Catalysis Letters 27 (1994) 345–354

A quantum-chemical study of adsorbed nonclassical carbonium ions as active intermediates in catalytic transformations of paraffins.

I. Protolytic cracking of ethane on high silica zeolites

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Received 7 February 1994; accepted 20 May 1994

Ab initio quantum-chemical calculations of protolytic cracking of ethane on Brønsted acid sites of high silica zeolites demonstrated the concerted mechanism of this reaction. The reaction coordinate represents the stretching of the O–H bond in combination with heterolytic splitting of the C–C ethane bond. This results in formation of methane and adsorption of the methyl group on the surface basic oxygen of the active site. The geometry of such activated complex is different from that of adsorbed carbonium ions which also represent highly excited surface complexes

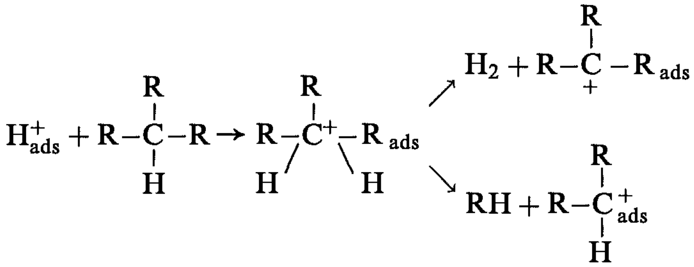
Keywords: zeolites; protonation; cracking; quantum chemistry; acidity

1. Introduction

Catalytic cracking of paraffins is traditionally considered as a chain reaction, with the adsorbed classical carbenium ions as the active intermediates. The chain initiation occurs through interaction of surface acid hydroxyls with olefins. They are always present in the reaction mixture under steady-state conditions as final products. The formation of adsorbed carbenium ions is followed by their cracking and chain propagation through hydride transfer in the rate-determining step:

$$\begin{aligned} &H^+ + \text{olefin} \rightarrow R^+_{ads} \\ &R^+_{ads} \rightarrow R^+_{1ads} + \text{olefin} \\ &R^+_{1ads} + RH \rightarrow R_1H + R^+_{ads} \quad \text{etc.} \end{aligned} \tag{1}$$

Recently, it was also shown that at low partial pressures of olefins and high temperatures, when the concentration of adsorbed carbenium ions is low, the mechanism of chain initiation is different. It involves adsorbed nonclassical carbonium ions that are formed by direct protonation of paraffins [1]. Their subsequent dehydrogenation or cracking with splitting off methane results in adsorbed carbenium ions which react further according to the above chain mechanism (1):



$$H^+_{ads} + R{-}\overset{\displaystyle R}{\underset{\displaystyle H}{C}}{-}R \rightarrow R{-}\overset{\displaystyle R}{\underset{\displaystyle H\ \ H}{C^+}}{-}R_{ads} \begin{cases} \nearrow H_2 + R{-}\overset{\displaystyle R}{\underset{+}{C}}{-}R_{ads} & \text{(2a)} \\ \searrow RH + R{-}\overset{\displaystyle R}{\underset{\displaystyle H}{C}}{}^+_{ads} & \text{(2b)} \end{cases}$$

The most convincing evidence for such chain initiation was obtained for cracking of light paraffins at very low conversions [2–4]. For instance, for cracking of isobutane at 450–500°C in a steady-state flow reactor, it was below 1% [2]. The main products were methane and propylene formed in equimolecular amounts with the apparent activation energy of 57 kcal/mol. This indicates that cracking proceeds through carbonium ion intermediates according to scheme (2b).

In the following publication of the same authors a similar mechanism of chain initiation was also proved for cracking of *n*-butane on a HZSM-5 zeolite [3]. The activation energies of ca. 35 kcal/mol for hydrogen + butene, methane + propylene, and ethane + ethylene formation were, however, much lower than those reported in ref. [2].

Finally, the direct protonation of C–H or C–C bonds on Brønsted acid sites was also proved for initial steps of *i*-butane and *n*-pentane cracking on dealuminated faujasites in ref. [4]. Unlike the above results, cracking of *i*-butyl carbonium ions produced both molecular hydrogen and methane, whereas cracking of *n*-pentyl carbonium ions yielded only methane. The resulting carbenium ions propagated the chains mainly by isomerization and hydrogen transfer with the chain length from 3 to 15 depending on the reaction conditions.

The above conclusions are based only on the analysis of the reaction products. Such data certainly cannot give any information on the nature and properties of adsorbed carbonium ions. In this connection in this work we report the results of quantum-chemical analysis of protonation and cracking of ethane on the surface of high silica zeolite.

Earlier, similar ab initio cluster quantum-chemical calculations demonstrated that ethyl carbenium ions produced from protonation of ethylene in high silica zeolites represent not the really existing active intermediates but rather unstable transition states [5]. In ref. [6], a similar conclusion was made for protonation of methane. The reported results demonstrated the validity of a concerted mechanism for hydrogen–deuterium hetero isotope exchange of methane with the surface hydroxyl groups of zeolites. This follows from the close values of theoretically estimated activation energy and rate of this reaction with those measured experimentally.

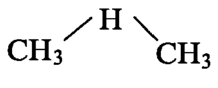
2. Method of calculation

The ab initio quantum-chemical calculations were performed with the GAUSSIAN 80 program and a 3-21 basis set. The geometries of both the free ethyl carbonium ion and the adsorbed complex were optimized with the gradient technique. The transition state of cracking was found by minimizing the norm of the gradient. Both procedures required rather extensive computations. Therefore, only the simplest case of adsorbed ethyl carbonium ion was considered and the bridging hydroxyl groups of a high silica zeolite were modelled by the simplest H_2O $Al(OH)H_2$ or H_2O $Al(OH)_3$ clusters. They were also used as the adsorption sites for ethyl carbonium ions.

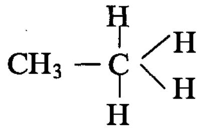
Both clusters are obviously too small for the quantitative description of proton transfer or cracking energetics. For instance, the proton abstraction energies calculated with the 3-21 basis set were respectively equal to 15.38 and 15.26 eV. This is considerably higher than the values of 12–13.5 eV estimated from spectroscopic data [7,8] or those of 11.9–13.8 eV calculated for larger clusters using more sophisticated basis sets [9]. Therefore, the following results should be considered only as a first preliminary attempt of qualitative quantum-chemical analysis, whereas the real quantitative treatment of adsorbed ethyl carbonium ions needs more accurate calculations.

3. Results and discussion

Although direct experimental data on the surface of adsorbed nonclassical carbonium ions are absent, the formation and reactions of these species in the gas phase have been well studied by mass spectrometry in refs. [10,11]. There are also numerous ab initio SC MO quantum-chemical calculations performed for free ethyl carbonium ions with very different degrees of accuracy [12]. They indicated that these species exist in two isomeric forms. The more stable isomer is represented by structure (I), in which two methyl fragments are bonded through a hydrogen atom. According to the highest level MP2/6-31G* calculations, this structure is nonlinear with a C–H–C angle of 105.8°. In the isomer (II), which is less stable by about 8 kcal/mol, only one methyl group is protonated resulting in a pentacoordinated carbon atom.



(I)

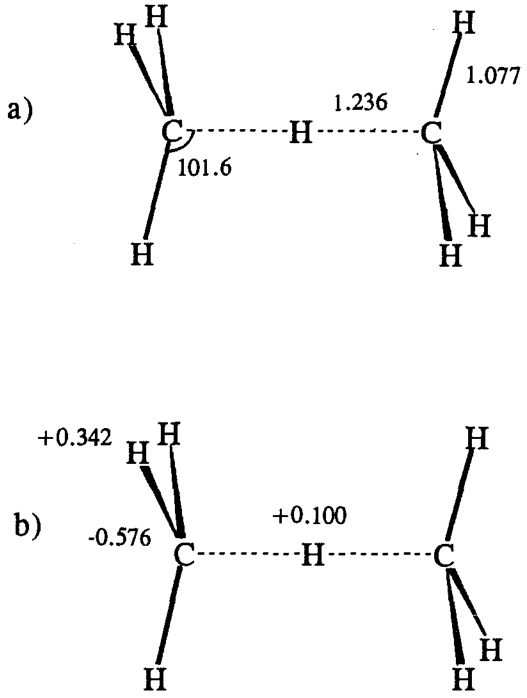


(II)

Both species are of interest for the problem under discussion. Indeed, the first structure could be considered as a model of cracking and hydride transfer, whereas the second one could be related to dehydrogenation.

Below we will start with adsorption on the surface of a high silica zeolite of the symmetrical isomer (I). Our more simple calculations also confirmed that it is more stable but resulted in the linear structure of this isomer presented by fig. 1.

It is reasonable to suppose that the C_{2v} symmetry of such ethyl carbonium ions should remain unchanged upon adsorption. Therefore, the two following structures of adsorbed complexes were considered: the complex with four hydrogens bonding with surface basic oxygens (fig. 2) and the complex with two hydrogen bonds of fig. 3.



$Q(CH_3) = +0.450$

Fig. 1. Geometry (a) and the charge distribution (b) in the most stable isomer of free nonclassical ethyl carbonium ion.

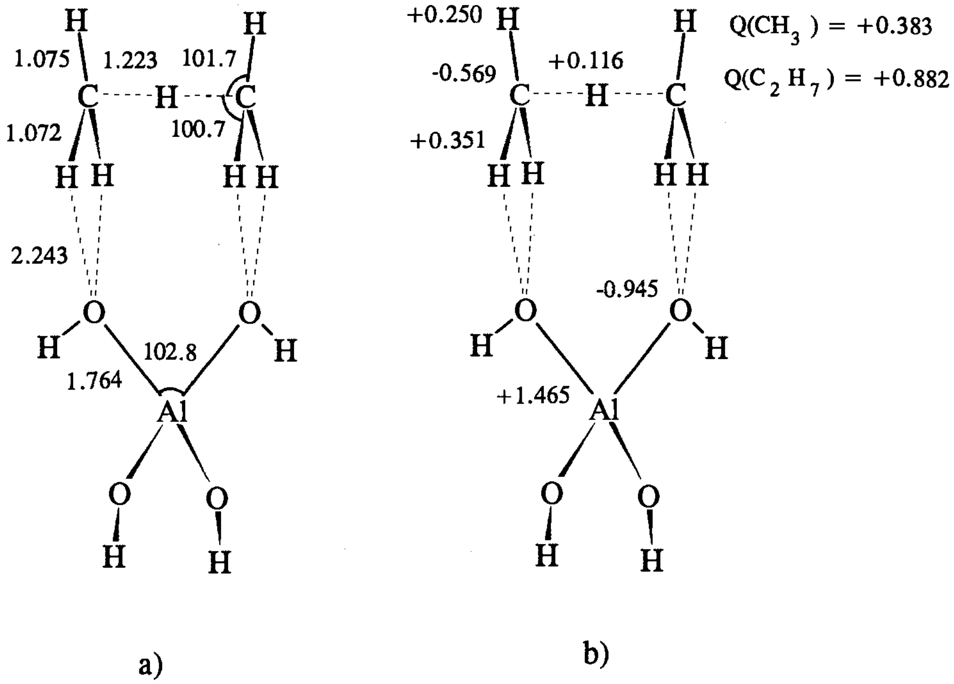


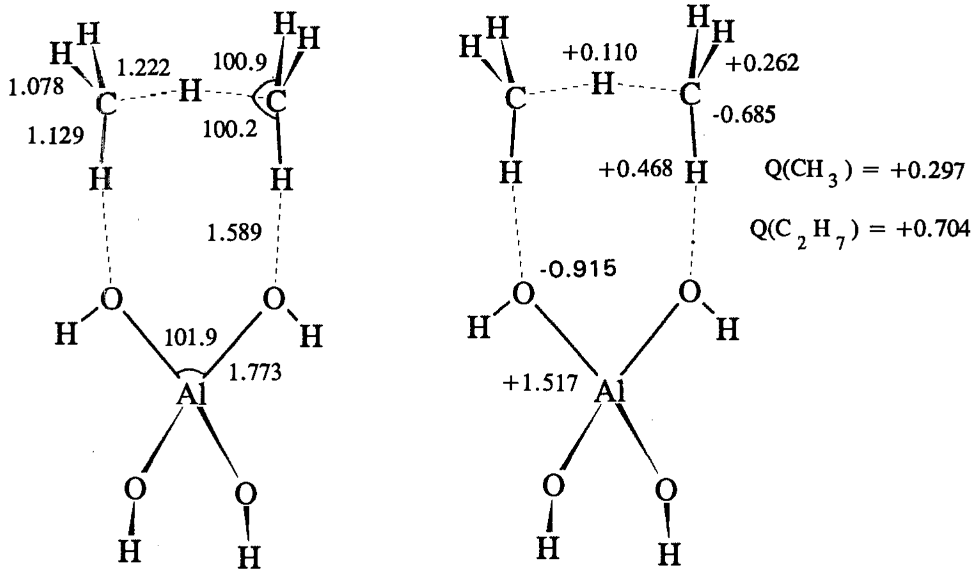
Fig. 2. Geometry (a) and charge distribution (b) in the adsorbed nonclassical ethyl carbonium ion bonded with the surface with four hydrogen bonds.

According to our calculations, formation of these species from free ethane molecule and a surface hydroxyl group of the cluster is highly endothermic (by 101.2 and 85.4 kcal/mol respectively). Thus, both complexes represent highly excited intermediates, while those with two hydrogen bonds are by about 15 kcal/mol more stable.

In addition, it was found that the four-hydrogen bonded complex of fig. 2 does not correspond to a local minimum of energy. Indeed, if the symmetry restriction is removed, it converts to the more stable double hydrogen bonded complex of fig. 3. The formation of the latter is connected with a local minimum of potential energy. Therefore, only this structure really corresponds to an adsorbed ethyl carbonium ion.

This is different from the case of adsorbed ammonium ions that has been discussed earlier in refs. [13–15]. These species are more stable when they form multiple hydrogen bonds with the surface of a zeolite. However, a direct comparison of ethane and ammonia protonation is hardly possible, since the proton affinity of ammonium is much higher and its adsorption as ammonium ion is exothermic.

At the first glance, both above-calculated protonation energies are too high. Indeed, if proton transfer is a limiting step, then the corresponding energy should be close to the activation energy of cracking. The latter is, however, much lower.



a) b)

Fig. 3. Geometry (a) and charge distribution (b) in the most stable adsorbed nonclassical ethyl carbonium ion.

For instance, according to refs. [2–4] for cracking of different butane isomers it is within 35–60 kcal/mol.

The following points should be, however, taken into account when comparing the calculated and experimental figures:

(i) The protonation of ethane is certainly more difficult than that of butane.

(ii) The clusters used in our calculations are too small. This results in about 1.5–2 eV higher proton abstraction energy than that estimated from spectral data or obtained from more accurate calculations performed for larger clusters with more sophisticated basis sets. Therefore, the above figures strongly overestimate the endothermicity of ethane protonation.

(iii) The effective activation energies reported in the literature represent the difference between the real activation energies and the heats of hydrocarbon adsorption. Therefore the real activation energy of cracking should be higher.

(iv) The 3-21 basis set used in our calculations cannot pretend for quantitative description of the interaction energy. Therefore, the above figures should be considered only as a qualitative illustration.

Thus, due to all these reasons, our calculations strongly overestimate the endothermicity of the proton transfer, and the real discrepancy between the calculated figures and experimentally measured activation energies is not as large as one could imagine at the first glance.

Table 1
Proton affinity of hydrocarbons [16]

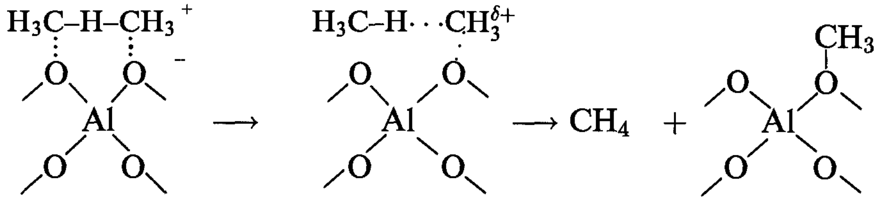
Hydrocarbon	Proton affinity (eV)
CH_4	5.1
C_2H_6	5.6
C_3H_8	6.1
C_2H_4	6.9
2-C_4H_8	7.8
C_3H_6	7.9
i-C_4H_8	8.5

Anyway, our results demonstrate that the adsorbed nonclassical carbonium ions represent highly excited unstable active intermediates. This is consistent both with a by 1.5 eV lower proton affinity of paraffins in comparison with corresponding olefins (table 1) and with the well known spectral data on weaker perturbation of hydroxyl groups by adsorbed paraffins compared to that by adsorbed olefins and other weak bases.

Let us now discuss in more detail the charge distribution in adsorbed complexes and their geometry. As one can see from comparison of figs. 1, 2, and 3, the interaction with the cluster results in a partial decrease of the positive charge of the free carbonium ion, although it still remains very high. This effect is mainly connected with the partial electron-density transfer from basic oxygen atoms of the cluster to the adsorbed species, thereby decreasing their positive charge to +0.882 in less stable and to +0.704 in more stable complexes, respectively. Thus, the higher relative stability of complexes with the double hydrogen bonds of fig. 3 is probably associated with their lower total positive charge.

The explanation of this difference consists in the different nature of the hydrogen bonding of adsorbed species with the surface. Indeed, the hydrogen bonds in the less stable complex of fig. 2 are longer, indicating a weaker bonding. In addition, in the more stable complex of fig. 3, the C–H bonds directed towards the surface are more strongly polarized. This is clearly evident from the higher positive charge of the corresponding protons which is equal to +0.468 *e* and +0.351 *e* in more stable and less stable complexes, respectively.

The relatively small decrease in positive charge of adsorbed ethyl carbonium ions in comparison with free cations is consistent with the rather insignificant perturbation of their geometry. As one can see from figs. 1 and 3 it is rather minor and manifests itself mainly in a small decrease of the C–H–C distance, in a very slight bending of the adsorbed species, and in a flattening of their methyl groups. In this connection, it is remarkable that the local energy minimum corresponding to the formation of adsorbed carbonium ions is very shallow. Therefore, a stronger perturbation of their geometry requires only a small amount of additional energy indicating the extremely high softness of the adsorbed species. For instance, even a relatively small displacement of the central hydrogen atom in the adsorbed ethyl carbonium ion towards one of the methyl groups strongly redistributes the positive charge and results in cracking with the formation of methane and adsorbed methyl cation:



(3)

According to our calculations, this reaction is strongly exothermic by 83 kcal/mol.

The search for a transition state of cracking required much more computation time than the calculations of adsorption and was therefore performed for the smallest H_2O $Al(OH)H_2$ cluster. It resulted in a geometry of the activated complexes that is quite different from those of both the adsorbed carbonium ion and the structure of fig. 2. This difference is mainly connected with the displacement of the central hydrogen atom towards one of the neighboring surface basic oxygens resulting in its insertion between the carbon atom of the methyl group and the surface oxygen (fig. 4). Simultaneously, the second methyl group is approaching the other oxygen atom of the adsorption site. In addition, this CH_3 becomes more flat

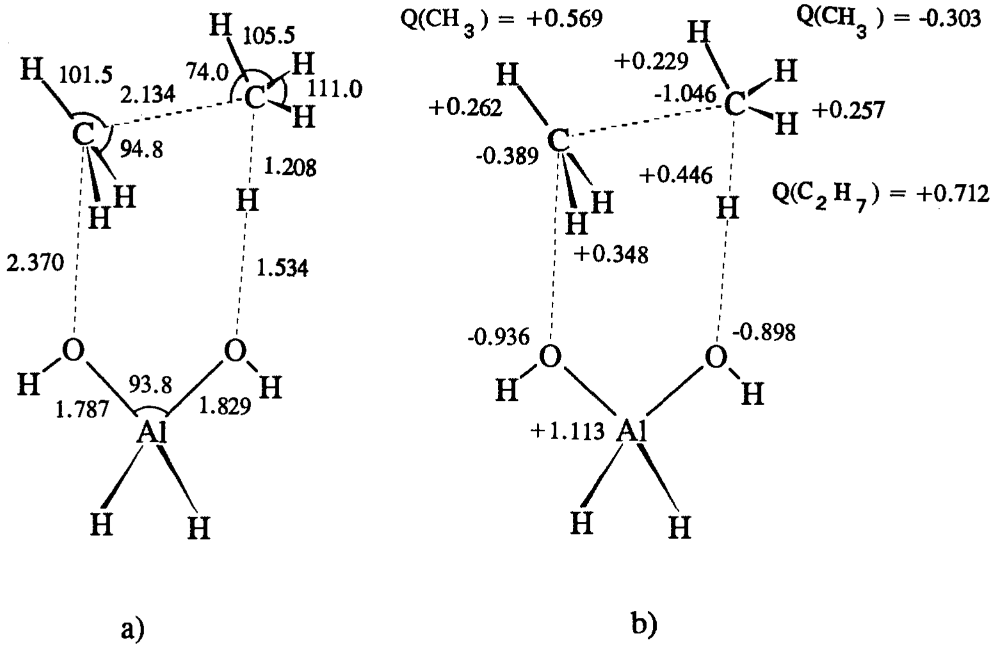


Fig. 4. Geometry (a) and charge distribution (b) in the transition state of protolytic cracking of ethane.

and forms a double hydrogen bond with the surface oxygen atom like in the structure of fig. 2. The total positive charge of the alkyl fragment in such transition state is practically the same as in the adsorbed carbonium ion (+0.712 *e*). However, this fragment is strongly polarized since the positive charge of the left methyl group increases from +0.297 *e* to +0.569 *e* (fig. 4). This should be correlated with the above-mentioned flattening of the methyl group, which makes it more similar to the free methyl carbenium ion.

Such a transition state should be considered as a two-point interaction of a free ethane molecule with the bridging acid hydroxyl group and the neighboring basic oxygen of the active site. This results in the simultaneous polarization and positive charging of the adsorbed molecule due to the partial proton transfer from the surface of the zeolite. Thus, the reaction coordinate of the protolytic cracking likely represents the concerted stretching of the O–H bond combined with heterolytic splitting of the C–C bond in the ethane molecule. This results in the formation of methane and adsorption of the methyl group on the surface basic oxygen of the active site.

It is remarkable that, in agreement with the above discussion, such a transition state is only by about 8 kcal/mol energetically less stable than the two-point adsorbed ethyl carbonium ion. Thus, its cracking really requires only a small activation energy. On the other hand, the geometry of the transition state is strongly different both from the adsorbed carbonium ion and from the less stable four-hydrogen bonded adsorbed species of fig. 2.

The energy profile of protolytic cracking obtained in this study is represented in fig. 5. In accordance with the above discussion, the absolute figures are strongly

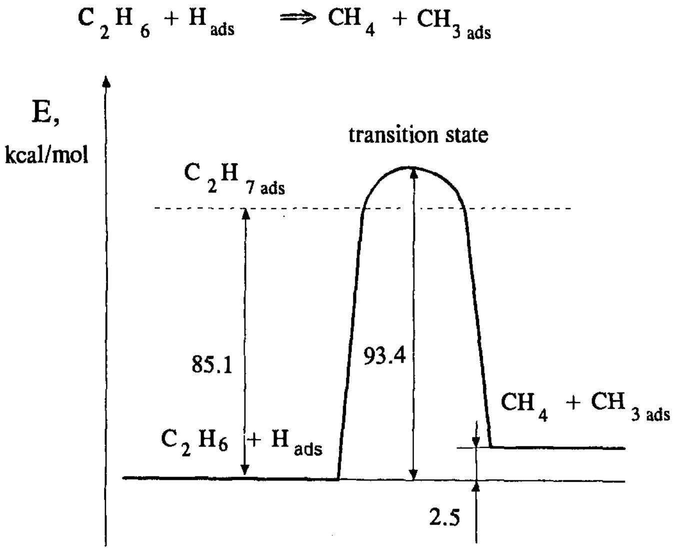


Fig. 5. The energy diagram of protolytic cracking of ethane on high silica zeolite.

overestimated. However, there is no doubt that both adsorbed nonclassical carbonium ions resulting from the proton transfer and the transition state of protolytic cracking of paraffins represent the highly excited unstable complexes and do not exist on the surface of the catalyst as real active intermediates. They should be rather considered as short-living complexes resulting from the interaction of adsorbed molecules with thermally excited acid hydroxyl groups or from the collisions of gaseous molecules with such excited OH groups in the case if the reaction takes place at elevated temperatures.

The cracking proceeds through the transition state of fig. 4 and does not require the formation of hydrogen bonded adsorbed carbonium ion. The species are probably connected with hydride transfer reaction, which will be discussed in a following publication.

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