JOURNAL OF CATALYSIS 77, 159–168 (1982)

A Kinetic Study of the Cracking, Isomerization, and Disproportionation of *n*-Heptane on a Chromium-Exchanged Y Zeolite

A. CORMA,[1] A. LÓPEZ AGUDO, I. NEBOT,* AND F. TOMÁS*

*Instituto de Catálisis y Petroleoquímica, Consejo Superior de Investigaciones Científicas, Madrid 6, Spain, and *Departamento Química Física, Facultad de Ciencias, Universidad de Valencia, Valencia, Spain*

Received July 1, 1981; revised Februay 24, 1982

The kinetic rate constants for the cracking, isomerization, and disproportionation of *n*-heptane over a CrHNaY (32% chromium exchanged) zeolite catalyst at 400, 450, and 470°C have been calculated. The interaction of *n*-heptane with a model Lewis acid such as BF_3 and progress along the reaction coordinate have been studied by means of molecular orbital calculations. From the kinetic results, i.e., activation energies and frequency factors, and the theoretical calculations, it can be concluded that the controlling step in these reactions is not the formation of the carbonium ion, but the subsequent transformation of this carbonium ion. In addition, the theoretical calculations show that the attack of a Lewis acid is more likely to occur on a carbon atom than on a C–H bond.

INTRODUCTION

Paraffin (alkane) cracking has been frequently chosen as a test reaction to measure the activity of different zeolite catalysts (*1–7*). The kinetics of the cracking of paraffins has been studied in many cases by measuring the rate of disappearance of the reactant (*1*, *8*). It has been shown in a previous paper (*9*) that such a method of measuring rates is inadequate since cracking is generally accompanied by other secondary reactions. A second problem with cracking reactions arises from the fact that the activity of the catalyst is strongly dependent on time on stream and, consequently, it is not surprising to find in the literature different values for the activity and activation energy depending on the time at which the activity was measured (*8*).

Despite the commercial importance of paraffin cracking and isomerization, these reactions are not well understood mechanistically. Even though the carbonium ion theory is generally used to explain satisfactorily the distribution of reaction products, in the case of paraffins the mechanism of the initiation step, i.e., the formation of the carbonium ion, is still a subject of discussion (*10*, *11*). Some authors (*10–14*) have considered that the initial carbonium ion is produced by proton donation to thermally produced olefinic species by a Brønsted acid site. In the view of others, however, the activation of paraffins requires hydride abstraction by a Lewis acid site on the catalyst surface or by a very strong Brønsted acid site (*10–12*, *14–17*). The protonation of a saturated hydrocarbon by a strong proton-donor acid has also been suggested (*10*, *18*) as a mechanism of carbonium ion formation. The attack by a Brønsted acid site to break a C–C bond may involve in this case a pentacoordinate intermediate homolog of CH_5^+ (*18*).

In the present work, the kinetic rate constant, frequency factors, and activation energies for the cracking and the accompanying isomerization and disproportionation reactions of *n*-heptane on a chromium-exchanged Y zeolite have been calculated in the absence of deactivation. The interaction of *n*-heptane with a strong Lewis acid such as BF_3 and progress along the reaction

---

[1] To whom all correspondence should be addressed.

0021-9517/82/090159-10$02.00/0

coordinate have been studied by means of molecular orbital calculations. From these theoretical calculations and the kinetic studies a new model for the formation of the carbonium ion in paraffin cracking is proposed.

METHODS

Molecular Orbital Calculations

For the theoretical calculations, standard geometries for the *n*-heptane molecule have been chosen (*19*). The geometry of BF_3 has been optimized by *ab initio* methods included in the program. The method of Bertrán *et al.* (*21*) has been used to calculate the interaction energy between BF_3 and *n*-heptane. This method gave satisfactory results for the approximation channels between the two reactants (*21, 22*). The wave functions, net atomic charges, and transition energies to excited states for these two molecules have been calculated by the CNDO/S method (*23*). More specifically, the CNDO/M (*24*) program with the parameterization implicit in it, and with expansion of the calculation to the 60 lower monoexcitations, has been used. Calculations involving the formation or breaking of C–H bonds have been carried out by the MINDO/3 method (*25*) with the program set GEOMO (*26*) and the standard parameterization implicit in the program. Also, the geometrical configurations of hydrocarbons and intermediates have been optimized by the gradient based method developed by Rinaldi (*27*) and included in the same program set GEOMO.

KINETIC CALCULATIONS

Cracking Reactions

Following the literature (*8, 17*), a first-order kinetic equation has been used to fit the overall cracking results, i.e., cracking to $C_3 + C_4$ plus $C_2 + C_5$

$$-\ln(1 - x) = k_l[S]\tau = k_l[S_0]\theta\tau \quad (1)$$

where x is the fraction of *n*-heptane cracked, k_l is the overall kinetic rate constant, [S] is the concentration of active sites at each time on stream, $[S_0]$ is the concentration of active sites at zero time on stream, τ is the contact time, and θ is the fraction of active sites available for cracking ($[S]/[S_0]$. In Eq. (1) the expansion factor has not been introduced since in the range of working conversions the changes in volume are generally small and it can be considered negligible. However, since the activity of the catalyst decays with time, the fraction of active sites available will be a function of the time on stream. We have used here the following decay equation:

$$\frac{-d\theta}{dt} = k_d\theta \quad (2)$$

which has been reported to fit the decay with paraffinic feeds (*28, 29*).

Integrating Eq. (2) between time zero and the final time on stream t_f yields

$$\theta = e^{-k_d t_f} \quad (3)$$

where k_d is a kinetic decay constant.

Introducing (3) in (1), we obtain

$$-\ln(1 - x) = k_l[S_0]e^{-k_d t_f}\tau. \quad (4)$$

The time on stream is related to the contact time by

$$\tau = P \cdot b \cdot t_f \quad (5)$$

where P is the catalyst/oil ratio in g/g, and b is a proportionality constant.

Introducing (5) in (4),

$$-\ln(1 - x) = k_l[S_0]e^{-k_d t_f}Pbt_f \quad (6)$$

where x is the instantaneous conversion, although experimentally only average conversions $\bar{x}$ were obtained. They are related by the following equation:

$$\bar{x} = \frac{1}{t_f}\int_0^{t_f} x\,dt. \quad (7)$$

In Eq. (6) k_l is the kinetic rate constant for the overall cracking, i.e., $k_l = k_{C_2+C_5} + k_{C_3+C_4}$ and was calculated by fitting the experimental conversion values to Eqs. (6)

and (7). The values for $k_{C_2+C_5}$ and $k_{C_3+C_4}$ can be calculated by taking into account the initial selectivities (IS) for the two cracking reactions yielding $C_2 + C_5$ and $C_4 + C_3$, obtained previously (*9*), and the following equations:

$$k_{C_2+C_5} = \frac{k_1[S_0] \cdot IS_{C_2+C_5}}{IS_{C_2+C_5} + IS_{C_4+C_3}} \quad (8)$$

$$k_{C_3+C_4} = k_1[S_0] - k_{C_2+C_5}. \quad (9)$$

Isomerization and Disproportionation Reactions

It is generally accepted that catalytic isomerization of paraffins is a first-order reaction with respect to the hydrocarbon concentration (*30*), which can be represented by

$$r_2 = k_2[S_0]C. \quad (10)$$

The disproportionation of paraffins is, however, a bimolecular reaction which presumably occurs via a Rideal mechanism instead of a Langmuir–Hinshelwood mechanism, since the latter would involve the interaction between two carbonium ions. Thus, one can write the following rate equation for the disproportionation reaction

$$r_3 = k_3[S_0]C^2. \quad (11)$$

Considering these two reactions and the cracking reaction ($r_1 = k_1[S_0]C$), the initial overall rate of loss of *n*-heptane at zero catalyst age can be expressed as:

$$-r_{n\text{-hep}} = C_0[S_0]\left[\sum_{i=1}^{i=2} k_i + C_0k_3\right] \quad (12)$$

where C_0 is the initial concentration of *n*-heptane. It is clear that the ratio between the rate of each reaction and the total rate of disappearance of *n*-heptane will be the initial selectivity for the products of that particular reaction:

$$(IS)_i = \frac{r_i}{-r_{n\text{-hep}}} = \frac{k_i[S_0]C_0}{C_0[S_0]\left[\sum_{i=1}^{i=2} k_i + C_0k_3\right]}. \quad (13)$$

This equation can be further simplified since in this work C_0 was maintained constant at 1 atmosphere. Consequently

$$\frac{r_i}{-r_{n\text{-hep}}} = k_i[S_0]/[S_0]\left[\sum_{i=1}^{i=2} k_i + C_0k_3\right]. \quad (14)$$

In this equation we know the initial selectivity (obtained experimentally), and the kinetic rate constant ($k_i[S_0]$) for the overall cracking reaction can also be calculated. Thus, the total rate of disappearance of *n*-heptane can be calculated from Eq. (14). Now, knowing the total rate of disappearance of *n*-heptane and the initial selectivities for the disproportionation and isomerization reactions, the kinetic rate constants for these two reactions can also be calculated with Eq. (14).

EXPERIMENTAL

The materials, as well as the catalyst preparation and the experimental procedure, have been previously reported (*9*). Samples of 1–3 g of CrHNaY zeolite, with 32% chromium exchange, were used. These were loaded in a glass tube and operated as an integral flow reactor. The *n*-heptane flow rate was varied from 1.10 to 1.846 g hr^{-1}. In a series of preliminary experiments it was established that in these conditions and by using a catalyst particle size of 80–120 mesh the rate of reaction is not controlled by either external or intraparticle diffusion.

In order to determine the extent of thermal cracking of *n*-heptane in the conditions used in this study, some experiments were performed in the absence of catalyst. It was found that at the higher temperature, 470°C, and slower flow rate used in this study the maximum thermal cracking conversion of *n*-heptane was less than 3%;

hence no corrections of the catalytic data reported have been attempted.

The kinetics of the n-heptane cracking reaction were studied at the reaction temperatures of 400, 450, and 470°C. The cumulative average yield for each product at different times on stream and constant space velocity were calculated from the average yields obtained, taking samples at regular intervals during the run (*9*). From these values at constant space velocity, the cumulative average yields at various constant catalyst/oil ratios were also calculated using the relationship between space velocity, catalyst/oil ratio, and time on stream (*31*). Also, to minimize the effect of secondary cracking reactions, only low conversion data (generally under 20%) were used. The cracking conversion data were taken as one-half of the sum of the previously corrected C_2,C_5 and C_3,C_4 fractions. The corrections of these fractions were made considering that the direct cracking reaction of n-heptane is accompanied by disproportionation reactions which also yield C_3, C_4, and C_5 hydrocarbons (*9*).

RESULTS AND DISCUSSION

Cracking Reactions

The corrected experimental cumulative average yields for the cracking products ($\bar{x}_{exp}$) at different catalyst/oil ratios and times on stream are summarized in Table 1. By fitting the $\bar{x}_{exp}$ data to Eqs. (6) and (7), the initial kinetic rate ($k_1[S_0]$) and decay (k_d) constants for n-heptane cracking obtained at the three temperatures used in this work are given in Table 2. For comparison purposes the average yields for cracking products predicted theoretically ($\bar{x}_c$) from Eqs. (6) and (7) are presented in Table 1. These values agree satisfactorily with the experimental data. The total rate of disappearance of n-heptane, as well as the initial kinetic rate constants for the dispropor-

TABLE 1

Experimental (ex) and Calculated (c) Average Yields for the Cracking of n-Heptane on a CrHNaY-32 Zeolite

Temperature											
400°C				450°C				470°C			
Cat/oil (w/w)	Time on stream (min)	$\bar{x}_{ex}$[a]	$\bar{x}_c$[b]	Cat/oil (w/w)	Time on stream (min)	$\bar{x}_{ex}$	$\bar{x}_c$	Cat/oil (w/w)	Time on stream (min)	$\bar{x}_{ex}$	$\bar{x}_c$
0.36	90.0	1.55	2.34	0.36	90.0	7.18	7.74	0.22	150.0	11.98	9.52
	150.0	4.81	3.87		180.0	10.19	11.09	0.27	120.0	12.35	9.61
	180.0	3.61	4.62		180.0	10.05	11.09	0.36	90.0	12.34	9.87
	195.0	3.28	4.99	0.43	150.0	10.27	11.23	0.40	180.0	18.53	19.00
0.40	255.0	9.42	7.18		150.0	10.89	11.23	0.48	150.0	19.02	19.50
0.43	150.0	3.72	4.60	0.52	120.0	11.16	11.26	0.80	90.0	19.24	20.50
0.52	105.0	3.53	3.99		120.0	11.40	11.26	0.83	120.0	24.97	26.47
	135.0	3.89	5.09	0.69	90.0	10.36	10.93				
0.65	90.0	3.84	4.43		90.0	11.31	10.93				
	105.0	3.52	4.86		150.0	18.10	17.46				
	165.0	6.90	7.52	0.77	120.0	17.90	16.00				
0.77	135.0	7.06	7.26								
0.91	270.0	15.89	16.27								
1.16	90.0	7.41	7.25								
	210.0	16.56	16.34								

[a] $\bar{x}_{ex}$ corresponds to the corrected experimental value $\bar{x}$ in Eq. (7).

[b] $\bar{x}_c$ corresponds to the value $\bar{x}$ calculated from Eq. (7).

tionation and isomerization reactions of *n*-heptane, determined by means of Eq. (14) and the corresponding values of initial selectivities (IS) from Table 2, are also given in this table. From the values of the kinetic rate constants of all the above mentioned reactions at the three reaction temperatures, the apparent activation energies and frequency factors were calculated and are presented in Table 3. The value for the overall cracking is 21.8 kcal mol^{-1}. Maatman *et al.* (*8*) reported for the cracking of *n*-heptane on a rare-earth X zeolite 16.3, 19.6, and 22.7 kcal mol^{-1} as the apparent activation energies at 30, 15, and 0 min of reaction time, respectively. Considering the errors associated with the determination of the activation energy, which will be even larger for a decaying catalyst, it can be accepted that the activation energies for the cracking of *n*-heptane on a rare-earth X and on a CrHNaY zeolite are the same. This implies that the nature of the active sites involved in the cracking of *n*-heptane on both rare-earth exchanged X zeolite and CrHNaY zeolite is the same. The difference in activity between the two catalysts would then be related to the total number of active sites rather than to the nature of these active sites. This result would, in turn, confirm the idea that, even though it is possible to see a wide range of acid strengths in zeolite catalysts by titration methods, only a small fraction of these sites plays an important role in the cracking of *n*-heptane. The decay constant for the cracking of *n*-heptane at 470°C has been found to be 16.79 × 10^{-4} sec^{-1}. This value can be compared with the values of 34.5 × 10^{-4} and 24.9 × 10^{-4} sec^{-1} reported for the cracking of a paraffinic gas–oil on an ultrastable HY and a La-exchanged Y zeolite, respectively, at 480°C (*15*).

TABLE 2

Initial Kinetic Rate Constants for Primary Reactions in the Catalytic Cracking of *n*-Heptane on a CrHNaY-32 Zeolite

Reaction	400°C				450°C				470°C			
	IS[a]	$k_i[S_0] \times 10^4$ $\frac{(\mathrm{mol}^{2-n})^b}{(\mathrm{g}^{2-n} \cdot \mathrm{sec})}$	$k_d \times 10^4$ (sec^{-1})	Total rate (× 10^4)	IS[a]	$k_i[S_0] \times 10^4$ $\frac{(\mathrm{mol}^{2-n})^b}{(\mathrm{g}^{2-n} \cdot \mathrm{sec})}$	$k_d \times 10^4$ (sec^{-1})	Total rate (× 10^4)	IS[a]	$k_i[S_0] \times 10^4$ $\frac{(\mathrm{mol}^{2-n})^b}{(\mathrm{g}^{2-n} \cdot \mathrm{sec})}$	$k_d \times 10^4$ (sec^{-1})	Total rate (× 10^4)
Global cracking	0.47	7.87 ± 2.42	0.8	16.74	0.59	21.64 ± 2.00	10.47	36.68	0.62	37.42 ± 5.62	16.79	60.35
Cracking to $C_2 + C_5$	0.09	1.51			0.14	5.14			0.23	13.88		
Cracking to $C_3 + C_4$	0.38	6.36			0.45	16.50			0.39	23.88		
Disproportionation	0.32	0,95 × 10^{-4}			0.30	1.82 × 10^{-4}			0.26	2,61 × 10^{-4}		
Isomerization	0.17	2,85			0.11	4.04			0.09	5.43		

[a] IS is the initial selectivity taken from Ref. (*9*).

[b] *n* is the reaction order.

Reaction Mechanism

Rate-controlling step. The cracking, isomerization, and disproportionation reactions are believed to occur through a carbo-

TABLE 3

Activation Energies and Frequency Factors for the Initial Rate Constant for the Reactions in the Cracking of *n*-Heptane on a CrHNaY-32 Zeolite

Reaction	Order of reaction	Activation energy (kcal/mol)	Frequency factor × $[S_0]$ (mol/g · sec)
Global cracking	1	21.8	8.06×10^3
Cracking to $C_2 + C_5$	1	30.0	6.94×10^5
Cracking to $C_3 + C_4$	1	18.7	6.68×10^2
Disproportionation	2	14.0	3.21×10^{-4}
Isomerization	1	8.7	1.78×10^{-1}

nium ion mechanism. A common step for these three reactions would then be the formation of the carbonium ion. As can be seen in Table 3, the activation energies for the three reactions are different. Thus, from these results two hypotheses can be made regarding the reaction mechanism. (i) If the formation of the carbonium ions were the rate-controlling step, a series of different carbonium ions would form on the catalyst surface, one type causing cracking, another isomerization, another disproportionation, another hydrogen transfer, another coking, etc. (ii) If it is assumed that the three reactions have a common carbonium ion intermediate which, once formed, can decompose, rearrange, or undergo a bimolecular disproportionation with a neutral molecule, it seems evident that the rate-controlling step would not be the formation of the carbonium ion but the cracking of the carbon chain or its rearrangement.

Current opinion, however, holds that the formation of the carbonium ion is the slowest step in the surface-catalyzed reaction sequence of paraffin cracking (*10*). This is based on the fact that olefins can form carbonium ions more easily than paraffins, which is the supposed explanation of the former cracking faster than the latter. To arrive at this conclusion it is necessary to assume that the carbonium ions formed on a paraffin and on an olefin behave equivalently and, furthermore, that the acid sites involved in both paraffin and olefin cracking reactions are the same. These assumptions have neither been satisfactorily proved, nor do they seem to be obvious.

An attempt to bring some light on these questions, particularly for the cracking reactions, has been made by means of molecular orbital calculations. The energies of formation of different carbonium ions, which can be formed on *n*-heptane by abstraction of a hydride ion by a model Lewis acid such as BF_3, have been calculated by the MINDO/3 method.

In the calculations all geometric parameters associated with the carbonium ion have been optimized. The results are summarized in Table 4. From these values it is clear that the most stable carbonium ion is that corresponding to the carbon number 4, which upon scission produces $C_2 + C_5$. However, its energy of formation is only 0.6 and 1.5 kcal/mol lower than that for carbon number 3 and carbon number 2, respectively, both of them producing by rupture $C_3 + C_4$. Therefore, if the controlling step in the cracking reaction were the formation of the carbonium ion we should expect a difference in the activation energies for the cracking reactions

$$C_7 \rightarrow C_5 + C_2$$

$$C_7 \rightarrow C_4 + C_3$$

much lower than the experimental value of

TABLE 4

Relative[a] Values for Enthalpy of Formation of the Different Carbonium Ions Which Can Be Formed from *n*-Heptane

Carbonium ion	ΔH (kcal/mol)
C_1^+	19.0
C_2^+	1.5
C_3^+	0.6
C_4^+	0.0

[a] Energy values are referred to the C_4^+ ion.

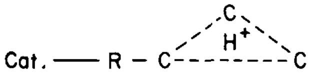
11.3 kcal/mol (see Table 3). Consequently, we believe that the rate-controlling step in the cracking of paraffins is the rupture of the C–C bond and not the formation of a carbonium ion. It must, however, be noted that the apparent activation energies given in Table 3 are not the activation energies for the rate-controlling step but the sum of the heat of formation of the intermediate carbonium ion and the activation energy for the controlling step.

We arrive at the same conclusion by examining the values of the entropy factors given in Table 3. From the transition state theory (*32*), in a catalytic reaction the frequency factor (A) is given by:

$$A = [S_0]\,\frac{k}{h}\,e^{\Delta S^{\#}/R}$$

where $[S_0]$ is the initial concentration of active sites, k is Boltzmann's constant, h is Planck's constant, and $\Delta S^{\#}$ is the entropy of activation. Table 3 shows that the frequency factor is higher for cracking than for isomerization or disproportionation. If the active sites involved in the formation of the carbonium ion in the three reactions are the same, then the differences in the value of the frequency factor for the three reactions should be related to the entropy factor. This entropy factor is higher for cracking than for isomerization or disproportionation. From these results we can conclude that energy requirements favor isomerization and disproportionation over cracking, while cracking is favored by the entropy. Furthermore, because of the difference in both activation energy and frequency factor, the relative rates for the three reactions will be temperature dependent, as will be the ratio of their initial yields. Therefore, cracking has the most favorable ΔS (A factor) of the three processes and hence should become increasingly favored as temperature increases.

The entropy results are in agreement with the idea that the isomerization, contrary to cracking, would take place without separation from the molecule of the methyl group which is going to migrate. In other words, as has been suggested (*33, 34*) during isomerization a new carbon–carbon bond is being formed at the same time that the former bond is breaking, presumably via a protonated cyclopropane complex.



Mechanism of carbonium ion formation. As indicated before, several authors have considered that the carbonium-ion formation from a paraffin requires the abstraction of a hydride ion by an acid site. We have studied theoretically this possibility by interacting the *n*-heptane molecule with BF_3, which is a typical strong Lewis acid.

Figure 1 shows the isoenergetic lines for the *n*-heptane–BF_3 interaction corresponding to the approach of the BF_3 molecule in parallel planes to those presented as planes A and B in Fig. 2. The BF_3 molecule has been maintained always parallel to the referred planes, and the position of the boron atom is indicated. No interaction channels of the Lewis acid site (boron atom) toward the hydrogen atoms can be observed. There are, however, clear interaction channels conducting the BF_3 to the carbon atoms in the opposite direction to the C–H bonds. The minima of energy are located over carbon 4 and over the symmetric equivalent carbons 2 and 6. Interaction on carbons 3 and 5 is also possible but energetically less probable. These results indicate that the attack of a Lewis acid site (or also a strong Brønsted site) is more likely to occur on a carbon atom than in the C–H bond, which would be expected according to the classical mechanism of carbonium ion formation via hydride abstraction. Thus, based on these results, the formation of a carbonium ion seems to take place via a pentacoordinate complex formed on a carbon atom of the paraffinic chain as illustrated in Fig. 3.

In other words, and generalizing this observation, the carbonium ion formation

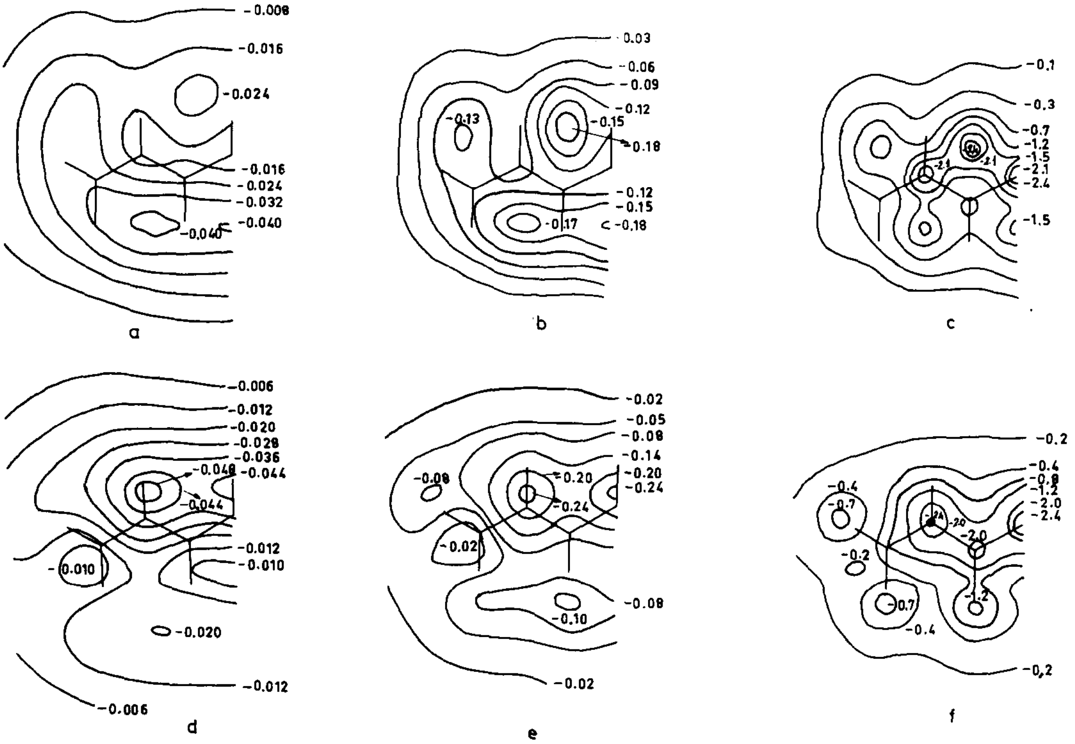


FIG. 1. Maps of isoenergetic (kcal mol^{-1}) lines for the van der Waals interaction between BF_3 and *n*-heptane. Distance (Z) from the BF_3 plane to the A plane: $Z = -3$ Å. (a); $Z = -2$ Å (b); $Z = -1$ Å (c). Distance from the BF_3 plane to the B plane: $Z = +3$ Å (d); $Z = +2$ Å (e); $Z = +1$ Å (f).

could be considered to occur by interaction of a carbon atom with the sites in the catalyst with positive density of charge or sites with electronic defects. These sites are able to interact with the carbon atoms and to produce their polarization. In some cases this polarization may be large enough to give rise to the carbonium ion produced usually in carbonium ion type reactions.

On the basis that the energy minima

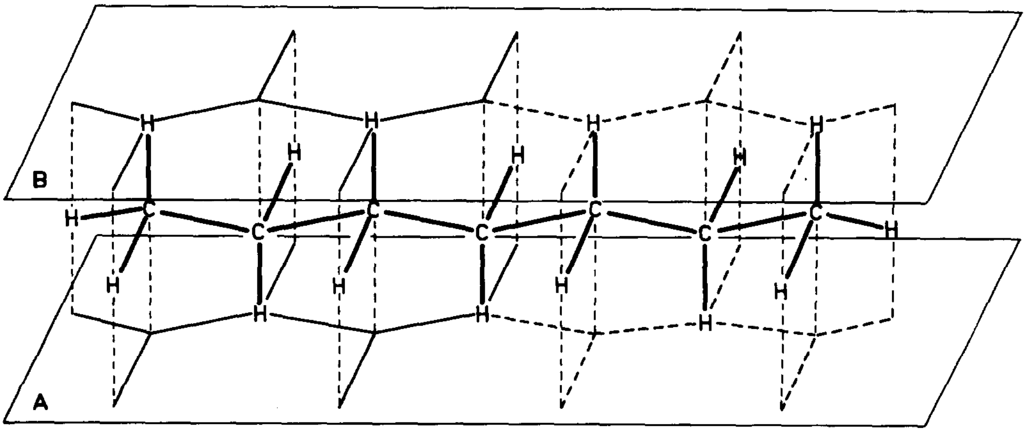


FIG. 2. Spatial orientation of the *n*-heptane molecule. The planes A and B are those referred to in Fig. 1.

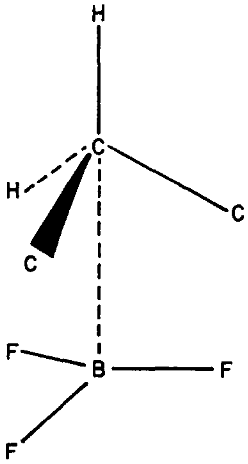


FIG. 3. A probable model for the interaction of *n*-heptane with BF_3.

shown in Fig. 1 are quite similar, and assuming that the rate of cracking is directly proportional to the number of carbonium ions, i.e., to the number of interaction complexes between *n*-heptane and BF_3, it would be expected, in a first approximation, that the rate of formation of $C_3 + C_4$ should be at least twice as high as that for the formation of $C_2 + C_5$. This conclusion is consistent with the observations deduced from the values of the kinetic rate constants given in Table 2.

CONCLUSIONS

In the present work the kinetic rate constants and activation energies for cracking, isomerization, and disproportionation of *n*-heptane on a CrHNaY-zeolite have been calculated. The activity of this catalyst for cracking of *n*-heptane decays about twice as slowly than that of a HY or a LaY zeolite for cracking of a paraffinic gas–oil. It has also been found that the rate-controlling step in cracking does not seem to be the formation of the carbonium ion, but the C–C bond breaking. Furthermore, the theoretical calculations effected show that the formation of the carbonium ion by a Lewis acid may more probably occur by direct attack on a carbon atom by the Lewis acid site than by hydride abstraction. This attack may produce a positive polarization of the carbon atom.

ACKNOWLEDGMENT

We gratefully acknowledge the help of Dr. C. Gutierrez in the preparation of the manuscript.

REFERENCES

1. Weisz, P. B., and Miale, J. N., *J. Catal.* **4,** 527 (1965).
2. Miale, J. N., Chen, N. Y., and Weisz, P. B., *J. Catal.* **6,** 258 (1966).
3. Tung, S. E., and McInich, E., *J. Catal.* **10,** 166 (1968).
4. Pickert, P. E., Rabo, J. A., Dempsey, E., and Schomaker, V., Proc. Intern. Congr. Catalysis, 3rd (Amsterdam 1964), Vol. 1, p. 714. North-Holland, Amsterdam, 1965.
5. Eastwood, S. C., Plank. C. J., and Weisz, P. B., *Proc. Eighth World Petroleum Congress* **4,** 245 (1971).
6. Oblad, A. G., *Oil Gas J.* **70,** 84 (1972).
7. Barthomeuf, D., and Beaumont, R., *J. Catal.* **30,** 288 (1973).
8. Maatman, R., Friesema, C., Mellema, R., and Maatman, J., *J. Catal.* **47,** 62 (1977).
9. López Agudo, A., Asensio, A., and Corma, A., *J. Catal.* **69,** 274 (1981).
10. Gates, B. C., Katzer, J. R., and Schuit, G. C. A., "Chemistry of Catalytic Processes," p. 31. McGraw–Hill, New York, 1979.
11. Jacobs. P. A., "Carboniogenic Activity of Zeolites," p. 109. Elsevier Scientific Publishing Company, Amsterdam, 1977.
12. Weisz, P. B., *Annu. Rev. Phys. Chem.* **21,** 175 (1970); *Chem. Tech.* 498 (1973).
13. Scherzer, J., and Ritter, R. E., *Ind. Eng. Chem. Prod. Res. Dev.* **17,** 219 (1978).
14. Greensfelder, B. S., Voge, H. H., and Good, G. M., *Ind. Eng. Chem.* **41,** 2573 (1949).
15. Borodzinski, A., Corma, A., and Wojciechowski, B. W., *Canad. J. Chem. Eng.* **58,** 219 (1980).
16. Venuto, P. B., and Habid, E. T., "Fluid Catalytic Cracking with Zeolite Catalysts," p. 104. Marcel Dekker, New York, 1979.
17. Voge, H. H., *in* "Catalysis" (P. H. Emmett, Ed.), Vol. VI, p. 407. Reinhold, New York, 1958.
18. Poutsma, M. L., *in* "Zeolite Chemistry and Catalysis" (J. A. Rabo, Ed.), p. 505. A. C. S. Monograph No. 171, Washington, D. C., 1976.
19. Pople, J. A., and Beveridge, D. L., "Approximate Molecular Orbital Theory," p. 111. McGraw–Hill, New York, 1970.
20. Henre, W. J., Latham, W. A., Ditchfield, R., Newton, M. D., and Pople, J. A., *QCPE* **13,** 236 (1973).

21. Bertran, J., Silla, E. B., and Fernández-Alonso, J. I., *Tetrahedron* **31,** 1093 (1973).
22. Montañana, R., Nebot, I., and Tomas, F., unpublished results.
23. Del Bene J., and Jaffe, H. H., *J. Chem. Phys.* **48,** 1807 (1968); **48,** 4050 (1968).
24. Jaffe, H. H., *et al., Quant. Chem. Prog. Exchange, Univ. Indiana* **13,** 315 (1976).
25. Bingham, R. C., Dewar, M. J. S., and Lo, D. H., *J. Amer. Chem. Soc.* **97,** 1285 (1975).
26. Rinaldi, D., Private communication.
27. Rinaldi, E., *Comp. Chem.* **1,** 101 (1977).
28. Weekman, W. V., *Ind. Eng. Chem. Proc. Des. Dev.* **7,** 90 (1968).
29. Pachovsky, R. A., and Wojciechowski, B. W., *J. Catal.* **37,** 120 (1975).
30. Condon, F. E., *in* "Catalysis" (P. H. Emmett, Ed.), Vol. VI, p. 43. Reinhold, New York. 1958.
31. Wojciechowski, B. W., *Catal. Rev.* **9,** 79 (1974).
32. Laidler, K. J., "Chemical Kinetics," McGraw–Hill, New York, 1950.
33. Brouwer, D. M., and Hogeveen, H., *Prog. Phys. Org. Chem.* **9,** 179 (1972).
34. Chevalier, F., Guisnet, M., and Maurel, R., Proc. Intern. Congr. Catalysis, 6th (London 1976), p. 478. Chemical Society, London, 1977.