is a typical example of alkane metathesis. Ethane reacts with silica-supported tantalum hydride ($[M]_{Si}H$, **1**) at 150 °C in the absence of hydrogen to give methane, propane, and trace amounts of butane.[9] Apparently, the first step of the process involves the cleavage of the C—H bond in the ethane molecule to form the surface compound $(\equiv SiO)_2Ta—Et$ (**2**) and H_2. In the second step, the ethane molecule can react with surface compounds **2** to give propane and the $(\equiv SiO)_2Ta—Me$ complex (**3**), which can be replaced by the next ethane molecule resulting in the formation of methane and regeneration of $(\equiv SiO)_2Ta—Et$ (Scheme 1).

Scheme 1



$[M]_{Si} = (\equiv SiO)_2Ta$

Metathesis of ethane could proceed by two possible mechanisms.[18] One mechanism involves two steps,

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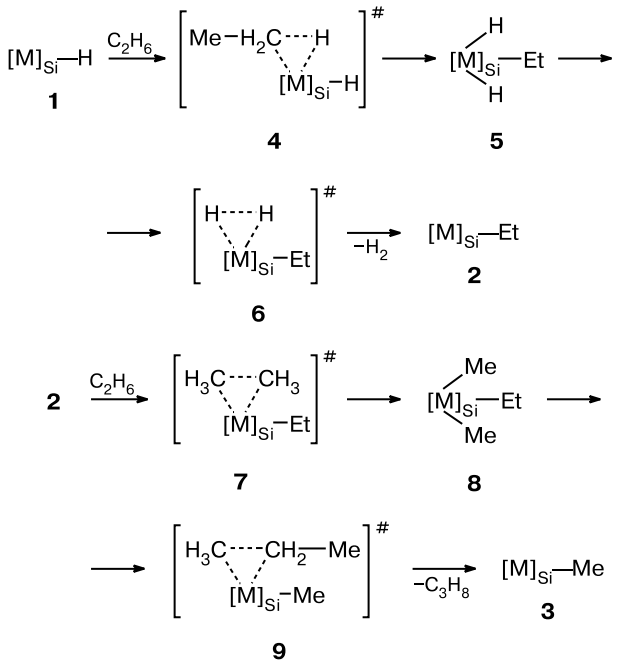
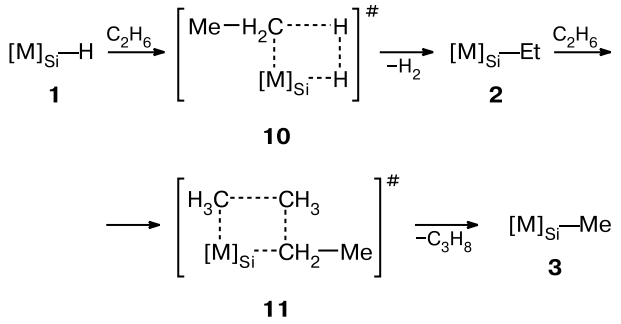
viz., the oxidative addition and reductive elimination (Scheme 2).

Scheme 2



An alternative mechanism assumes the one-step concerted reaction proceeding through the formation of a four-center transition state (Scheme 3).

Scheme 3



The above-described pattern reflects the general direction of transformations of hydrocarbons, whereas the detailed data on the structures of active centers, transition states (TS), and pathways of transformations are lacking in the literature. Taking into account advances achieved in modeling the modified silica surface,[19—21] we carried out a theoretical study of the structures of clusters, which model the chemically modified silica surface (complexes **1**, **2**, **3**, and **5**), and examined the mechanism of the reaction of complex **1** with ethane giving rise to complex **2**.

Calculation procedure

All calculations were carried out by the density functional theory (DFT) using the B3LYP exchange-correlation functional with the 6-31G basis set supplemented by polarization functions on all atoms, except for the Ta atom for which the LanL2DZ pseudopotential was used.[22] The calculations were performed with full geometry optimization, unless otherwise stated. All calculations were carried out with the use of the Gaussian 98 program package.[23]

The modified silica surface was modeled by the $(H_4Si_2O_5)(OH)_2$ cluster (**12**). The latter represents a fragment of the SiO_2 β-crystobalite structure[21] (Fig. 1) in which the Si—O broken bonds are terminated by H atoms (indicated by solid lines in Fig. 1). The geometric parameters of the terminal OH groups thus obtained were fixed in the calculations. This cluster was chosen because the structure of silica gel used in experiments on modification of the surface resembles most closely the structure of crystobalite containing a large number of isolated terminal OH groups. The distances from the atoms of the surface group (active center) to the nearest atoms of the crystobalite surface are in the range of 3.5—4.5 Å. Our test calculations of large clusters demonstrated that further enlargement of the cluster has virtually no effect on the structure of the surface fragment. Hence, it can be assumed that cluster **12** with two termi-

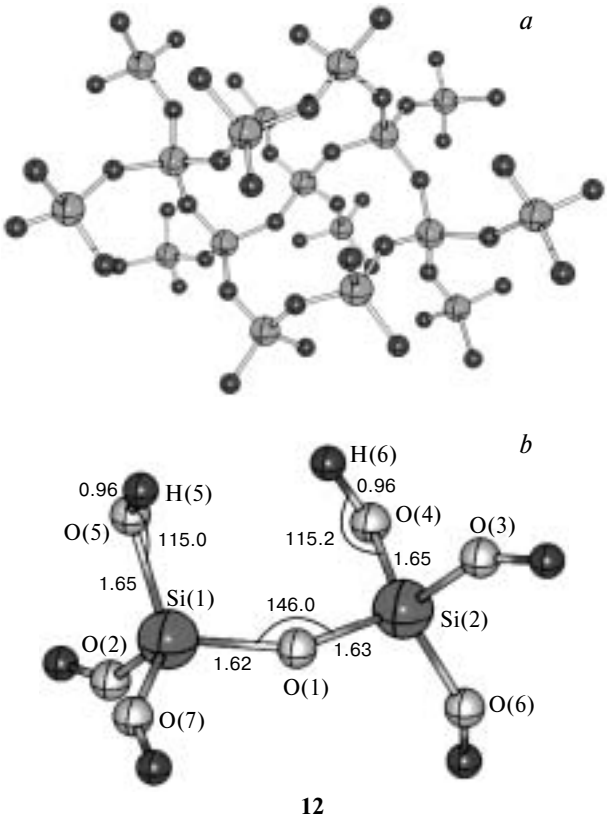
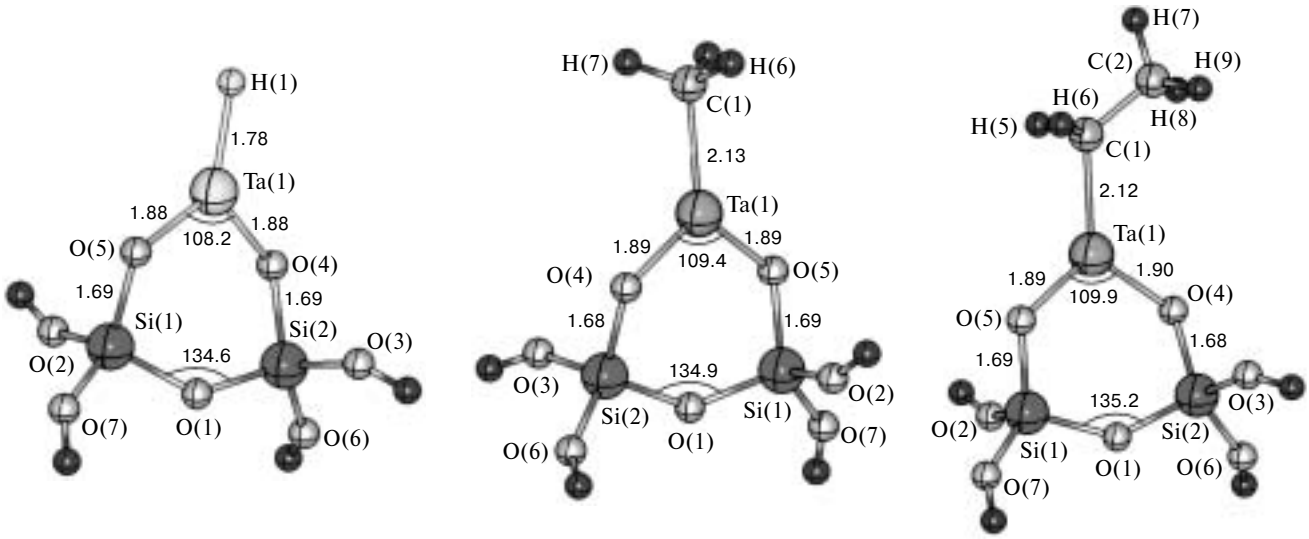


Fig. 1. Structures of β-crystobalite (*a*) and cluster **12**, which models a silica surface (*b*). Here and in Figs. 2—4, the bond lengths/Å are given; the corresponding angles/deg are displayed above the arcs.



13 **14** **15**

Fig. 2. Optimized structures of the clusters, which model the hydride (**13**), methyl (**14**), and ethyl (**15**) surface complexes of tantalum.

nal OH groups presented in Fig. 1 allows one to model typical organometallic active centers.

Results and Discussion

In studying the reaction of ethane with surface tantalum monohydride (Fig. 2, cluster **13**), it is necessary to consider two possible mechanisms, *viz.*, activation of one of the C—H bonds followed by the oxidative addition of ethane to form the Ta—C and Ta—H bonds (formation of the tantalum ethyl dihydride complex) and metathesis of ethane at the C—C bond including the intramolecular hydrogen exchange when the coordination number of the metal atom remains constant (four-center TS). The optimized geometric parameters of the organotantalum derivatives of cluster **12** (clusters **13—15**), which model the main intermediates of the catalytic cycle of ethane metathesis (see Scheme 1), are presented in Fig. 2. The replacement of the terminal H atoms of cluster **12** with organometallic groups leads to elongation of the Si(2)—O(4) and Si(1)—O(5) bonds by 0.03—0.05 Å and to slight changes in the bond lengths in the first coordination sphere of the Si atoms. The bond lengths in the second coordination sphere of these atoms remain virtually unchanged. This indicates that the properties of the surface organometallic compounds are adequately modeled by small clusters. In addition, the calculated Ta—O bond length (1.88 Å) and the stretching frequency of tantalum hydride (ν(Ta—H) = 1854 cm^{-1}) are consistent with the experimental data (1.89 Å and 1800 cm^{-1}, respectively).[11] The replacement of the H atoms in surface tantalum monohydride by the Me and Et groups

Table 1. Calculated energies (ΔE, ΔH, ΔG, and ΔS) of the reagents, products, intermediate structures, and transition states of the activation step involved in the two-step mechanism of ethane metathesis

Parameter /kcal mol^{-1}	Reagents		Cluster					
	13 + C_2H_6	**15** + H_2	**16**	**17**	**18**	**19**	**20** (TS1)	**21** (TS2)
ΔE	25.8	29.2	2.0	2.1	0	1.1	38.7	33.7
ΔE + ZPE*	27.0	25.5	1.9	1.9	0	1.0	38.8	33.0
ΔH_{298}	27.3	27.4	1.8	1.9	0	1.0	38.6	33.0
ΔG_{298}	16.1	18.0	2.0	2.1	0	1.0	38.9	33.7
ΔS_{298}**	37.5	31.5	−0.8	−0.7	0	0.2	−0.8	−2.1
ΔH_{423}	26.9	27.8	1.8	1.9	0	1.0	38.4	33.1
ΔG_{423}	11.4	14.0	2.1	2.2	0	0.9	39.0	33.9
ΔS_{423}**	36.4	32.6	−0.8	−0.7	0	0.3	−1.4	−2.0
Rate constants/s^{-1}	$k'_{298} = 1.2 \cdot 10^{-4}$, $k'_{423} = 5.1 \cdot 10^{-2}$	$k''_{298} = 1.3 \cdot 10^{-12}$ $k''_{423} = 2.7 \cdot 10^{-5}$	—	—	—	—	—	—

* Correction for the energy of zero-point vibrations.
** Cal $(mol\ K)^{-1}$.

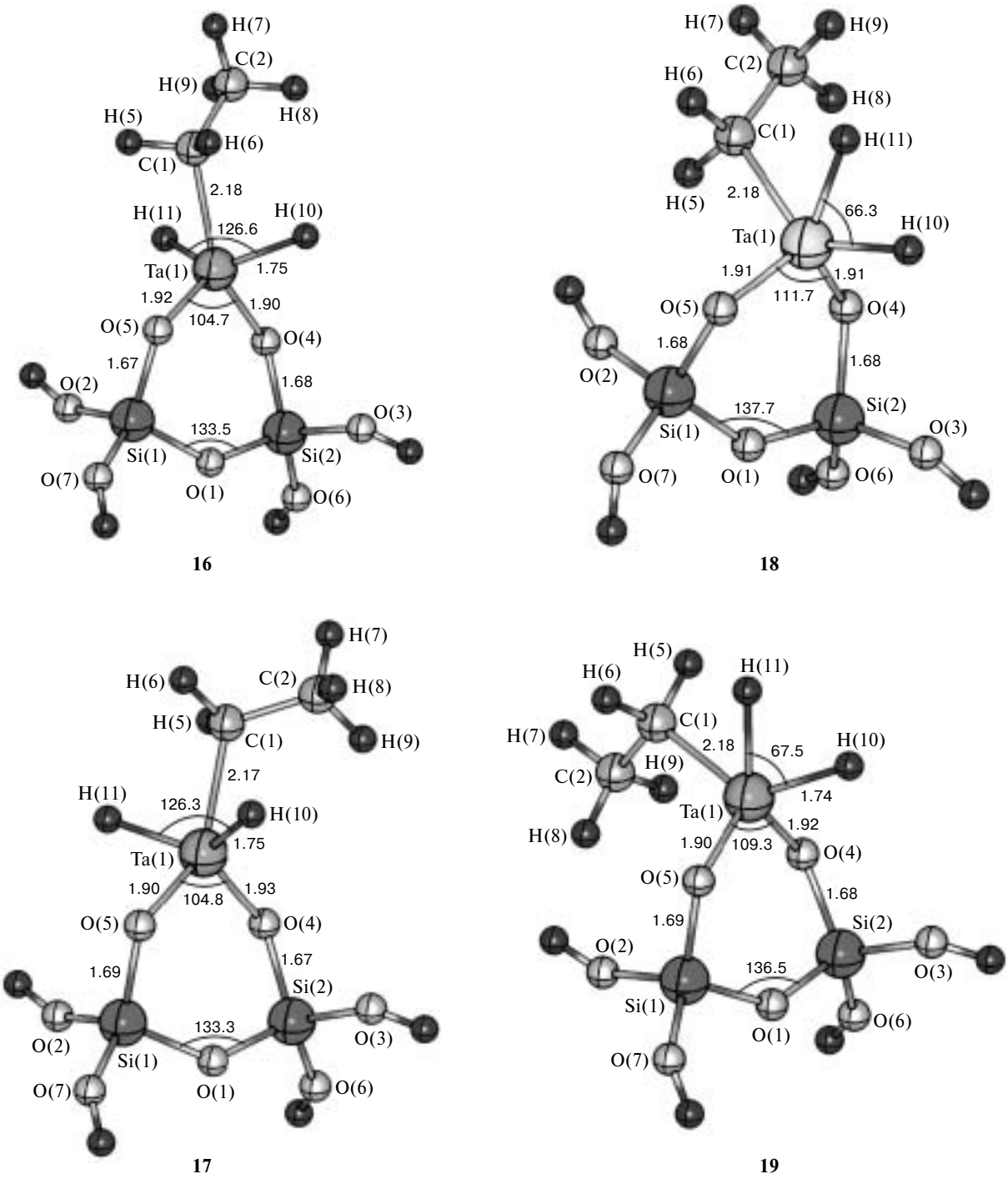
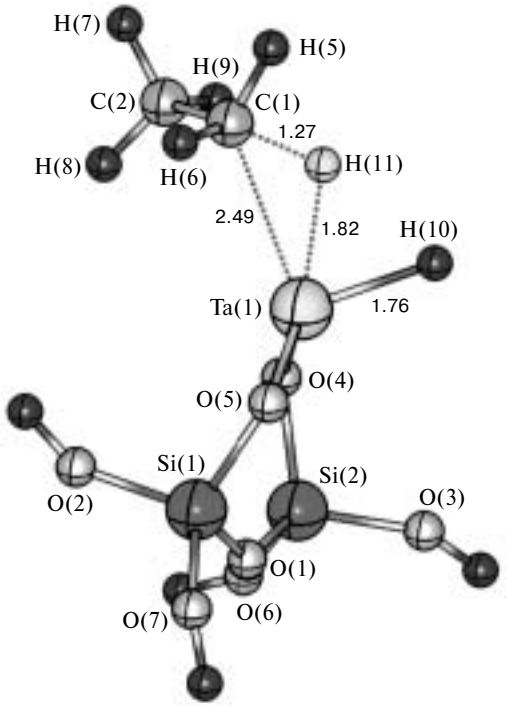


Fig. 3. Optimized structures of the clusters, which model the surface ethyl dihydride derivatives of tantalum (**16—19**).

only slightly influences the geometric parameters of the clusters.

No stationary points corresponding to adducts of ethane and molecular hydrogen with clusters **13** and **15**, respectively, were found on the potential energy surface (PES). It is known[24—26] that B3LYP calculations substantially underestimate the energies of interactions in complexes of this type. We also failed to localize the four-center TS of the reaction proceeding *via* a concerted one-step mechanism. Let us consider the two-step mechanism. The calculations predicted four different stable configurations of the dihydride complex, *viz.*, two axial and two equatorial (Fig. 3, clusters **16—19**). Their energies differ by no more than 2 kcal mol^{-1}. Cluster **18** corre-



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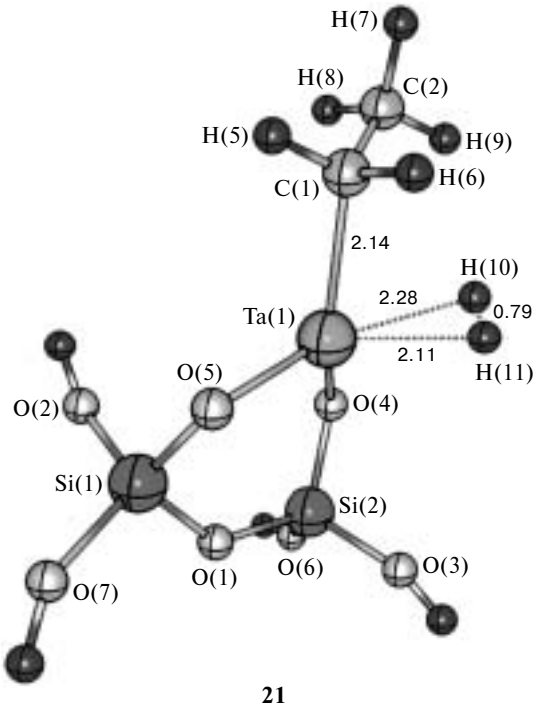

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Fig. 4. Transition states TS1 (**20**) and TS2 (**21**) of the two-step mechanism.

sponds to the most stable configuration. We also found two TS, *viz.*, TS1 and TS2 (Fig. 4, clusters **20** and **21**), each being characterized by one imaginary frequency i453 (cluster **20**) and i151 cm^{-1} (cluster **21**). In addition, we

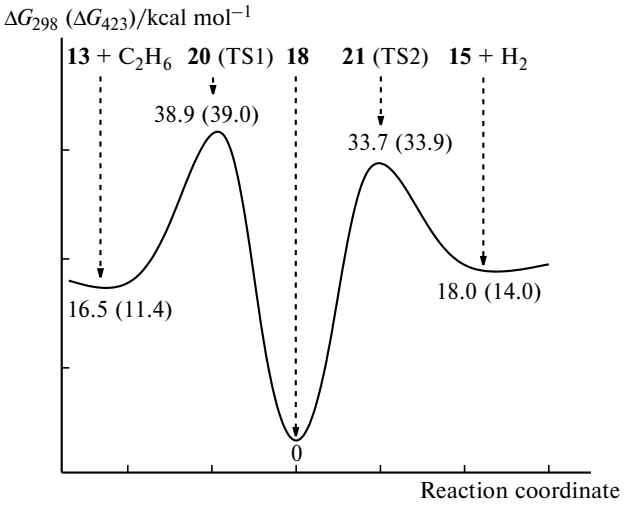

Fig. 5. Profile of the potential energy surface for the activation step involved in the two-step mechanism (Gibbs energies (ΔG) for the reaction temperature (150 °C) are given in parentheses).

analyzed the reaction pathways by the method of the internal reaction coordinate[27,28] and found that structures **20** and **21** are actually the transition states of the oxidative addition of ethane (**13** + C_2H_6 ⟶ **18**) and reductive elimination of hydrogen (**18** ⟶ **15** + H_2).

The relative energies, energies corrected for zero-point vibrations, and free Gibbs energies for all structures are given in Table 1. The PES profile of the activation step of the two-step mechanism (**13** + C_2H_6 ⟶ **18** ⟶ ⟶ **15** + H_2) is shown in Fig. 5, where the Gibbs energies calculated for the reaction temperature (150 °C) are given in parentheses.[9] The energy of the Ta^V compound acting as an intermediate in the two-step mechanism appeared to be 18 kcal mol^{-1} lower than the energies of the reaction products, which means that the process is virtually thermodynamically forbidden. The activation energies are 22.4 and 33.7 kcal mol^{-1} (calculated for 25 °C). Hence it follows that the reaction cannot proceed *via* the two-step mechanism with substantial rates (rate constants calculated according to the TS theory are $1.2 \cdot 10^{-4}$ and $1.3 \cdot 10^{-12}$ s^{-1}) (see Table 1). According to the results of calculations, the two-step mechanism is impossible due to unfavorable thermodynamic and kinetic factors. Apparently, the one-step concerted mechanism of ethane activation is more probable. The adequate description of this mechanism requires the use of higher-level calculation methods, *viz.*, at least the restricted Hartree—Fock (RHF) method including the electron-correlation effect at the level of the second-order Möller—Plesset perturbation (MP2) theory. Because of limited possibilities of the computer used, we did not perform such calculations.

To summarize, the results of calculations of silica-supported tantalum hydride demonstrated that such sur-

face compounds can be satisfactorily modeled by small clusters based on the β-crystobalite structure. The results of calculations of the reaction pathways by the density functional theory indicate that the ethane metathesis cannot proceed *via* a two-step mechanism involving the formation of pentavalent tantalum compounds as intermediates.

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