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A Theoretical Description for the Monomolecular Cracking of C–C Bonds over Acidic Zeolites

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The pathway to monomolecular C–C bond cracking over Brønsted acid sites has been characterised theoretically using the AM1 molecular orbital method. The model describes not only the transition of the proton from the acid site to the paraffin, but also the collapse of the resulting carbonium ion directly to a smaller alkene and alkane. This model thus predicts that the protolysis is not driven by an acid–base pair type reaction, as witnessed with ammonia and alkene activation. The data amassed allowed a quantitative description of the primary product distributions for the alkanes butane and hexane which shows good agreement with experimental data. © 1995 Academic Press, Inc.

INTRODUCTION

The importance of zeolites in the catalytic cracking of paraffins has led to extensive research into the subject (1–13). One of the most important findings of such work is the realisation that the reaction consists predominantly of two mechanisms running in concert (1–7). The first of these is bimolecular and is propagated by β-scission and hydride transfer. The second proposed route is, by contrast, a monomolecular mechanism and lies in the formation of nonclassical carbonium ions by protonation of C–C and C–H bonds by Brønsted acid sites. Such structures were first proposed by Olah in the late sixties and are characterised by a pentacoordinated carbon or three-centre two-electron bond. Molecules of this nature, however, are extremely unstable and their direct detection has so far been limited to low temperature mass spectrometry experiments (14–16). As such, the existence of carbonium ions in the cracking mechanism has been proposed solely on the basis of the products thought to be formed from their collapse. The detection of the monomolecular reaction is further hindered by products of the bimolecular reaction which tend to dominate at high conversions (3, 6–8). Recent experimental work has thus tended to concentrate on small molecules at low conversion rates where primary reactions are prevalent and product distributions easier to analyze. Recently, several notable publications on butane cracking have been able to isolate the monomolecular mechanisms and have shown the first order products to be hydrogen, methane, and ethane (1, 2). These results can be attributed to the collapse of carbonium ions formed from the protonation of *sec*-C–H, *p*-C–C, and *sec*-C–C bonds, respectively.

The use of molecular orbital techniques can be of unique benefit in the study of such short-lived reaction systems as they allow us to look at not only reactive intermediates (in this case the carbonium ion) but also their formation and subsequent collapse. At present the route to C–H bond cracking remains elusive and hence the main body of this work concentrates on the complete characterisation of protolytic C–C bond attack. Finally a quantitative picture of the reaction rates and product distributions is proposed and applied to the cracking of butane and hexane.

METHODS

Previous theoretical work on this subject (11–13) has tended to concentrate solely on the study of the carbonium ion itself, using only a proton to represent the acid site. A model designed to map the complete reaction, however, must contain a more complex description of the acid and for this reason the basic model $H_3SiOHAlH_3$ (Fig. 1) was used. All calculations were performed on the SPARTAN (17) package running on a Silicon Graphics Indigo system. The AM1 method (18) was employed because of its superiority in representing carbonium ions when compared to all other semiempirical and *ab initio* methods with the exception of those incorporating correlation (19–21). The latter were considered too costly computationally. No constraints on symmetry were imposed on the structure at any point. The position of the transition states on the reaction coordinate was checked via optimisation on either side of the saddle point and by examination of their associated negative vibrational mode. All minima and saddle points were subject to full optimisation.

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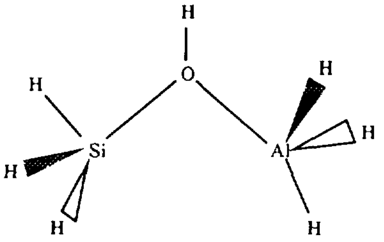

FIG. 1. Representation of the Brønsted acid site $H_3SiOHAlH_3$.

RESULTS AND DISCUSSION

Butane Cracking

n-Butane was investigated not only because it contains two different C–C bonds and thus provided us with a chance to compare the two possible reaction schemes theoretically, but also because it allowed comparison with experimental data. The cracking of the outer C–C bond is characterised in Figs. 2 and 3, which show the energetics and the relevant structures of the reaction profile. It must first be noted that the initial activation energy is clearly too high when compared with experimental data (1, 2), an error which can be linked to several factors. First, although the AM1 method may describe the system fairly well it must be appreciated that accurate energetics, especially those associated with transition state structures, where correlation is very important, are difficult to attain for all but the most sophisticated levels of theory. This should, however, have no effect on the qualitative description of the reaction profile. (A more subtle quantitative approach for calculating product distributions is also found to be possible and is explained in more detail later). Second, the cluster used in our studies is clearly an inadequate representation of a true acid site. Recent theoretical investigations into the acidity of H-ZSM-5 by Brand *et al.* (22), for example, have shown that large sections of the zeolite are needed (over 20 tetrahedral centres) to produce reasonable deprotonation energies. Such pieces are clearly infeasible for use in this type of study where the positions of discrete transition states are being sought. A further problem may be associated with the models lack of other tetrahedral oxygen (T(O)) atoms other than that connected with the acid site itself. This may cause trouble if alkane activation is a reaction driven by an acid–base type mechanism such as is associated with the protonation of ammonia (23) and alkenes (24) (i.e., where adjoining (TO) atoms provide a site for charge stabilisation of protonated species). Our results show this is not the case for alkane protonation, where complete charge separation occurs.

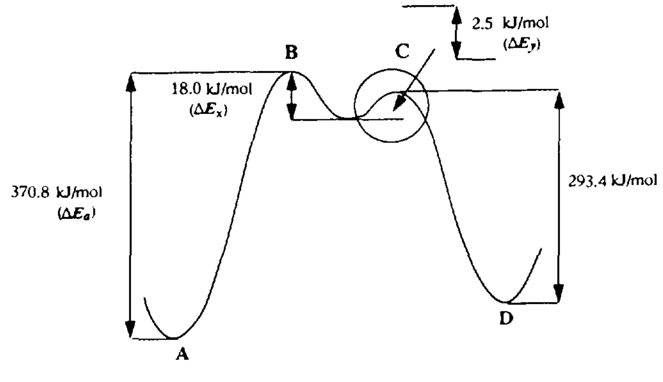

FIG. 2. Reaction profile for the cracking of the outer C–C bond of butane.

The text below describes the cracking of the outer C–C bond of butane (Fig. 3). Structure **A** shows the alkane situated above the acid site. The adsorption energy is, as expected, very low and is calculated to be only 1 kcal/mol. The transition structure **B** represents the approach of the proton to the C–C bond, which has lengthened from 1.52 to 1.99 Å. The O–H bond length has also increased to 1.72 Å, although this value can fluctuate depending on the C–C bond studied. Optimisation of **B** leads to the stable minimum **C** and the formation of the carbonium ion, the geometry of this ion and that of the deprotonated acid site being almost identical to that of their structures calculated separately. Mulliken and electrostatic charge analysis predict almost complete charge separation and an ionic bond of 82 kJ/mol is calculated to exist between the charges. The consequent transition state **D** which is formed shows the breaking of a three-centre C–H bond and is followed by the loss of a β-hydrogen (indicated in Fig. 3) from the resulting carbenium ion, thus producing an olefin **E.** The instability of the carbonium ion is further underlined here, as the breaking of the C–H bond involves an energy barrier of only 0.6 kcal/mol.

This result is pleasing as it is consistent with experimental data (1, 2). First, it prohibits the formation of propane, as there is no pathway for the collapse of the methyl ion; but more importantly, it implies that product distributions for a *wholly* monomolecular reaction will contain identical amounts of paraffins and their associated olefins. Experiments conducted by Haag and Kranilla (1) on butane led to similar conclusions and a more quantitative comparison with their results is shown below.

Figures 2 and 3 show the cracking of the outer C–C bond (producing methane and propene) and similar diagrams can be constructed for the cracking of the central C–C bond (producing ethane and ethane). From these two schemes it was then possible to construct a kinetic picture of the relative reaction rates of the two monomolecular routes to butane cracking. The production of meth-

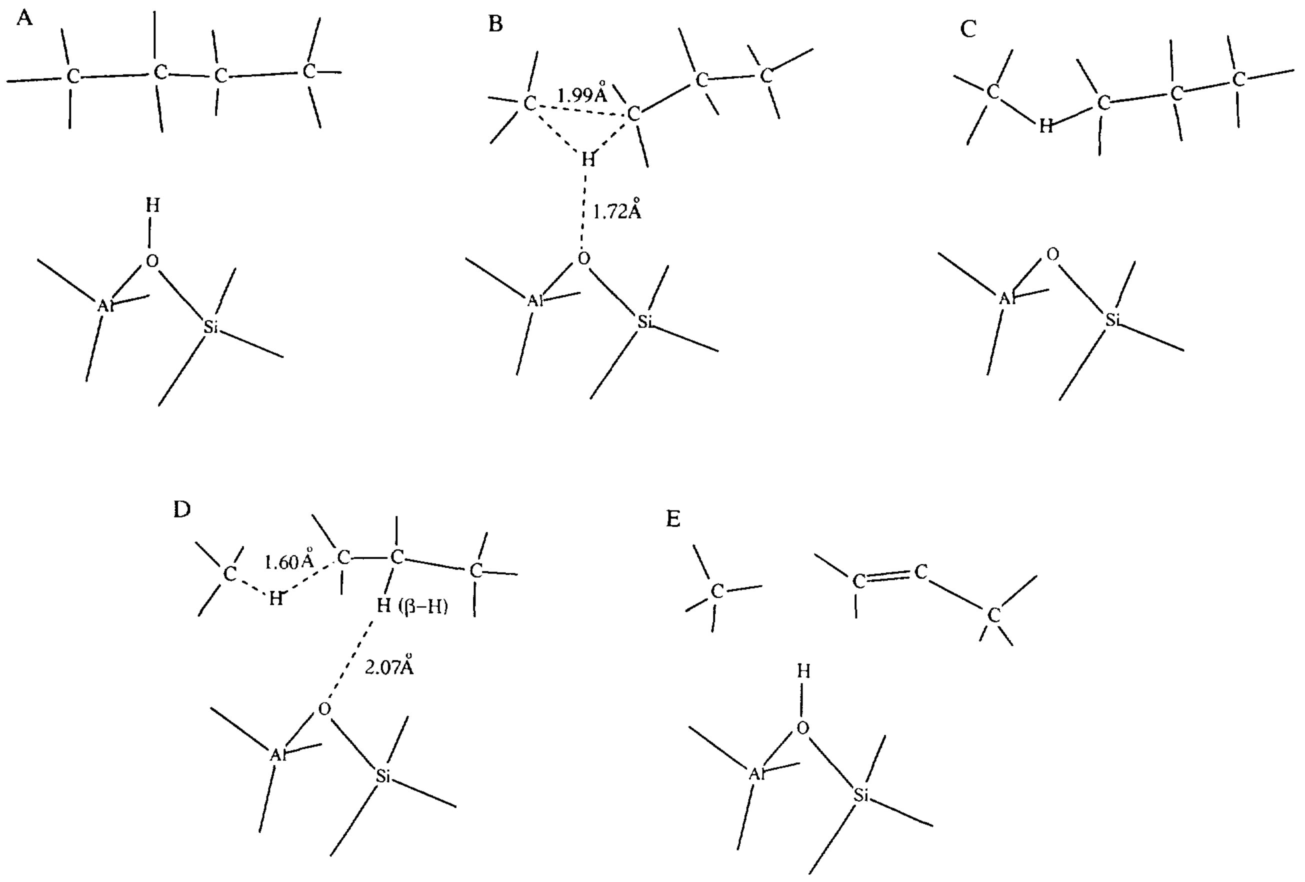

FIG. 3. Representation of the collapse of the carbonium ion by protonation of the outer C–C bond. The restoration of the acid site leads to two of the primary products, methane and propene.

ane and ethane can be expressed in the two rate equations below:

$$\frac{d[\text{methane}]}{dt} = k_a \cdot [\text{butane}]. \qquad [1]$$

$$\frac{d[\text{ethane}]}{dt} = k_b \cdot [\text{butane}]. \qquad [2]$$

Hence from [1] and [2]

$$\frac{d[\text{methane}]}{dt} \Big/ \frac{d[\text{ethane}]}{dt} = k_a/k_b. \qquad [3]$$

The rate constants k_a and k_b can then be calculated by the Arrhenius equation:

$$k_a = A_a \cdot \exp^{-\Delta E_a/RT}. \qquad [4]$$

$$k_b = A_b \cdot \exp^{-\Delta E_b/RT}. \qquad [5]$$

Hence from [4] and [5]

$$\frac{k_a}{k_b} = \frac{A_a}{A_b} \cdot \exp^{-(\Delta E_a - \Delta E_b)/RT}. \qquad [6]$$

Problems that may have been associated with the size of the activation energies are hence overcome as the relative rates of the two possible reactions are defined by the *difference* in activation energies and not their implicit size; i.e., the error in the predicted stability of the deprotonated piece is due to the nature of the acid site alone and not to the specifics of a reaction. Hence the subtraction of two energies calculated for the same site by a particular level of theory will result in the cancellation of the particular error.

The values of the pre-exponential Arrhenius constants can be represented in terms of the entropy of activation ΔS^{act}. Entropies were calculated via statistical thermodynamics using a set of normal vibrational frequencies:

$$\frac{A_a}{A_b} = \exp^{(\Delta S_a^{\text{act}} - \Delta S_b^{\text{act}})/R}. \qquad [7]$$

The treatment above, however, does not take into account the possible back reaction afforded by the collapse of the carbonium ion back to the reactant alkane. This can be treated in a similar manner as before where the fraction of molecules completing the reaction (for the case of the outer bond) is given by $k_y/(k_y + k_x)$ (Fig. 2), where

$$\frac{k_y}{k_x} = \frac{A_y}{A_z} \cdot \exp^{-(\Delta E_y - \Delta E_x)/RT}. \qquad [8]$$

Last, the value for A_a is doubled, as experimental calculations are specific to the whole molecule, where there are two primary bonds to one secondary C–C bond. The final values of k_a and k_b are then used to calculate the mol% of primary products and are recorded in Table 1.

The theoretical results show good agreement not only with the experimental product distributions but also with the individual factors of activation energy and the pre-exponential factor. Results show how the selectivity is controlled by two forces; the middle bond is favoured due to the greater stability of the carbonium ion formed while the reaction of the outer bond is driven by the larger disorder of the transition state. It was therefore concluded that, apart from the appearance of steric factors for larger alkanes and fluctuations in the entropic contribution, by and large, product *distributions* are subject to the nature of the alkane studied and independent of the acid medium used. As such the primary products can be characterised simply by functions like Eq. [6] for all reaction conditions. The confidence instilled in the method coupled with its relative simplicity thus presented us with an opportunity to investigate the cracking of larger alkanes where experimental evidence is not so clear.

Hexane Cracking

Unlike butane, the cracking of hexane is harder to define. This is due to the difficulty, even at low conversions, of confining the bimolecular mechanism. Distributions of products hence tend to depend to a large degree on reaction conditions and the olefin/alkane ratio expected from a purely monomolecular reaction is rarely observed. Attempts to rationalize results by assignment of products to the individual mechanism are subject to personal interpretation and comparisons with theoretical results are, as such, open to a wider discussion. Recent work by Meusinger *et al.* (2), however, reports that results for the cracking of hexane indicate that paraffin products can be attributed solely to the monomolecular reaction. Theoretical results were calculated as shown in Table 2. Experimental results were recorded for a number of SAPOs (whose basic acid site can be represented as in Fig. 1) and as such the data were expressed as an average of all results.

TABLE 2

Summary of Theoretical Data for the Cracking of Hexane

Bond	Property (calculated at 773 K and 1 atm)[a]			
	A_a/A_x	$(\Delta E_a - \Delta E_x)$/kJ/mol	k_a/k_x	mol% of product
Outer (methane)	1.0	0.00	1.0	31
Second (ethane, butane)	2.78	9.01	0.67	46 (23, 23)
Middle (propane)	4.54	8.03	1.33	23

[a] A_a, ΔE_a, and k_a represent the properties of the outer bond while A_x, ΔE_x, and k_x are the properties of the respective bonds quoted.

Here again theoretical and experimental results are in good agreement, the only anomaly being the large amount of butane predicted by the model. This may be linked with an underestimation of the energy barrier representing the collapse to butane, which was in fact found to be identical to that for ethane formation. Looking back at the individual values of the rate constants (Table 3) we can see that, as in butane cracking, central bonds are energetically favoured, in contrast to the outer bonds, where the reaction producing methane is mainly driven by the high entropies of activation resulting from the disorder of the transition states. Further vindication of the

TABLE 1

Comparison of Theoretical and Experimental Kinetic Data for the Cracking of Butane

Acid site	Property (calculated at 769 K and 1 atm)			
	A_a/A_b	$(\Delta E_a - \Delta E_b)$/kJ/mol	k_a/k_b	mol% ethane/methane
$H_3SiOHAlH_3$ (AM1)	5.26	10.4	1.0	49/51
Expt.[a]	3.23	8.0	1.1	52/48

[a] Ref.(1).

TABLE 3

Primary Product Distributions for Hexane Cracking

	mol% of product	
	AM1	Expt.[a]
Methane	31	36
Ethane/butane	23/23	25/9
Propane	23	30

[a] Ref.(2).

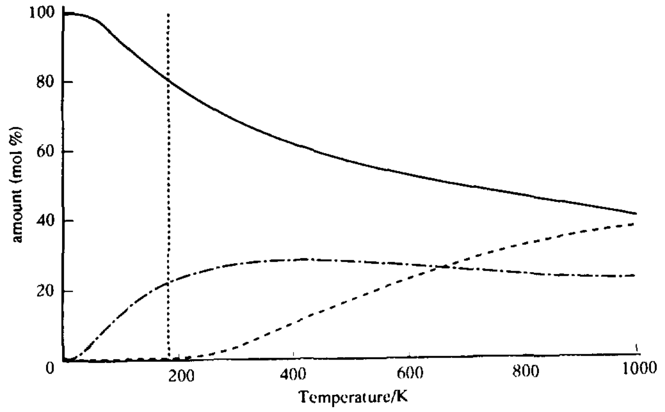

FIG. 4. Plot of product distribution against temperature. (---) = methane, (—·—) = ethane + butane, (——) = propane. The vertical line indicates the product distribution at 195 K.

results can be sought by the analysis of the temperature dependence of the molar selectivity. Resulting calculations show that the ratio A_a/A_x is unaffected by temperature, leaving the relative reaction rates to be defined by single Boltzmann functions controlled by differences in activation energies. Results are displayed in Fig. 4 and show the three competitive exponential functions. At high temperatures the expression $\exp(-\Delta E/RT) \rightarrow 1$ and the product distributions hence tend to the values expressed by the entropic ratios, which explains the small variance of the mol% in the temperature range 750 → 850 K as noted by Meusinger *et al.* (2). As the temperature decreases, however, the reaction becomes dominated by those products resulting from the lowest energy transition state. This is highlighted by the rapid decrease in the mol% of methane and the subsequent rise in ethane and butane production. Information from the graph was then used to compare results with those found by Olah *et al.* (25), whose work on the protolytic cracking of hexane was carried out at around 195 K. Their findings were that the product distributions were in the order

$$(C_4H_{10} + C_2H_6) > C_3H_8 \gg CH_4.$$

This is echoed by the theoretical model and indicates that the predicted ordering of the activation energies is correct and hence subsequently the ordering in magnitude of the pre-exponential constants of the Arrhenius equation.

CONCLUSION

First, and most importantly, the theoretical model serves to validate and explain all the steps of the monomolecular C–C cracking reaction and allows us to witness them at a molecular level. Such evidence is invaluable in defining not only the systems reviewed here but also for a whole range of paraffins to which it can be equally applied. The surprising accuracy with which the model predicts the mol% of products not only shows a success for the AM1 molecular orbital method but also adds further evidence that, while activation energies are dependent largely upon the acidity of the site, the actual distribution of products depends only on the relative basicity of the C–C bonds themselves. From this it also follows that the lower activation energies noted for the central bonds in the cracking of both hexane and butane are due to the greater electron density around them. This effect is somewhat balanced by the higher entropy of activation for the outer bonds of both molecules. The two effects of both entropy and enthalpy of activation are being investigated for higher alkanes alongside continued efforts to characterise the pathway for C–H attack.

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