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Theoretical studies of pentene cracking on zeolites: C–C β-scission processes

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Abstract

The C–C bond-breaking step of pentene adsorbed on a model zeolite cluster is examined using ab initio and density functional theory (DFT/B3LYP) electronic structure techniques as an example of the β-scission process that arises in cracking of alkanes and alkenes. After pentene has been protonated by the acid site, the reactant for the cracking process corresponds to a pentyl cation covalently bound to the oxygen of the zeolite, $ZO^{-}-C_5H_{11}^{+}$. The product of the C–C bond-breaking process is propene plus an ethyl cation bound to a neighboring oxygen. The energy of the transition state relative from B3LYP calculations is 60 kcal/mol relative to the pentyl cationic reactant. For the case of the branched olefin methyl pentene, the transition state energy is slightly lower (55 kcal/mol), but the overall reaction energy is essentially the same as for pentene. The results are compared to the case of the gas phase pentyl carbenium ion. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: β-scission processes; Pentyl carbenium ion; Pentene cracking; Density functional theory

1. Introduction

The nature of the molecular species involved in the cracking of hydrocarbons into smaller fragments over zeolite catalysts has been studied extensively in this technologically important process, as the advent of zeolites has revolutionized the petroleum refining technology. While the mechanism of acid-catalyzed process involving carbocationic species was proposed nearly 50 years ago, there have been extensive studies in the catalysis literature involving heterogeneous processes and analogs with solution superacid chemistry to elucidate these mechanisms more clearly and to attempt to detect the intermediates involved in these reactions [1–4]. Also in recent years there has been an increasing number of theoretical studies on the nature of the acid sites in zeolites [5,6], the interactions of these acid sites with adsorbates including hydrocarbons [7,8], and on simple reactions of hydrocarbon species using model systems to represent the zeolite [9,10]. The most common approach has been to employ molecular clusters to describe the zeolite, although solid-state calculations with periodic boundary conditions have been applied in specific instances to zeolite systems.

In this study we report the results of ab initio and density functional studies on one aspect – the "β-scission" C–C bond-breaking step – that arises in the cracking process of alkanes and alkenes. We will focus on the species arising from pentene adsorption on an acid site and the subsequent cracking of this C_5 species as an illustration of the carbon–carbon bond-breaking step. In alkene cracking some of the key steps that are postulated to occur at acid sites in zeolite catalysts

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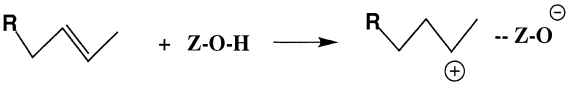
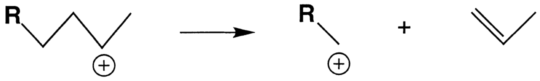
involve the initial adsorption of the alkene on the acid site of the zeolite Z–O–H to form the "carbenium ion" species:



β-scission of the C–C bond at the beta position relative to the cationic site to form a smaller alkene and another carbenium ion:

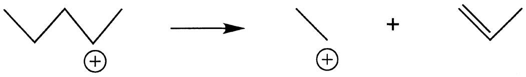


and chain termination by deprotonation of the product cation, the reverse of the adsorption reaction.

The currently accepted mechanisms for alkane cracking are similar in that they also involve carbenium ions and the same β-scission step (2) above, but the initiation step leading to the cationic species can occur by a variety of processes including hydride abstraction by some other cationic species. Alternatively, direct protonation from the zeolite to the alkane can occur to form a "carbonium ion" intermediate which can then either undergo dehydrogenation to form a carbenium ion species or cracking into two smaller hydrocarbons. Both the hydride abstraction and the direct protonation lead to carbenium-like species that can then undergo conventional β-scission. This catalytic step then produces another cationic species which can attack another alkane molecule.

The nature of the carbonium and carbenium ion species has been a matter of considerable speculation since such species corresponding to "free" carbocations have not been observed directly by IR or NMR probes [11]. Rather the carbenium ion species that have been observed experimentally or characterized theoretically [12,13] consist of an "alkoxy" species corresponding to an alkyl cation R^+ bound to an anionic site $[Z–O]^-$ in the zeolite, where Z–O denotes the –Al–O–Si– site in the zeolite framework.

In our studies we employ a simple three-T-site (or T3-site, T for tetrahedral) to represent the immediate vicinity of the acid site in faujasite. This is modeled by a cluster comprised of the Si–O–Al–OH–O–Si skeleton with the unsatisfied bonds terminated by hydrogens. The resulting neutral cluster has the overall formula $H_3Si–O–AlH_2–OH–SiH_3$. For comparison, we have studied the reaction of the 2-pentyl cation undergoing β-scission in the gas phase to form propene and the ethyl cation:



and the corresponding reaction on the zeolite cluster. The structures of the reactants, products and transition states are determined using ab initio electronic structure techniques. In addition the related β-scission reaction of 4-methyl-2-pentyl cation to form propene and the propyl cation is also studied to compare the formation of a secondary cationic species with that of forming a primary alkyl cation (in the case of pentene).

2. Computational details

The structures of the C_5 and C_6 hydrocarbon species in these reactions have been optimized in a 6-31G* Gaussian basis at the Hartree–Fock level using the GAUSSIAN 94 program [12]. Similarly for the interactions of these with the zeolite cluster, where the T3 cluster is described as $H_3Si–O–AlH_2–OH–SiH_3$, the structures of the hydrocarbon–zeolite species were also optimized in Hartree–Fock calculations in the 6-31G* basis. While we have explored the imposition of structural constraints to keep the geometry of the cluster strictly within the crystalline geometry of the zeolite framework (as determined by X-ray diffraction) [5], unconstrained optimization for stable minima and for saddle points corresponding to transition states has been found to have advantages in that the structures can be checked by calculating vibrational frequencies to verify that they are in fact minima or transition states. In the case of transition states, structures having one negative force constant in the second derivative Hessian matrix are found using the quadratic synchronous transit (QST3) method [13]. Hybrid density functional calculations, employing a modified form [14] of the Becke-Lee-Yang-Parr functional (B3LYP) [15,16], have been performed at the geometries obtained to provide a realistic estimate of correlation effects. In addition the vibrational frequencies of the transition state are calculated at the final structure to verify that there is only one negative force constant in the Hessian matrix.

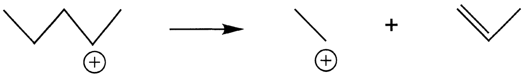
For comparison to measured experimental quantities at temperatures for which cracking processes are carried out, to the calculated energies should be added zero point and thermal corrections using calculated vibrational frequencies. Similarly estimates of true activation energies using transition state theory approaches can be made.

3. Results

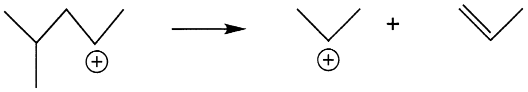
The β-scission reactions of pentene and methyl pentene have been examined in the gas phase and on the zeolite cluster. They are first studied using ab initio Hartree–Fock (HF) techniques; to investigate the effect of correlation we also carried out calculations using a hybrid density functional (B3LYP) approach at the geometries determined at the HF level.

3.1. Gas phase reactions

The cracking reaction of the 2-pentyl ion, a secondary carbenium ion, produces propene and the ethyl cation, a primary carbenium ion:



while methyl pentene produces propene and a secondary propenium ion:



The energetics are summarized in Table 1. While each reaction is endothermic in the gas phase, the calculated endothermicity is greater (47 kcal/mol) for the pentyl ion reaction compared to the methylpentyl reaction (26 kcal/mol). This result is consistent with the expected order of stability primary<secondary<-tertiary for carbenium ions. This is also in agreement with the thermochemical estimates [17] for the gas phase reaction energies of +48 kcal/mol for the pentene ion and ~30 kcal/mol for the methylpentene ion. The calculated values do not include zero-point or thermal corrections which are needed to compare directly with the experimental values, but these corrections are not expected to affect the differences in the calculated endothermicities significantly.

3.2. Zeolite reactions

We now compare these reaction energies for the same species adsorbed on the zeolite cluster. The structure for the reactant, the pentyl cation bound to the T3 cluster, is shown in Fig. 1, and the key geometric parameters are summarized in Table 2. The reactant structure might be described either as an ionic

Table 1
Energetics (kcal/mol) of pentene cracking reactions on model zeolite clusters from calculations on optimized geometric structures in the 6-31G* basis

	Gas phase reaction		Zeolite reaction	
	Calc. (HF)	Expt. [a]	Calc. (HF)	Calc. (B3LYP)
(a) *Pentene cracking reaction*				
2-Pentyl “ion”	0.0	0.0	0.0	0.0
Transition state	[+47]	–	+64.0	+60.0
Ethyl “ion”+propene	+47.4	+48	+19.1	+21.0
Pentene+Z–O–H physisorbed	–	–	+11.6	
Pentene +Z–O–H	–	–	+17.2	
(b) *Branched pentene cracking reaction*				
4-Methyl-2-pentyl “ion”	0.0	0.0	0.0	0.0
Transition state	–	–	+58.2	55.3
2-Propyl “ion”+propene	25.9	29–30	+18.6	20.1

[a] From Ref. [18].

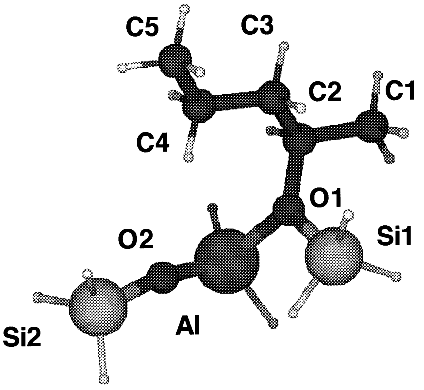


Fig. 1. Reactant for pentene cracking reaction – pentyl “ion” on Si–O–Al–O–Si cluster.

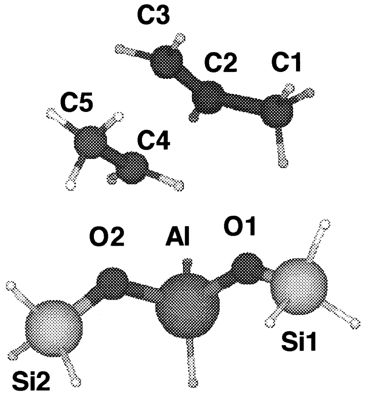


Fig. 2. Transition state for pentene cracking reaction.

Table 2
Selected bond distances (in Å) for the pentene cracking reaction (the numbering scheme for the atoms is shown in Fig. 2)

	Reactant	Transition state	Product
Al–O_1	2.007	1.779	1.726
Al–O_2	1.720	1.817	1.926
O_1–C_2	1.466	4.017	4.618
C_2–C_3	1.524	1.339	1.320
C_3–C_4	1.530	2.414	4.220
O_2–C_4	3.768	2.403	1.452
Si_1–O_1	1.703	1.611	1.612
Si_2–O_2	1.608	1.621	1.702

complex of the Z–O(–) cluster with the $C_5H_{11}^+$ cation, or more appropriately, as an alkoxy species Z–O–R where R=C_5H_{11} bound to the O of the Al–O_1–Si_1 linkage as X_3–Al–O_1(R)–Si_1–X_3. In the latter picture the Al–O bond is more of the dative type, as shown by the long Al–O_1 (2.007 Å) bond length compared with the other Al–O_2 bond length of 1.720 Å and also with the Si–O–C_5H_{11} single bond linkages for Si–O_1 (1.703 Å) and C_2–O_1 (1.466 Å).

Similarly the transition state and product structures are shown in Figs. 2 and 3. The product (Fig. 3) corresponds to the β-scission of the C_3–C_4 bond of the pentyl ion initially bound to the zeolite. The propene molecule and ethyl cation are formed, with the latter again forming an alkoxide bond to the other oxygen atom, O_2, adjacent to the Al on the zeolite cluster. Again one sees a lengthening of the Al–O_2 bond from 1.817 Å in the reactant to 1.962 Å in the product.

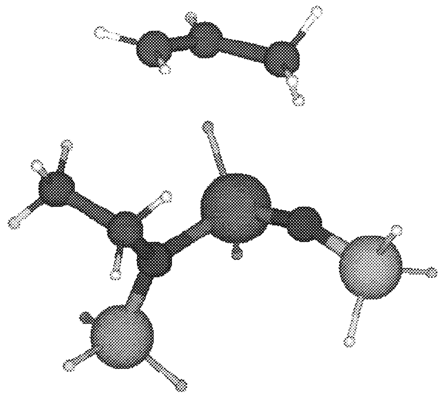


Fig. 3. Product for pentene cracking reaction – ethyl “ion” on Si–O–Al–O–Si cluster plus propene molecule.

The overall thermochemistry for the pentene cracking process (Table 1) on the zeolite cluster is still endothermic, but now is only +19 kcal/mol, much lower than the value (+48 kcal/mol) for the gas phase reaction. Furthermore the methyl pentene reaction on the zeolite has essentially the same overall reaction energy as the unsubstituted pentene, in contrast to the gas phase reaction, where the formation of the secondary cation product was more favorable by 21.5 kcal/mol according to the calculations.

The energy of the transition state (Fig. 2) between the two forms, as obtained from the calculations, is calculated to be 64 kcal/mol above the starting 2-pentyl alkoxide structure. For the methyl pentene case, the activation energy at the Hartree–Fock level is slightly, but significantly, lower – 58 kcal/mol compared to 64 kcal/mol. With density functional theory (B3LYP) the calculated activation energies are 60 kcal/mol (pentene) and 55 kcal/mol (methylpentene).

4. Discussion

The results in the preceding section described the species involved in the β-scission cracking of the C_3–C_4 bond in the 2-pentyl ion in the gas phase and adsorbed on a zeolite cluster (see Table 1). In addition the related process involving the 4-methyl-2-pentyl ion was explored to examine the differences where a secondary vs. primary product is formed. The energetics of the zeolite-catalyzed reaction of pentene are depicted in Fig. 4.

For the methyl–pentene reaction, the calculated endothermicity is essentially the same as for pentene, in contrast to the gas phase reaction where the latter reaction was favored since a secondary cation was formed. In the presence of the zeolite, a C^+–O^- bond is formed between the formally ionic structures so that the difference between primary and secondary ions is not as evident.

While the starting point in this discussion has been the adsorbed 2-pentyl "ion" (or 2-pentoxy species), the actual process would start with pentene and the Z–O–H species which can form a "physisorbed" pentene Z–O–H species. The latter species undergoes reaction by protonating the double bond in pentene to form the adsorbed 2-pentyl ion. This process is depicted in Fig. 4. The interaction between pentene and the Z–O–H species leads to the "physisorbed" form, which is 6.2 kcal/mol exothermic. The subsequent transformation to the 2-pentyl species, the starting point for the cracking step, is exothermic by 11.6 kcal/mol.

In contrast to the small differences in overall reaction energies, a significant but small difference was found for the relative energies of the transition states for the unsubstituted vs. substituted pentene cracking reactions at both the Hartree–Fock and density functional theory levels of calculation, with the latter process having a calculated barrier 6 kal/mol lower than for pentene itself. This could indicate that the primary reason for the differences in reactivity of a branched hydrocarbon compared to an unbranched hydrocarbon in this particular case arises more from kinetic factors than thermodynamic considerations. For a cracking reaction at 500°C a difference of

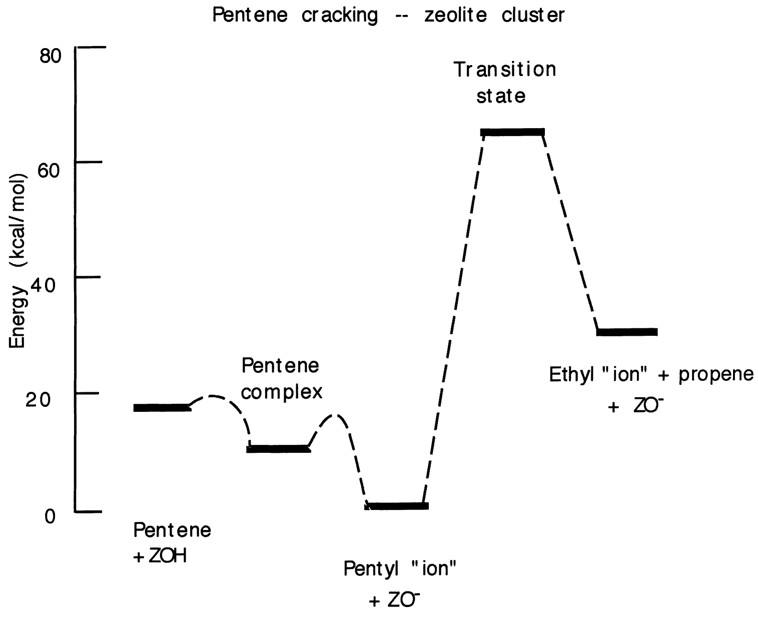


Fig. 4. Reaction pathways for pentene cracking processes.

6 kcal/mol would correspond to a difference in reaction rates of about 50:1 if one used a simplistic approach comparing the differences in activation barriers for the two processes.

In comparing to experimental studies of cracking we first note that pentene was chosen both as a potential example for C–C cracking in larger hydrocarbons as well as for understanding C_5 chemistry itself. For smaller alkanes and alkenes experimental evidence in recent years [18–21] suggests that the classic β-scission process is less important compared to direct cracking and dehydrogenation by protonation from the zeolite. In larger hydrocarbons the "effective" activation energies from experimental studies can typically range from 25–35 kcal/mol [1], much smaller than the calculated values of 55–60 kcal/mol calculated here.

In making these comparisons it is difficult to sort out what the rate-determining step is and whether the effective activation energy corresponds to a particular fundamental kinetic step. Also, these differences may arise that pentene is not a prototypical example of cracking in the larger hydrocarbons, but that it cracks with a somewhat different mechanism. Blaszkowski et al. [10] have also pointed out that there are significant differences of 5–10 kcal/mol depending on whether one defines the effective activation energy relative to the initial gas phase reactants compared to the adsorbed species. We note here that the pentene cracking transition state lies only 47 kcal/mol relative to the energy of the gas phase pentene+zeolite cluster (Table 1).

While there have been numerous calculations in the literature of protonation cracking and dehydrogenation of alkanes as noted earlier, the present calculations are among the first to address the carbon—carbon bond-breaking step in hydrocarbon cracking using reliable theoretical methods in accurate basis sets. Preliminary results of the calculations in this paper have been reported [22]. Although a relatively small "three-T-site" cluster model is used for the zeolite, this is a typical cluster size for current theoretical investigations [6–10] of hydrocarbon chemistry at acid sites in zeolites. In a recent paper published since the original submission of our work, Frash et al. [23] examine β-scission processes for C_4 and C_5 alkoxide species employing similar clusters at both Hartree–Fock and DFT (B3LYP) levels of calculation. Their activation energies from DFT calculations range from 52 to 70 kcal/mol, depending on basis set and cluster size. These values may be compared to the transition state energies of 55–60 kcal/mol obtained in these calculations (Table 1) by applying an estimate of the zero-point energy (ZPE) correction of about 4 kcal/mol [23] to obtain actual activation energies of 51 and 56 kcal/mol for the pentene and methylpentene species, respectively. We note that activation energies of 54.5 and 60.1 kcal/mol were obtained [23] for intermediates in reactions using the same 6-31G* basis set used in our calculations.

5. Summary

Theoretical studies of the β-scission carbon–carbon bond-breaking step in hydrocarbon cracking have examined the reaction of pentene and methyl pentene on a model cluster representing the acid site of a zeolite surface. The structures and reaction pathway have been investigated at Hartree–Fock and density functional (B3LYP) levels. The overall reaction is endothermic by 19 kcal/mol for both molecules, and the transition state energy is about 60 kcal/mol. The reactant corresponds to a pentyl cation, formed by protonation of pentene, covalently bound to an oxygen atom adjacent to an Al site in the zeolite. Similarly the ethyl cationic product is stabilized by bonding to another oxygen atom near the Al. In this way the zeolite serves to provide both a means of generating these cationic species and stabilizing them over the course of the reaction.

The reaction path in the zeolite differs from the gas phase β-scission of the 2-pentyl carbenium ion which has a higher reaction energy (47 kcal/mol) but essentially no additional barrier besides the overall endothermicity. The calculated barrier of the cracking reaction on the zeolite cluster is 6 kcal/mol lower for the case of "branched" methyl pentene cracking compared to "straight chain" pentene cracking, while the overall reaction energies are quite similar. These results suggest that kinetic rather than thermodynamic factors may play a significant role in the cracking chemistry of hydrocarbons in zeolite catalysts.

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