The Mechanism of Paraffin Reactions on HY Zeolite

J. ABBOT AND B. W. WOJCIECHOWSKI

Department of Chemical Engineering, Queen's University, Kingston, Ontario, Canada K7L 3N6

The selectivity and kinetics of catalytic cracking of a range of paraffin feedstocks are explained by assuming that cracking occurs only at Brønsted sites. We propose that the cracking reaction is initiated through the formation of a pentacoordinated carbonium ion and that subsequent events parallel the reaction of the same paraffin in liquid superacid media. For linear paraffins in the range C_6–C_{16}, direct bond cleavage of the initial carbonium ion produces a gas phase paraffin and an adsorbed carbenium ion which can desorb as an olefin. Rearrangement of the carbonium transition state before cracking is postulated to produce branched paraffins as initial products. Hydride transfer between an adsorbed carbenium ion and a feed molecule leads to the cracking of that feed molecule via β-scission of the resulting carbenium ion. This constitutes a kind of chain mechanism. However, this process is slower than the direct cracking of linear paraffins via protolysis. The reaction of linear paraffins is inhibited by the competitive adsorption of product olefins, which also enhance the chain mechanism route but not enough to cause an overall acceleration in cracking rate when olefins are added to a linear paraffin during cracking. For short-chain branched paraffins such as 2-methylpentane, 3-methylpentane, and 2,3-dimethylbutane, C–H bond cleavage to produce molecular hydrogen occurs in parallel with C–C cleavage. In contrast to linear ions, the carbenium ion formed by hydride ion abstraction from a branched feed molecule via the chain process undergoes β-scission more rapidly than does the cleavage of the branched feed molecule through protolysis. Thus the addition of small amounts of olefin to some small branched paraffins produces a significant acceleration in cracking rate. The kinetic model which applies to the reactions of linear paraffins on HY is therefore not valid for these branched paraffins which are prone to acceleration of cracking by adsorbed carbenium ions.   © 1989 Academic Press, Inc.

INTRODUCTION

The mechanism of the cracking reactions of paraffins on solid acid catalysts is still under debate. Most recent studies have focussed on mechanisms of hydrocarbon reactions on zeolites, reflecting the commercial importance of these catalysts, both in the refining of gas oils, and, more recently, in processes such as MTG. It has been proposed that initiation of paraffin cracking can occur at either Brønsted or Lewis acid centres (1–5) on the catalyst surface. Interaction of a paraffin with a Brønsted site can result in cracking of the saturated molecule via protolysis (1, 2, 5), after initial formation of a pentacoordinated carbonium ion. This leads to a smaller paraffin molecule and an adsorbed carbenium ion at the active site. Alternatively, evolution of molecular hydrogen may occur (1), leading to a carbe-

nium ion, which may then undergo cracking via β-scission. In both cases, the cracking process is initiated by a mechanism which leads to the formation of a carbenium ion at the Brønsted site. Once this is formed, the cracking process may be propagated by a chain reaction (2) involving hydride ion transfer from a paraffin feed molecule to the adsorbed ion, leading to a product paraffin molecule and a new carbenium ion, which, in turn, can undergo cracking. However, the extent of this propagation sequence is not known; it is also possible that desorption of the residual ion as an olefin occurs after each cracking event, so that the original Brønsted site is reconstituted (5) without any chain of reactions involving residual carbenium ions. Notice that in the chain process the carbenium ion can act as a Lewis site or as a Brønsted site.

It has been suggested (6) that cracking

1

reactions of paraffins are initiated via thermal cracking of the feed to produce olefins. Adsorption of these unsaturated product molecules at Brønsted sites would then enable cracking to proceed totally via a chain reaction. Support for this proposal is provided by certain experiments which show that addition of small traces of olefin to a saturated feed can produce a significant acceleration in the rate of paraffin cracking (7–9). However, other studies have found that little or no influence can be detected when an olefin is introduced (10–12), while kinetic studies have provided evidence for inhibition by unsaturated product species (13, 14).

Initiation of reactions of paraffins on zeolite catalysts may also occur through hydride ion extraction at preexisting Lewis acid sites connected with the lattice of the catalyst (2). Although it seems clear that this process does occur on various catalysts leading to skeletal isomerization of the saturated molecule (15), the evidence for this mechanism as the dominant mode for cracking of paraffins on zeolites is less convincing.

We have recently undertaken a series of studies on reactions of paraffins on HY zeolite, in which both selectivity and kinetic phenomena have been examined in detail (12, 13, 16). Although we have said that initiation via a carbonium ion mechanism at Brønsted sites provides a plausible explanation for our selectivity results (5), we have, until now, left unspecified the detailed description of the reaction mechanism.

THEORY

Selectivity

For each reaction product, the time-averaged yield sampled from $t = 0$ to t_f, the run duration, can be plotted against $\overline{X}_R$, the integral conversion of feed. These plots can be enveloped by a single curve, the optimum performance envelope (OPE), which describes the selectivity behaviour of prod-
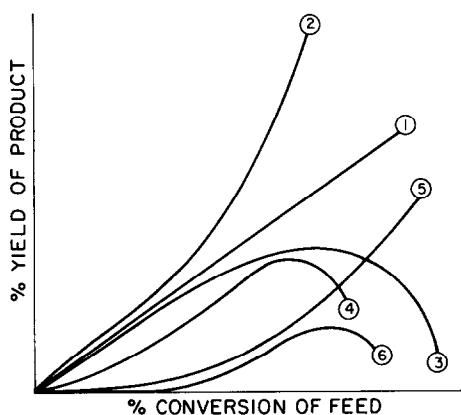

FIG. 1. Theoretical optimum performance envelope (OPE) curves of various products. The OPEs shown refer to the products: (1) stable primary product, (2) stable primary plus secondary product, (3) unstable primary product, (4) unstable primary plus secondary product, (5) stable secondary product, and (6) unstable secondary product.

ucts to be described by characteristic curves, illustrated in Fig. 1. The initial selectivity of a product, given by the slope of the OPE at zero conversion is nonzero for a primary product and zero for secondary or subsequent products.

Kinetics

We have shown (13) that reactions of n-paraffins on HY at 400°C can be described by

$$\frac{dX}{d\tau} = \frac{(1 + Gt)^{-N} A(1 - X)/(1 + \varepsilon X)}{1 + B(1 - X)/(1 + \varepsilon X)}, \quad (1)$$

where

X is the fractional conversion of the paraffin,

τ is the feed contact time,

t is the time on stream,

ε is the volume expansion coefficient,

G and N are aging parameters, and

A and B are constants related to the rate constant for reaction, and the Langmuir adsorption constants for reactant and products.

The constants A and B are defined by the expressions

$$A = \frac{\sum_i k_i K[C_0]}{1 + \sum_j K_j n_j [C_0]} \qquad (2)$$

and

$$B = [C_0] \frac{K - \sum_j K_j n_j}{1 + \sum_j K_j n_j [C_0]}, \qquad (3)$$

where

k_i are the individual rate constants for the i parallel modes of conversion of the feed,

K and K_j are Langmuir adsorption constants for the feed C and each product P_j, respectively,

n_j is a stoichiometric factor accounting for the number of product molecules of type j formed from the feed molecule, and

$[C_0]$ is the initial concentration of the reactant.

RESULTS AND DISCUSSION

Initiation in Linear Paraffins

The kinetic model presented in the theory section is based on the assumption that only one type of site on the catalyst surface is active during this catalytic process. Figure 2 shows that for reaction of n-paraffins on HY in the temperature range 400–500°C experimental results are well fitted by this model. Optimum values of kinetic parameters are given in Table 1. Under these conditions, cracking is found to be the domi-

nant process accounting for >95% of the initial selectivity, with skeletal isomerization and coke formation accounting for the remainder.

In the development of our model, it is assumed that the active sites have uniform decay and adsorption characteristics. As the catalyst decays, activity is lost due to loss of active sites, so that only some fraction of the original sites remains after a given time on stream (13, 17–19). Table 1 shows significant consistency in the magnitudes of the aging parameters (N and G) obtained for different linear paraffin feedstocks. We note that all the linear paraffins show a B value of -1 and that as chain length increases the value of m, the order of the decay reaction with respect to active site concentration, increases. The first we interpret as being a sign of severe competition by products for adsorption on active sites. The second indicates increasing involvement of pore blockage in the decay of catalyst activity. A Langmuir type adsorption process was assumed for this kinetic model, and we have shown (13) how the magnitude of parameter B is related to the Langmuir adsorption constants for reactant and products.

Extensive recent studies (2–4) of the reaction of n-heptane on HY, and other zeolites have lead to the opposite conclusion, that two distinct types of sites—Brønsted sites and Lewis sites—are active during initial cracking. The evidence for this is based

TABLE 1

Kinetic Parameters for Reactions of Paraffins on HY Zeolite[a]

Paraffin	Temp. (°C)	A (mol/g cat/min)	B	N	G (min⁻¹)
n-Octane	400	0.22	−0.994	0.80	1.11
n-Dodecane	400	0.66	−0.996	0.88	1.43
n-Hexadecane	400	1.72	−0.998	0.42	1.52
n-Hexane	500	1.36	−0.900	1.07	0.88
2,2,4-Trimethylpentane	300	12.6	−0.630	0.96	42.1
2,2,4-Trimethylpentane	400	287.0	−0.998	0.81	2011

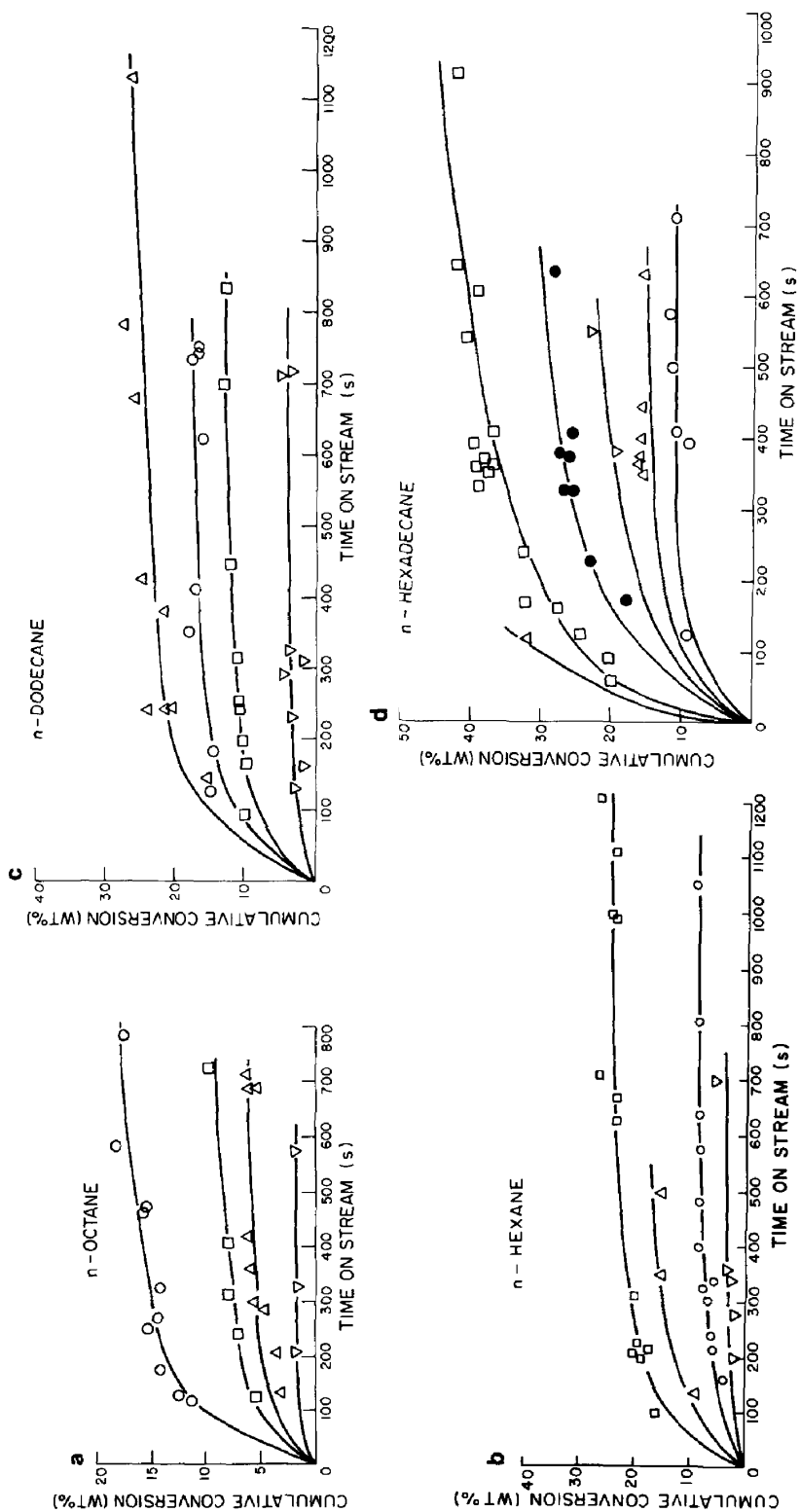[a] All reactions were carried out at 1 atm pressure.

FIG. 2. Theoretical curves and experimental points for cracking of n-paraffins on HY: (a) n-octane at 400°C. Catalyst/reactant ratios: (○) 0.2760, (□) 0.0690, (△) 0.0345, (▽) 0.0035. (b) n-Hexane at 500°C. Catalyst/reactant ratios: (▽) 0.0148, (○) 0.0368, (□) 0.1850. (c) n-Dodecane at 400°C. Catalyst/reactant ratios: (△) 0.140, (○) 0.00650, (□) 0.0033. (d) n-Hexadecane at 400°C. Catalyst/reactant ratios: (▲) 0.135, (●) 0.0333, (▽) 0.0165, (△) 0.0066, (○) 0.0032.

on consideration of initial selectivities, combined with the application of a "one-site" model for fitting kinetic data. It seems on reflection to be unlikely that two different types of sites, having distinct adsorption and aging characteristics, will have a sum of their two Langmuir expressions, one for each site type, reduce to the simple "one-site" form of Eq. (1). We therefore propose to examine the consequences of the postulate that only one type of site is active for the cracking of linear paraffins on HY.

There is significant evidence that cracking reactions of paraffins on zeolites occur on Brønsted sites. Several studies have shown that the cracking activity of zeolites is strongly dependent on catalyst pretreatment temperature (20, 21). Activity is generally found to decline as pretreatment temperature is increased above 500°C, corresponding to the conversion of Brønsted sites into Lewis sites, as the catalyst undergoes dehydration (20, 21). A recent study has shown that for n-octane cracking on pentasils, there is a direct relationship between the number of Brønsted sites present and catalytic activity (22). The same study also concluded that Lewis acid sites were relatively unimportant during the cracking reaction. It has also been reported (23) that it is the strong Brønsted sites which are active in cracking of n-heptane on HY at 450°C, from studies of aging and coke formation during the cracking reaction.

It would appear reasonable therefore to assume that if only one type of site is active during cracking reactions of n-paraffins on HY, these must be Brønsted sites. This proposal is in keeping with the recent interest in the idea that reactions of paraffins can be initiated at Brønsted sites via formation of a pentacoordinated carbonium ion (1, 2, 5). Such protonation of saturated molecules to give carbonium ions has been extensively studied at low temperatures in superacid media (24, 25). At the same time it is becoming apparent that there is a great deal of similarity in product distributions of re-

actions in superacids and those on zeolites. This suggests that similar intermediates are involved in both systems. For example, if we compare the product distribution for reaction of n-octane in the superacid FSO_3H/SbF_5 at 25°C (24, 25) with the initial product distribution for reaction on HY at 400°C (16) C_3, C_4, and C_5, fragments are dominant in both cases, while C_1, C_2 and molecular hydrogen are either absent or formed as very minor products. Our recent studies have shown that the similarity between the two reaction systems also applies to branched paraffins and cycloparaffins (26, 27). Supporting evidence for the possibility of a carbonium ion intermediate during paraffin cracking has been provided by theoretical studies (2, 28). Using molecular orbital calculations, it has been found that for the cracking of n-heptane, bond cleavage via formation of a protonated intermediate is energetically more favourable than through the formation of a carbenium ion, produced by hydride ion extraction at a Lewis acid site. The involvement of Lewis sites in cracking reactions of n-paraffins is therefore in doubt.

A recent series of studies of reactions of n-heptane on various zeolites concluded that both Brønsted and Lewis acid sites are active during the initiation of the cracking process (2–4). This conclusion was reached by considering initial product selectivities, particularly the initial ratios of paraffin/olefin formed, as well as the presence of branched species in the primary products. We must therefore reconcile initial selectivity results with the proposal that only Brønsted sites are involved in initiating cracking in paraffins.

We have recently examined the initial cracking selectivities for n-octane and n-dodecane on HY at 400°C (16). Initial selectivity values for reaction of n-dodecane are shown in Table 2. In that work we find that the initial ratios for paraffin/olefin are not unity. However, two important factors must be considered before making any mechanistic conclusions. First, more than

TABLE 2

Product Types and Initial Weight Selectivities for
Reaction of n-dodecane on HY

Product	Type[a]	Initial selectivity
Ethane	2S	—
Ethylene	2S	—
Propane	(1 + 2)S	0.0180
Propylene	1U	0.0753
n-Butane	(1 + 2)S	0.0321
Isobutane	(1 + 2)S	0.0753
Trans-2-butene	1U	0.0527
Cis-2-butene	1U	0.0316
Isobutene	1U	0.1205
n-Pentane	(1 + 2)S	0.0210
2-Methylbutane	(1 + 2)S	0.0853
Trans-2-pentene	1U	0.0231
Cis-2-pentene	1U	0.0141
3-Methyl-1-butene	2U	—
2-Methyl-1-butene	1U	0.0271
2-Methyl-2-butene	1U	0.0597
1-Pentene	1U	0.0073
n-Hexane	1U	0.0210
2-Methylpentane	(1 + 2)S	0.0452
3-Methylpentane	(1 + 2)S	0.0228
2,3-Dimethylbutane	2S	—
C_6 olefins	1U	0.0916
n-Heptane	1S	0.0110
2-Methylhexane	(1 + 2)S	0.0251
3-Methylhexane	(1 + 2)S	0.0191
2,3-Dimethylpentane	(1 + 2)S	0.0073
2,4 Dimethylpentane	(1 + 2)S	0.0085
C_7 olefins	1U	0.0339
Methylcyclohexane	T	—
Dimethylcyclopentanes	T	—
n-Octane	2S	—
2-Methylheptane	(1 + 2)S	0.0080
3-Methylheptane	(1 + 2)S	0.0091
4-Methylheptane	2S	—
2,3-Dimethylhexane	2S	—
2,4-Dimethylhexane	2S	—
2,5-Dimethylhexane	2S	—
Dimethylcyclohexanes	T	—
Trimethylcyclopentanes	T	—
Toluene	2S	—
C_8 aromatics	2S	—
C_9 aromatics	2S	—
C_{10} aromatics	2S	—
$C_{10} + C_{11}$ paraffins	2S	—
C_{12} (skeletal isomerization)	1U	0.0361
Coke	(1 + 2)S	0.0169
		0.9987

[a] 1 = primary; 2 = secondary; S = stable; U =
unstable; T = trace amounts detected by GC/MS.

one olefin may be produced from each feed molecule, particularly when long chain paraffins are used as feedstock. This results from the sequential cracking of the carbenium ion produced after the first cracking event, rather than desorption of a long chain olefin. Second, hydrogen transfer reactions resulting in unsaturated species such as aromatics and coke must be considered, if these species are produced initially. In the absence of irreversible hydrogen transfer from the catalyst itself, an overall stoichiometric balance for hydrogen in the feed and in the initial products must be maintained. This means that, for initial cracking of n-paraffins such as n-heptane and n-octane, where simple cleavage into a paraffin and an olefin is the dominant primary process, any deviation from unity for the initial paraffin/olefin ratio must first be corrected for the effects of hydrogen transfer processes leading to aromatics and coke. We have reported, for example, that for reaction of n-hexadecane on HY (29), the paraffin/olefin ratio is significantly higher at 300°C than at 400°C. This was fully accounted for by a complete mass balance showing that the formation of unsaturated coke and aromatics is much higher at the lower reaction temperature and is accompanied by the saturation of some of the product olefins, leading to a high paraffin/olefin ratio.

The second issue which must be examined is the appearance of branched species as primary products. The initial formation of these has been used as evidence of the participation of Lewis acid sites during the initiation of paraffin cracking (4). This proposal comes from the view that if cracking is initiated at Brønsted sites alone then the linear feed molecule which undergoes protolysis will produce a smaller linear paraffin as an initial product species, leaving a residual carbenium ion at the Brønsted sites. If this ion has four or more carbon atoms, rearrangement to a branched structure prior to desorption is favoured as it will result in a more stable carbenium ion,

which can then desorb as a branched olefin. There is thus no difficulty in explaining the appearance of branched olefins as primary products, branched paraffins are another matter.

The appearance of branched paraffin species as initial products via the protonation of a linear feed molecule requires more detailed consideration. For reactions of linear paraffins in superacid media, detailed initial product distributions, including the relative proportions of all isomers, have unfortunately not been reported (24, 25). It also appears that in considering the cracking mechanism of linear paraffins by a carbonium ion intermediate, the possibility of rearrangement of the transition state has not been carefully considered. It is tacitly assumed that protonation of a linear paraffin can *only* result in a linear product paraffin as the first product of protolysis (4).

More detailed information on product distributions from linear paraffins in liquid superacid media, particularly with regard to distribution of isomers, would be helpful at this point, and we are currently undertaking such studies. Theoretical calculations must also be done. However, if we compare the proposed mechanisms for cracking and for alkylation in superacid media (30), we see that the first process is the reverse of the second, with a common transition state, comprising a three centre complex between two carbon atoms and the proton. For cracking, separation of this complex leads to the formation of a carbenium ion and a smaller saturated fragment. during alkylation, the same complex is formed as a carbenium ion is approached by a saturated molecule. It seems possible that during the cracking process, as the carbenium ion and the saturated fragment begin to separate, realkylation can occur. If this occurs at the same carbon atom, the original protonated linear species is reconstituted. If it occurs at another carbon atom, a protonated branched isomer is produced, and subsequent cracking will yield branched paraffinic fragments.

We have previously suggested the possibility of rearrangement of carbonium ions produced by protonation of linear paraffins at Brønsted acid sites on zeolite catalysts (5) on the basis of other experimental results. It was observed that in cracking a mixture of linear paraffins, linear paraffins are produced preferentially on HZSM-5 whereas branched paraffins were favoured on HY. We explained this by assuming that rearrangement of the carbonium ion formed by initial protonation of the linear paraffin was much more difficult within the narrow pore structure of HZSM-5. It has been suggested in other work that isomerization of n-paraffins is caused by protonation of a paraffin on solid superacid polymers with proton donor strengths comparable to those of liquid superacid media (10).

Chain Reactions in Linear Paraffins

Consider now the cracking mechanism for linear paraffins on HY after initiation has occurred. It has been proposed by some investigators (2–4) that reaction may proceed via a chain mechanism. One way this process may proceed is by a hydride ion transfer to a surface carbenium ion from another feed molecule. The new parent carbenium ion will then release and take the place of the now saturated surface fragment and undergo normal cracking via β-scission, etc. In this way a chain is established. Evidence for this is provided by the observation that addition of small traces of olefin to paraffin feedstocks can in certain cases produce a significant acceleration of paraffin cracking. This effect has been reported for reaction of n-octane on HY (9), butane on mordenite (8), and for cracking of n-hexadecane on amorphous silica alumna (7). However, we have been unable to detect such an effect (12) when a small amount of l-hexene was added to n-hexane, for reaction on HY at 500°C (Fig. 3). Our observation is similar to reports for addition of isobutene to n-heptane during cracking on a rare-earth-exchanged Y zeolite
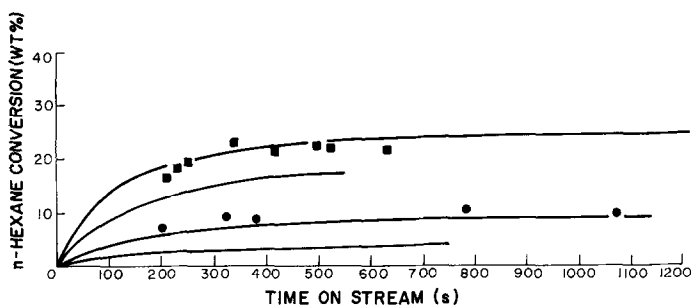
FIG. 3. Curves for catalytic conversion of n-hexane on HY zeolite at 500°C, with experimental points for n-hexane feed after addition of 1% 1-hexene. Catalyst/reactant ratios correspond to those in Fig. 2b.

(11) and for addition of 1-butene to n-butane for reaction on a solid superacid (11).

From our kinetic model, we find that the reaction of n-paraffins on HY in the range 400–500°C is inhibited (13) as product olefins are formed. A similar conclusion was reached for n-hexadecane on silica–alumina (14). We believe that, for linear paraffins, reaction on HY proceeds via protonation of feed molecules on catalyst sites even after initiation has occurred and that this process is inhibited by competition for adsorption at the same Brønsted sites by product olefins whose concentration increases with conversion (28). It is difficult in such a case to assign any importance to the chain mechanism in relation to direct protolysis.

The Influence of Chain Length on the Rate of Cracking

From the optimum values for kinetic parameters in Table 1 for reaction of n-octane, n-dodecane, and n-hexadecane on HY at 400°C, we can now draw some conclusions regarding the average rate constant for cracking and the influence of chain length on its value. From inspection of Eq. (2), it is clear that the parameter A is a function of all adsorption terms as well as of the rate constants k_i, which can be expressed for the reactant as

$$\sum_i k_i = \frac{A}{B} \cdot \frac{K_o}{K} \cdot (-\Sigma n_j)$$

on the assumption that $K \ll K_o$.

It has been shown that heats of adsorption for paraffins on zeolites increase approximately linearly with chain length (31). For lack of comparable information for chemisorption we assume that the energy of chemisorption of K for n-octane, n-dodecane, and n-hexadecane is also proportional to the length of the hydrocarbon chain. It can also be seen that the major contribution to product adsorption is due to short chain olefins in the range C_3–C_6, which probably have similar chemisorption constants K_i (32). If this is so, then the values of $\Sigma K_j n_j$ will be $K_o \Sigma n_j$ and proportional to the initial molar selectivity for olefins in each n-paraffin (Table 3). From Eq. (4), we can now calculate the relative values for Σk_i as shown in Table 3. Finally, we divide those values by the number of "crackable bonds," Σb_i, leading to fragments of C_3 or larger. The values of $\Sigma k_i/\Sigma b_i$ can be identified with k_i in the mechanism shown in Fig. 4, showing that this value increases with chain length. A similar trend can be seen for reactions of n-paraffins in the range C_3–C_{14} on a rare-earth-exchanged X zeolite at 900°F (33). These results indicate that internal bonds in a linear paraffin are more susceptible to cracking than those closer to the

TABLE 3

Calculation of Cracking Rate per Bond in n-Paraffins

	n-Octane	n-Dodecane	n-Hexadecane
A/B	0.221	0.663	1.723
Σn_j	0.88	1.5	1.9
K	1	1.64	2.72
Σk_i	0.195	0.606	1.203
Σb_j	3	7	11
$\Sigma k_i/\Sigma b_i$	0.065	0.087	0.109
Normalized rate per bond	1	1.24	1.69

ends of the chain. It is not clear why this phenomenon persists so far into the molecule or how much further it may persist.

Branched Paraffins

We have studied reactions of 2-methylpentane, 3-methylpentane, and 2,3-dimethylbutane on HY at 500°C. Figure 5 shows plots of experimental cumulative conversions for these branched paraffins as a function of time on stream. It is immediately apparent that these sets of curves differ from those presented in Fig. 2 for the linear paraffins. The curvature of the lines in Fig. 2 is always monotonic, and our simple kinetic model can be applied, as we have previously described (*13*). For the branched paraffins, however, the plots of
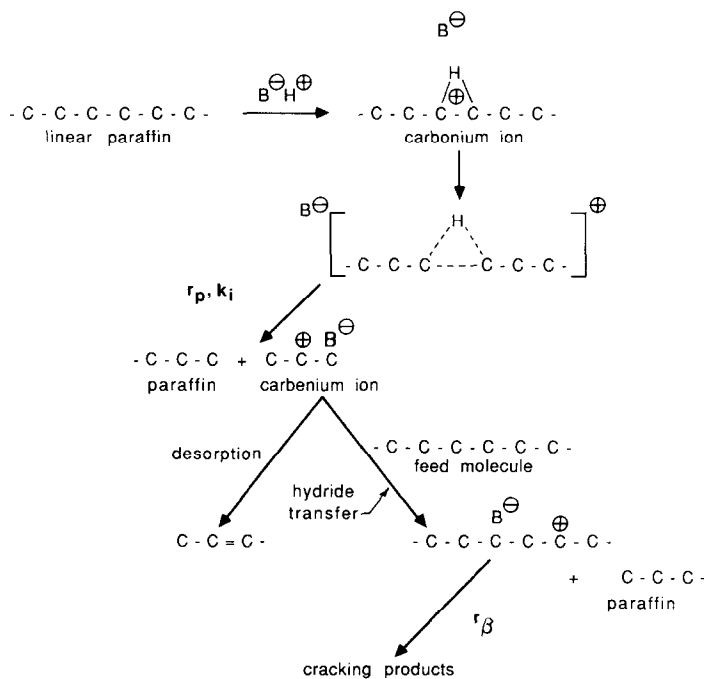

FIG. 4. Reaction mechanism for cracking of a linear paraffin on HY zeolite.
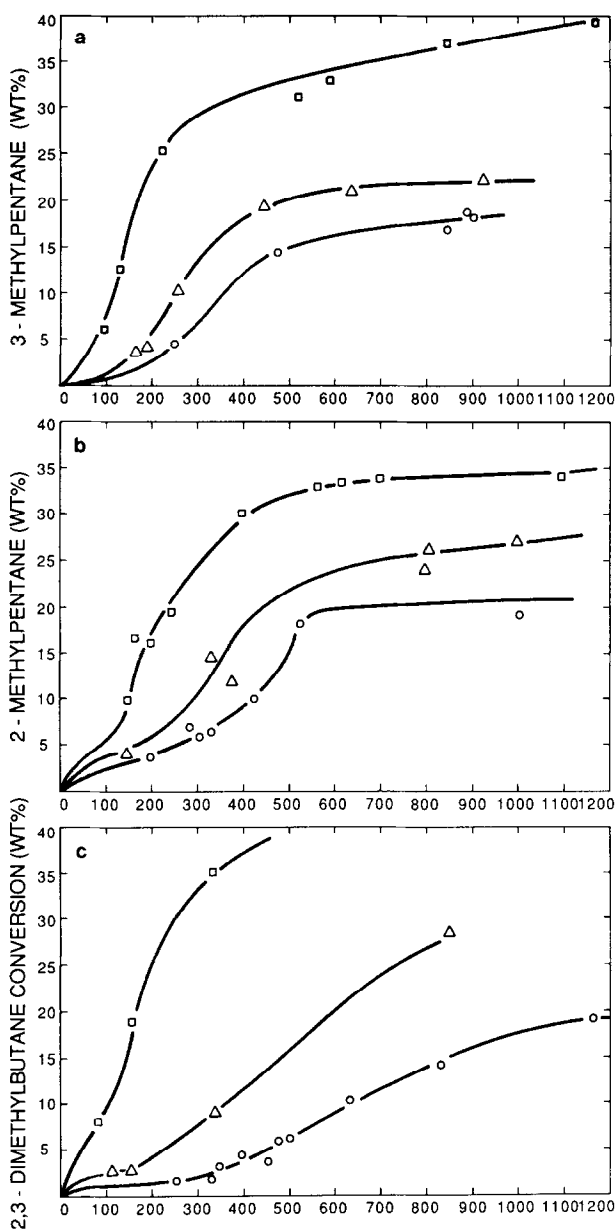
FIG. 5. Conversion of branched C_6 paraffins on HY at 500°C as a function of time on stream (a) 3-methylpentane, (b) 2-methylpentane, and (c) 2,3-dimethylbutane. Catalyst/reactant ratios: (□) 0.0385, (△) 0.0154, (□) 0.0077.

conversion against time on stream at each level of catalyst/reactant exhibit "induction periods," i.e., regions where the curvature is obviously concave. We have not observed this type of phenomenon previously in any reaction of a pure hydrocarbon on a zeolite catalyst, and the simple kinetic model successfully applied in the case of linear paraffins is no longer valid.

Initial selectivities for reaction of 2-methylpentane on HY at 500°C (26) show that cracking to produce two C_3 fragments

is the dominant initial process and that molecular hydrogen is an initial product. As we have shown previously (26) molecular hydrogen appears to be produced during initial reaction of a paraffin on HY when the molecule contains a hydrogen ion attached to a tertiary carbon atom. Its formation can be accounted for by interaction of the feed molecule with a Brønsted site as shown in Fig. 6. A carbonium ion is produced which can either undergo C–H bond cleavage to produce hydrogen and a carbenium ion (1), or C–C bond cleavage to produce propane and a carbenium ion (1). From the presence of initial selectivity for hydrogen, it can be seen that both these processes must take place (26) even if initiation of cracking occurs on Brønsted sites alone.

The possibility of C–H bond cleavage of the carbonium ion formed from 2-methylpentane, in parallel with C–C bond cleavage, does not, however, explain the observed kinetic phenomena. This can be explained by assuming either an increase in the number of active sites after initiation of the cracking reaction has occurred, or that the existing sites are modified by product formation in such a way that activity is enhanced. The model we have applied successfully to the reactions of linear paraffins allows only for a decrease in the number of active sites due to aging and for a reduction in available sites due to competitive adsorption of product species (13). It does not allow for the possibility that the number of sites increases after initiation, nor for the possibility that sites can be modified so that their activity is promoted.

It appears unlikely that more active sites, identical to those initially present, can be introduced during reaction (16). This leaves the modification of the original Brønsted sites through interaction with a product species as a plausible explanation. In the above discussion of linear paraffin cracking we argued that during the cracking of a linear paraffins, adsorption of product olefins to produce a carbenium ion at a Brønsted site causes inhibition. We believe that for linear paraffins $r_p > r_\beta$ on Fig. 4, so that adsorption or retention of product olefin at a Brønsted site causes inhibition of cracking. For the branched paraffins, the reverse appears to be true, i.e., $r_\beta \gg r_p$, so that hydride ion abstraction followed by cracking of the branched C_6 carbenium ion oc-
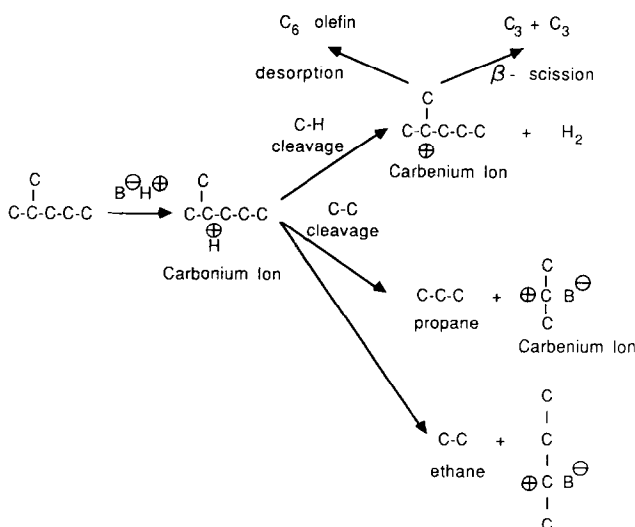

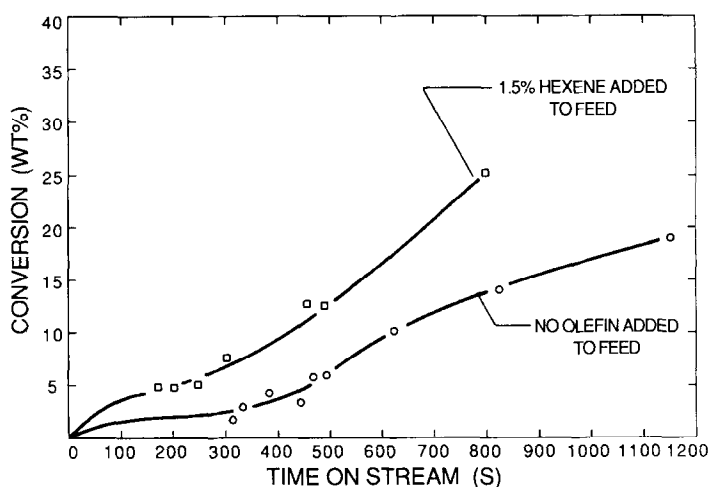FIG. 6. Initiation of cracking for a branched paraffin at a Brønsted site.

FIG. 7. The influence on conversion of adding 1.5% 1-hexene to 2,3-dimethylbutane for reaction on HY at 500°C.

curs more rapidly than cleavage of the feed molecule via direct protolysis at a Brønsted site.

It seems that this difference between the linear paraffins and the branched paraffins is due to the relative ease of removal of the tertiary hydride ion, leading to the formation of a tertiary carbenium ion. It is known that removal of a tertiary hydride ion in a paraffin occurs very much more easily than removal of a secondary hydride (28). If this interpretation of the observed kinetic effect is correct, we would expect that addition of small traces of olefin to branched paraffins will cause an acceleration of the cracking reaction. Figure 7 shows the effect of introducing 1.5% 1-hexene to the 2,3-dimethylbutane feed. It is clear that the cracking reaction is significantly enhanced by the initial presence of the olefin. Thus, in contrast to the linear paraffins, the branched paraffin reaction appears to proceed mainly via a chain reaction involving surface carbenium ions acting as Lewis acids forming carbenium ions on feed molecules by hydride ion abstraction. If the surface carbenium ions were to act as Brønsted sites, it is hard to visualize how they could be so effective as catalytic sites, if the original Brønsted sites on the catalyst were not.

We note at this point that the reaction of 2,2,4-trimethylpentane on HY at 300 and 400°C (26) shows kinetic behaviour typical of linear paraffins. Figure 8 shows that the curves representing conversion at different catalyst to reactant ratios are similar to those for linear paraffins in Fig. 2 and there is no evidence of any "induction" period typical of the C_6 branched paraffins (Fig. 4). Table 2 also shows that the value of the parameter B for reaction of 2,2,4-trimethylpentane on HY at 400°C is close to -1, so that the kinetic behaviour of this branched molecule is similar to that of the linear paraffins. This is an unexpected result at first
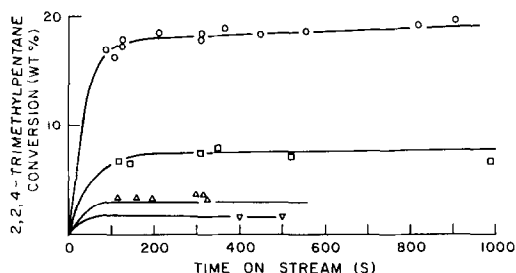

FIG. 8. Theoretical curves and experimental points for reaction of 2,2,4-trimethylpentane on HY at 300°C. Catalyst/reactant ratios: (∇) 0.0148, (△) 0.0350, (□) 0.106, (○) 0.360.

sight, especially since we also find that molecular hydrogen is not observed as an initial product of this reaction on HY at 400°C. This however agrees with observations in liquid superacid media, where it was shown that for highly substituted molecules, C–H bond cleavage to produce molecular hydrogen is no longer a facile process even though the molecule contains a tertiary hydrogen in the structure (24, 25). Steric constraints may effectively "shield" access to the tertiary hydrogen, so that product distributions obtained for highly substituted paraffins are more typical of linear paraffins than of the monomethyl paraffins (24, 25). At the same time conversion proceeds by a protolytic mechanism similar to that of linear paraffins.

Skeletal Isomerization of Paraffins

Although we propose the existance of direct skeletal isomerization of carbonium ions formed on paraffins, there is also some evidence that skeletal isomerization of paraffins occurs on Lewis acid sites, via hydride ion extraction and the rearrangement of the resulting carbenium ion. For example, with the superacid systems P_2O_5/Al_2O_3 and $AlCl_3/Al_2O_3$, Lewis acid sites are thought to be responsible for the catalytic activity which promotes skeletal isomerization of n-alkanes at low temperatures (34, 35). Studies of skeletal isomerization of paraffins on the solid superacid SbF_5–SiO_2–Al_2O_3 (36, 37) have shown that reaction occurs via hydride ion extraction at Lewis acid centres. However, as pointed out recently (38) one cannot be sure that all traces of water have been completely eliminated from these catalysts, so that Brønsted sites may still be present and produce the observed catalytic activity. It would therefore seem reasonable to suggest that the observed skeletal isomerization of n-paraffins on HY (Table 2) also occurs on Brønsted sites through rearrangement of the carbenium ion.

CONCLUSIONS

In summarizing our findings on the product distributions and the kinetics of conversion of a variety of linear and branched paraffins, we come to the following conclusions. On HY zeolite at 400–500°C, linear paraffins are mainly (above 90% or so) converted on one type of site. This site is capable of both cracking the feed molecule and isomerizing the initial paraffin product. Lewis acid sites would also be capable of carrying out both processes. However, there is much evidence to show that Brønsted acids are vitally important to catalytic cracking. We are therefore forced to choose between the two and conclude that the dominant active site in linear paraffin cracking is a Brønsted site. Furthermore, we must take it that the pentacoordinated carbonium ion formed on a Brønsted site by a linear paraffin will not yield molecular hydrogen by hydride ion elimination but will permit isomerization of the leaving moiety before its elimination as a paraffin. These are not obvious conclusions and need to be examined both by experiment and by MO calculation.

Branched molecules containing an unshielded tertiary hydrogen react on two types of sites. One is present on the original catalyst and leads to the production of initial molecular hydrogen and to cracking. The same Brønsted sites proposed as agents of linear paraffin cracking could play the necessary role. The reason for the appearance of molecular hydrogen as an initial product is no doubt connected with the ease of extraction of a hydride ion when a tertiary hydrogen is present in a molecule. This same ease of hydride extraction is responsible for the appearance of the second type of site active in the cracking of branched paraffins. The second type of site is a carbenium ion, sitting on a Brønsted site, and acting as a Lewis acid toward a feed molecule. This leads to a chain mechanism wherein a branched feed molecule approaches a surface carbenium ion, gives up

a hydride ion, allows the desorption of the surface moiety as a paraffin and takes its place as a carbenium ion. This ion then isomerizes, cracks, and eventually may desorb or undergo a subsequent chain propagating reaction.

The difference between linear and branched paraffin cracking reactions is therefore that whereas surface carbenium ions occupy Brønsted sites and inhibit the cracking of linear paraffins, they do not inhibit but in fact promote the cracking of branched paraffins. This is made obvious by the effect of added olefins to the two types of feeds. Small amounts of olefins added to linear paraffins have no effect on reaction rate, large amounts inhibit the reaction. In contrast, small amounts of olefins added to branched paraffins speed up the reaction, as does the accumulation of product olefins as conversion increases. We conclude that carbenium ions on Brønsted sites are even more effective in catalyzing the cracking of branched paraffins than the preexisting Brønsted sites of the catalyst itself.

Finally, we note that branched paraffins can contain shielded tertiary hydrogens. In these molecules the reaction proceeds by the same mechanism as in linear paraffins. That is to say no molecular hydrogen is present in the initial products of the reaction and only one type of site is involved in the cracking reaction.

REFERENCES

1. Haag, W. D., and Dessau, R. M., in "Proceedings, 8th International Congress on Catalysis, Berlin, July 1984 II–305. Dechema, Frankfurt-am-Main, 1984.
2. Corma, A., Planelles, J., Sanchez-Marin, J., and Tomas, F., J. Catal. 93, 30 (1985).
3. Corma, A., and Fornes, V., in "Catalysis by Acids and Bases" (B. Imelik, Ed.), p. 409 (1985).
4. Corma, A., Planelles, J., and Tomas, F., J. Catal. 94, 445 (1985).
5. Abbot, J., and Wojciechowski, B. W., Ind. Eng. Chem. Prod. Res. Dev. 24, 501 (1985).
6. Scherzer, J., and Ritter, R. E., Ind. Eng. Chem. Prod. Res. Dev. 17, 219 (1978).
7. Pansing, W. F., J. Phys. Chem. 69, 392 (1965).
8. Weisz, P., Chem. Tech., 498 (1973).
9. Anufriev, D. M., Kuznetsov, P. N., and Ione, K. G., J. Catal. 65, 221 (1980).
10. Magnotta, V. L., and Gates, B. C., J. Catal. 46, 266 (1977).
11. Corma, A., Monton, J. B., and Orchilles, A. V., Appl. Catal. 23, 255 (1986).
12. Abbot, J., and Wojciechowski, B. W., Canad. J. Chem. Eng., in press.
13. Abbot, J., and Wojciechowski, B. W., J. Catal. 104, 80 (1987).
14. Voge, H. H., in "Catalysis" (P. H. Emmett, Ed.), Vol. VI, Chap. 5. Reinhold, New York, 1958.
15. Takahashi, O., and Hattori, H., J. Catal. 68, 144 (1981).
16. Abbot, J., and Wojciechowski, B. W., J. Catal. 107, 451 (1987).
17. Wojciechowski, B. W., Catal. Rev. Sci. Eng. 9(1), 79 (1974).
18. Pachovsky, R. A., Best, D. A., and Wojciechowski, B. W., Ind. Eng. Chem. Process Des. Dev. 12(3), 254 (1973).
19. Viner, M., and Wojciechowski, B. W., Canad. J. Chem. Eng. 60, 127 (1982).
20. Hopkins, P. D., J. Catal. 12, 325 (1968).
21. Benesi, H. A., J. Catal. 8, 368 (1967).
22. Klyachko, A. L., Kapustin, G. I., Brueva, T. R., and Rubenstein, A. M., Zeolites 7(2), 119 (1987).
23. Magnoux, P., Cartraud, P., Mignard, S., and Guisnet, M., J. Catal. 106, 235 (1987).
24. Olah, G. A., Halpern, Y., Shen, J., and Mo, Y. K., J. Amer. Chem. Soc. 95, 4960 (1973).
25. Olah, G. A., Halpern, Y., Shen, J., and Mo, Y. K., J. Amer. Chem. Soc. 93(5), 1251 (1971).
26. Abbot, J., and Wojciechowski, B. W., J. Catal., 113, 353 (1988).
27. Abbot, J., and Wojciechowski, B. W., Canad. J. Chem. Eng., in press.
28. Planelles, J., Sanchez-Marin, J., Tomas, F., and Corma, A., J. Chem. Soc. Perkin Trans. II, 333 (1985).
29. Abbot, J., and Wojciechowski, B. W., J. Catal., 109, 274 (1988).
30. Olah, G. A., in "Carbocations and Electrophotic Reactions." Verlag Chemie, Wiley, New York, 1974.

31. Barrer, R. M., and Sutherland, J. W., *Proc. R. Soc. Ser. A* **237,** 439 (1956).

32. Derrah, R. I., Loughlin, K. F., and Ruthven, D. M., *J. Chem. Soc. Faraday Trans. 1* **68**(10), 1947 (1972).

33. Nace, D. M., *Ind. Eng. Chem.* **8,** 31 (1969).

34. Krzywicki, A., Marczewski, M., and Malinowski, S., *React. Kinet. Catal. Lett.* **8,** 25 (1978).

35. Krzywicki, A., and Marczewski, M., *J. Chem. Soc. Faraday Trans.* **76,** 1311 (1980).

36. Hattori, H., Takahashi, O., Takagi, M., and Tanabe, K., *J. Catal.* **68,** 132 (1981).

37. Takahashi, O., and Hattori, H., *J. Catal.* **68,** 144 (1981).

38. Lombordo, E. A., Pierantozzi, R., and Hall, W. K., *J. Catal.* **110,** 171 (1988).