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A quantum-chemical study of adsorbed nonclassical carbonium ions as active intermediates in catalytic transformations of paraffins.
II. Protolytic dehydrogenation and hydrogen–deuterium hetero-isotope exchange of paraffins on high-silica zeolites

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HF/3-21G quantum-chemical analysis of the protolytic attack of acid protons in zeolites at the C–H bonds in methane and ethane indicated that the resulting transition states depend on the sign of the bond polarization. If a hydride ion is split off from the paraffin, then the transition state resembles the adsorbed carbonium ion and the reaction results in molecular hydrogen and in formation of the surface alkoxy group. The case, when a proton tends to split off from the paraffin, corresponds to the hetero-isotope exchange of paraffins with surface OH groups. This is a concerted acid–base reaction with a transition state different from adsorbed carbonium ion.

Keywords: quantum-chemical calculations; protolytic dehydrogenation; zeolites; paraffins

1. Introduction

As has been already discussed in our previous paper [1], the protolytic cracking of paraffins on zeolites,

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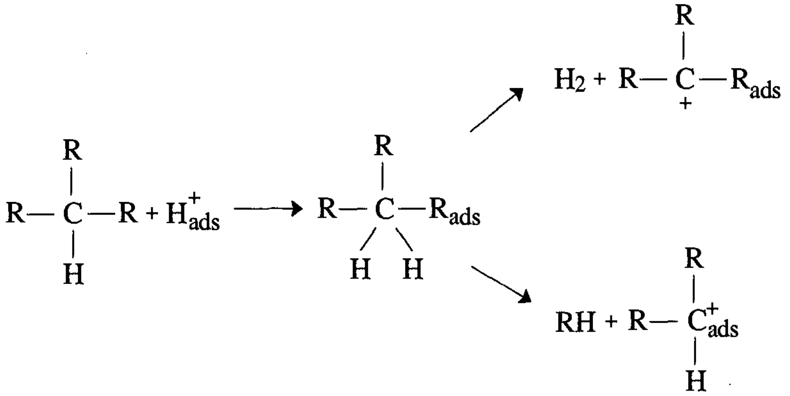
$$\mathrm{RH} + \mathrm{H}^+_{\mathrm{ads}} \rightarrow \mathrm{R_1H} + \mathrm{R}^+_{2\,\mathrm{ads}}, \tag{1}$$

represents only one of the possibilities to produce adsorbed aliphatic carbenium ions. The alternative consists in protolytic dehydrogenation, which also yields an adsorbed alkyl fragment and molecular hydrogen:

$$\mathrm{RH} + \mathrm{H}^+_{\mathrm{ads}} \rightarrow \mathrm{R}^+_{\mathrm{ads}} + \mathrm{H_2}. \tag{2}$$

Usually, both these reactions are considered to proceed through the common active intermediate represented by an adsorbed nonclassical carbonium ion [2–5]:



$$\mathrm{R{-}\overset{R}{\underset{H}{C}}{-}R} + \mathrm{H}^+_{\mathrm{ads}} \longrightarrow \mathrm{R{-}\overset{R}{\underset{H\;\;H}{C}}{-}R_{ads}} \nearrow \mathrm{H_2} + \mathrm{R{-}\overset{R}{\underset{+}{C}}{-}R_{ads}} \tag{3a}$$

$$\searrow \mathrm{RH} + \mathrm{R{-}\overset{R}{\underset{H}{C}}{}^{+}_{ads}} \tag{3b}$$

However, as will be shown below, the real mechanisms of dehydrogenation and cracking are quite different, since eq. (1) corresponds to proton attack at the C–H bond of the paraffin, whereas reaction (2) to attack at the C–C bond. Therefore, the geometry of the corresponding transition states is also quite different resulting in a different way of interaction of the hydrocarbon fragments with the surface.

In ref. [6] this problem was discussed using as a reference the results on the kinetics of *n*-butane transformations on high-silica zeolites. Indeed, according to ref. [7], the apparent activation energy of *n*-butane protolytic cracking (about 35 kcal/mol) is considerably higher than that of dehydrogenation (about 25 kcal/mol). This could be considered as evidence of the different reaction mechanisms and the different nature of the corresponding transition states. However, in ref. [5] the activation energies of both these reactions were found to be practically equal. Thus, the arguments based on the study of kinetics cannot be considered as decisive and the question about the transition states of protolytic cracking and dehydrogenation still remains open.

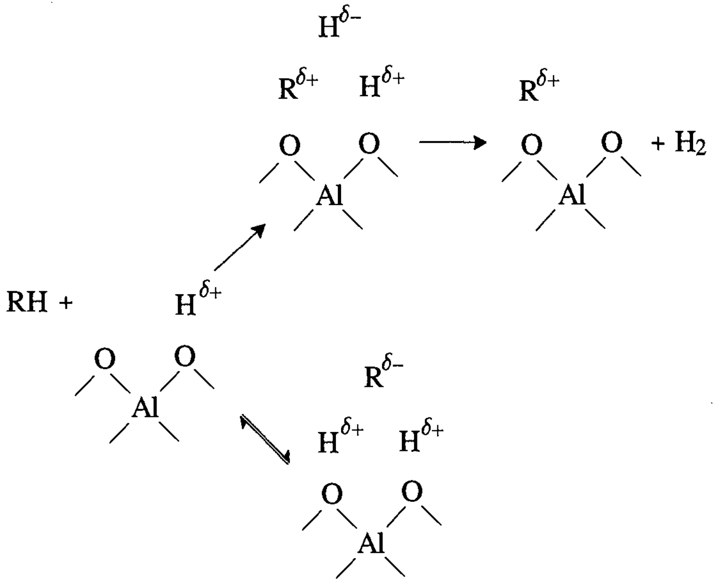
In this connection, the aim of this paper is a comparative quantum-chemical analysis of the carbon–carbon and carbon–hydrogen bond activation in methane and ethane resulting from protolytic attack at these bonds of acid protons in high silica zeolites. The results obtained are compared with those on protolytic cracking of ethane and hetero-isotope exchange of methane earlier reported in refs. [1,8].

2. Method of calculations

As in ref. [1], ab initio quantum-chemical calculations were performed with a GAUSSIAN 80 program and 3-21G basis set. The geometry of both the initial clusters and adsorbed complexes was optimized by the gradient technique. The transition states of cracking and of hydrogen–deuterium hetero-isotope exchange were found by minimizing the norm of the gradient. This procedure required rather extensive computations. Therefore, the bridging acid hydroxyl groups of the high-silica zeolite were modeled by the simplest $H_2O\ Al(OH)H_2$, cluster. As was already discussed in ref. [1], this cluster is too small for the proper reproduction of the deprotonation energy and energetics of proton transfer. Similar to ref. [1], the following results should be considered, therefore, only as a very first qualitative attempt, whereas the more precise quantum-chemical analysis of protolytic dehydrogenation requires more sophisticated basis sets and more expanded clusters.

3. Results and discussion

The carbon–hydrogen bond of paraffins may interact with bridging acid hydroxyl groups of zeolites in two different ways, resulting in splitting off either the hydride ion or proton. This depends on the sign of the C–H bond polarization created by interaction of adsorbed molecules with surface acid hydroxyl groups and the neighbouring basic oxygen of the active sites:



(4a)

(4b)

Let us start with the first of these alternatives, which represents the abstraction of the hydride ion. The subsequent recombination of $H^{\delta-}$ with the split off proton results in formation of molecular hydrogen and adsorption of an aliphatic alkyl fragment on the neighbouring basic surface oxygen of the zeolite.

The geometry and the charge distribution in the transition state for methane dehydrogenation found in this work is depicted in fig. 1. Such an activated complex represents a combination of a proton transfer from the acid hydroxyl group to the adsorbed methane with simultaneous heterolytic cleavage of one of its C–H bonds. Indeed, the proton transfer is evident from the relatively high positive charge of the adsorbed $CH_5^{\delta+}$ fragment (+0.545 *e*) and from the considerable stretching of the O–H bond in the activated complex (from 0.974 Å for the free OH group to 1.316 Å).

One of the CH bonds of methane is also strongly stretched (from 1.09 to 1.751 Å) and polarized (the corresponding hydrogen atom has a negative charge of −0.278 *e*, while a positive charge of +0.505 *e* is induced on the methyl group). The partially split CH_3 fragment becomes flat and its geometry resembles that of free methyl carbocation.

The short distance between partially split proton and hydride ion in such acti-

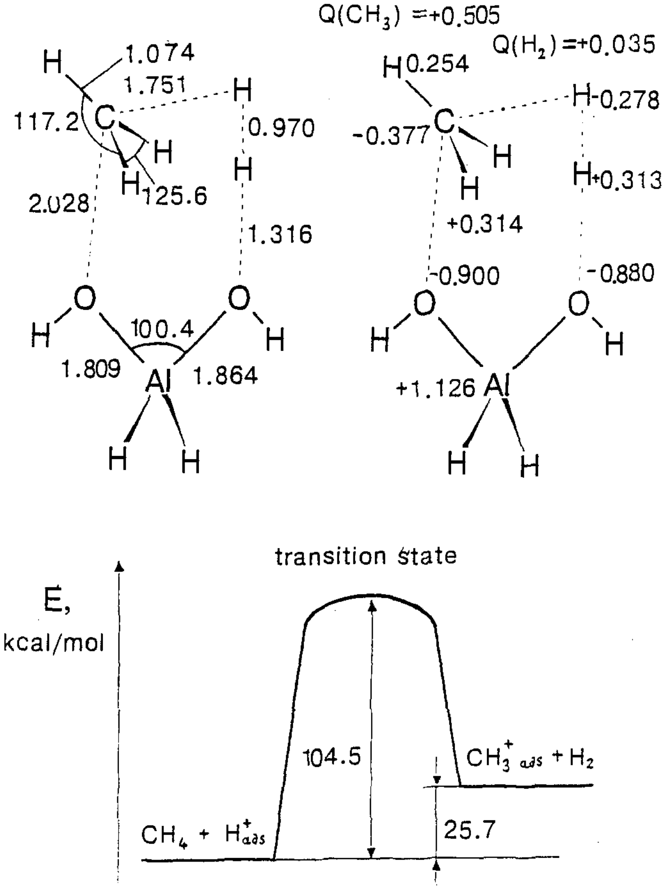


Fig. 1. The transition state of methane protolytic dehydrogenation.

vated complex indicates the formation of molecular hydrogen. It is only slightly perturbed, since the interatomic H–H distance of 0.970 Å is close to that in the free hydrogen molecule. This conclusion is also supported by the small total positive charge of the resulting H_2 fragment. It is equal to only +0.035 *e*, despite the fact that the abstracting molecule is rather strongly polarized (the proton directed towards the oxygen atom of the cluster has a positive charge of +0.313 *e*, whereas the other hydrogen atom a negative charge of −0.278 *e*).

In other words, the reaction coordinate of protolytic methane dehydrogenation at first represents a stretching and polarization of one of the C–H bonds when methane interacts with the proton of the acid hydroxyl group and the neighbouring basic oxygen atom of the active site. This is combined with the simultaneous stretching of the O–H bond in the surface hydroxyl group of the Brønsted active site. It is certainly not surprising that formation of such strongly perturbed activated complex requires a very high activation energy. According to our calculations it is equal to 104.49 kcal/mol, however, as has been discussed in ref. [1], the real value is approximately twice less.

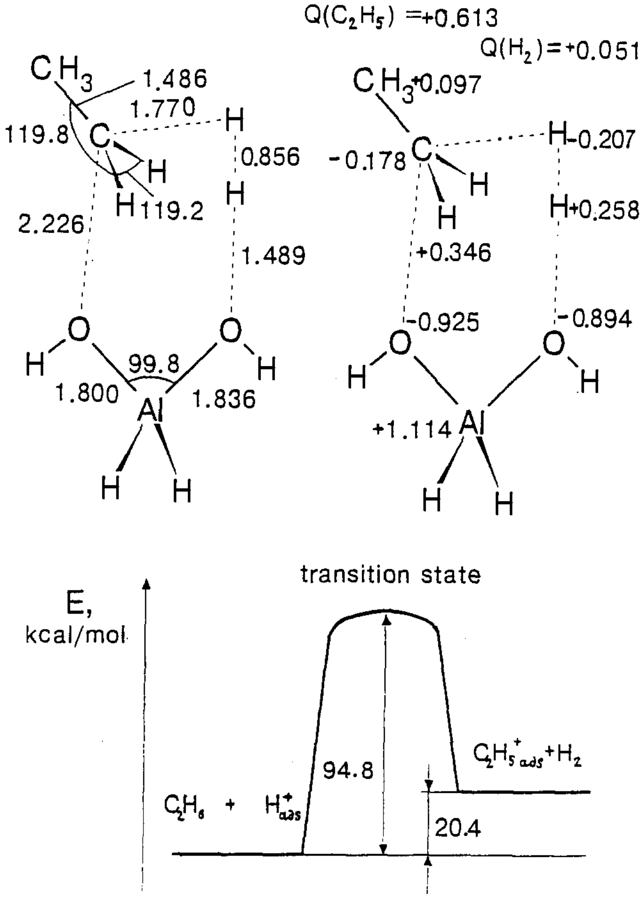


Fig. 2. The transition state of ethane protolytic dehydrogenation.

Table 1
Comparison of the activated complexes of ethane cracking and dehydrogenation

Reaction	Structure of the activated complex	$q_{C_2H_7}$ (*e*)	$q_{C_2H_5}$ (*e*)	r_{C-O} (Å)	r_{O-H} (Å)
protolytic cracking	III	+0.712	–	2.37	1.534
dehydrogenation	IV, fig. 2	+0.664	+0.613	2.226	1.489

The second part of the reaction coordinate represents the decomposition of the activated complex. This results in splitting off the hydrogen molecule and in the adsorption of the methyl carbenium ion on the neighbouring basic oxygen as a covalent methoxy group.

A similar transition state was also obtained for dehydrogenation of ethane (fig. 2). It very much resembles that of protolytic methane dehydrogenation with the following minor differences:

(i) The tendency of proton transfer for ethane is somewhat stronger. This follows from the higher positive charge of the $C_2H_7^{\delta+}$ fragment in comparison with $CH_5^{\delta+}$ (figs. 1 and 2, tables 1 and 2) and is consistent with the higher proton affinity of ethane (5.6 eV in comparison with 5.1 eV for methane).

(ii) Interaction of the resulting ethyl carbenium ion with the basic surface oxygen of the active site is weaker than for the methyl carbocation. This is evident from the longer $O-C_2H_5^{\delta+}$ distance in the transition state of ethane dehydrogenation in comparison with that of methane, and reflects the weaker binding of the ethyl carbocation with the surface of the zeolite.

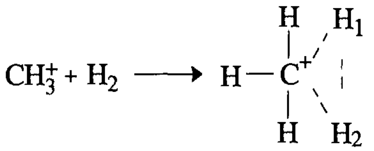
(iii) The transition state of ethane dehydrogenation is even more close to the complete splitting off of the molecular hydrogen. This is evident from the slightly shorter H–H distance and from the stronger stretching of the OH bond in such activated complex. The polarization of the resulting hydrogen molecule is also slightly weaker.

(iv) Finally, the most important difference is the lower activation energy of ethane protolytic dehydrogenation in comparison with that calculated for methane (94.79 and 104.49 kcal/mol, respectively). This is consistent with the higher reactivity of ethane in comparison with methane.

Table 2
Comparison of the activated complexes of methane dehydrogenation and the one of methane hetero-isotope exchange

Reaction	Structure of activated complex	q_{CH_5} (*e*)	r_{C-H} (Å)	r_{O-H} (Å)	q_H (*e*)
free cluster	–	–	–	0.97	+0.486
dehydrogenation	fig. 1	+0.505	1.751	1.316	+0.313
isotope exchange	fig. 3	−0.573	1.527	1.146	+0.506

Both of the above transition states represent very close analogs of free methyl and ethyl carbonium ions, which have been earlier thoroughly studied by high pressure mass spectrometry [9]. According to these data and to results of ab initio quantum-chemical calculations [10], the free methyl carbonium ion represents a complex of methyl carbenium ion with molecular hydrogen:

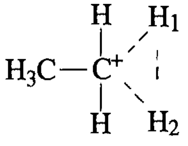


(5)

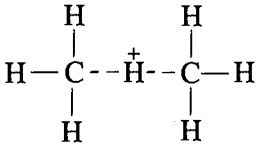
The H–H bond distance (in the hydrogen molecule fragment) calculated with the 6-31G* basis set is 0.853 Å. This is only slightly longer than the bond length in the free hydrogen molecule calculated at the same level of theory (0.730 Å) and is much shorter than the bond length in H_2^+ (1.041 Å). In addition, the C–H_1 and C–H_2 distances are also considerably longer than normal C–H bonds [10]. This also confirms the above structure. Despite the relatively weak perturbation of molecular hydrogen, such a complex is rather stable, since reaction (5) is exothermic by 44 kcal/mol [11].

The geometry of the free methyl carbonium ion is very close to that calculated by us for the activated complex of protolytic methane dehydrogenation presented in fig. 1 (the H_1–H_2 distance equal to 0.735 Å and C–H_1 and C–H_2 bond lengths of about 1.75 Å). The main difference with the free ion consists in the lower positive charge of the adsorbed carbonium ion and in the polarization of the resulting H_2 fragment. Both these effects have been created by interaction with the basic surface oxygen atoms of the active site. Thus, the transition state of methane dehydrogenation represents a very close analogy of the free methyl carbonium ion with only a small perturbation in the geometry and charge distribution resulting from the interaction with the surface of the zeolite.

The same is also true for the transition state of protolytic ethane dehydrogenation, which also very much resembles the isomeric form I of ethyl carbonium ion:



(I)

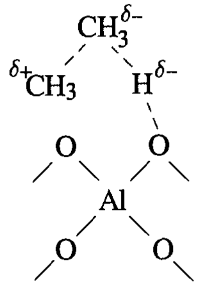


(II)

(6)

This structure also represents a complex of ethyl carbenium ion with molecular hydrogen. However, it is considerably weaker than in the case of the methyl carbonium ion, since the energy of dissociation into ethyl carbenium ion and molecular hydrogen is equal to only 8 kcal/mol [10]. This is well consistent with results of our quantum-chemical calculations for the transition state of ethane dehydrogenation depicted in fig. 2. They indicated the shorter H_1–H_2 distances and the longer C - - H_1 and C - - H_2 distances in comparison with the adsorbed methyl cation of fig. 1. Thus, the transition state of the protolytic dehydrogenation of ethane also represents a close analogy of isomer I of the free ethyl carbonium ion.

Let us now compare the transition state of ethane dehydrogenation with the one for ethane protolytic cracking, which was earlier reported by us in ref. [1]. (See also Table 1.) As was shown in ref. [1], the latter represents a polarized analog of isomer II of the free ethyl carbonium ion, where the resulting methane molecule is almost split off:



(7)

The geometry of the positively charged methyl group in such activated complex and that of the ethyl group in the transition state of ethane dehydrogenation depicted in fig. 2 are very similar. Both alkyl groups have a high positive charge of about +0.6 *e* and are almost flat, thus resembling the free methyl carbenium ion. The calculated C- -O distances of about 2.2–2.3 Å are also very close to each other. Therefore, it is not surprising that our calculations resulted in close activation energies of ethane protolytic dehydrogenation and cracking (94.79 and 93.4 kcal/mol, respectively). This is well consistent with the experimental results on *n*-butane transformations on high-silica zeolites reported in ref. [4], but disagrees with ref. [7].

Unfortunately, the level of our calculations does not permit to make any definite conclusions about the absolute values of these activation energies. Nevertheless, there is no doubt that the geometry of transition states of protolytic cracking and dehydrogenation is quite different, although both of them could be considered as the analogs of free carbonium ions.

If the sign of C–H bond polarization in the activated complex is opposite to that for the case of dehydrogenation, this may result in splitting off the proton instead of abstraction of the hydride ion. A quantum-chemical analysis of this possibility for the reaction of hetero-isotope exchange with methane was recently carried out in ref. [8]. In agreement with the experimental results, it was concluded that this reaction follows a concerted mechanism with a rather low activation energy.

To make possible the comparison of these data obtained with a more precise 6-31G* basis set for a larger $H_3Si(OH)Al(OH)_2OSiH_3$ cluster with the above simpler calculations, the transition state of hetero-exchange reported in ref. [8] was reproduced for the smaller H_2O $Al(OH)H_2$ cluster and simpler 3-21G basis set (fig. 3). The corresponding activation energy of hetero-exchange is equal to 37.12 kcal/mol in excellent agreement with the earlier reported value of about 35 kcal/mol.

The geometry of both transition states is also quite similar. The main difference consists in a somewhat weaker stretching of the O–H bond in the activated complex for the smaller cluster (according to our calculations this bond length is equal to 1.146 Å in comparison with 1.201 Å obtained in ref. [8]). On the contrary, the C–H bonds directed towards the active site for the smaller cluster are longer. Both of these results reflect the higher proton abstraction energy from the smaller cluster and, consequently, the less extent of proton transfer to adsorbed methane.

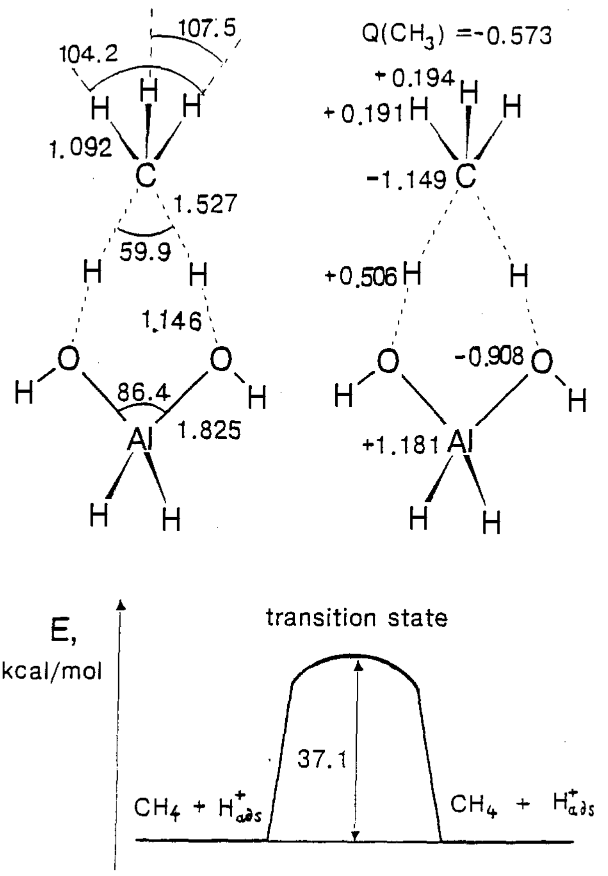


Fig. 3. The transition state of hydrogen–deuterium hetero-isotope exchange.

The smaller cluster and the simpler basis set also nicely reproduce the charge distribution in the activated complex of hetero-exchange. Thus, even the simplest calculations allow to discuss the different ways of C–H bond activation.

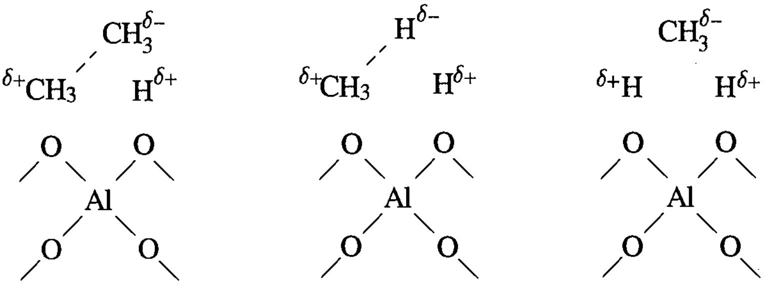
This can be done from the comparison of figs. 1 and 3 (see also table 2). The depicted results indicate absolutely different mechanisms of dehydrogenation and isotope exchange. Indeed, as was already discussed above, the transition state of dehydrogenation represents a very close analog of the free methyl carbonium ion with only rather small differences in geometry and charge distribution. On the contrary, the hetero-exchange is a concerted reaction involving a simultaneous transfer of two protons: one from the acid hydroxyl group to paraffin and another in the opposite direction from methane to the basic surface oxygen of the active site. The corresponding transition state results from the simultaneous stretching of the C–H bond in methane and of the O–H bond of the hydroxyl group. On the top of the activation barrier the lengths of both C–H bonds directed towards the surface of the zeolite are equal. The similar is true for both O–H distances. However, they are stretched much weaker than in case of dehydrogenation (only for about 20% instead of 35%). This should be considered rather as an indication of proton splitting from methane, than methane protonation.

This conclusion is also consistent with the opposite charges of CH_3 fragments in both activated complexes. For hetero-exchange, this charge is negative, instead of being positive for the transition state of dehydrogenation. The geometry of CH_3 groups in both activated complexes is also quite different. In case of dehydrogenation, the methyl group is flat as one should expect for the methyl carbenium ion, while for hetero-exchange, the pyramidal shape typical of covalent bonded carbon practically remains unchanged. Thus, the hetero-isotope exchange is by no means an acid-catalysed reaction, but instead represents a concerted mechanism that is intermediate between acid and base catalysis. The similar conclusion was very recently made in ref. [13].

Finally, the concerted mechanism of hetero-exchange is also well consistent with the recent experimental results obtained in refs. [14–16]. These data demonstrated, that for iso-paraffins the hetero-exchange proceeds surprisingly easy at temperatures of about 100°C, i.e. approximately by 300–400°C lower than cracking or dehydrogenation. This also clearly demonstrates the different mechanisms of the hetero-exchange and dehydrogenation and consequently confirms the different nature of the corresponding transition states.

4. Conclusion

The results of this paper in combination with those previously reported in ref. [1] show that the interaction of paraffins with bridging hydroxyl groups of zeolites may result in the following different surface complexes:



(III) (IV) (V)

(8)

Neither of them could be considered as the really existing active intermediate, but instead they represent highly excited transition states.

Structure III corresponds to the activated complex of protolytic cracking. It results from the attack of a proton at the carbon–carbon bond of a paraffin in combination with polarization of the adsorbed molecule by the basic oxygen of the active site. The dehydrogenation reaction represents then the heterolytic splitting of the C–C bond with formation of the adsorbed alkyl fragment and desorption from the surface of methane.

The reaction coordinate of structure IV corresponds to the proton attack at the C–H bond of a paraffin. This results in heterolytic splitting of this bond with abstraction of a hydride ion. The consequent adsorption of the alkyl fragment on the neighbouring basic oxygen of the active site is followed by evolution of molecular hydrogen. This is another way to produce adsorbed carbenium ions from paraffins.

Due to the high positive charges of the corresponding hydrocarbon fragments and to their geometry, both of these transition states could be considered as analogs of two isomeric forms of nonclassical carbonium ions. On the other hand, the way of interaction of the initial paraffins and the activated complexes with the acid–base pairs of the active sites is quite different. Therefore, the traditional explanation of protolytic cracking and dehydrogenation by the common carbonium ion intermediate should be revised in favor of the above discussed more realistic structures of the activated complexes.

Structure V of the transition state of hetero-isotope exchange represents a very specific case of the concerted reaction. It neither corresponds to the purely acid, nor to the purely base catalysis. In this case, both the strength of the Brønsted acid and that of neighbouring basic oxygen are important. Therefore, the transition state of this reaction could not be considered as a protonated paraffin and hardly has any direct relation to protolytic cracking and dehydrogenation.

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