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Quantum-chemical study of the nonclassical carbonium ion-like transition states in isobutane cracking on zeolites

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The "ab initio" quantum chemical calculations at MP2/6-31++G**//HF/6-31G* level were performed for some elementary steps of isobutane cracking on zeolites. The results demonstrated that adsorbed carbonium ions represent not the observable reaction intermediates, but the high-energy transition states of the corresponding elementary reactions. Calculated activation energies are in reasonable agreement with experimental data.

1. INTRODUCTION

Catalytic cracking of paraffins on solid acids such as zeolites and amorphous silica-alumina catalysts is widely used by chemical industry for oil refining. It is generally accepted that this is a chain reaction, which involves adsorbed carbenium ions as active intermediates [1]. This conclusion is based mainly on the study of kinetics and the composition of the final products.

A considerable effort in understanding of some details of the reaction mechanism has been recently made for cracking of light paraffins on zeolites. For these relatively simple molecules one can discriminate between different ways of chain initiation on the basis of the distribution of reaction products at conversions below 1%. Such experiments indicated that at high temperature and low pressure the chain initiation mainly proceeds through direct protonation of light paraffins, which involve adsorbed pentacoordinated nonclassical carbonium ions [2]:

$$RH \; + \; H^+_{ads} \; \Longrightarrow \; RHH^+_{ads} \begin{cases} \Longrightarrow \; H_2 \; + \; R^+_{ads} & (1) \\ \Longrightarrow \; R_1H \; + \; R_2{}^+_{ads} & (2) \end{cases}$$

It was also found that for isobutane the apparent activation energies of protolytic cracking and dehydrogenation according to reactions (1) and (2) are very close to each other (39.6 and 37.5 kcal/mol, respectively) [3]. In [4,5] a kinetic model of isobutane cracking was worked out, which includes 21 elementary steps. A good fitting of computed reaction parameters with experimental data was achieved. The initial steps of isobutane, n-butane and n-pentane cracking were also studied in [6,7,8].

Kinetic regularities represent only one source of information concerning the mechanism of cracking. Another source is quantum-chemical analysis of various elementary steps of the reaction. This has been done, however, only in a few published papers, which are mainly devoted to the study of adsorbed carbenium ions. For instance, it was concluded in [9] that these species are activated complexes, whereas the stable surface intermediates resulting from ethylene and bridging hydroxyl groups of zeolites are the covalently bonded alkoxides. They are formed from the surface π-complexes through the carbenium ion-like transition state, which strongly resembles in its geometry and charge distribution the classical ethyl carbenium ion. In [10] similar conclusions were also made for formation of surface sec-propyl and tert-butyl fragments.

The adsorbed nonclassical carbonium ions have also been the subject of quantum-chemical investigations. In [11] the concept of carbonium ion-like transition state was applied to hetero-isotope exchange of CD_4 with protons in zeolites, and in [12,13] - to protolytic cracking and dehydrogenation of ethane. The activation energies for two latter reactions were found to be very high. This looks, however, quite natural, since cracking and dehydrogenation of ethane are certainly very difficult reactions. Consequently, more realistic models involving higher hydrocarbons should also be studied.

Indeed, possible pathways of n-butane cracking were discussed in [14]. In [15] the protolytic cracking of higher paraffins was also analysed by means of semi-empirical calculations. Below we report a more detailed "ab initio" quantum-chemical study of the nature and the role of adsorbed carbonium ions in protolytic cracking, protolytic dehydrogenation and hydride transfer elementary steps of isobutane transformations on zeolites, which involve the adsorbed tert-butyl carbenium ions and isobutyl carbonium ions.

2. MODELS AND COMPUTATIONAL DETAILS

The "ab initio" quantum chemical calculations were performed with the GAUSSIAN 92 program. Due to the relatively large size of the hydrocarbon fragments (up to 8 carbon atoms for hydride transfer), the Broensted acid sites of zeolites were modelled by the simplest $H(OH)Al(OH)_3$ cluster. The geometries of the investigated structures were fully optimised at SCF theory level using standard 6-31G* basis set. The gradient technique was applied for these optimisations. Transition states were found by minimising the gradient norm. Analytical frequency calculations were performed in order to verify the nature of the obtained stationary points. In addition, the Intrinsic Reaction Coordinate method (IRC) [16] was applied for passing from each transition state to the initial and the final products.

Single point calculations were carried out for all optimised structures using second-order Moeller-Plesset perturbation theory with a 6-31++G** basis set. Zero-point vibration corrections (ZPE) obtained from frequency calculations were included in final activation energies and heat effects (unscaled frequencies were used). The potential-fitted atomic charges obtained according to CHELPG scheme [17] at HF/6-31++G**//HF/6-31G* level were applied for analysis of charge distributions in the calculated structures.

3. RESULTS

Similar to protolytic cracking of ethane [12], the protolytic cracking of isobutane was considered as a proton attack at the C-C bond. The C_4H_{11} fragment in the transition state TS-I in Figure 1 is oriented almost perpendicularly to O1-Al-O2 plane. Because of the high total positive charge (+0.909 e) and geometry it very much resembles a nonclassical $C_4H_{11}^+$

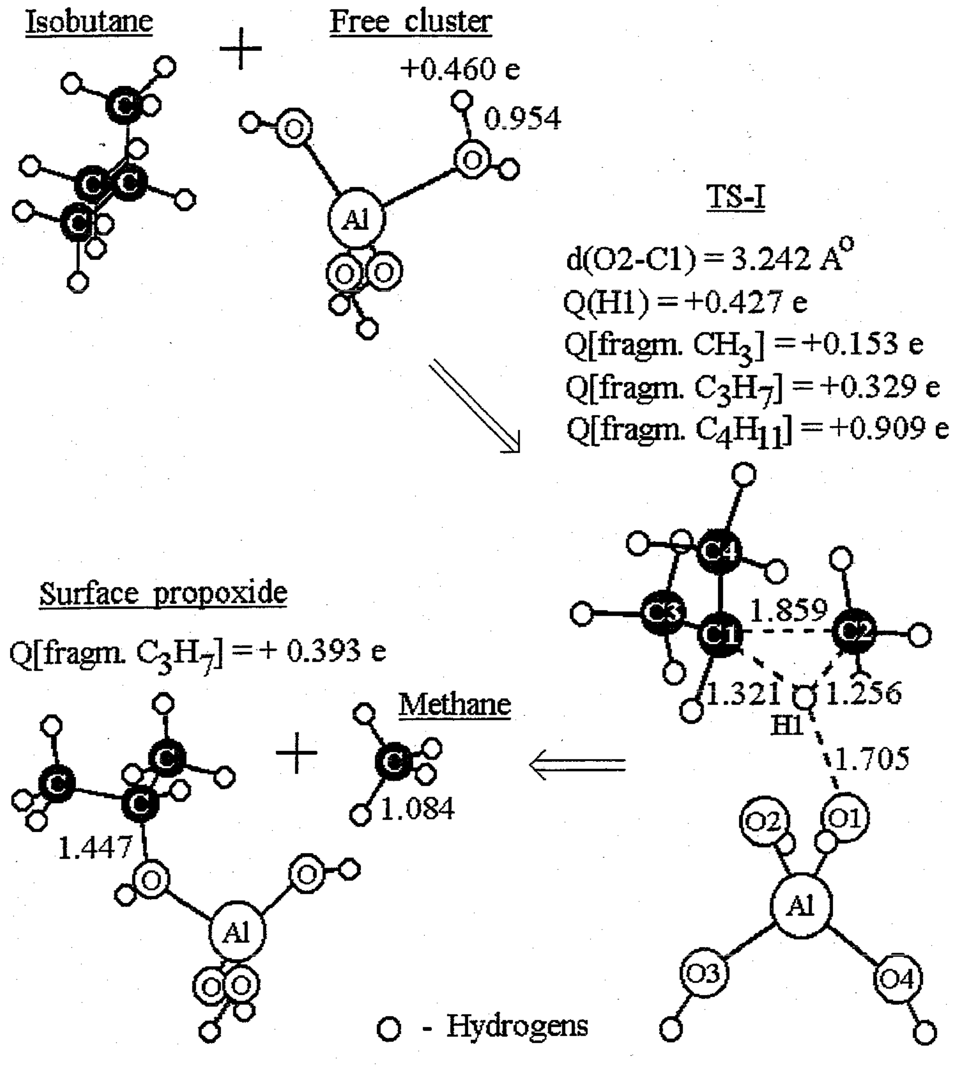

Figure 1. Protolytic cracking of isobutane.

carbonium ion, where the sec-propyl and methyl groups are also connected with each other by a hydrogen atom [18].

On the other hand, due to the interaction of the bridging H1 hydrogen with the O1 oxygen atom of the cluster, the adsorbed hydrocarbon fragment is strongly polarised. This results in the non-linear geometry of the adsorbed carbocation with a rather high positive charge of +0.427 e at the bridging H1 hydrogen atom. One can also distinguish a strongly perturbed positively charged methane-like fragment ($Q(CH_4)$ = +0.580 e) with the C2-H1 bond stretched by 0.172 A.

The decomposition of this transition state occurs by abstraction of methane and by the approach of the sec-propyl fragment to the O2 oxygen atom of the cluster. This results in the surface sec-propyl alkoxide and demonstrates the bifunctional Broensted acidic - Lewis basic nature of the active site.

The reaction of protolytic cracking of isobutane is practically thermoneutral with activation energy equal to 57.5 kcal/mol. This is much lower than the earlier reported in ref. [12] value for the cracking of ethane of 93.4 kcal/mol obtained with the 3-21G basis set and with only partial geometry optimisation. Therefore, we reproduced our previous calculations at the MP2/6-31++G**//HF/6-31G* level with full geometry optimisation. In this case the activation energy for ethane cracking was found to be equal to 80.3 kcal/mol. This is still much higher than for isobutane cracking, and should be explained by the more difficult generation of methylcarbenium ion-like fragment in comparison with sec-$C_3H_7^+$ carbocation.

The reaction path for protolytic dehydrogenation is depicted in Figure 2. The geometry of the transition state TS-II for this reaction is quite different. It indicates rather the protolytic attack at the H2 hydrogen atom of isobutane itself than at the C1-H2 bond. This activated complex resembles a polarised hydrogen molecule placed between tert-butyl carbenium ion and the negatively charged cluster. Indeed, the H1 atom has a positive charge +0.231 e, while the H2 atom a negatively charged (Q(H2) = - 0.189). This results in only a small total charge of the abstracting H_2 fragment (+0.042), and in a H1 - H2 distance slightly longer by 0.053 A with respect to free hydrogen molecule. At the same time, the tert-butyl group in this transition state has a very high positive charge of +0.872 e. The protolytic dehydrogenation is endothermic by 6.9 kcal/mol.

Intrinsic Reaction Coordinate analysis shows that after splitting off the hydrogen molecule, the tert-butyl group moves to the O1 oxygen atom, i.e. to the same oxygen which was connected with acidic proton in the initial cluster. Consequently, protolytic dehydrogenation can not be considered as a concerted reaction. However, the hydrogen bonding of a hydrocarbon fragment with basic O2 and O3 oxygen atoms of the cluster is important for the geometry of the transition state.

One can rationalise a difference between protolytic cracking and dehydrogenation in the following way. In the latter case the proton attack results in a polarisation of the C1-H2 bond with a displacement of electronic density from the carbon towards hydrogen atom. This is in contradiction with electronegativities of these atoms. In addition, in the transition state of 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 unfavourable for dehydrogenation with respect to cracking. As a consequence we obtained an activation energy for dehydrogenation of 66.8 kcal/mol, which is considerably higher than that for cracking.

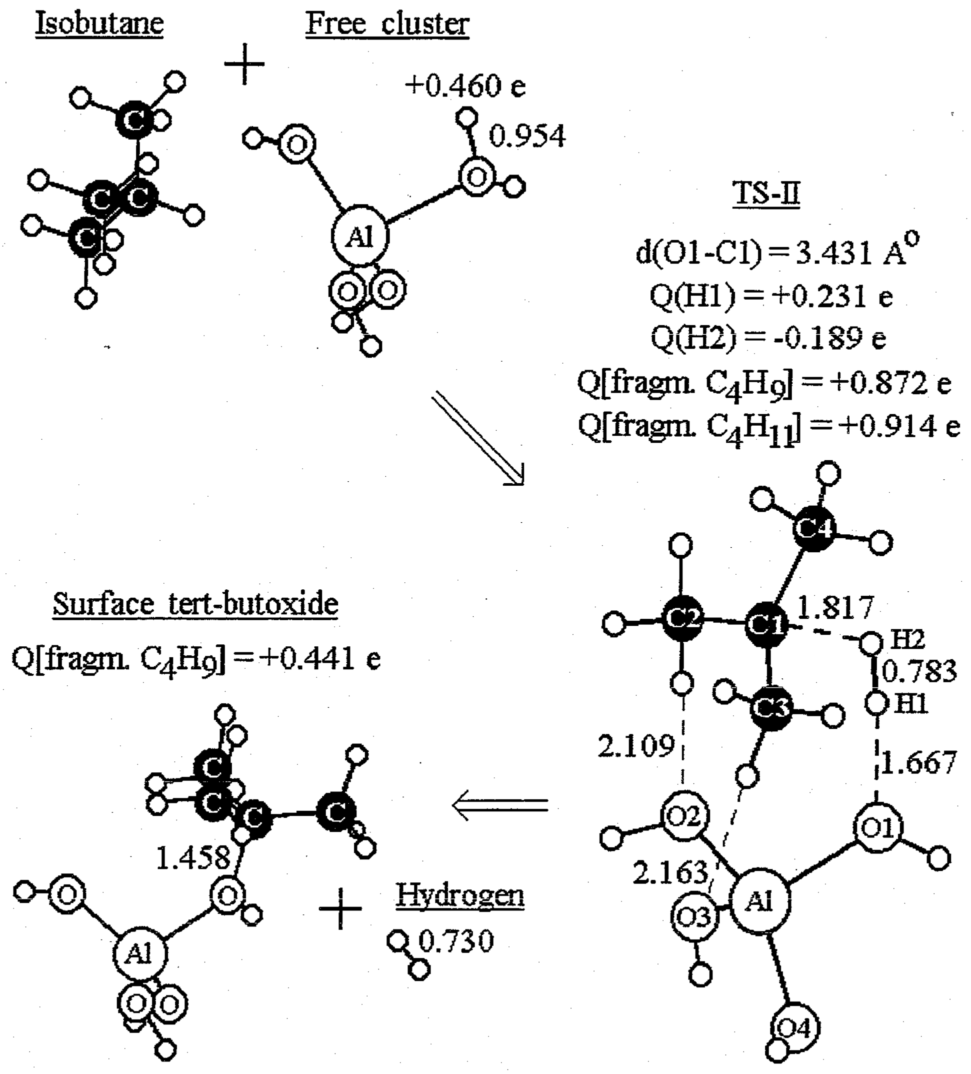

Figure 2. Protolytic dehydrogenation of isobutane.

The reaction path for isobutane dehydrogenation found here is similar to that previously reported for dehydrogenation of ethane and methane in [13,19]. On the other hand, the activation energy of 66.8 kcal/mol for isobutane dehydrogenation is much lower than 94.8 kcal/mol, previously obtained with the 3-21G basis set and only partial geometry optimisation in [13]. Therefore, we also reproduced the calculations for ethane dehydrogenation at the

MP2/6-31++G**//HF/6-31G* level with full geometry optimisation. The obtained value of 83.8 kcal/mol makes the difference in activation energies for ethane and isobutane dehydrogenation more reasonable.

The hydride transfer was studied for degenerated reaction between surface tert-butyl alkoxide and isobutane:

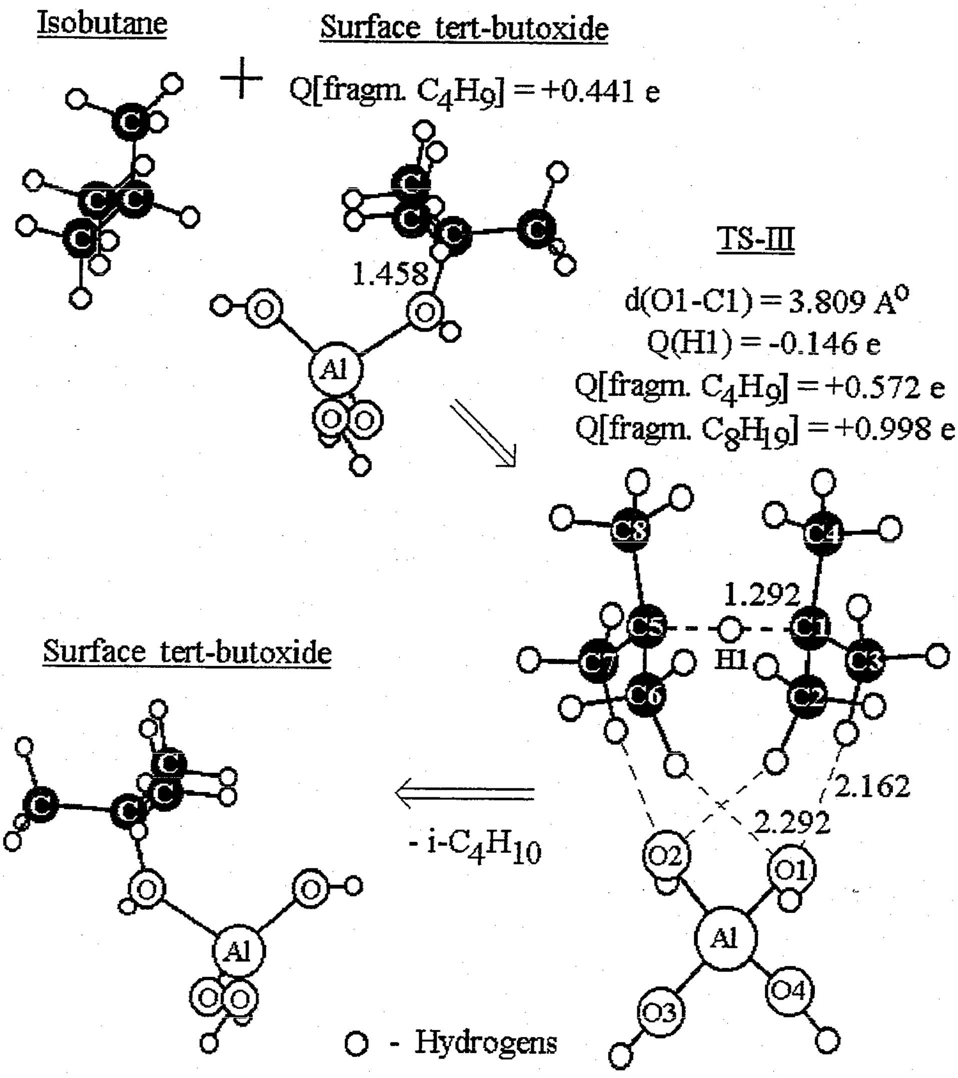

Figure 3. Hydride transfer from isobutane to surface tert-butoxide.

$$t\text{-}C_4H_9{}^+{}_{ads} + i\text{-}C_4H_{10} \Longrightarrow i\text{-}C_4H_{10} + t\text{-}C_4H_9{}^+{}_{ads} \qquad (3)$$

The reaction starts with an attack of isobutane on the C-O bond of the covalently bonded tert-butyl alkoxide. This results in a strong 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 oxygen atoms O1 and O2 of the cluster (see transition state TS-III in Figure 3). The polarisation of C-O bond is even stronger than in the course of isobutane protolytic dehydrogenation. In other words, for hydride transfer the tert-butyl group becomes even more "carbenium ion-like" than in the transition state of dehydrogenation. However, due to the different orientation relative to the cluster, the resulting unstable carbenium ion abstracts the hydride ion from the attacking isobutane molecule instead of adsorbing on the neighbouring basic oxygen.

The geometry and charge distribution in the hydrocarbon fragment of such an activated complex very much resemble those in the nonclassical carbonium ion resulting from protonation of the central C-C bond in hexamethylethane. The positive charge is equally divided 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 C1-H1 bond of 1.292 A in comparison with the normal C-H bond length of 1.089 A.

The total positive charge of such adsorbed carbonium ions is very high (+0.998 e). 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 modelling of isobutane cracking in [4]. One has, however, to bear in mind that the latter model was calculated with some very rough assumptions.

4. DISCUSSION

A comparison of our results with available literature data is given in Table 1. All of the calculated activation energies are considerably higher than those following from the experimental results. This is most likely connected with the unrealistically small size of the cluster used in our calculations, which results in about 1 eV higher proton abstraction energy than that obtained for larger clusters. In addition, one has to bear in mind that the activation energies reported in [3] are the apparent values. Therefore, they should be corrected for the heat of isobutane adsorption of about 12-14 kcal/mol [20]. This makes the discrepancy between calculated and experimental values quite reasonable.

As was already mentioned above, the activation energy of 30 kcal/mol for hydride transfer was obtained from kinetic modelling, based on rather rough simplifying assumptions. Therefore, the discrepancy between the above calculated value and the one reported in [4] should not be considered too seriously.

It is even more significant that in addition to reasonable agreement with experimentally measured values, our results provide a first real understanding of the nature of adsorbed nonclassical carbonium ions and of their role in some elementary steps of cracking. This is particularly important, since even in very recent publications, the adsorbed carbenium and carbonium ions are still considered as actual stable intermediates (see [1] and references therein).

Table 1.
Comparison of calculated heat effects (ΔH, kcal/mol) and activation energies ($E^{\#}$, kcal/mol) with available literature data.

Reaction	Parameter	Our results	Kinetic model	Experiments at low conversions
1 (cracking)	$E^{\#}$	57.5	38.1	39.6
1	ΔH	1.3	-2.4	-
2 (dehydrogenation)	$E^{\#}$	66.8	38.9	37.5
2	ΔH	6.9	-7.6	-
3 (hydride transfer)	$E^{\#}$	48.4	~30	(less than 40)

Only quite recently it was demonstrated that the real stable intermediates in heterogeneous acid-catalysed transformations of hydrocarbons on zeolites are the covalently bonded alkoxides or surface esters (see [21,22] and references therein). They are the precursors of adsorbed carbenium ions, which are formed from these more stable species as transition states by partial dissociation or stretching of C-O bonds. This results in separation of charges and in formation of metastable ion pairs with "carbenium ion-like" alkyl fragments. This conclusion is supported by the IR study of proton transfer from Bronsted surface acid sites to adsorbed hydrocarbons [21], by quantum chemical calculations [9,10] and by ^{13}C MAS NMR measurements [23,24].

Represention of reactive carbenium ions by the transition states is very different from the traditional interpretation in the literature. The latter does not even discuss the real reaction coordinate with the initial formation of π-complexes (if the carbonium ions are formed from olefins) and the subsequent transformation of these species into surface alkoxides through carbenium ion-like transition states.

Adsorbed nonclassical carbonium ions are also high-energy transition states resulting from proton attack at C-C or C-H bonds of paraffins according to reactions (1,2) or arising from interaction of paraffins with carbenium ion like excited surface alkoxides as in the case of hydride transfer (3). The geometry and charge distribution in such "carbonium ion-like" transition states resemble to even a larger extent those of the corresponding free ions than in case of adsorbed carbenium ions. On the other hand, the formation of such "carbonium ion like" transition states requires somewhat higher activation energies than for the "carbenium ion-like" transition states resulting from protonation of alkenes (see refs. [9,10]).

It is also very important that neither the adsorbed carbenium ions, nor adsorbed carbonium ions are considered as really free species, since both of them are strongly electrostatically bonded with the surface. For instance, according to our estimation, the abstraction of tert-butyl carbonium ions from the top of the activation barrier in reaction (1) requires an additional energy of about 4 eV. A close electrostatic interaction energy was estimated for adsorbed $C_8H_{19}^+$ ion involved in the transition state of hydride transfer (3).

Such a strong Coulombic interaction substantially modifies the geometry and reactivity of adsorbed species. For instance, it explains the perpendicular orientation of the positively charged hydrocarbon fragments towards O1--Al--O2 plain of the cluster as due to diminishing of steric hindrances and to the more effective interaction of positive and negative charges in the excited ion pairs.

The strong Coulombic interactions results also in a different geometry and charge distribution in the above discussed transition states. It should be also stressed that both the above calculated and the experimentally measured activation energies are considerably higher than those reported for similar reactions in super-acid solutions [25]. This also reflects the strong interaction of adsorbed species with the surface and the higher activation energies in comparison with liquid super acids. Thus, the general term "adsorbed carbonium ion" in reality includes many structures and in each case should be specified depending on the selectivity of the reaction and on the nature of the resulting final products.

5. CONCLUSION

The "ab initio" quantum chemical calculations performed for cracking of isobutane result in reasonable values for the activation energies of protolytic cracking, dehydrogenation and hydride transfer. The calculations also demonstrate that the adsorbed carbonium ions represent not the reaction intermediates, but the transition states of the corresponding elementary reactions. Although the geometry and charge distribution in such activated complexes very much resemble those of free carbocations, the adsorbed species are strongly held at the active sites by Coulombic interaction. This results in different structures of the transition states for different elementary reactions and modifies the reactivity of the adsorbed species in comparison with free carbocations.

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