A COMPUTATIONAL STUDY OF ETHANE CRACKING IN CLUSTER MODELS OF ZEOLITE H-ZSM-5*

Stanislaus A. Zygmunt,[1,2] Larry A. Curtiss,[2] and Lennox E. Iton[2]

[1]Department of Physics and Astronomy, Valparaiso University, Valparaiso, IN 46383
[2]Materials Science and Chemistry Divisions, Argonne National Laboratory, Argonne, IL 60439

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DISCLAIMER

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S. A. ZYGMUNT*, L. A. CURTISS+ and L. E. ITON+

*Valparaiso University, Valparaiso, IN, USA; szygmunt@exodus.valpo.edu
+Argonne National Laboratory, 9700 S. Cass Ave., Argonne, IL, USA

ABSTRACT

Protolytic cracking of ethane by zeolites has been studied using quantum-chemical techniques and a cluster model of the zeolite Brønsted acid site. Previous computational studies have utilized small cluster models and have not accounted for the long-range effects of the zeolite lattice. These studies have found reaction barriers for cracking which are significantly higher than experimental values. In this work we used a larger zeolite cluster model containing five tetrahedral (Si, Al) atoms (denoted 5T) and searched for stationary points along one possible reaction path for cracking at the HF/6-31G(d) level of theory. This path involves a multi-step cracking reaction, in which the proton is first transferred from the acid site to the adsorbed ethane molecule to form an ion-pair equilibrium complex. Subsequently the proton attacks the C-C bond to complete the cracking process. The activation barrier for cracking was calculated, including corrections for (i) vibrational energies at the experimental reaction temperature of 773 K; (ii) electron correlation and an extended basis set at the B3LYP/6-311+G(3df,2p) level; and (iii) the influence of the surrounding zeolite lattice in H-ZSM-5. The barrier we obtain, 53 ± 5 kcal/mol, is significantly smaller than previous theoretical results and is in good agreement with typical experimental values for small hydrocarbons. Work is currently in progress to extend this study by carrying out geometry optimizations of these complexes using the B3LYP method of density functional theory.

INTRODUCTION

The transfer of a proton from the Brønsted acid site to an adsorbed molecule is an important step in acid catalysis by zeolites. However, this process is not yet fully understood at an atomic level. In particular, protonated intermediate species have not yet been well characterized. In the case of hydrocarbon cracking, does proton transfer lead to a stable intermediate carbonium ion, or a short-lived transition-state? Such a question is difficult to answer using spectroscopic techniques, but can be addressed through the use of ab initio quantum chemistry. As a first step toward future investigations of cracking reactions involving larger hydrocarbons, we have carried out a detailed theoretical study of the potential surface of ethane interacting with the Brønsted acid site of a cluster model of a zeolite.

Previous theoretical work in this area has used small cluster models for the zeolite acid site which do not include a complete set of four neighboring oxygen atoms around the substitutional aluminum site [1-6]. This is significant because our previous work on the interaction of the water dimer with the Brønsted acid site in zeolites showed that when proton transfer takes place, there are important interactions between the protonated molecule and three of the four oxygen neighbors [7]. In addition, several earlier studies of hydrocarbon cracking used the HF/3-21G method, with its small basis set, for geometry optimization, and thus obtained equilibrium geometries which differ significantly from those obtained with the larger 6-31G(d) basis [1-2,5]. The most ambitious study to date used local density functional theory (DFT) with a basis set similar to 6-31G(d) to examine ethane cracking in a 3T cluster [4]. However, the reaction barrier found in this study (70 kcal/mol) is significantly higher than typical experimental values for the true activation barrier of propane and n-butane over H-ZSM-5 at 773K (~47 kcal/mol) [8]. The theoretical overestimate of the barrier is likely due to several factors, including the presence of only two oxygen neighbors around the aluminum site in the zeolite cluster, the well-known defects of the local DFT method used in the study, the neglected influence of the zeolite lattice, and the correction for extended basis sets which we have found to be significant in zeolite-adsorbate systems [9-10].

The goal of the present study is to treat the simplest possible hydrocarbon cracking reaction using a more realistic zeolite cluster model, including the approximate effects of electron correlation, a large basis set, and the electrostatic influence of the surrounding lattice. This should provide a benchmark to indicate the ability of present-day theoretical methods to give quantitatively accurate results for cracking reaction barriers, and thus the degree to which theoretically-suggested reaction mechanisms are reliable. The same methods applied here will be used in the future to investigate cracking of larger hydrocarbon molecules.

THEORETICAL METHODS

For this work we used ab initio molecular orbital theory and gradient-corrected DFT [11]. After obtaining each of the optimized geometries at the HF/6-31G(d) level of theory, we also calculated the harmonic zero-point energy (ZPE) of each system. Transition state structures have only one imaginary vibrational frequency, corresponding to the reaction coordinate. The cluster model for the zeolite framework used in this study, denoted 5T, has five tetrahedral (Si, Al) atoms and is terminated by H atoms at its periphery. It is larger than the 3T or 1T clusters used in all

previous ab initio studies of hydrocarbon cracking by zeolites, and is a more realistic model of the acid site environment in the actual catalyst.

In calculating the activation barrier for cracking, we have employed several additional corrections. In addition to the standard correction for scaled zero-point vibrational energies (ΔZPE), a vibrational energy correction at the experimental reaction temperature of 773 K (ΔE_{773}) was calculated. Next, a correction for the combined effects of electron correlation and an extended basis set (Δ(COR+BS)) was calculated at the B3LYP/6-311+G(3df,2p) level. Finally, we calculated an approximate correction for the finite cluster size of our model (ΔCS) which reflects the influence of the zeolite lattice on the barrier energy. This cluster size correction was determined by extrapolating the barrier energy from the 5T zeolite cluster model to a much larger larger 38T zeolite cluster with atomic positions derived from experimental diffraction studies of H-ZSM-5. The details of this procedure will be published elsewhere [12]. The change in the barrier energy due to this increase in cluster size was taken to be a good estimate of the long-range influence of the zeolite lattice in a real crystal.

RESULTS AND DISCUSSION

A schematic potential energy surface for one possible pathway for protolytic cracking of ethane by an acidic zeolite is shown in Figure 1. HF/6-31G(d) optimized structures corresponding to the stationary points on this potential surface are shown in Figures 2-7. The ethane molecule forms a weakly bound adsorption complex with the Brønsted acid site in which the proton remains on the zeolite framework ($ZH\cdots C_2H_6$). As ethane approaches the acid site more closely, the acidic proton is detached from the zeolite, causing the system first to pass through a transition state for proton transfer (TS PT) and then form an ion-pair equilibrium complex (IP 1). After this first step of proton transfer, the acidic proton moves further from the zeolite framework, passing through through an as-yet unidentified transition state (TS MID) to reach a second ion-pair equilibrium complex (IP 2). From this point C-C bond is finally broken via a cracking transition state (TS CRACK) to yield CH_4 weakly adsorbed on the zeolite ($ZCH_3\cdots CH_4$). In the resulting zeolite (ZCH_3), the acidic proton has been replaced by a methyl cation. Note that at each step of this process, the C-C bond elongates slightly, from an initial distance of 1.53Å to 2.23Å in the cracking transition state.

The HF/6-31G(d) activation barrier for proton transfer, neglecting zero-point energy corrections, is 74.6 kcal/mol. The ion-pair complex IP 1 formed by proton transfer is only 0.3

kcal/mol lower in energy than the transition state. However, when zero-point energies are included, the transition state complex is actually 0.5 kcal/mol lower in energy than the ion-pair complex. A similar situation exists for the IP 2 complex, which is only 0.2 kcal/mol more stable than the cracking transition state TS CRACK. It is therefore possible that these ion-pair complexes may not correspond to true stable equilibrium structures. This indicates that the top of the potential energy surface is actually very flat, and that the rate-limiting step in the cracking reaction is the transfer of the acidic proton from the zeolite to the adsorbed hydrocarbon molecule. The existence of a stable ion-pair complex has previously been reported in a theoretical study by Collins and O'Malley [2] using a smaller basis set and a very small 1T cluster model for the zeolite. Kazansky et al.[6] also found such a complex to be stable using the 1T cluster model.

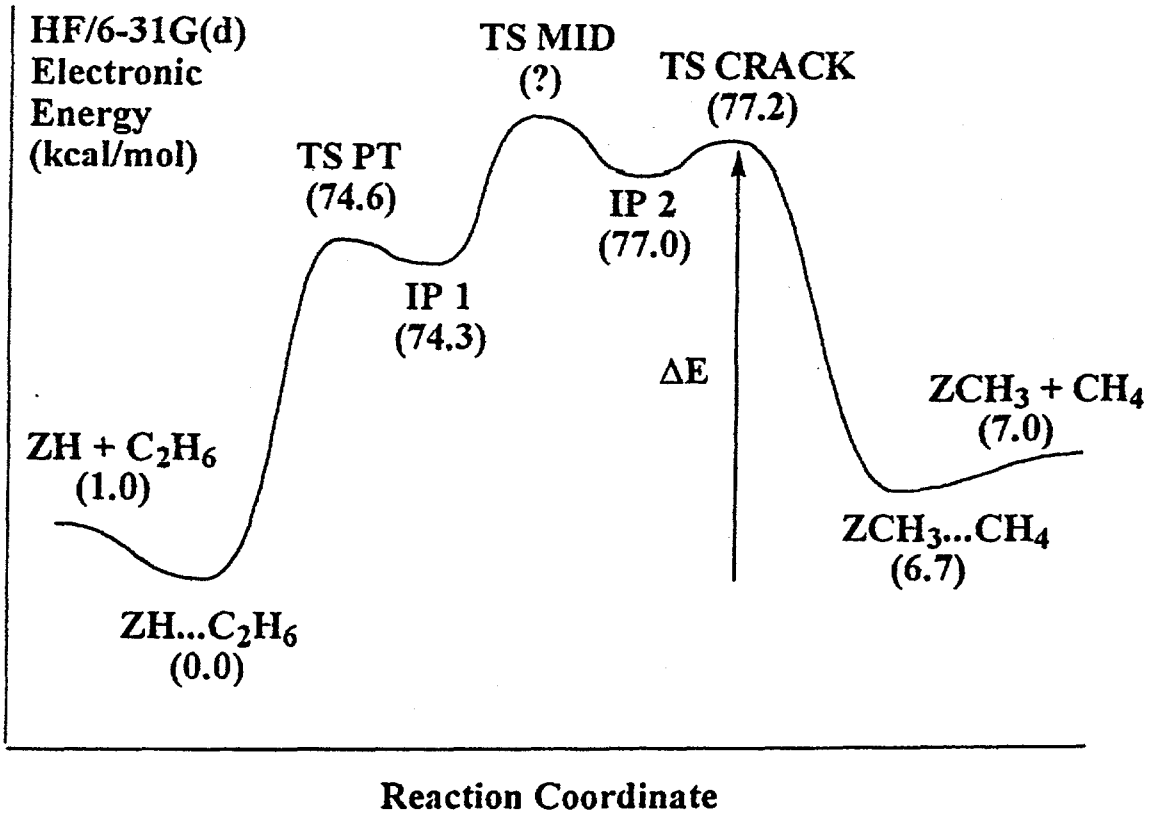

Figure 1 Schematic potential energy surface for protolytic cracking of ethane. (TS PT = proton transfer transition state complex; IP1, IP2 = ion-pair equilibrium complexes; TS CRACK = cracking transition state complex; ΔE = activation barrier for cracking)

We have not yet found the structure of the TS MID transition state complex, which connects the IP 1 and IP 2 structures, but based on preliminary calculations we expect it to be very close to the energy of the cracking transition state complex. Thus our value for the true activation barrier

for protolytic cracking of ethane at the HF/6-31G(d) level of theory (ΔE in Figure 1) is 77.2 kcal/mol. This value is significantly lower than that of Kazansky et al. [6], who found it to be 83 kcal/mol at the HF/6-31G(d) level in a 3T cluster. This confirms our expectation that the use of the 5T cluster leads to a lower reaction barrier when compared to smaller cluster models.

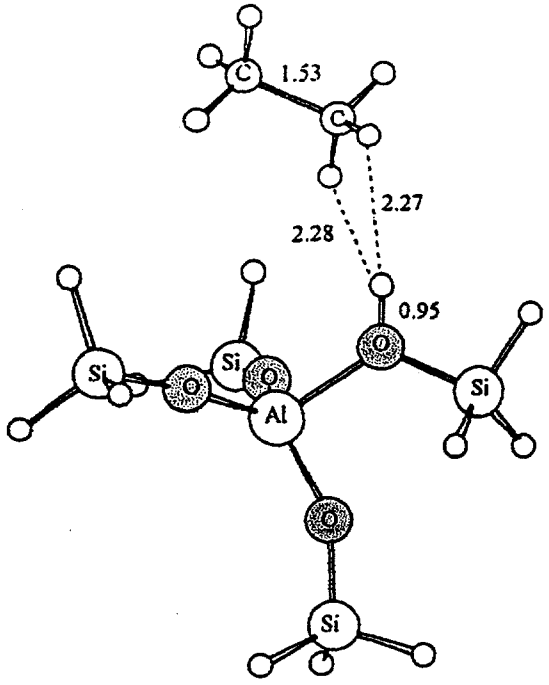

Figure 2. $ZH\cdots C_2H_6$ equilibrium complex.

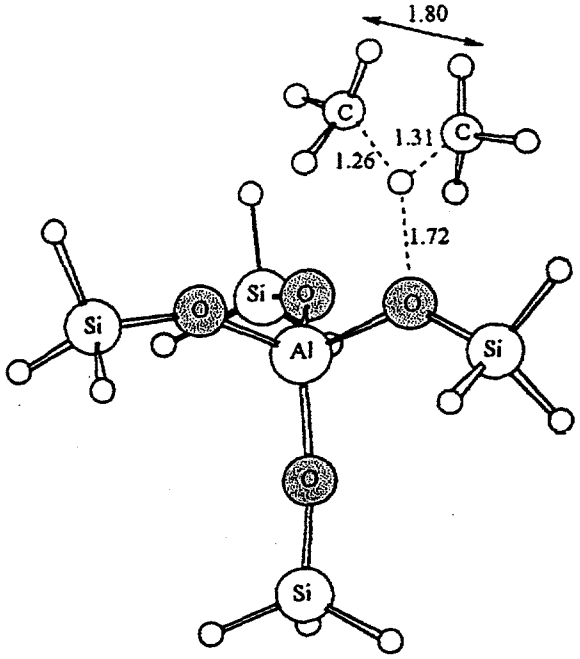

Figure 3. TS PT proton transfer transition state.

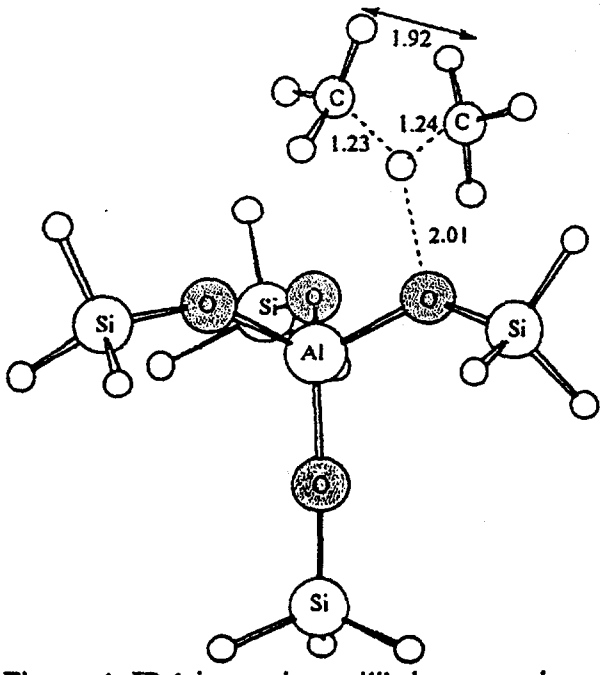

Figure 4. IP 1 ion-pair equilibrium complex.

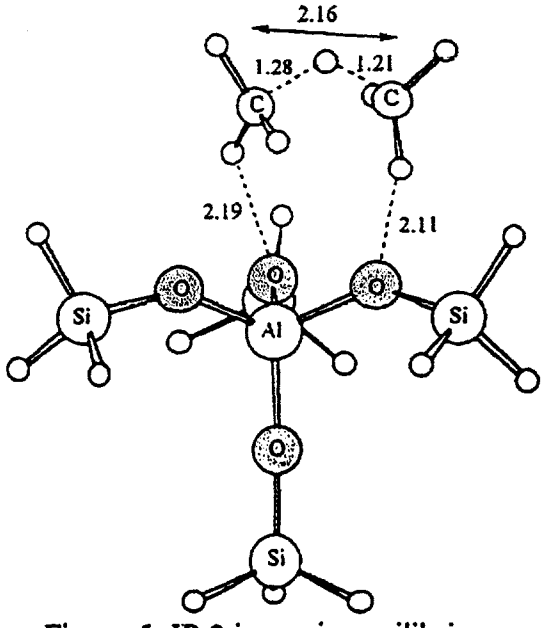

Figure 5. IP 2 ion-pair equilibrium complex.

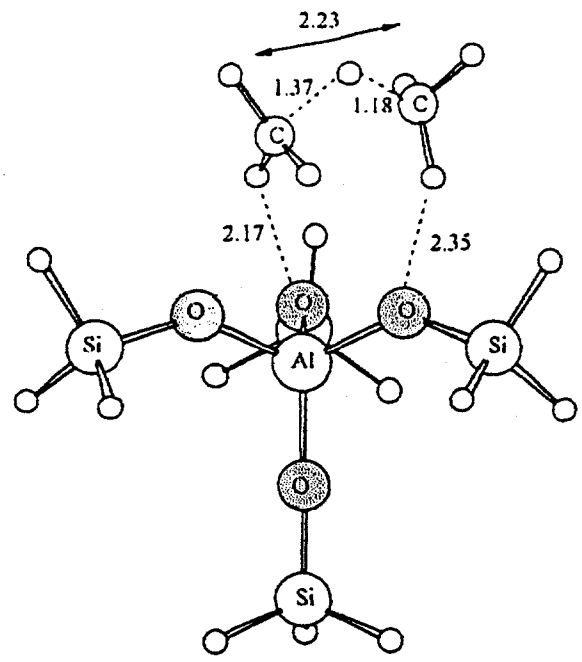

Figure 6. TS CRACK cracking transition state.

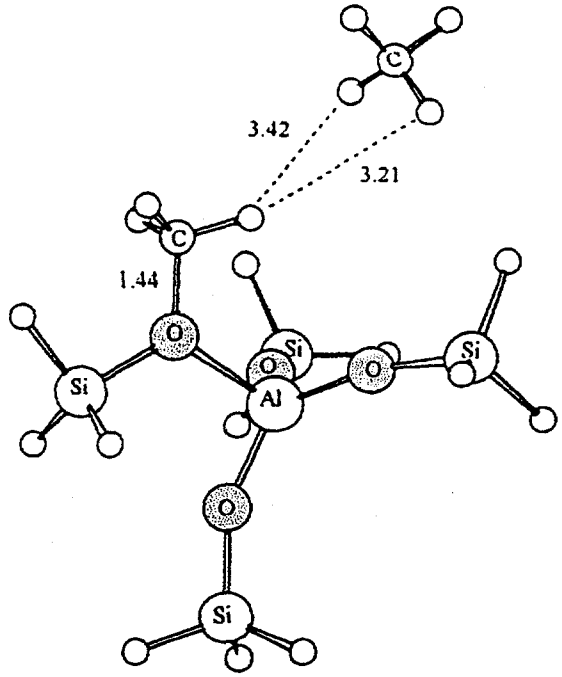

Figure 7. $ZCH_3\cdots CH_4$ equilibrium complex.

The influence of the calculated correction terms on the barrier energy is displayed in Table 1. The combined effects of electron correlation and basis set extensions (Δ(COR+BS)), zero-point vibrational energies (ΔZPE), thermal corrections to 773K (ΔE_{773}), and the zeolite lattice (ΔCS) reduce the barrier to 53 ± 5 kcal/mol. The estimated uncertainty of 5 kcal/mol reflects the approximations made in calculating the correction terms. To our knowledge there is no experimental value for the cracking barrier of ethane in the literature, so we can compare only to the experimental value of 47 kcal/mol for propane and n-butane in H-ZSM-5 [8]. However, our preliminary calculations for propane cracking indicate that the relative energies of complexes involving protonated propane are approximately 2.5 kcal/mol *lower* than the energies of corresponding complexes involving protonated ethane. This, along with the uncertainties in our correction terms, brings our result for ΔE into good agreement with the experimental activation barrier.

Our results emphasize that the long-range influence of the zeolite lattice causes a significant reduction in the calculated barrier due to the electrostatic stabilization of the ionic transition state complex for cracking. Along with the use of the smaller 3T cluster model, we believe this is a major reason for the deficiency of previous theoretical estimates of the cracking barrier for ethane in zeolites. Published theoretical values of 70 kcal/mol [4-5] and 75.4 kcal/mol [6] neglected the zeolite lattice in which the finite cluster model is embedded.

Our study is currently being extended by carrying out geometry optimizations of the complexes reported here using the B3LYP/6-31G(d) method. This will help us assess the influence of electron correlation on the geometries and relative energies of these structures. The results reported here demonstrate the reliability of ab initio quantum chemistry for the prediction of reaction pathways and energy barriers for hydrocarbon cracking in zeolites.

Cracking Barrier and Corrections	Energy (kcal/mol)
ΔE [HF/6-31G(d)]	77.2
Δ(COR+BS)	-8.0
ΔZPE	-2.1
ΔE_{773}	-1.2
ΔCS	-12.7
ΔE [theory] ethane	53 ± 5
ΔE [expt.] propane, n-butane	47

Table 1. Calculated energy barrier for protolytic cracking of ethane in H-ZSM-5.

CONCLUSIONS

We have examined the protolytic cracking of ethane by zeolite H-ZSM-5 via a multi-step process of proton transfer and formation of a metastable ion-pair complex, followed by C-C bond breaking and formation of methane and a surface methyl cation. The calculated barrier energy of 53 ± 5 kcal/mol is in good agreement with available experimental values for small alkanes. Use of the 5T cluster model lowers the calculated barrier at the HF/6-31G(d) level compared to the commonly used 3T model of earlier studies, which emphasizes the importance of a realistic zeolite cluster model for accurate quantum chemical studies of hydrocarbon cracking. Energy corrections for electron correlation, an extended basis set, and the long-range influence of the zeolite lattice are very large in this system and *must* be included in order to obtain quantitative agreement with experiment. We have shown for the first time that activation barriers for hydrocarbon cracking reactions in zeolites can be calculated with quantitative accuracy by ab initio methods.

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