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Adsorbed carbocations as transition states in heterogeneous acid catalyzed transformations of hydrocarbons

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Abstract

Ab initio quantum chemical calculations indicated that adsorbed carbenium and carbonium ion active intermediates of acid-catalyzed transformations of hydrocarbons on zeolites are not the really existing highly reactive species but the transition states of the corresponding elementary steps. Adsorbed carbenium ion-like activated complexes can be formed both via proton addition to the double bonds of olefins or as energetically excited unstable ion pairs resulting from partial dissociation of the carbonyl bonds in more stable alkoxy species. In contrast, the highly energetically excited adsorbed carbonium ion-like transition states result only from proton attack at the C–C or C–H bonds of paraffins. The quantum chemical calculations provided the information on geometry and electronic structure of these activated complexes which depend on the elementary reactions in which these transition states are involved. The calculated heat effects and activation energies for the main elementary steps in acid catalyzed transformations of hydrocarbons on zeolites, i.e. of double bond shift, skeletal isomerization and cracking of olefins or protolytic dehydrogenation, protolytic cracking of paraffins and hydride transfer from isoparaffins to carbenium ions are in a reasonable agreement with the experiment. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

The modern mechanisms of heterogeneous acid-catalyzed transformations of hydrocarbons on zeolites and other solid acids involve adsorbed carbocations as active intermediates [1]. For instance, it is generally believed that in catalytic transformations of olefins these species are the adsorbed carbenium ions which are formed by proton addition to the double bonds:

$$>C=C< \quad + \quad H^{+}{}_{ads} \quad \longrightarrow \quad R^{+}{}_{ads} \qquad (1)$$

The subsequent reactions of carbenium ions well explain the composition of final products and the selectivity of the corresponding reactions.

There is also convincing evidence that the active intermediates of acid-catalyzed transformations of paraffins are adsorbed carbonium ions which result from direct protonation of paraffins [2]:

$$RH + H^{+}_{ads} \rightarrow RH^{+}_{2\,ads} \qquad (2)$$

These species are then involved in protolytic cracking and protolytic dehydrogenation, yielding adsorbed carbenium ions:

$$RH + H^{+}_{ads} \rightarrow RH^{+}_{2\,ads} \rightarrow R_{1}H + R^{+}_{2\,ads} \qquad (3)$$

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$$RH + H^+_{ads} \rightarrow RH^+_{2\,ads} \rightarrow R^+_{ads} + H_2 \qquad (4)$$

Up to recently, it was also believed that both adsorbed carbenium and carbonium ions are really existing short-lived intermediates with properties similar to those of free gaseous species or of weakly solvated carbocations in solutions of superacids while the interaction of adsorbed carbocations with the surface of heterogeneous catalysts usually was not discussed.

A real account of interaction of adsorbed carbocations with the surface of heterogeneous catalysts became possible only recently due to the development of quantum-chemical calculations. Another important source of information on the nature of these species comes from IR spectroscopy and MAS ^{13}C NMR which allow a direct study of proton transfer to adsorbed hydrocarbons and the nature of resulting intermediates. The aim of this paper is to discuss these results in connection with the mechanism of the acid-catalyzed transformations of hydrocarbons on zeolites.

2. Nature of adsorbed carbenium ions

2.1. *Why adsorbed carbenium ions are surface alkoxyls but not ion pairs?*

Originally the carbenium ion mechanisms of the acid catalyzed organic reactions were formulated and developed for homogeneous catalysis. Only later were these ideas transferred to heterogeneous systems. Therefore, let us come back to the very beginning of the carbenium ion theory.

At first the hypotheses about the formation of carbenium ions in solutions was put forward in 1922 by Meerwein who observed that the rate of the liquid phase camphenhydrochloride rearrangement into isobornylchloride increased in parallel with dielectric constants of different solvents [3]. Later on, the carbenium ion mechanisms were also discussed for S_NI substitution and S_EI elimination by Ingold, Huse and other authors (see for instance [4]) and for a number of other organic reactions by Whitmore [5,6]. One should, however, bear in mind that all these conclusions were supported only by the composition and stereochemistry of the resulting final products or by indirect arguments based on the kinetics of corresponding reactions, since at that time, direct spectral methods for the investigation of active intermediates had not yet been developed. Therefore, the next important step in further evolution of carbenium ion chemistry was a direct observation of carbocations in solutions of super acids by NMR and other spectral techniques by Olah and his co-workers (see, for instance, the review paper [7]). These authors reported numerous examples of a direct spectral study of different carbocations including aliphatic carbenium ions in solutions of SbF_5–HF, which they called a ‘‘magic acid’’. On the other hand, in weaker acids or in more basic solvents, the formation of alkyl carbenium ions was not observed due to interaction of these species with solvating molecules.

Indeed, solvation certainly favors the heterolytic dissociation of polar molecules but also strongly modifies the properties of the resulting ion species. For instance, the electron affinity of a free proton is equal to 13.6 eV. In contrast, the corresponding value for a hydrated proton in liquid water is only about 6 eV. This difference is due to solvation effects, since, after neutralization of the positive charge of the hydrated proton by an electron, the energy of proton hydration is replaced by a much smaller value of the heat of water condensation. Thus, solvation, on one hand, favors the heterolytic dissociation of water but, on the other hand, converts the resulting protons and hydroxyl ions into chemically much less active hydrated species.

For aliphatic carbenium ions, the effect of solvation is quite similar. These species are known as rather strong Lewis acids. Therefore, in basic solutions they are converted into alcohols:

$$R^+ + OH^- \rightarrow ROH \qquad (5)$$

whereas in neutral water solutions, they form hydrated oxonium ions:

$$R^+ + nH_2O \rightarrow ROH_2^+(n-1)H_2O \qquad (6)$$

This results in S_N2 mechanisms of the acid-catalyzed transformations of alcohols or olefins instead of S_NI carbenium ion mechanism in moderately concentrated acids. For instance, our recent ^{13}C NMR study of *tert*-butanol dehydration in 70% sulfuric acid indicated that this reaction, which was traditionally considered as a classical carbenium ion transformation, occurs through the formation of oxonium ion intermediates [8]. In other words, the account of the solvation allows one to conclude that *tert*-butanol dehydration does not proceed by the following S_N1 mechanism:

$$t\text{-}C_4H_9OH + H^+ \rightarrow t\text{-}C_4H_9^+ + H_2O$$
$$t\text{-}C_4H_9^+ + t\text{-}C_4H_9OH \rightarrow i\text{-}C_8H_{16} + H_2O + H^+ \qquad (7)$$

but by an S_N2 mechanism in which hydrated oxonium ions play the role of active intermediates:

$$t\text{-}C_4H_9OH + H_5O_2^+ \rightarrow t\text{-}C_4H_9OH_2^+2H_2O$$
$$t\text{-}C_4H_9OH_2^+2H_2O + t\text{-}C_4H_9OH \rightarrow i\text{-}C_8H_{16} + H^+4H_2O \qquad (8)$$

For the transformations of hydrocarbons on zeolites and on other solid acids, the situation is quite similar. The only difference consists in the replacement of solvation by water by the interaction of adsorbed carbenium ions with basic surface oxygen of the solids. Therefore, depending on the basicity of the surface oxygen, proton transfer to adsorbed olefins results in the formation of more or less covalent surface alkoxides rather than carbenium ions. The former species form similar covalent carbonyl bonds with the surface oxygen as with oxonium ions in aqueous solution.

There are several ways to estimate the covalent character of this bond. One of them is based on the Sanderson electronegativity equalization principle according to which the interaction of adsorbed carbenium ions with surface basic oxygens should result in partial neutralization of their positive charge due to the electron density transfer from oxygen to adsorbed species:

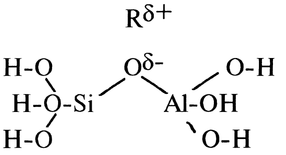
$$R^+ + O^=_{surf} \rightarrow RO^-_{ads} \qquad (9)$$

According to Ref. [9], the extent of such electron transfer, δ, could be estimated from the following expression which includes electronegativities χ and hardness η of the hydrocarbon fragments and the solid:

$$\delta = \frac{\chi_{R^+} - \chi_{surf}}{2(\eta_{R^+} + \eta_{surf})}. \qquad (10)$$

Our estimations showed that the corresponding electronegativity and hardness for zeolites are close to those of liquid water [10]. Therefore, the polarity of the carbonyl bond in surface alkoxyls and in liquid phase oxonium ions are also close to each other. In other words, proton transfer from surface Brønsted acid sites to adsorbed olefins yields covalently bonded surface alkoxy groups with only partially polarized carbonyl bonds rather than ion pairs.

This conclusion was also supported by direct quantum chemical calculations. First, this was done in our papers [11,12] by the semiempirical CNDO method for methyl, ethyl and isopropyl fragments R adsorbed on the following cluster as a model of a high silica zeolite:



(11)

The results obtained also confirmed the covalent nature of the alkyl fragments which follows from the calculated short covalent C–O bond length, tetrahedral H–O–C and C–C–C angles and from the relatively low Mulliken charges (see Table 1). Moreover, for different alkyl fragments, these parameters are very close to each other.

At first glance, this contradicts the generally accepted ideas according to which the carbenium ion properties of an isopropyl group are much stronger than those of ethyl or methyl groups. However, one should discriminate between the similar geometries and charges of the ground states of alkoxy fragments and the energies of their heterolytic dissociation. Indeed, for an isopropyl group, the energy of heterolytic abstraction is almost by 2 eV lower than that for the methyl group. This indicates that the differences in the carbenium ion properties of methyl, ethyl and isopropyl groups are related to different positions of the energetically excited heterolytic terms, whereas

Table 1
CNDO calculations for alkyl groups adsorbed on high silica zeolite [11,12]

Alkyl fragment	CH_3^+	$C_2H_5^+$	$C_3H_7^+$
qR	+0.32	+0.33	+0.33
qO	−0.42	−0.41	−0.41
qC	+0.18	+.013	+0.07
$r_{C–O}$	1.465	1.476	1.487
D_{het}eV	7.25	6.05	4.93

the covalent ground states of these species are rather similar.

Later on this conclusion was also confirmed by more sophisticated ab initio quantum chemical calculations which will be discussed below. In addition, the covalent nature of surface alkyl groups was supported by numerous experimental results obtained by MAS ^{13}C NMR which easily discriminate between adsorbed carbenium ions and the covalently bonded alkoxides, since the ^{13}C chemical shifts of the positively charged carbon atoms in aliphatic carbenium ions are as high as 300–350 ppm instead of 70–80 ppm for alkoxides.

Indeed, a MAS NMR study of active intermediates resulting from the interaction of ^{13}C enriched propene [13], *tert*-butanol [14,15] and isobutanol [16,17] with acid hydroxyl groups in hydrogen forms of zeolites indicated that the ^{13}C chemical shifts are quite low and equal to only about 70–80 ppm. This also confirms the formation of adsorbed alkoxy species instead of carbenium ions.

Thus, in contrast to results obtained by Olah et al. for solutions of the "magic acid", the proton transfer to adsorbed olefins or the abstraction of hydroxyl groups from alcohols adsorbed on the surface of zeolites does not result in the formation of ion pairs. The reason for this difference is connected with different reaction conditions and the different solvation of carbenium ions in liquid super acids in comparison with the interaction of these species with the surfaces of zeolites. In addition, the strength of the "magic acid" is certainly much higher than that of the hydrogen forms of zeolites.

2.2. *Adsorbed carbenium ions as transition states in proton transfer to adsorbed olefins or in decomposition of surface alkoxides*

Since the heterolytic abstraction of adsorbed alkyl fragments from the surface requires very high energies of about 6–7 eV, the complete heterolytic rupture of carbonyl bonds in the surface alkoxides never happens, even in high-temperature reactions. Instead, the corresponding elementary steps involve only a partial dissociation or stretching of carbonyl bonds, resulting in the formation of energetically excited ion pairs, while the alkyl fragments in these unstable ion pairs resemble, by their geometry and the high positive charge, free carbenium ions.

Such activation of carbonyl bonds in surface alkoxides represents a further development of our earlier published concept [18] according to which partially dissociated or stretched chemical bonds are usually more polar than the corresponding covalent ground states. Therefore, the real meaning of the stronger ionic character of the isopropyl group in comparison with the methyl group in the above mentioned example consists not of a higher positive charge of the isopropyl fragment itself but of an easier polarization of the stretched or partially dissociated carbon–oxygen bond. This results in easier generation of the energetically excited ion pairs with chemical properties, geometries and positive charges resembling those of free or weakly solvated isopropyl carbenium ions in solution of the magic acid.

These ideas were developed in more detail in our paper [19] by means of ab initio quantum chemical calculations of ethylene protonation by bridging surface hydroxyl groups of a high silica zeolite and of the reverse reaction of decomposition of the surface ethoxy fragments. In accordance with the above discussion, the results of calculations demonstrated that the most stable species resulting from proton transfer to adsorbed ethylene are covalently bonded ethoxy groups (Fig. 1(c)), while the proton transfer involves the transition state of Fig. 1(b), which resembles a free ethyl carbenium ion. Similarly to the semiempirical calculations, the latter conclusion follows from the relatively high positive charge of the ethyl fragment and from the flatter geometry of the ethyl group in such transition state with a C–C bond length intermediate between those of the single and double bonds.

The same transition state is also formed in the reverse reaction of surface ethoxy group decomposition. Thus, the carbenium ion-like transition state could be formed from "both sides", i.e. from proton addition to the double bond of ethylene and from the partial dissociation of the carbonyl bond in the surface ethoxy group.

An important feature of such an energetically excited unstable adsorbed ethyl carbenium ion-like transition state is that it corresponds to the very top of the potential barrier. Therefore, this species could not have a higher positive charge or be "more free" than in structure 1 (b), since further stretching of the

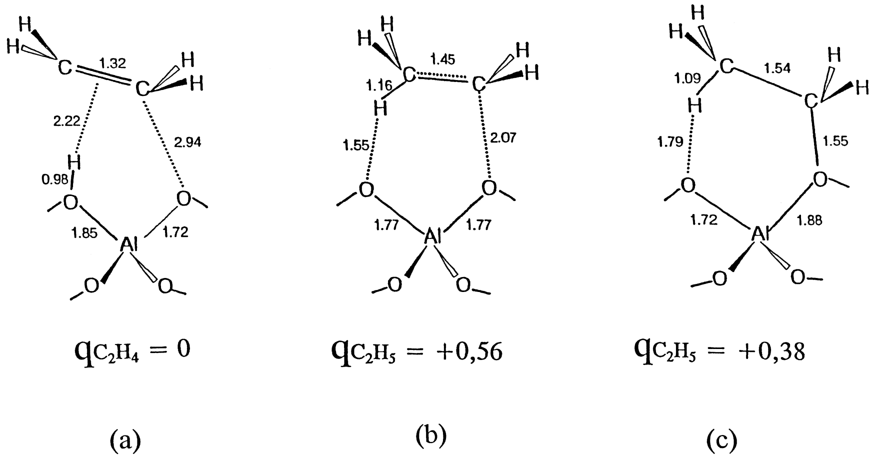


Fig. 1. Reaction path of proton addition to ethylene adsorbed on bridging hydroxyl of a high-silica zeolite. Quantum chemical calculations at 3-21G level. Here and further distances in Angstroms, Mulliken charges in multiples of the electron charge.

carbonyl bond results in a back proton transfer to the zeolite surface, with the formation of a π-complex rather than desorption of a free ion.

In contrast to the ethyl group, the separation of positive and negative charges for isopropyl fragment in the energetically excited ion pair is larger, due to the higher proton affinity of propylene in comparison to ethylene. Thus, the formation of the carbenium ion-like isopropyl fragment not only requires a lower energy for a similar separation of charges but also results in a higher positive charge of the isopropyl fragment at the top of the energy barrier before abstraction of proton back to the surface of the zeolite.

3. On the real carbenium ion mechanisms of acid-catalyzed transformations of olefins on zeolites

Acid-catalyzed transformations of olefins on zeolites are usually explained by a number of elementary reactions of the adsorbed carbenium ions assumed to be active intermediates. These reactions include hydride ion shift, β-scission of olefins from carbenium ions, skeletal isomerization of carbenium ions, addition of carbenium ions to olefins, etc. In most cases, the carbenium ion species involved in these reactions are considered as free, while their interaction with the zeolite surface is ignored.

Below we will consider more realistic mechanisms in which, in accordance with the above discussion, adsorbed carbenium ions represent energetically excited transition states, whereas the final reaction products are formed by different routes for the decomposition of such energetically excited activated complexes.

3.1. Double bond shift in olefins

This reaction represents a stabilization of an adsorbed carbenium ion-like transition state due to the abstraction of a proton back to the basic surface oxygen of the zeolite and desorption of the resulting olefin from the surface. Of course, for an ethoxy group, this would not result in the formation of a new product. However, if a proton is first added according to Markovnikov rule to the methylene group of 1-butene and then abstracted from another methylene group of the resulting alkoxide, 2-butene is produced.

For zeolites, the ab initio quantum chemical calculations of the reversible proton addition and abstraction were performed for ethylene [19,20], propylene [20,21] and isobutene [21,22]. The latter case is most closely related to 1-butene isomerization. Therefore, let us consider it in more detail.

The energy diagram of the isobutene interaction with the surface bridging hydroxyls of a high silica

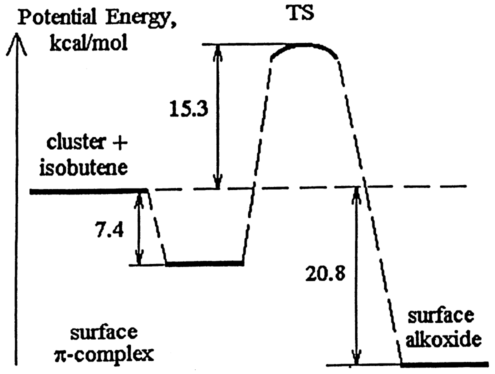


Fig. 2. Energy diagram of isobutane protonation on high-silica zeolite.

zeolite, reconstructed from the results of our calculations, is depicted in Fig. 2. The geometries of the resulting transition state and alkoxide are presented in Fig. 3.

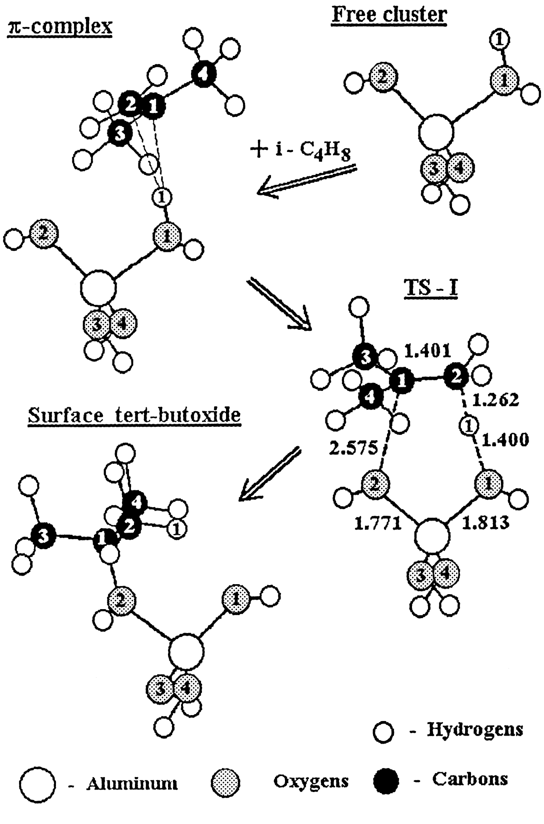


Fig. 3. Reaction path of isobutene protonation on high-silica zeolite. Calculations at the MP2/6-31++G**//6-31G* level.

As in the case of ethylene, the reaction starts with the formation of π-complex. This elementary step does not require any activation energy and, at the MP2/6-31++G**//6-31G* level with zero point corrections, is exothermic by 7.4 kcal/mol. The π-complex then transforms into a covalently bonded *tert*-butyl group. Similarly to ethylene, the conclusion about the covalent nature of the C–O bond in this most stable final structure follows from the short C–O distance of 1.458 A, from the geometry of the *tert*-butyl fragment with covalent angles at tertiary carbon atom close to 109°, and from only a moderate positive charge of the alkyl group (+0.441 e). The reaction of proton transfer is exothermic by 20.8 kcal/mol.

The transformation of the π-complex into a covalently bonded surface *tert*-butyl fragment occurs through the transition state of Fig. 3 with an activation energy of 22.7 kcal/mol. The geometry of this transition state resembles that of the classical *tert*-butyl carbenium ion, while the positive charge of the *tert*-butyl fragment (+0.821 e) is much higher than that of the covalently bonded alkoxide (+0.441 e). In addition, the C_4H_9 group becomes almost flat as one may expect for the classical *tert*-butyl cation.

The cyclic structure of this transition state indicates a bifunctional nature of the active site. Indeed, its Brønsted acid part protonates the adsorbed olefin, whereas the interaction with the neighboring basic oxygen converts the resulting carbenium ion into the surface alkoxide. This is assisted by the "switching" of the A1–O bonds of the cluster which are almost equally long in the transition state, but considerably differ from each other in the initial and final structures (in both cases the A1–O bond with three-coordinated oxygen is longer).

The reaction coordinate of the reverse reaction of the decomposition of the surface alkoxy group includes the stretching of the carbonyl bond, the transfer of the proton back to the surface basic oxygen of the active site, and the transformation of the single C–C bond in the adsorbed carbenium ion-like transition state into a double bond. In accordance with experimental data, the activation energy of the double bond shift should then be close or equal to that of the decomposition of the surface alkoxide.

The energy diagram of Fig. 2 very much resembles that for the interaction of olefins with surface OH groups of zeolites recently discussed by Hall and

Engelhardt in [23]. Indeed, in both cases, the reaction occurs through the same sequence of elementary steps with similar values of heat effects or activation energies: olefin→π-complex (the heat effects are 7.4 or 9 kcal/mol, respectively); π-complex→surface alkoxide (heat effects of formation from olefin and hydroxyl group are equal to 20.8 and 20 kcal/mol, respectively with activation energies of 15.3 and 12 kcal/mol, respectively).

On the other hand, both schemes substantially differ in the interpretation of the nature of adsorbed carbenium ions. According to our and other quantum chemical calculations [19–22], these species represent transition states, whereas Hall et al. consider them as metastable reaction intermediates with lifetimes which depend on the acid strength of the initial OH groups (the stronger are the OH groups, the longer is the lifetime of such carbenium ions and the more chemically active they are).

Of course, a study of kinetics alone cannot discriminate between these alternatives. This is possible only by means of quantum chemical calculations which thus allow the next step in understanding the real mechanisms of carbenium ion reactions. In addition, they provide information on the geometry of carbenium ion-like transition states and on the nature of interaction of alkyl fragments with the surface. The results of quantum chemical calculations also give reasonable estimates of the heat effects and activation energies of the double bond shift.

3.2. *Skeletal isomerization of olefins*

Experimental studies of skeletal isomerization of olefins indicated that this reaction proceeds via either monomolecular or bimolecular (dimerization-cracking) mechanisms. Monomolecular skeletal isomerization was found to be more common. Indeed, *n*-pentene and higher hydrocarbons isomerize on zeolites via a monomolecular path, which includes a protonated cyclopropane ring [24,25].

The initial step of this reaction is probably similar to that of the double bond shift, resulting in the formation of a covalently bonded alkoxy group. These species then transform into transition states representing energetically excited ion pairs which contain carbenium ion-like alkyl fragments. Then a cyclopropane ring is formed, a proton being donated back to the zeolite. Reopening of the cyclopropane ring by protonation of another bond of the cycle results in skeletal isomerization.

A quantum chemical analysis of this mechanism was carried out in Refs. [26] and [27]. We present below the results of the calculations at the B3LYP/6-31G* level for the zeolite $H_3Si(OH)A1H_2(OSiH_3)$ cluster without any symmetry constrains [27].

The obtained results indicated two conformations of the transition state of cyclopropane ring closure. The first "near-in-plane" conformation (Fig. 4(b)) has all three carbon atoms localized close to the O1–A1–O2 plane of the cluster: their deviations from the plane are within 0.15–0.40 Å and the angle between the O1–A1–O2 and C1–C2–C3 plains is only 7.5°. The corresponding reaction path starts from the elongation of the O2–C2 bond of the surface prop-1-oxy; after that, a new C2–C1 bond is formed while the H1 hydrogen is transferred to the surface O2 oxygen. Since cyclopropane is a strained molecule, its formation from the surface alkoxy group is rather endothermic: +22.7 kcal/mol at the B3LYP/6-31G* level.

The second "out-of-plane" conformation of the transition state of Fig. 4(d) has a rather large angle between the C1–C2–C3 and the O1–A1–O2 planes ($\sim$80°). The reaction path associated with this transition state also involves the elongation of the O1–C2 bond in the surface prop-1-oxy, formation of the new C2–C1 bond and transfer of the H1 hydrogen to the surface O1 oxygen. However, in this path, the hydrogen atom is transferred to the same O1 oxygen which was bonded to the C2 carbon in the initial state. In addition, the O2 oxygen is not bonded to any carbons or hydrogens in both the initial and final states, but the strong hydrogen bond (1.891 A) between this oxygen and H2 hydrogen reduces the corresponding activation energy.

The total B3LYP/6-31G* activation energy for the cyclopropane ring closure is slightly lower if the reaction proceeds via an "out-of-plane" transition state than via a "near-in-plane" one: 54.9 vs. 59.6 kcal/mol. Both values are much higher than the experimentally measured activation energy of skeletal isomerization of carbenium ions in solution of "magic acid" which is equal to 14–17 kcal/mol [28]. However, when comparing these figures, one should bear in mind that in solution the carbenium ions are weakly solvated by molecules of HF, whereas on

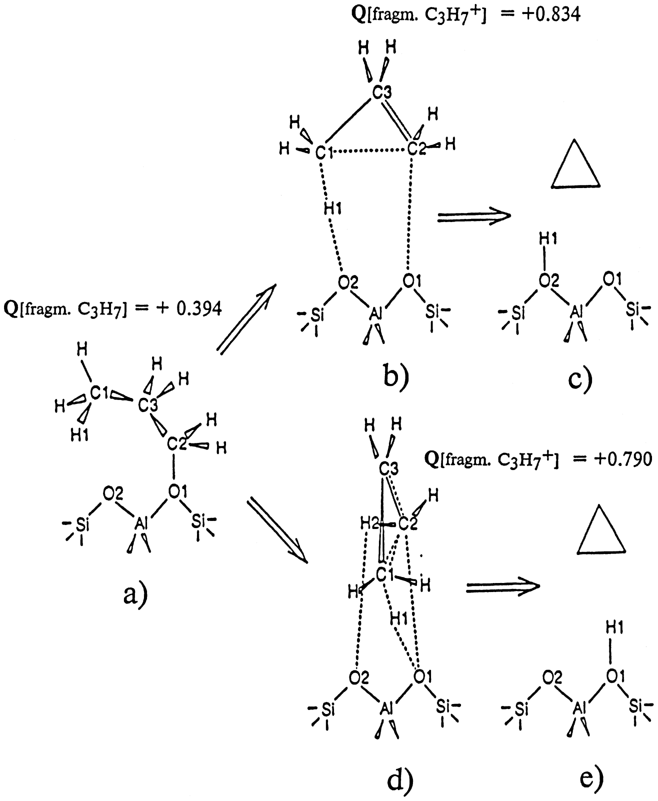


Fig. 4. Reaction path of skeletal isomerization of olefins via cyclopropane ring formation. Calculations at the MP2/6-31++G**//6-31G* level.

the surface of zeolite the generation of the ion pairs via partial dissociation of carbonyl bonds in covalent alkoxides requires an activation energy of about 25 kcal/mol. This value should be added to activation energy of the ring closure in free carbenium ions. Therefore, the higher value of the quantum chemically estimated activation energy of the propane ring closure in zeolites looks quite reasonable.

3.3. Cracking of olefins

The mechanism of this reaction also can be rationalized by a modified carbenium ion theory which involves carbenium ion-like transition states. Similarly to the double bond shift and skeletal isomerization reaction, this reaction also starts with formation of the most stable surface alkoxides. These species are then transformed into high-energy activated complexes or into transition states with carbenium ion-like alkyl fragments which are involved in the reaction of β-scission.

In Ref. [29], several paths for β-scission of 1-but-1-oxy and pent-2-oxy were discussed by means of density functional B3LYP and Hartree-Fock quantum chemical calculations with 6-31G* basis sets for $H(OH)A1H_2(OH)$ and $H_3Si(OH)A1H_2(OSiH_3)$ clusters. The results obtained indicated that the potential energy surface for this reaction is very complicated while the reaction may proceed through several cyclopropane-like transition states with the calculated activation energies in the range of 50–60 kcal/mol. One of them is presented in Fig. 5.

Similarly to skeletal isomerization, the cracking of alkoxy group also starts with elongation of the carbon–oxygen bond, resulting in the carbocationic cyclopropane-like transition state depicted in Fig. 5. The main difference in comparison with the skeletal isomerization through the "in-plain" transition state

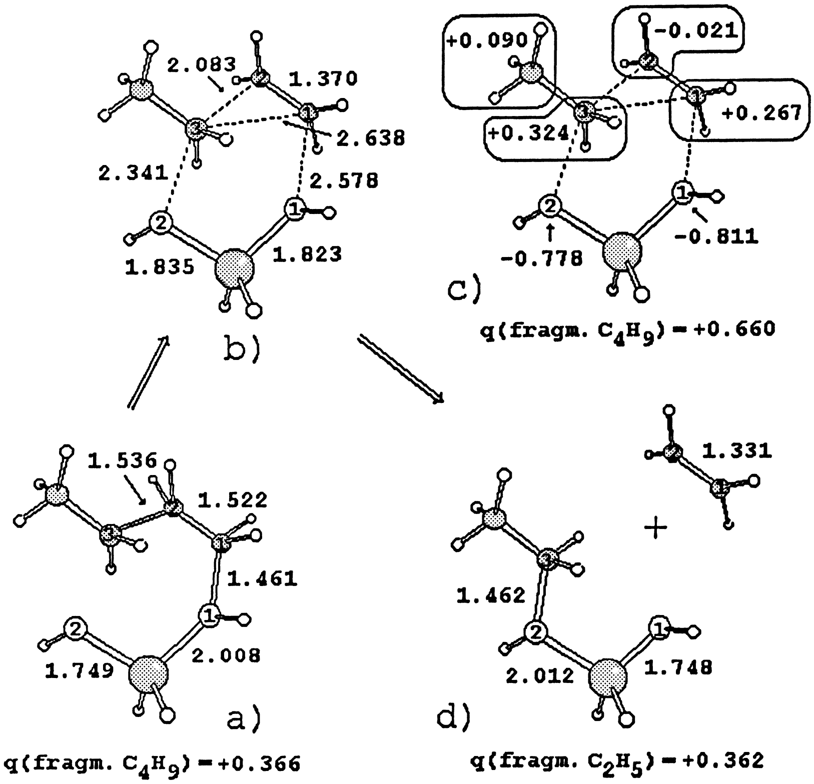


Fig. 5. Reaction path of the β-scission reaction found at the B3LYP/6-31 level: (a) Initial alkoxide; (b) transition state distances; (c) transition state charges; (d) final alkoxide and olefin.

of Fig. 4 consists of the additional formation of the new carbon–oxygen bond of C3 with O2 resulting in different bond lengths in the cyclopropane ring which is then decomposed into olefin and a new adsorbed alkyl group.

This is another way to stabilize the excited ion pairs through β-scission of smaller alkyl fragments and desorption from the surface of lighter olefin. Here, the neutralization of the positively charged carbon atom of the excited carbocation occurs due to formation of the double bond. Simultaneously, the positive charge migrates to the abstracted alkyl fragment, which then forms a new surface alkoxy group when interacting with the basic oxygen.

The mechanism discussed explains naturally the easier cracking of branched olefins which have higher proton affinities than linear olefins. Therefore, the abstraction of protons from the excited branched carbenium-ions occurs with more difficulty than the cleavage of C–C bonds. It also naturally explains the close relation between cracking and skeletal isomerization and predicts for cracking the importance of the interaction of the abstracting carbenium ion with a neighboring basic oxygen of the active site. Therefore, the selectivity of these reactions should be related to a geometry of active sites and to the different basic strengths of the neighboring surface oxygen atoms.

The calculated activation energy of about 60 kcal/mol is considerably higher than that estimated from the modeling of the kinetics of isobutane cracking [30]. The most important reason for this difference is the difference in the acid strength between that of the cluster used in calculations and that of the real zeolite.

3.4. Oligomerization of olefins

This reaction represents the reverse of cracking. It also starts with the formation of a surface alkoxide, which then may be transformed into a carbenium ion-like transition state. If this species reacts with another olefin molecule, a larger alkyl fragment is formed. After decomposition, the surface alkoxide converts into a higher olefin as final product of the reaction.

Since the thermal excitation of the tertiary surface alkyl fragment into an ion pair occurs more readily than that of secondary and primary alkoxides, the rate of oligomerization of branched isoolefins is higher than that for linear olefins.

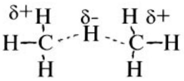
4. Adsorbed carbenium and carbonium ions as transition states in cracking of paraffins

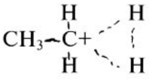
Catalytic cracking of paraffins is usually considered as a chain reaction with adsorbed carbenium ions as active intermediates. As already discussed above, these species are formed as transition states by excitation of the more stable alkoxides. The carbenium ion-like transition states are then involved in secondary reactions of skeletal isomerization, cracking or oligomerization.

Addition of protons to olefins is only one possible way to produce adsorbed carbenium ions. An alternative consists of the direct protonation of paraffins. At first, this gives rise to adsorbed nonclassical carbonium ions, which then transform into carbenium ions by secondary reactions (3) and (4) of protolytic cracking or dehydrogenation. The most convincing evidence in favor of this reaction were obtained for cracking of light paraffins at very low conversions which allowed one to estimate the activation energies of protolytic cracking and dehydrogenation of ca. 35 kcal/mol [31].

As with carbenium ions, the structure and properties of adsorbed carbonium ions, are usually considered in relation to free species without taking into account the interaction with the catalyst surface. In this connection, let us consider the data on the structure and properties of free carbonium ions in the gas phase which are mainly available from quantum chemical calculations and mass-spectrometry.

Already the very first quantum chemical calculations indicated that free carbonium ions exist in the two following isomeric forms [32]:


(I)


(II)

Structure (I) is a complex of methyl carbenium ion with a strongly polarized molecule of methane. The positive charge is equally shared between two methyl groups while the central hydrogen is slightly negatively charged. According to the MP2 6-31G* calculations, this complex is nonlinear with a C–H–C angle of 105.8°.

In contrast, structure (II) is a weaker complex of ethyl carbenium ion with a slightly perturbed hydrogen molecule. The positive charge in this cation is mainly localized at the ethyl group, while the hydrogen molecule is almost neutral with the H–H distance practically equal to that in unperturbed hydrogen. It was also demonstrated by both quantum chemical calculations and mass spectrometry that structure (I) is by 8 kcal/mol more stable than structure (II) and that heavier carbonium ions are less stable than ethyl carbonium ions. This is well explained by weaker Lewis acids properties of the tertiary and secondary carbenium ions in comparison with those of the primary ions.

Since the proton affinities of paraffins are 1–2 eV less than those of olefins, the energetics of the formation of carbonium ion is less favorable than that of carbenium ions (see Table 2). Therefore, one might conclude that, similarly to carbenium ions, adsorbed carbonium ions also are transition states resulting from proton transfer to paraffins. Moreover, due to lower proton affinities the activation energies of paraffin protonation should be even higher than those for the formation of carbenium ion-like transition states.

One might also suppose that complex (I) corresponds to proton attack at the C–C bond of ethane while complex (II) can be produced by proton attack at the C–H bond. In other words, this means that complex (I) should resemble a carbonium ion-like transi-

Table 2
Proton affinities of some hydrocarbons

Hydrocarbon	Proton affinity (eV)
CH_4	5.3
C_2H_6	5.6
C_3H_8	6.1
C_2H_4	6.9
C_3H_6	7.8
C_4H_8	7.99
i-C_4H_8	8.3

tion state of protolytic cracking of ethane, whereas structure (II) resembles the transition state of protolytic dehydrogenation. In Refs. [33] and [34] these assumptions were used for quantum chemical analysis of the protolytic cracking and dehydrogenation of ethane on the smallest $H_2O(AlH)_3$ cluster, which models the Brønsted acid sites of a high-silica zeolite. However, we will discuss below more recent results for protolytic cracking and protolytic dehydrogenation of isobutane published in Refs. [22] and [35]. The corresponding ab initio calculations were also performed for the smallest $H_2Al(OH)_3$ cluster with HF/6-31++G**//6-31G* basis set.

4.1. Protolytic cracking of isobutane

Protolytic cracking of isobutane starts with a proton attack at one of the C–C bonds. The C_4H_{11} fragment in the resulting transition state of Fig. 6 is oriented almost perpendicularly to the O1–Al–O2 plane. By the high total positive charge of +0.909 e and by its geometry, this fragment very much resembles a non-classical $C_4H_{11}{}^+$ carbonium ion in which the isopropyl and methyl groups are connected via a hydrogen atom. One can also distinguish a strongly perturbed positively charged methane-like fragment ($Q(CH_4)=+0.580$ e) with a C2–H1 bond, stretched by 0.172 Å, that is formed in the reaction.

On the other hand, due to the hydrogen bonding of H1 bridging hydrogen atom with the O2 basic oxygen of the cluster (d(O2–H1)=1.705 Å), the adsorbed carbocation has a nonlinear geometry (with a C1–H1–C2 angle of 92.3°). Relatively weaker hydrogen bonds with the surface oxygens are also formed by three other hydrogens (H2, H3 and H6 in Fig. 6). This results in the polarization of corresponding C–H bonds. Therefore, the positive charge +0.211 e at the H3 hydrogen of the methyl group directed towards the surface is somewhat higher than those of the H4 (+0.146 e) and H5 (+0.147 e) hydrogens directed out from the surface. Similarly, the positive charge of the H6 hydrogen directed towards the surface (+0.102 e) is higher than those of the H7 (+0.084 e) and H8 (+0.065 e) hydrogens. This also indicates the polar-

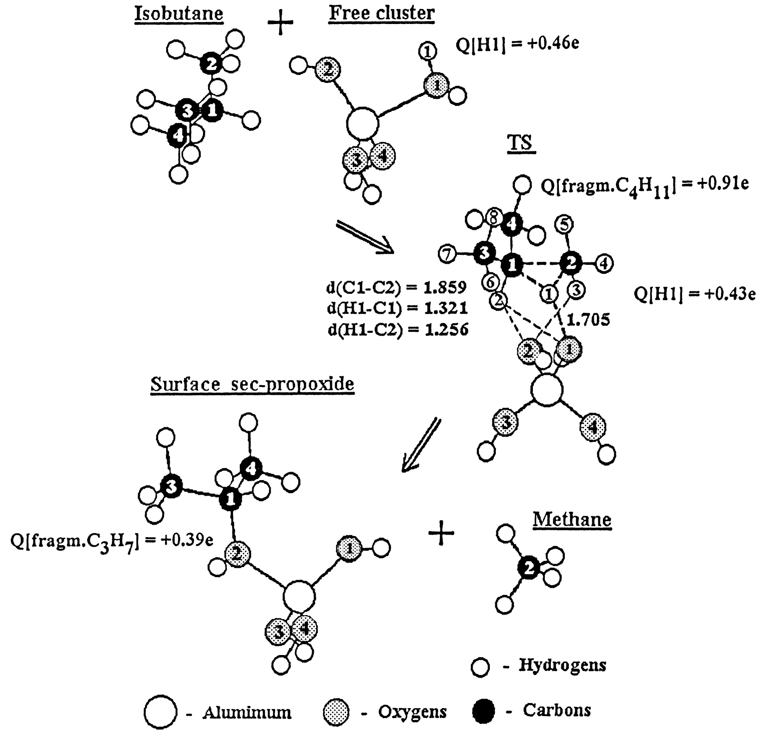


Fig. 6. Reaction path of the protolytic cracking of isobutane. Calculations at MP2/6-31++G**//6-31G* level.

ization of the hydrocarbon fragment due to interaction with the surface.

The decomposition of the transition state occurs by abstraction of methane and by the approach of the isopropyl fragment to the basic O2 oxygen of the cluster. This results in the formation of surface *sec*-propyl alkoxide and demonstrates a bifunctional nature of the Brønsted acidic–Lewis basic active site.

According to our calculations, the protolytic cracking of isobutane is practically thermoneutral, with an activation energy of 57.5 kcal/mol. This is considerably higher than the value of about 40 kcal/mol obtained at very low conversion or the value estimated from modeling the kinetics [35]. However, one has to bear in mind that the experimentally measured value is an apparent activation energy. Therefore it should be increased by about 12–14 kcal/mol for the heat of isobutane adsorption [36]. In addition, the smallest $H(OH)Al(OH)_3$ cluster used in our calculation has lower acidity than the real zeolite. The account of both these corrections makes the discrepancy between calculated and experimental values quite small. Thus, the "ab initio" cluster quantum chemical calculations reasonably describe the activation energies and heat effects of the protolytic cracking of isobutane.

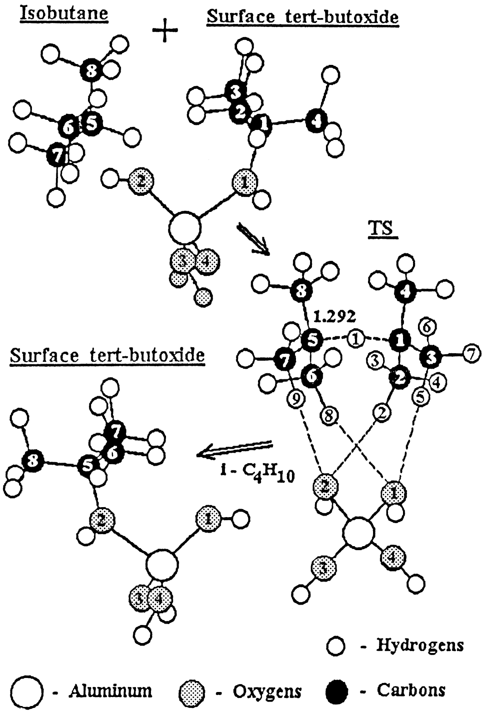


Fig. 7. Reaction path of the protolytic dehydrogenation of isobutane. Calculations at MP2/6-31++G**//6-31G* level.

4.2. Protolytic dehydrogenation

The reaction path for protolytic dehydrogenation is depicted in Fig. 7. The geometry of the transition state of this reaction is quite different from that for cracking. It indicates a protolytic attack at the H2 hydrogen atom of the isobutane rather than at the C1–H2 bond. The resulting activated complex resembles a polarized hydrogen molecule placed between the *tert*-butyl carbenium ion and the negatively charged cluster. Indeed, the H1 atom has a positive charge +0.231 e while the H2 atom is charged negatively (Q(H2)=−0.189 e). This results in only a small total charging of the abstracting H_2 fragment (+0.042 e), and in only a slightly longer (by 0.053 Å) H1–H2 distance with respect to the free hydrogen molecule. The *tert*-butyl group in such a transition state has a very high positive charge of +0.872 e. The protolytic dehydrogenation is endothermic by 6.9 kcal/mol.

Thus, both the transition states of cracking and of dehydrogenation contain highly positively charged butyl fragments with the average formula of $C_4H_{11}^+$, which could be considered as the analogs of adsorbed carbonium ions. On the other hand, not only the final products of reactions (3) and (4) but also the structures of these carbonium-ion-like fragments are quite different since the former results from protolytic attack at the C–C bond of isobutane whereas the latter is yielded by protolytic attack at the C–H bond.

The Intrinsic Reaction Coordinate analysis shows that after abstraction of the hydrogen molecule, the isobutyl group moves to the O1 oxygen atom, i.e., to the same oxygen which was bonded in the initial cluster to the acidic proton. Consequently, protolytic dehydrogenation could not be considered as a concerted reaction. On the other hand, the hydrogen bonds of a hydrocarbon fragment with basic O2 and O3 oxygen atoms of the cluster (d(O2–H6)=2.109 Å; d(O3–H3)=2.163 Å) are quite important for the geometry of this transition state. Therefore, as in the case of the transition state for protolytic cracking, the hydrogen atoms directed towards the surface have somewhat higher positive charges than other hydrogens. For example, the H3 hydrogen has a charge of +0.266 e, whereas the charges of the H4 and H5 atoms connected to the same C2 atom are only +0.127 and +0.123 e, respectively.

One can rationalize the difference between the transition states of dehydrogenation and cracking in the following way. In the case of dehydrogenation, the proton attack results in the polarization of the C1–H2 bond with a displacement of electronic density from the carbon towards the hydrogen atom. This is in contradiction to the electronegativities of these atoms. In addition, in the transition state for dehydrogenation, the positively charged central carbon atom of the *tert*-butyl fragment is rather far from the negatively charged active site due to the steric repulsion of three methyl groups, whereas the *sec*-propyl fragment in the transition state for cracking is closer to the cluster. The two latter factors are unfavorable for dehydrogenation with respect to cracking. As a consequence, we obtained an activation energy 66.8 kcal/mol for dehydrogenation, which is considerably higher than that obtained for cracking (57.5 kcal/mol).

4.3. Hydride ion transfer

One more example of the reaction involving adsorbed carbonium ion-like transition states is the transfer of a hydride ion from a paraffin to carbenium ion resulting in the propagation of the reaction chain:

$$R^+ + i\text{-RH} \rightarrow \text{RH} + i\text{-R}^+ \qquad (12)$$

Unlike protolytic cracking or dehydrogenation, this is a secondary reaction. Therefore, its experimental study is more difficult, and the only available estimate of its activation energy of about 30 kcal/mol was made from modeling of isobutane cracking [30].

The hydride transfer will be discussed below for a degenerated reaction between surface *tert*-butoxide and isobutane:

$$t\text{-C}_4\text{H}_{9\,\text{surf}} + i\text{-C}_4\text{H}_{10} \rightarrow i\text{-C}_4\text{H}_{10} + t\text{-C}_4\text{H}_{9\,\text{surf}} \qquad (13)$$

The reaction starts with the isobutane attack at the C–O bond of the covalently bonded *tert*-butyl alkoxide. This results in a considerable increase of the C–O distance and in the change of the *tert*-butyl group orientation relative to the active site in such a way that two of its methyl groups form hydrogen bonds with the O1 and O2 oxygen atoms of the cluster (Fig. 8). Such perturbation is much stronger than in the case of *tert*-butyl alkoxide formation or decomposition, since the total positive charge of the hydrocarbon fragment is very high (+0.998 e). In other words, the *tert*-butyl group becomes even more "carbenium-ion-like" than in the transition state of formation decomposition of the surface alkoxide. On the other hand, due to the different orientation relative to the cluster, the resulting unstable carbenium ion, instead of being adsorbed by the neighboring basic oxygen, abstracts the hydride ion from the attacking isobutane yielding the symmetric (symmetry C_2) transition state depicted in Fig. 8.

The geometry and charge distribution in the hydrocarbon fragment of such an activated complex also very much resemble those of the nonclassical carbonium ion of structure (I) resulting from protonation of the central C–C bond in hexamethyl ethane. The positive charge is equally distributed between both *tert*-butyl fragments, whereas the charge of the hydrogen atom which links these groups is slightly negative (−0.146 e). The hydride nature of this bridging hydrogen is also evident from the longer C–H bond of 1.292 A in comparison with the normal C–H bond length of 1.089 A.

Four hydrogen atoms in such a transition state (H2, H5, H11 and H14) form weak hydrogen bonds with the surface O1 and O2 oxygens (d(O1–H2)=d(O2–H11)=2.162 A; d(O1–H5)=d(O2–H14)=2.297 A). This interaction determines the geometry of the transition state and results in higher positive charges of the hydrogen atoms involved in the hydrogen bonds. For example, q(H2)=+0.170 e, while q(H3)=+0.091 e and q(H4)=+0.068 e.

Thus, although the transition state for the hydride transfer as well as the transition state for the isobutane cracking arises from the protonation of the C–C bond of an alkane and has a very high positive charge, the hydrocarbon fragments of these transition states interact quite differently with the zeolite surface. Indeed, in the case of cracking, the H1 hydrogen atom has a high positive charge and interacts strongly with an oxygen atom of the surface. On the contrary, in the transition state of hydride transfer, the H1 hydrogen atom has a negative charge, and therefore, practically does not interact with the surface. As a result, these activated complexes decompose by different pathways: via a proton transfer between the cluster and hydrocarbon

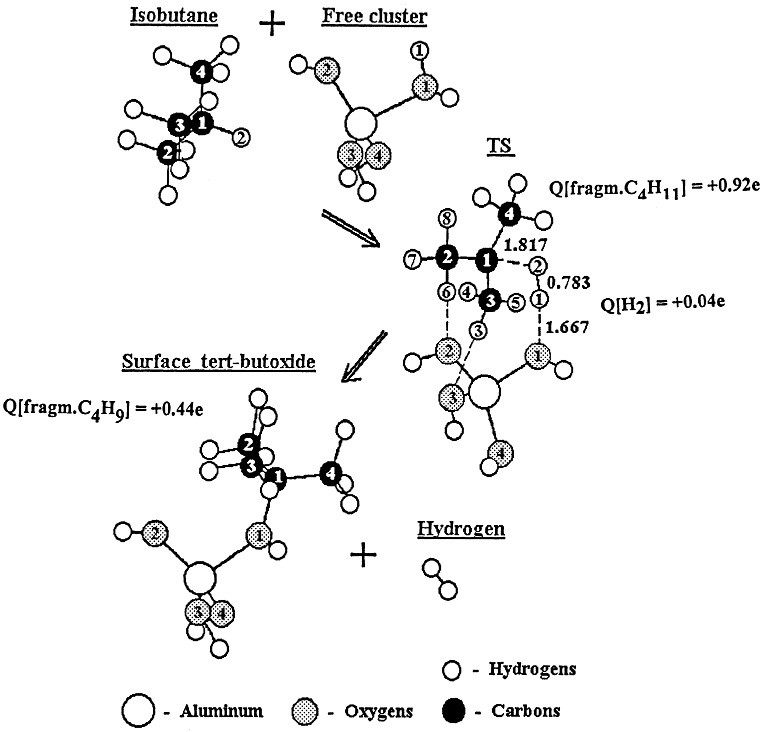


Fig. 8. Reaction path of the hydride ion transfer between isobutane and isobutyl group. Calculations at MP2/6-31++G**//6-31G* level.

for protolytic cracking and via an intermolecular hydride transfer in the latter case.

The calculated activation energy of hydride transfer is equal to 48.4 kcal/mol. This is considerably higher than the value of about 30 kcal/mol used for modeling of isobutane cracking in Ref. [30]. One has, however, to bear in mind that the latter model implied some very rough assumptions.

5. Conclusions

The results of the above quantum chemical calculations provide a much improved understanding of the real nature of adsorbed carbenium and carbonium ions and of their role in some elementary steps of acid-catalyzed transformations of olefins and paraffins. This conclusion is quite important, since, even in the very recent publications, the carbenium ions are still considered as relatively stable intermediates.

In contrast, the above results demonstrate that the real stable intermediates in the heterogeneous acid-catalyzed transformations of hydrocarbons on zeolites are covalently bonded alkoxides or surface esters. These species are precursors of adsorbed carbenium ions, which are formed by partial dissociation or stretching of C–O bonds. This results in the separation of charges and in the formation of transition states with "carbenium-ion-like" alkyl fragments.

Together with our previous publications [33–35], the results obtained give a much better understanding of the real nature of adsorbed nonclassical carbonium ions. These species also are highly excited transition states resulting from proton attack at C–C or C–H bonds of paraffins according to reactions (3) and (4) or arising from interaction of paraffins with excited surface alkoxides as in the case of hydride transfer. The geometry and charge distribution in such "carbonium-ion-like" transition states are also very similar to those in the corresponding free ions, whereas the activation energies of proton transfer to paraffins are even higher than for the "carbenium-ion-like" transition states resulting from protonation of alkenes.

It is very important that, neither the adsorbed carbenium ions, nor the adsorbed carbonium ions could be considered as free species since they are strongly electrostatically bonded to the surface. For instance, according to our estimates, the abstraction of *tert*-butyl carbenium ion from the top of the activation barrier in the reaction of double bond shift in olefins requires an additional energy of about 4 eV. Nearly the same values for electrostatic interaction were also estimated for adsorbed carbonium ions involved in the transition states of protolytic cracking, protolytic dehydrogenation and hydride transfer.

Such a strong coulombic interaction substantially modifies the geometry and the reactivity of adsorbed species. For instance, it explains the perpendicular orientation of the positively charged hydrocarbon fragments relative to the O1–A1–O2 plane of the cluster in the transition states of cracking or of hydride transfer due to diminishing of steric hindrances and to the more effective interaction of positive and negative charges in the excited ion pairs. At the same time, both transition states arising from protonation of C–C bond are considerably different due to different types of interaction of the hydrocarbon fragment with the surface.

It is also very important that both the above-calculated activation energies and those experimentally measured for the high temperature transformations of paraffins on zeolites are considerably higher than those obtained for the similar reactions in super acid solutions. Indeed, the activation energies for protolytic cracking of neopentane with the formation of methane and *tert*-butyl cation in a $HF–SbF_5$ solution is equal to 21 kcal/mol [37] and only to 14 kcal/mol in a $HSO_3F–SbF_5$-solution [38]. The activation energy of the protolytic dehydrogenation of isobutane in $HF–SbF_5$ reported in [39] is equal to 18.3 kcal/mol, whereas for the hydride transfer from isobutane to *tert*-butyl cation in the $SO_2–CH_2Cl_2–AsF_5$ solution, it is only 3.6 kcal/mol [39]. All these values are much lower than for high temperature reactions on zeolites.

This difference should be accounted for by the strong coulombic interaction of the adsorbed species with the surface, resulting in considerably higher activation energies in heterogeneous catalytic reactions than in liquid superacids. Thus, the commonly used mechanisms, in which the reactions of adsorbed carbenium and carbonium ions are considered in a similar way to those for free carbocations, is certainly a very rough simplification.

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