

# Reactivity of Alkanes on Zeolites: A Theoretical *ab Initio* Study of the H/H Exchange

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*Ab initio* calculations were performed to study the H/H exchange between light alkanes (methane, ethane, propane, and isobutane) in protonated zeolites. The Brønsted acid site of the zeolite was represented by a T3 cluster (T = Si, Al). The results of the calculations, at the B3LYP/6-31G\*\* and MP2/6-31G\*\*//HF/6-31G\*\* levels, indicated that the transition state resembles a pentacoordinated carbonium ion. The enthalpy of activation was similar, regardless of the alkane and the type of hydrogen being exchanged. The  $\Delta H^\ddagger$  values, at room temperature, ranged from 32.2 kcal/mol for methane to 36.2 kcal/mol for the exchange of the tertiary hydrogen of isobutane, both at the B3LYP/6-31G\*\* level. These results are not in complete agreement with experiments, as it has been shown that for isobutane only the primary hydrogens exchange at temperatures near ambient. This disagreement may be attributed to the fact that the cluster model employed in the calculations neither includes the electrostatic effects of the zeolite cavity nor takes into account steric repulsion associated with the framework.

## Introduction

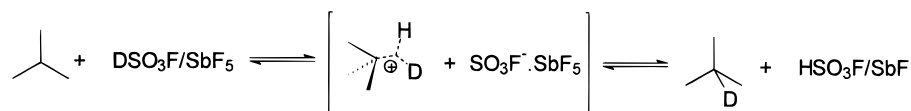
The electrophilic activation of alkanes in liquid superacid systems was independently discovered by Olah<sup>1</sup> and Hogeveen<sup>2</sup> in the 1960s. On the basis of product selectivity and isotopic labeling experiments, Olah proposed<sup>3</sup> a qualitative scale of  $\sigma$  bond reactivity following the order  $\text{tert-C-H} > \text{C-C} > \text{sec-C-H} > \text{prim-C-H} > \text{CH}_4$ . An interesting reaction accompanying alkane ionization in liquid superacids is the H/D exchange.<sup>4</sup> At  $-78^\circ\text{C}$ , isobutane exchanges with  $\text{DSO}_3\text{F/SbF}_5$  almost exclusively at the methine position.<sup>4</sup> To explain this result, Olah proposed the formation of the 2-H-isobutonium cation as intermediate or transition state (Scheme 1). More recently, Sommer and collaborators showed<sup>5</sup> that, at  $-10^\circ\text{C}$ , isobutane exchanges both the tertiary and the primary hydrogens, indicating that at higher temperatures the superacid medium can attack both C–H bonds of isobutane.

Zeolites catalyze many industrial hydrocarbon reactions, especially cracking and isomerization processes.<sup>6</sup> Nevertheless, the reactivity of the  $\sigma$  bonds on the zeolite surface is still poorly understood. We have shown that tertiary alkanes undergo H/D exchange with deuterated zeolites below the cracking threshold.<sup>7</sup> Notwithstanding, the selectivity is different from that observed in liquid superacid. The exchange takes place only in the primary and secondary positions adjacent to the tertiary center, which remains unexchanged.<sup>8</sup> This can be explained by a mechanism involving tertiary carbenium ions and olefins (Scheme 2), similar to the mechanism of exchange with deuterated sulfuric acid.<sup>9</sup> In liquid superacid, the deprotonation of the carbenium ion, to form an olefin, is virtually excluded, but on the zeolite and sulfuric acid solutions, the acid strength is not high enough to prevent this reaction and the exchange mechanism follows a different pathway. However, the central problem on how the carbenium ion is first formed from the alkane interaction with the zeolite surface remains unanswered.

Theoretical methods have been widely employed to study reactions catalyzed by zeolites. Because of the complex structure of the zeolite, most of the work has been performed considering

a finite model, representing only a part of the structure. One of the models most used to represent the zeolite acid site in catalysis studies is the T3 cluster, where T stands for Al or Si atoms. This cluster-model is large enough as to encompass the neighborhood of the Brønsted acid site, but still small enough to allow the use of high-level *ab initio* treatments. Many catalytic reactions have been studied using this type of cluster, aiming at the understanding of the mechanism and the nature of the intermediates and transition states (TS) formed. Recent examples are the cracking<sup>10</sup> and isomerization<sup>11</sup> of alkanes, protonation, and reactions of methanol,<sup>12</sup> water,<sup>13</sup> benzene,<sup>14</sup> and olefins.<sup>15</sup> Most of these studies concluded that cationic species are not normally formed as intermediates but only as transition states. This could be a consequence of the cluster model used, as it neglects contributions from the electrostatic potential of the zeolite cavity, which may stabilize more ionic TS and intermediates. For instance, in a recent combined quantum mechanics/molecular mechanics (QM/MM) study,<sup>16</sup> differences in the acidity of some zeolites, measured in terms of enthalpy of ammonia adsorption, were found as a function of the framework structure, implying that the zeolite framework plays an important role in proton-transfer reactions. On the other hand, more recent results<sup>17</sup> of cationic species within the channel of periodic chabazite show that the additional stabilization given by the zeolite framework, with respect to the cluster model, strongly depends on the level of calculation, the zeolite composition, and the coverage, reaching a maximum of 7.8 kcal/mol at the most favorable conditions.

The H/H exchange of methane<sup>18</sup> and ethane<sup>19</sup> with the zeolite Brønsted acid site has already been investigated by several groups using different theoretical approaches. All these studies have indicated that a free carbonium ion is not formed as intermediate and that the TS has a pentacoordinated carbonium ion character. Nevertheless, the majority of the experimental results of H/D exchange between alkanes and zeolites is carried with tertiary alkanes, while methane and ethane present only primary carbon atoms. Therefore, it would be interesting to carry

**SCHEME 1: Proposed Pathway for H/D Exchange of Isobutane with DSO<sub>3</sub>F/SbF<sub>5</sub>****SCHEME 2: Mechanism of H/D Exchange on Zeolites**

out a theoretical investigation of the H/H exchange with other alkanes in order to improve our knowledge about the reactivity of  $\sigma$  bonds on protonated zeolites. Propane and isobutane were selected for this study because they are the two simplest alkanes to exhibit secondary and tertiary carbon atoms and also because there are experimental results<sup>7,8</sup> available for comparison.

Although the H/H exchanges of methane<sup>18</sup> and ethane<sup>19</sup> have been previously investigated, the calculations were performed either at the Hartree–Fock or at the DFT level with functionals other than B3LYP. Therefore, these two molecules were also considered in the present study. Their consideration will provide not only a fair comparison along the alkane series, by treating them at the same level of calculation, but also a test for the dependence of the DFT results on the choice of the functional.

**Computational Methods**

To simulate the zeolitic acid site, a T3 cluster (T = Si, Al) was used (Figure 1). The border silicon atoms were saturated with hydrogens to avoid dangling bonds. All the calculations were performed at the B3LYP/6-31G\*\* and MP2/6-31G\*\*//HF/6-31G\*\* levels, using the GAUSSIAN 94 package.<sup>20</sup> The geometries of the T3 cluster and of the alkanes were first separately optimized. From those optimized geometries, the structures corresponding to the adsorption minimum of each alkane molecule and the zeolitic cluster were obtained. The latter structures were then used in the search for the transition states (TS). The transition states were obtained using the Berny and the eigenvector follower (EF) algorithms and characterized as having only one imaginary frequency, which corresponds to the reaction mode. A vibrational analysis was performed for all structures and the frequencies scaled by 0.89 to obtain the zero-point energy (ZPE) and thermal corrections to 298.15 K. Charges at the atomic centers were calculated by fitting to the density derived electrostatic potential with the CHelpG scheme<sup>21</sup> using the B3LYP wave functions.

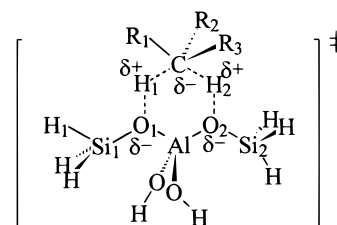
**Results and Discussion**

The calculations showed that a free carbonium ion is not formed as a discrete intermediate, but that the H/H exchange on zeolites occurs through a TS with carbonium ion character, for all the alkanes studied, in agreement with previous results for methane<sup>18</sup> and ethane,<sup>19</sup> using different levels of theory. Table 1 shows the calculated enthalpies of activation ( $\Delta H^\ddagger$ ) and the charge developed on the attacking carbon atom for the H/H exchange between the studied alkanes and the T<sub>3</sub> cluster. From the results on Table 1, one can see that the enthalpy of activation does not show significant variations, either with the carbon chain length or the type of hydrogen atom being exchanged, being about 30 kcal/mol for all the hydrocarbons considered. This result implies that the reactivity of the alkane C–H bonds on the zeolite surface is the same, regardless of being a primary, secondary, or tertiary bond. For instance, the enthalpy of

**TABLE 1: Calculated Enthalpy of Activation ( $\Delta H^\ddagger$ ), Corrected for Zero-point Energy (ZPE) and 298.15 K, Reaction Coordinates, and Electrostatic Potential Derived (CHelpG) Charges for the H/H Exchange with the T<sub>3</sub> Cluster**

reaction <sup>a</sup>	$\Delta H^\ddagger$ (kcal/ mol) <sup>b</sup>	$\Delta H^\ddagger$ (kcal/ mol) <sup>c</sup>	reaction coordinates (cm <sup>-1</sup> ) <sup>c</sup>	charge formation on the attacked carbon <sup>c,d</sup> ( $\delta q$ )
CH <sub>4</sub> + HT3	31.1	32.3	–1703	–0.187
C <sub>2</sub> H <sub>6</sub> + HT3	31.4	32.3	–1590	–0.058
CH <sub>3</sub> CH <sub>2</sub> CH <sub>3</sub> + HT3	30.6	32.2	–1590	–0.068
CH <sub>3</sub> CH <sub>2</sub> CH <sub>3</sub> + HT3	30.6	33.3	–1484	–0.042
(CH <sub>3</sub> ) <sub>2</sub> CH + HT3	29.8	32.3	–1567	–0.043
(CH <sub>3</sub> ) <sub>3</sub> CH + HT3	31.5	36.2	–1412	+0.047

<sup>a</sup> The italic hydrogen refers to the one being exchanged. <sup>b</sup> MP2/6-31G\*\*//HF/6-31G\*\*. <sup>c</sup> B3LYP/6-31G\*\*//B3LYP/6-31G\*\*. <sup>d</sup>  $\delta q$  = (absolute charge of the carbon atom in the TS) – (absolute charge of the carbon atom in the reactant).



**Figure 1.** Transition state for H/H exchange of alkanes with zeolites.

activation for exchanging the primary hydrogen atom varies at most by 1 kcal/mol along the series C<sub>1</sub>–C<sub>4</sub>. If one looks at the results for propane, the  $\Delta H^\ddagger$  value for the exchange of the secondary hydrogen is 33.3 kcal/mol and just 32.2 kcal/mol for the primary at the B3LYP/6-31G\*\* level of calculations. For the exchange of the tertiary hydrogen of isobutane, the  $\Delta H^\ddagger$  was 36.2 kcal/mol, a value slightly higher than the one for the exchange of the primary hydrogen atom (32.3 kcal/mol). This difference can be attributed to some steric hindrance associated with the exchange at the tertiary center due to the methyl substituents. Also from Table 1, one sees that for all the hydrocarbons studied there was a small degree of charge formation in the TS. Except for the attack at the methine position of isobutane, an increase in the electronic density on the attacked carbon atom in the TS was observed, relative to the ground state. This implies that the TS should be poorly sensitive to the electronic effect of substituents, reflecting an almost constant activation energy for all the C–H bonds. This kind of negative charge distribution in the TS has already been observed for the H/H exchange of methane<sup>18</sup> at different theory levels. Table 1 also shows that the two levels of calculations used in this work show similar results for the enthalpy of activation for the H/H exchange. We also carried out calculations using a T5 cluster, where the two hydroxyls, linked to the aluminum atom, were replaced by two OSiH<sub>3</sub> groups. The  $\Delta U^\ddagger$  for the exchange of the tertiary hydrogen of isobutane was 39.7 kcal/mol, at the

**TABLE 2: Geometrical Parameters (Interatomic Distances in Å and Bond Angles in Degrees) for the TS for the Exchange of Methane with a T3 Cluster, Using Different Functionals**

geometrical parameter <sup>a</sup>	Becke–Perdew <sup>b</sup>	B3LYP <sup>c</sup>
O <sub>1</sub> –H <sub>1</sub>	1.310	1.314
C–H <sub>1</sub>	1.336	1.336
C–H <sub>2</sub>	1.337	1.342
O <sub>2</sub> –H <sub>2</sub>	1.310	1.311
C–O <sub>1</sub>	2.641	2.648
C–O <sub>2</sub>	2.645	2.651
Si <sub>1</sub> –O <sub>1</sub>	1.674	1.675
Si <sub>2</sub> –O <sub>2</sub>	1.676	1.674
Al–O <sub>1</sub>	1.818	1.830
Al–O <sub>2</sub>	1.726	1.831
Si <sub>1</sub> –O <sub>1</sub> –Al	125.3	129.6
O <sub>1</sub> –Al–O <sub>2</sub>	92.3	91.4
Al–O <sub>2</sub> –Si <sub>2</sub>	124.9	129.2

<sup>a</sup> See Figure 1. <sup>b</sup> Reference 18d. <sup>c</sup> Present result.**TABLE 3: Geometrical Parameters (Interatomic Distances in Å and Bond Angles in Degrees) for the TS for the H/H Exchange of Ethane, Propane, and Isobutane with a T3 Cluster at B3LYP/6-31G\*\* Level of Calculation**

geometrical parameter <sup>a</sup>	ethane	propane 1° C–H	propane 2° C–H	isobutane 1° C–H	isobutane 3° C–H
O <sub>1</sub> –H <sub>1</sub>	1.356	1.357	1.378	1.360	1.440
C–H <sub>1</sub>	1.316	1.315	1.310	1.309	1.298
C–H <sub>2</sub>	1.316	1.317	1.304	1.318	1.324
O <sub>2</sub> –H <sub>2</sub>	1.356	1.357	1.408	1.371	1.429
C–O <sub>1</sub>	2.667	2.666	2.679	2.663	2.723
C–O <sub>2</sub>	2.667	2.669	2.708	2.688	2.749
Si <sub>1</sub> –O <sub>1</sub>	1.672	1.672	1.669	1.670	1.665
Si <sub>2</sub> –O <sub>2</sub>	1.670	1.670	1.666	1.668	1.665
Al–O <sub>1</sub>	1.828	1.827	1.828	1.827	1.820
Al–O <sub>2</sub>	1.828	1.827	1.828	1.827	1.820
Si <sub>1</sub> –O <sub>1</sub> –Al	130.5	130.6	131.3	129.8	128.1
O <sub>1</sub> –Al–O <sub>2</sub>	91.6	91.7	91.7	91.6	92.1
Al–O <sub>2</sub> –Si <sub>2</sub>	129.5	129.2	128.7	131.8	127.5

<sup>a</sup> See Figure 1.

B3LYP/6-31G\*\*//B3LYP/6-31G\*\* level. This value is similar to the  $\Delta U^\ddagger$  of 37.1 kcal/mol for the same reaction calculated with the T3 cluster, indicating that the use of a larger cluster did not lead to significant changes in the activation energy. Therefore, the use of a more computationally costly T5 cluster does not seem to be justified in the scope of this work.

Table 2 shows some of the geometrical parameters of the TS for the exchange of methane using DFT with different functionals. From the results on Table 2, one sees that the geometry of the TS shows little dependence on the level of calculation employed, except for the Al–O<sub>1</sub> and Al–O<sub>2</sub> bond lengths which are much shorter when the Becke–Perdew (BP) functional is used. The enthalpy of activation at the BP level was found to be<sup>18d</sup> approximately 29 kcal/mol, slightly lower than the presently obtained at the B3LYP level of calculation. The same trend is observed for the exchange of ethane.

Table 3 shows the geometry of the TS for the exchange of the other alkanes studied, at the B3LYP level of calculation. The observed variations in the C–O<sub>1</sub>, C–O<sub>2</sub>, O<sub>1</sub>–H<sub>1</sub>, and O<sub>2</sub>–H<sub>2</sub> bond lengths clearly reflect the difference in steric hindrance when going from a primary to a tertiary hydrogen atom. These distances are larger in the TS for exchanging the tertiary hydrogen atom of isobutane, followed by the values for the exchange of the secondary hydrogen atom in propane, implying that, for these two reactions, the pentacoordinated complex is further away from the zeolite structure. Therefore, the stabilization provided by the interaction with the zeolite structure is

smaller and the activation energy is higher. Exactly the same trend is observed at the HF level of calculation.

The calculations for the H/H exchange with methane show a good correlation with the experimental results.<sup>18a</sup> Nevertheless, for the H/D exchange with tertiary and linear alkanes, the experimental results<sup>6,7</sup> indicate a different scheme for the C–H bond reactivity on zeolites. Tertiary alkanes readily exchange at 100 °C and lower temperatures,<sup>7,22</sup> while linear alkanes require higher temperatures<sup>8b,c</sup> (ca. 200 °C). The most probable mechanism for exchange of tertiary alkanes on zeolites is shown in Scheme 2, involving adsorbed carbenium ions and olefins. This mechanism explains why exchange at the tertiary position is never observed. Addition of small amounts of olefins increases the rate of exchange without altering the regioselectivity, indicating that the rate-determining step is prior to the olefin formation.<sup>8c,d</sup> Therefore, at least for tertiary alkanes, a more ionic TS could be operative, favoring the protonation of the tertiary C–H bond and formation of the adsorbed *tert*-butyl carbenium ion (Scheme 2).

On the other hand, the H/D exchange of isobutane with HF/SbF<sub>5</sub> takes place through a TS resembling a carbonium ion coordinated with the counterion, as evidenced in recent high-level ab initio calculations.<sup>23</sup> Indeed, the TS for exchange in liquid superacids is similar to the TS shown in Figure 1. The hydrogen atoms of the three-center bond are coordinated with the counterion. Hence, a free carbonium ion is not formed in the H/D exchange in liquid superacids. Nevertheless, isobutane can be ionized to the *tert*-butyl cation in HF/SbF<sub>5</sub> solutions. The TS for ionization seems to involve a higher degree of charge separation than the TS for exchange and might occur with a weaker interaction with the counterion. The present calculations using the T<sub>3</sub> cluster neither include the electrostatic effects of the zeolite cage nor take into account steric repulsions associated with the zeolite framework. Therefore, covalent interactions may be strengthened relative to more ionic ones. It is possible that the electrostatic field inside the zeolite cavity may facilitate the formation of a more ionic TS favoring the protonation of tertiary C–H bonds, leading to the adsorbed carbenium ion plus hydrogen (dehydrogenation reaction). Indeed, it has been recently demonstrated<sup>24</sup> that the ionizing power of zeolites is similar to, or even higher than, that of water/methanol mixtures.

Calculations for the dehydrogenation of methane<sup>18d,f</sup> and ethane<sup>19</sup> to form the adsorbed methyl and ethyl cation (alkoxy species) plus hydrogen using a T3 cluster showed an activation energy of 74.8 kcal/mol (GVB+CI)<sup>18f</sup> and 81.9 kcal/mol (NLDA-BP)<sup>18d</sup> for methane and 70.9 kcal/mol (NLDA-BP)<sup>19</sup> for ethane. The TS for dehydrogenation exhibits a much higher ionic character than the TS calculated for the H/H exchange. It is possible that, for tertiary systems, the activation energy for dehydrogenation becomes lower than the activation energy for the H/H exchange, as the electrostatic fields inside the cages would better stabilize the more ionic TS, explaining the experimental data for H/D exchange.

Further evidence for the difference in behavior of linear and branched alkanes comes from a recent Monte Carlo and molecular dynamics study.<sup>25</sup> It was shown that, in ZSM-5 and silicalite, the branched alkanes adsorb, preferentially, at the channel intersections whereas the linear ones are more or less equally distributed in the straight and sinusoidal channels. This result implies that linear and branched alkanes should undergo catalytic reactions at different sites within the zeolite, a situation that cannot be described by a T3 cluster. Indeed, calculations<sup>26</sup> with a large cluster, representing a real part of the zeolite Y structure (sodalite + hexagonal prism), indicated that the



oxygens of the framework are not equivalent. Therefore, a symmetrical TS, as pictured in Figure 1, would not be favored as it will lead to a proton attached to a different topological oxygen, increasing the energy of the system. Thus, depending on the size and shape of the alkane molecule, the results of calculations with the T3 cluster should be interpreted with care. This model not only underestimates ionic interactions but cannot take into account steric effects associated with the different types of acid sites and topological framework oxygens. While the electrostatic effect of the zeolite cavity should affect almost equally the studied alkane molecules, the steric effect should be larger for the branched and longer linear chains.

Recent experimental<sup>27</sup> kinetic isotopic effect data of isobutane dehydrogenation in liquid superacid and zeolites indicated that the TS is different in both media. The TS on zeolites does not resemble a pentacoordinated carbonium ion and has a more linear geometry than the TS in liquid superacid, whose geometry is closer to the calculated<sup>28</sup> geometry of a free 2-H-isobutonium cation. This is an additional experimental evidence that a TS for H/H exchange, similar to that pictured in Figure 1, is not favored on the zeolite surface.

## Conclusions

Calculations of the H/H exchange between a T3 cluster representing the zeolite Brønsted acid site and different alkanes (methane, ethane, propane, and isobutane) were carried out. The enthalpy of activation, at B3LYP/6-31G\*\* levels of calculation, was similar (ca. 30 kcal/mol) regardless of the type of C–H bond being involved. The TS exhibits little degree of charge separation and, except for the exchange of the tertiary hydrogen of isobutane, there was a small negative charge over the attacking carbon atom. The results are not in complete agreement with the available experimental data of H/D exchange with linear and tertiary alkanes, as the latter exchange faster and because the tertiary hydrogen is never exchanged in these alkanes, indicating a different mechanistic pathway. This disagreement may be attributed to the fact that the cluster-model employed in the calculations neither includes the electrostatic effects of the zeolite cavity nor takes into account steric repulsion associated with the zeolite framework. Thus, results of ab initio calculations with T3 and other smaller clusters should be interpreted with great care, as they may lead to erroneous conclusions regarding the mechanism of zeolite catalyzed reactions.

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