CONF-970443--

LA-UR- 97-3879

Title:

Theoretical Studies of Pentene Cracking on Zeolites: C-C Beta-Scission Processes

RECEIVED
DEC 16 1997
OSTI

Author(s):

P. Jeffrey Hay
Antonio Redondo
Yuejin Guo

Submitted to:

Catalysis Today

Proceedings from symposium on "Computational Chemistry Modeling in Heterogenous Catalysis," San Francisco, CA (April, 1997)

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

Los Alamos
NATIONAL LABORATORY

Form 836 (10/96)

DISCLAIMER

Theoretical Studies of Pentene Cracking on Zeolites: C-C Beta-Scission Processes

P. Jeffrey Hay, Antonio Redondo and Yuejin Guo

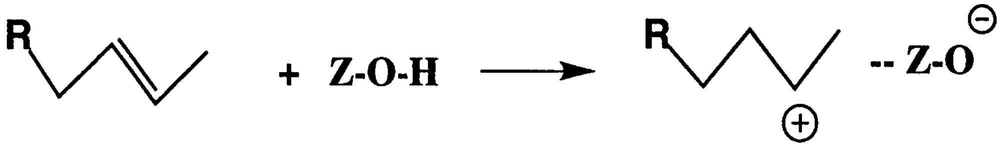
Theoretical Division, T-12, MS B268
Los Alamos National Laboratory, Los Alamos, NM 87545

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 such as faujasite to carry out these transformations more selectively has revolutionized the petroleum refinining technology. While the nature of the acid-catalyzed process involving proposed carbocationic species has been proposed for nearly fifty years, 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 have 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 "beta-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 initial adsorption of the alkene on the acid site of the zeolite Z-O-H to form the "carbenium ion" species



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

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 beta-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 hydrocarbon Either of the hydride abstraction or direct protonation lead to carbenium-like species that can then undergo conventional conventional beta-scission in a catalytic step that produces another cationic species which can then 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 $[Z\text{-}O]^-$ 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) to represent the immediate vicinity of the acid site in faujasite comprised of the Si-O-Al-OH-O-Si skeleton with the unsatisfied bonds terminated by hydrogens. The resulting neutral cluster has the overall form $H_3Si\text{-}O\text{-}AlH_2\text{-}OH\text{-}SiH_3$. We study the reaction of the 2-pentyl cation undergoing beta-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 techniqes. In addition the related beta-scission reaction of 4-methyl-2-pentyl cation to form propene and the propyl cation is also studied to compare the situation of forming 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 GAUSSIAN94 program [12]. Similarly for the interactions of these with the zeolite cluster, where the T3 cluster is described as $H_3Si\text{-}O\text{-}AlH_2\text{-}OH\text{-}SiH_3$, the structures of the hydrocarbon-zeolite species are also optimized in HF calculations in the 6-31G* basis. While we have explored imposing structural constraints to attempt to give a more realistic form to the cluster [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 (B3LYP) calculations, employing a modified form [14] of the Becke-Lee-Yang-Parr functional [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 of 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. These issues will be explored more fully in future work [17] where other steps of pentane and pentene catalysis in zeolites will be explored in greater detail.

3. RESULTS

The β-scission reactions of pentene and methyl pentene have been examined in the gas phase and on the zeolite cluster, first studied using ab initio Hartree-Fock (HF) techniques, and also using 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 [18] 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 Figure 1. Similarly the transition state and product structures are shown in Figures 2 and 3, respectively, where the atomic numbering scheme is given in Figure 2. The reactant structure might be described either as an ionic 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 in Figure 1 one has single bond Si-O-C_5H_{11} linkages witha Si-O_1 and C_2-O_1 bond lengths of 1.703 and 1.466 Å, respectively, compared with a rather long Al-O (2.007 Å) bond length. In Table 2 some of the other key geometric parameters are summarized for the reaction.

The product (Figure 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-O2 bond from 1.817 Å in the reactant to 1.962 Å in the product.

The overall thermochemistry for the pentene cracking process (Table 2) 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 (Figure 2) between the two forms, as obtained from the calculations, is calculated to be 64 kcal/mole above the starting 2-pentyl alkoxide structure. For the methyl pentene case, the activation energy at the Hartree-Fock (HF) 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 have summarized the structures and energetics of 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. 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.

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" 9or 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 will not be treated here in detail, but will be described elsewhere. Briefly, however, we find the process leading to the "physisorbed" form to be 6.2 kcal/mol exothermic (see Table 1) and the subsequent transformtion to the 2-pentyl species to be 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 HF and DFT 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 hydrocarbons compared to an unbranched hydrocarbon in this particular case arises more from kinetic factors than thermodynamic considerations. For a cracking reaction at 500C a difference of 6 kcal/mol would correspond to a difference in reaction rates of 150:1 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 prototypical system 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 [19-22] 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. VanSanten [10] has 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).

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 activation barriers corresponding to the transition state energy are about 60 kcal/mol, but with the barrier 6 kcal/mol lower for the case of methyl pentene cracking. These results suggest that kinetic rather than thermodynamic factors may play a significant role in the cracking chemistry of hydrocarbons in zeolite catalysts.

ACKNOWLEDGMENTS

This work was supported by the Biological and Chemical Technologies Research Program of the Office of Industrial Technologies of the U.S. Department of Energy and the Catalysis Thrust at Los Alamos National Laboratory under Laboratory Directed Research and Development Funds.

REFERENCES

1. A. Corma and B. W. Wojciechowski, Catal. Rev.-Sci. Eng. 27 (1985) 29.
2. B. C. Gates, Catalytic Chemistry (Wiley: New York, 1991), Chapter 5
3. J.S. Buchanan, J. G. Santiesteban, and W.O. Haag, J. Catal. 158 (1996) 279.
4. F. C. Jentoft and B.C. Gates, Topics in Catal. 4 (1997) 1.
5. A. Redondo and P. J. Hay, J. Phys. Chem. 97 (1993) 11764.
6. R.A. vanSanten and G. J. Kramer, Chem. Rev. 95 (1995) 637.
7. V. B. Kazansky, Acc. Chem. Res. 24 (1991) 379.

8. P. Vikruela-Martin, C.M. Zicovich-Wilson and A. Corma, J. Phys. Chem. 97 (1993) 13713.
9. V. B. Kazansky, M.V. Frash, and R. A. van Santen, Appl. Catal. A 146 (1996) 225.
10. S.R. Blaszkowski, M.A.C. Nascimento and R. A. van Santen, J. Phys. Chem. 100 (1996) 3463.
11. J. F. Haw, B.R. Richardson, I.S. Oshiro, N.D. Lazo and J.A. Speed, J. Am. Chem. Soc. 11 (1989) 2052.
12. Gaussian 94, Revision D.3, M. J. Frisch *et al.*, Gaussian, Inc., Pittsburgh, PA 1995.
13. QST3 method
14. P.J. Stephens, F.J. Devlin, C.F. Chabalowski, and M. J. Frisch, J. Phys. Chem. 98 (1994) 11623.
15. C. Lee, W. Yang, and R.G. Parr, Phys. Rev. B 37 (1988) 785.
16. A.D. Becke, J. Chem. Phys. 98 (1993) 5648.
17. A. Redondo, P. J. Hay and Y. Guo, in preparation.
18. JANAF
19. H. Krannila, W. O. Haag and B.C. Gates, J. Catal. 135 (1992) 115.
20. P.V. Shertukde, G. Marcelin, G.A. Sill and W. K. Hall, J. Catal. 136 (1992) 446.
21. B. W. Wojciechowski and J. Abbot, Can. J. Chem. Eng. 63 (1985) 462.
22. B. W. Wojciechowski and J. Abbot, J. Catal. 108 (1987) 346.

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

	Gas phase reaction		Zeolite reaction	
	Calc. (HF)	Expt[a]	Calc. (HF)	Calc. (B3LYP)
	Pentene cracking reaction			
2-pentyl "ion"	0.	0.	0.	0.
Transition state	[+47]	--	+64.0	+60.
ethyl "ion" + propene	+47.4	+48	+19.1	+21.
pentene -- Z-O-H adsorbed	--	--	+11.6	
pentene + Z-O-H	--	--	+17.2	
	Branched pentene cracking reaction			
4-methyl-2-pentyl "ion	0.	0.	0.	0.
Transition state	---	--	+58.2	55.3
2-propyl "ion" + propene	25.9	29-30	+18.6	20.1

[a]Ref. 18

Table 2. Selected bond distances (in Angstroms) for the pentene cracking reaction.

	Reactant	Transition state	Product
Al-O1	2.007	1.779	1.726
Al-O2	1.720	1.817	1.926
O1-C2	1.466	4.017	4.618
C2-C3	1.524	1.339	1.320
C3-C4	1.530	2.414	4.220
O2-C4	3.768	2.403	1.452
Si1-O1	1.703	1.611	1.612
Si2-O2	1.608	1.621	1.702

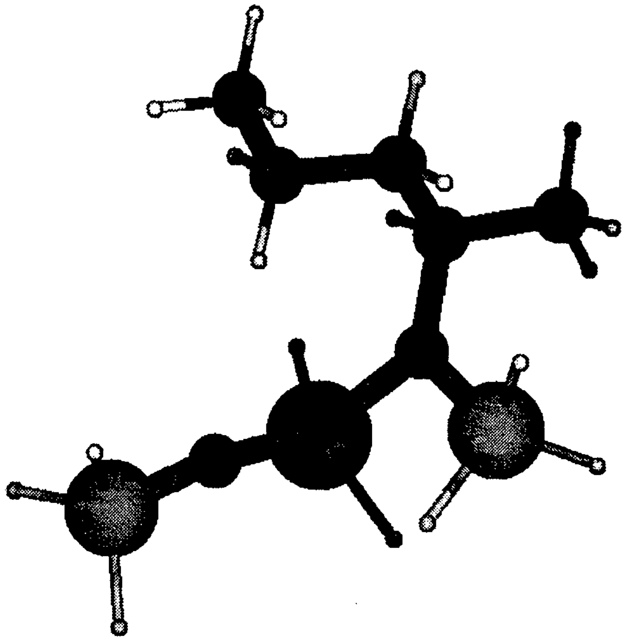


Figure 1. Reactant for pentene cracking reaction--pentyl "ion" on Si-O-Al-O-Si cluster

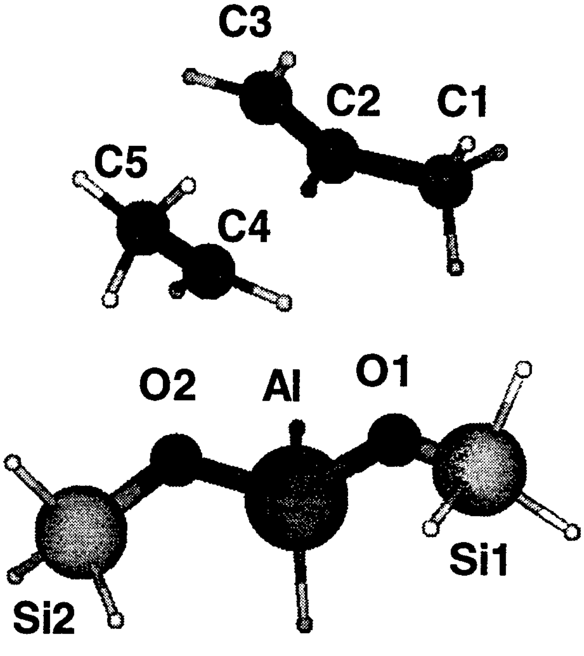


Figure 2. Transition state for pentene cracking reaction--atom numbering scheme is shown.

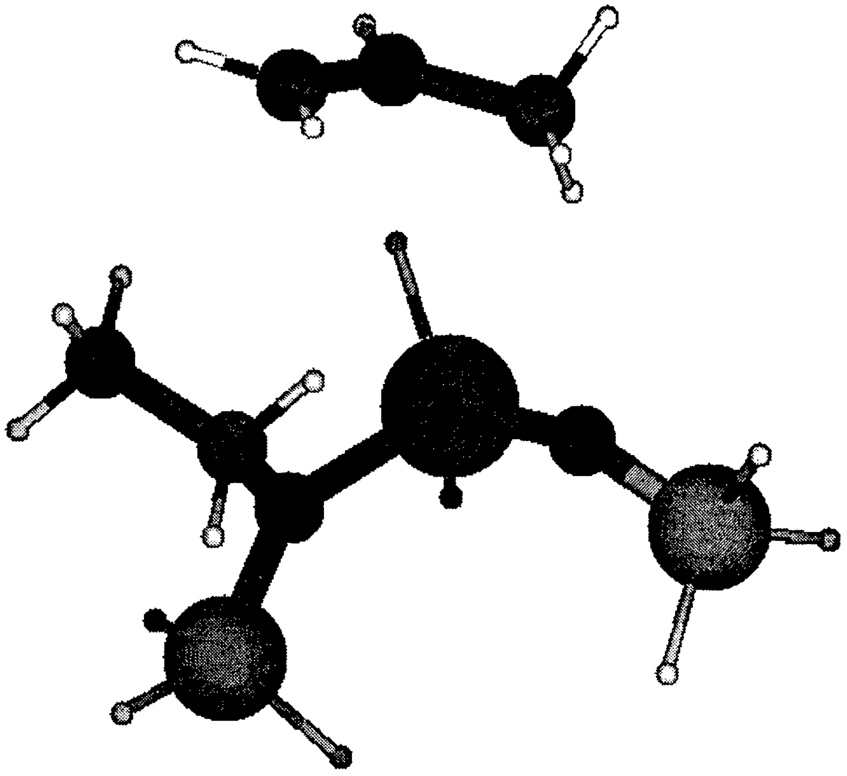


Figure 3. Product for pentene cracking reaction--ethyl "ion" on Si-O-Al-O-Si cluster plus propene molecule.

Report Number (14) LA-UR--97-3879

CONF-970443--

Publ. Date (11) 19970[illegible]4

Sponsor Code (18) DOE/MA; DOE/MA, XF

JC Category (19) UC-910; UC-901, DOE/ER

19980619 064

DOE