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Mechanistic Considerations in Acid-Catalyzed Cracking of Olefins

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The relative rates of cracking and resultant product distributions for cracking C_5–C_8 olefins over ZSM-5 at 510°C were quantified and rationalized in terms of carbenium ion mechanisms. Conditions were chosen to minimize bimolecular reactions. Cracking rates increase more dramatically with carbon number for olefins than for monomolecular cracking of paraffins, as more energetically favorable modes become available for β-scission of the carbenium ion formed by proton donation to the olefin. Product distributions were used to determine the relative rates of various modes of β-scission, as classified by the types of carbenium ions involved. For hexene and heptene feeds, the most-favorable β-scission mode available (C-type, involving just secondary carbenium ions, for hexene feed; B-type, involving secondary plus tertiary carbenium ions for heptene) accounted for 70–80% of the cracking. Product distribution was independent of which hexene or heptene isomer was fed, since double-bond and skeletal isomerization precedes significant cracking. For 1-octene feed, however, the olefin was nearly all cracked via secondary-tertiary and tertiary-secondary β-scission (after isomerizing to a dimethylhexene) before it isomerized further to the 2,4,4-trimethylpentene isomer, which would be required to undergo the most energetically favored (tertiary-tertiary) form of cracking. A semiquantitative prediction of rates and product distribution for 1-octene cracking could be made, using rates for the various types of β-scission calculated from results with C_6–C_7 feeds.

INTRODUCTION

Olefins are produced in the FCC unit from the cracking of feed molecules. Many of the primary olefin products are large enough (C_{5+}) that they undergo further cracking. This secondary olefin cracking, which proceeds over the Y-containing base catalyst and over additives such as ZSM-5, has a major impact on the yield and composition of the FCC gasoline and C_4-gases. Olefin reactions over medium-pore zeolites are also at the heart of many other fuel-related processes. These include MTG and MTO for converting methanol to gasoline and to olefins, respectively; MOGD for converting light olefins to gasoline and distillate; and processes for olefin interconversion, for shifting 1-butene to 2-butene, and for increasing C_4–C_5 branching (1). Paraffin cracking, isomerization, and dehydrocylization can also proceed via olefinic intermediates. Cracking of olefins may be desired or not desired, depending on the process. Selection of catalysts and operating conditions can be assisted by knowledge of olefin cracking patterns.

Olefin interconversion and cyclization at temperatures around 200–400°C have been the subject of numerous studies, especially in connection with the conversion of methanol and light olefins to gasoline over ZSM-5 (2–6). Cracking of higher olefins over acid catalysts at high temperature (>400°C) presents experimental challenges due to high reaction rates, and has received less attention in the literature than paraffin cracking. Haag *et al.* (7) compared cracking rates at 538°C of linear and branched C_6–C_9 paraffins and C_6 olefins over ZSM-5 crystallites of different sizes to distinguish between shape selectivity caused by diffusion limitation and by constraint on the size of the transition state complex. Abbot and Wojciechowski (8) found that pentene and hexene cracked over ZSM-5 at 404°C via a dimerization-cracking route, while cracking of C_7–C_9 olefins was much faster and appeared to be a monomolecular process. They related the observed rates of reaction of linear and branched octene feeds over H–Y at 300°C to differing strengths of adsorption (9). Buchanan (10) determined olefin cracking rates and selectivities over a steamed ZSM-5 FCC additive at 538°C. At this temperature, hexene cracking was predominantly monomolecular. Nayak and Moffat (11) cracked C_6–C_8 olefins over various ZSM-5 catalysts at around 400°C, and found that the activity per aluminum atom increased with a decrease in the Al content of the zeolite.

It is widely accepted that olefin cracking over catalysts with Brønsted acidity involves the protonation of the double bond to form a tricoordinate carbenium ion, with subsequent scission of a carbon–carbon bond in the beta position, to form a free olefin and a smaller carbenium ion. While paraffin cracking at high temperature and low pressure occurs by a monomolecular process involving a protonated, pentacoordinated carbonium ion intermediate, paraffin cracking can also proceed via tricoordinate carbenium ions, especially at lower temperatures, higher paraffin

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pressure, and over catalysts with large pores (12). In carbenium ion cracking, extensive skeletal isomerization and shifting of the position of the carbenium center may precede the bond scission. The carbenium ion remnant donates a proton to the catalyst to desorb as a smaller olefin.

Protonation of olefins, and the reverse reaction, the deprotonation of carbenium ions, are extremely fast reactions. This is indicated by the fact that the rate of double-bond isomerization of olefins exceeds that of other olefin conversion reactions by orders of magnitude. Thus, the carbenium ions can be considered to be in equilibrium with the corresponding olefins and, for equilibrated olefins, with each other. The detailed nature of the intermediate species, often depicted simply as a free carbenium ion, is the subject of continuing investigation (13). The ground state is proposed to be covalently bound to an anionic lattice oxygen, forming an alkoxy species; higher energy moieties are an ion pair, and a more or less ''free'' carbenium ion which resembles the transition state. Thus, it is the concentration and reactivity of the latter that determines the reaction rate. The stability, and hence relative concentrations, of carbenium ions increases strongly in the order $1° < 2° < 3°$, so processes which involve the formation of a primary cation are energetically unfavorable.

Carbenium ion intermediates are involved in isomerization and cracking of paraffins as well as olefins over acid catalysts and dual-function (metal/acid) catalysts. Martens and Jacobs (14) discuss carbenium ion mechanisms in detail, drawing on results from both low-temperature (195 K) reactions in superacids and paraffin hydrocracking over dual-function solid catalysts. They point out the importance of protonated cyclopropane intermediates in skeletal isomerization.

In treating the isomerization and hydrocracking of C_9–C_{16} paraffins over Pt/ZSM-5, Weitkamp *et al.* (15) introduced terminology which is useful in organizing the various types of carbenium ion scission. β-scission, where the initial carbenium ion is tertiary and the carbenium ion remaining after scission is also tertiary, is denoted as type A. Type B1 scission starts with a secondary ion and finishes with a tertiary ion, while type B2 moves from a tertiary to secondary ion. Type C involves a secondary to secondary transformation, and type D is secondary to primary. We adopt this terminology in the discussion below, but find it necessary to increase the number of categories to include, for instance, primary-tertiary transformations, which we designate as type E.

In the present study, an effort is made to quantify the relative rates of the various types of beta-scission involved in cracking of olefins at elevated temperatures. Cracking rates for C_5–C_8 olefins over ZSM-5 at 510°C were determined, using low hydrocarbon partial pressures (10–100 Torr) to minimize bimolecular reactions. ZSM-5 of high $SiO_2/Al2O_3$ and hence of low activity was used to minimize diffusion effects (7). For each feed, all of the plausible carbenium ion beta-scission steps were enumerated and then related to the observed reaction rates and product distributions, in order to obtain estimates of the relative contribution of each mode of beta-scission. This work with C_5–C_8 olefin cracking may be compared with a detailed study of hydrocracking of C_8–C_{10} paraffins over Pt/USY where olefins are involved as intermediates (16, 17).

TABLE 1

Cracking Rate Constants for Hydrocarbons over HZSM-5 at 510°C and 10 Torr Partial Pressure

Carbon number	Rate constant k, sec^{-1} Paraffin	Olefin	Ratio of rate constants, olefin/paraffin
4	0.08	—	—
5	0.30	9.5	32
6	0.84	231.0	275
7	1.49	1823.0	1220
8	2.25	5732.0	2550

METHODS

Cracking reactions were run at atmospheric pressure in an 8 mm i.d. quartz reactor with a central thermowell. The reactor was heated by a tubular furnace. Nitrogen carrier gas passed through a bubbler containing the feed hydrocarbon, and then through a temperature-controlled condenser kept at a lower temperature than the bubbler. A second stream of diluent nitrogen was used to adjust the hydrocarbon partial pressure to the desired value (typically 10–100 Torr). For olefin cracking, powdered catalyst (5–30 mg) was diluted with about 1 cc of 50/80 mesh quartz chips. For paraffin cracking, around 0.5 g of 14/30 mesh catalyst was used. The conversion of the various feeds was maintained within a kinetically useful range by adjusting the amount of catalyst and the flow rate. On-line analysis of products was done using a Varian 3700 gas chromatograph with a 60 m, 0.25 mm i.d. nonpolar capillary column.

Experiments were carried out using a ZSM-5 catalyst with a molar silica : alumina ratio of 650 : 1. First order rate constants were calculated using a contact time in seconds, defined as (gas flow at reaction temperature, cc/sec) (catalyst density, 1.78 g/cc)/(catalyst loading, g). The catalyst density here is the density of the zeolite crystals.

RESULTS

First-order rate constants for monomolecular cracking of C_4–C_8 paraffins and C_5–C_8 olefins over ZSM-5 at 510°C are listed in Table 1, and values are plotted in Fig. 1. As

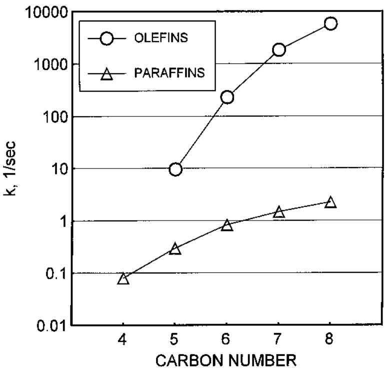

FIG. 1. Cracking rule constants for linear hydrocarbons over 650 : 1 ZSM-5 at 510°C.

expected, paraffins crack much more slowly than olefins. The rate of paraffin cracking increases only moderately with carbon number. At the relatively high temperature and low pressure chosen for these experiments, paraffin cracking proceeds mainly via proton donation to form a pentacoordinated carbonium ion (12). Since the true activation energies and transition states in monomolecular cracking are essentially independent of carbon number (18), this weak dependence of the rate on carbon number is mostly due to the increase in sorption constants. By contrast, the rate of olefin cracking increases dramatically, especially for C_5 through C_7. In addition to an increase in the sorption constants, which is similar to that of the corresponding paraffins, increasing the size of the olefin can allow much more facile cracking modes of the carbenium ion intermediate, as discussed below.

Product distributions are listed in Table 2, along with percent branching of the butenes. Product selectivities obtained from C_6–C_8 olefin cracking typically changed little with level of conversion. Selectivities towards paraffins were less than 1 mol%, except for pentene, which had a methane selectivity of about 3 mol% (Table 2). The product distribution for 2-pentene (mainly ethylene and propylene) indicates monomolecular cracking dominates under our experimental conditions, although some dimerization-cracking is indicated by the butene product and the excess of propylene over ethylene. The formation of other products such as pentane and cyclopentene indicates the occurrence of significant secondary reactions during pentene cracking.

For hexene and larger olefin feeds, however, over 99% of the cracking occurs by a single cracking step to produce two smaller olefin molecules per feed molecule cracked. Under our reaction conditions, secondary bimolecular reactions of the products are negligible, as indicated by the good molar balances between pairs of expected fragments, the absence of paraffins which might result from bimolecular reactions, and the constancy of the fragmentation pattern when the conversion is varied. A small amount of skeletal isomerization of the butene product is observed with hexene cracking. Since C_7 and C_8 cracking occur at much shorter contact time, secondary butene isomerization is not significant with these feeds. Thus, the olefinic products from cracking of C_6–C_8 olefins are kinetically determined and mechanistically significant.

The equilibrium percentage of isobutene in total butenes is about 43% at 510°C. The percentage of isobutene in butenes from 1-hexene cracking (around 30%) falls well below the equilibrium value. Cracking of 1-heptene produces mainly isobutene (about 75%), even though the feed molecule is linear.

DISCUSSION

These results can be rationalized in terms of carbenium ion mechanisms. Shown in Figure 2 and Figures 4–6 are possible carbenium ion structures and types of beta-scission for C_5, C_6, C_7 and C_8 species. Transformations which would involve both initial and final primary carbenium ions or (except for pentene cracking) the formation of a methyl carbenium ion are omitted, because of unfavorable energetics, but reactions involving formally primary carbenium ions had to be recognized to account for the cracked products. The nomenclature of Weitkamp *et al.* (15) is followed in the main, but several new categories have been added. Secondary-to-primary scissions are referred to as type D2, rather than the original D, and primary-to-secondary processes are termed D1. It was felt that primary–secondary processes should not be barred from consideration, unless they can be shown to be much less probable than secondary–primary scissions. The population of secondary carbenium ions is greater than that of primary carbenium ions, which would tend to favor secondary–primary processes, but this may be balanced by the greater energy barrier for the actual scission, relative to primary–secondary cracking. Primary–tertiary (E1) and tertiary–primary (E2) processes are introduced, partly to explain the formation of isobutene during hexene cracking. The cracking patterns of the individual olefin feeds are discussed in detail below.

Pentene Cracking

Figure 2 shows three modes of β-scission of a C_5 carbenium ion via D-type cracking, all involving a primary cation. This accounts for the slow rate of monomolecular cracking of pentene. A fourth mode, primary-to-primary, is expected to be much more difficult and will not be considered in the following. The slow rate of monomolecular cracking allows dimerization-cracking and various side reactions to become significant with pentene feed. Some of these side reactions are shown in Fig. 3.

The third cracking type, D3, results in a methyl cation,

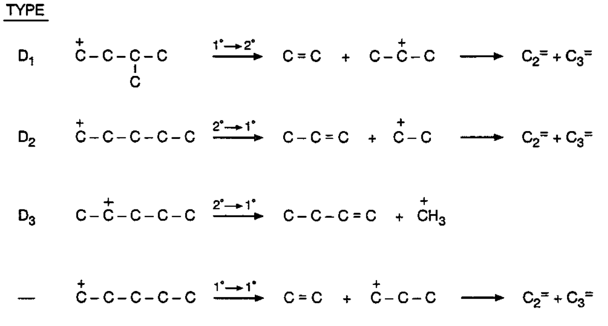

FIG. 2. Modes of β-scission of C_5 carbenium ion.

which is energetically highly unfavorable. Nevertheless, the formation of about 3% methane may result from this type of cracking. The presence of the anionic zeolite framework can stabilize methyl or primary carbenium ions, such that the energy differences among the different types of carbenium ions is less than indicated by measurements of the heats of formation of free, gas-phase carbenium ions (19). Instead of eliminating a proton, the methyl carbenium ion can add to pentene to form a C_6 species, or abstract a hydride ion (hydrogen transfer), preferably from the most abundant hydrocarbon, pentene. The resulting pentenyl cation can undergo cyclization to cyclopentene (Fig. 3I). Additional hydrogen transfer between two pentene molecules yields pentane and additional cyclopentene (Fig. 3II).

Hexene Cracking

For the hexyl cation (Fig. 4), there are six modes of β-scission which involve a primary cation, and one C-type scission, where only secondary cations are involved. The availability of this C-type scission of the 4-methyl-2-pentyl carbenium ion is mainly responsible for the dramatic increase in cracking rates in going from pentene to hexene.

The rate of hexene skeletal isomerization is much faster than its cracking rate (8, 10), so the rate of isomerization to form the 4-methyl-2-pentyl cation probably does not limit the cracking rate. For a 1-hexene feed, significant amounts of the other normal isomers (2-hexene and 3-hexene, both cis and trans) appear at short contact times (less than 5% conversion to C_5-cracking products), followed by branched isomers at longer contact time. This double bond shift is much faster than skeletal isomerization (14). A near-equilibrium hexene isomer distribution can be obtained at 26% conversion to C_5-cracking products (10). These observations indicate that adsorption (with formation of a carbenium ion) and desorption of olefins on an acid catalyst are fast processes. These data rule out a mechanism whereby a given carbenium ion resides on an acid site long enough to undergo double bond shift, formation of a methyl side chain, methyl shift, and eventual cracking, with no desorption intervening. The appearance in the gas phase of the hexene isomers prior to appreciable cracking indicates, rather, than a C_6 entity undergoes numerous adsorption and desorption events on Brønsted acid sites, and only during a few of its adsorption episodes does a methyl branch form or shift to give skeletal isomers. Cracking occurs even less frequently.

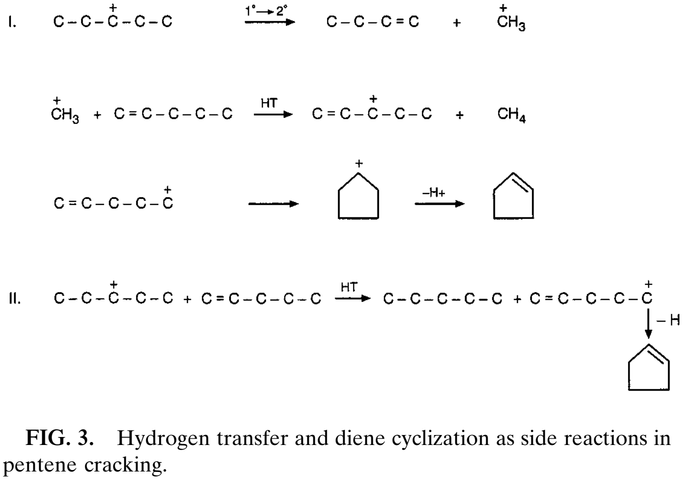

FIG. 3. Hydrogen transfer and diene cyclization as side reactions in pentene cracking.

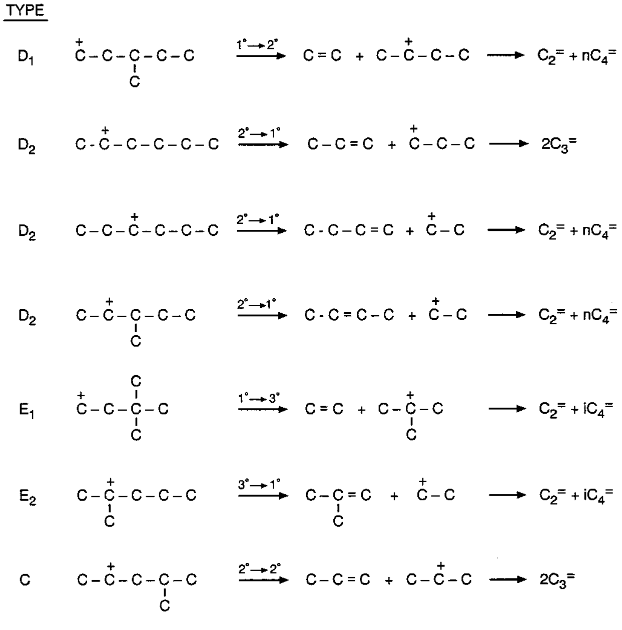

FIG. 4. Modes of β-scission of C_6 carbenium ion.

Order of magnitude estimates of the relative rates of the various modes of β-scission shown in Fig. 4 can be made by relating them to the observed rates of formation of propylene, *n*-butene, and isobutene. Propylene, *n*-butene, and isobutene are produced from 1-hexene in proportions of about 42 : 3 : 1, from the selectivities listed in Table 2.

Iso-butene is produced only by the E1 and E2 scissions, *n*-butene by the D1 and two D2 scissions, and propylene

TABLE 2

Olefin Cracking over HZSM-5 at 510°C and 10 Torr Partial Pressure

Feed	Conv. wt%	Selectivity, mol%				i-$C_4^=$/$C_4^=$%
		$C_2^=$	$C_3^=$	$C_4^=$	$C_5^=$	
2-$C_5^=$ [a]	7.7	31.7	38.3	11.9	—	35.4
1-$C_6^=$ [b]	20.1	7.0	83.6	7.9	0.6	26.0
1-$C_6^=$	34.0	7.4	83.2	8.0	0.7	28.3
1-$C_6^=$	65.5	7.5	83.4	7.9	0.7	34.2
1-$C_7^=$	94.1	0.9	47.3	47.7	0.9	74.2
1-$C_8^=$	85.0	trace	27.5	44.4	28.0	44.0

[a] Other observed products include methane 3.2 mol%, ethane 0.3%, iso- and *n*-pentane 3.7%, cyclopentene 7.2%, methylcyclopentene 2.7%, cyclohexene 0.2%, and hexadiene 0.7%.

[b] Measurement at 5 Torr hydrocarbon partial pressure.

by one D2 and the C scission. Since hexene isomerizes much faster than it cracks, it is reasonable to assume that all seven forms of the hexyl carbenium ion can exist in contact with the acid site of the catalyst. If the further assumption is made that the rates of all D1 and D2 reactions (lumped as "D") are equal, and likewise that the rates of the E1 and E2 ("E") reactions are equal, a set of three equations can be formulated and solved to obtain the relative rates of the C, D, and E scissions as 40:2:1, respectively. The C scission accounts for about 80% of the total hexene cracking rate.

Heptene Cracking

Heptene has two B and two C scission modes, compared to only one C mode available for hexene. Figure 5 shows, for heptene cracking, five D or E type scissions leading to ethylene plus pentene, and four D or E scissions leading to propylene plus butene. Two C scissions produce propylene and *n*-butene, while two B-type scissions give propylene and isobutene. Using the same set of assumptions described above, the iso-butene/total butenes ratio listed in Table 2 for heptene cracking (74.2%) indicates that, on average, a B-type scission is about three times faster than a C-type. Thus, the heptyl cation, with 2 C and 2 B scission modes available, might be expected to crack around eight times faster than the hexyl cation, whose cracking is dominated by a single C-type scission. This corresponds closely to the experimental ratio of heptene to hexene cracking rates of 7.9, from the data in Table 1.

Cracked over ZSM-5 at 400°C, 2,3-dimethyl-2-pentene and 4,4-dimethyl-2-pentene feeds gave the same product distribution as that shown in Table 2 for 1-heptene. This suggests that with heptene, as with hexene, isomerization is rapid compared with cracking.

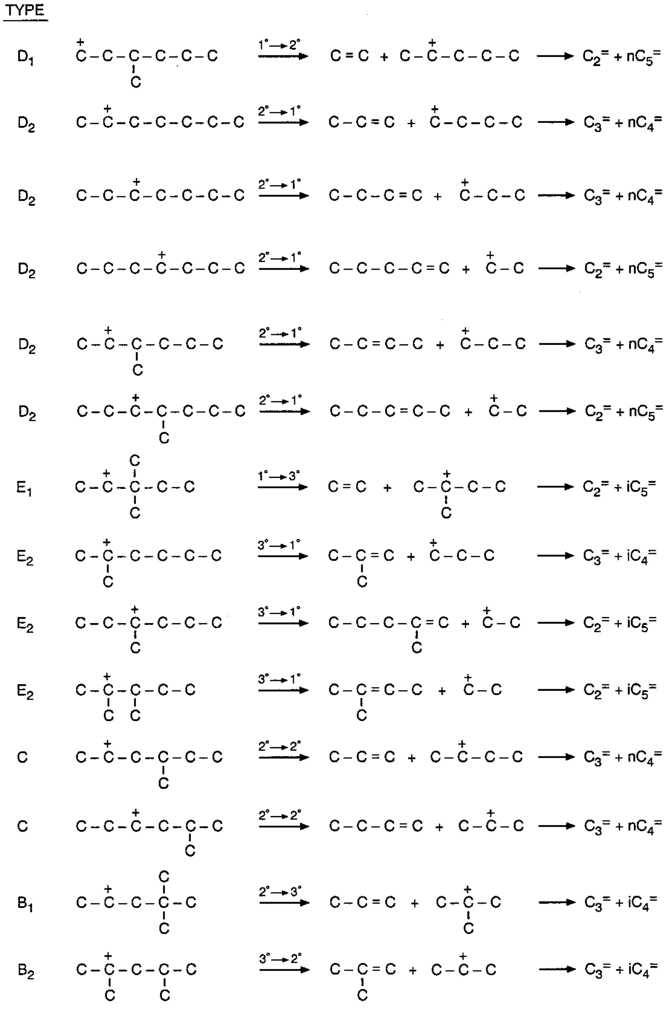

FIG. 5. Modes of β-scission of C_7 carbenium ion.

Octene Cracking

The isomerization of 1-octene leads to a large number of isomers. The structural isomers consist of linear octene, three methylheptenes, five dimethylhexenes, four trimethylpentenes, and two isomers with ethyl side chains. The predominant beta scission structures for octenes of different degrees of branching are depicted in Fig. 6, together with the resulting cracked products. The possibility of undergoing a more facile type of scission (D < C < B < A) increases with the degree of branching. Dimethylhexenes and most trimethylpentenes crack via B-type scission. For only one isomer, 2,4,4-trimethyl-2-pentene, is tertiary-tertiary or A-type scission possible. Six B-type beta-scissions are possible, three of which lead to propylene plus pentene, with the other three each giving one iso-butene plus one *n*-butene. Of the eight C-type scissions, six yield propylene plus pentene, and two each give two *n*-butenes. In general, D- and C-type cracking yields only linear products; B-type

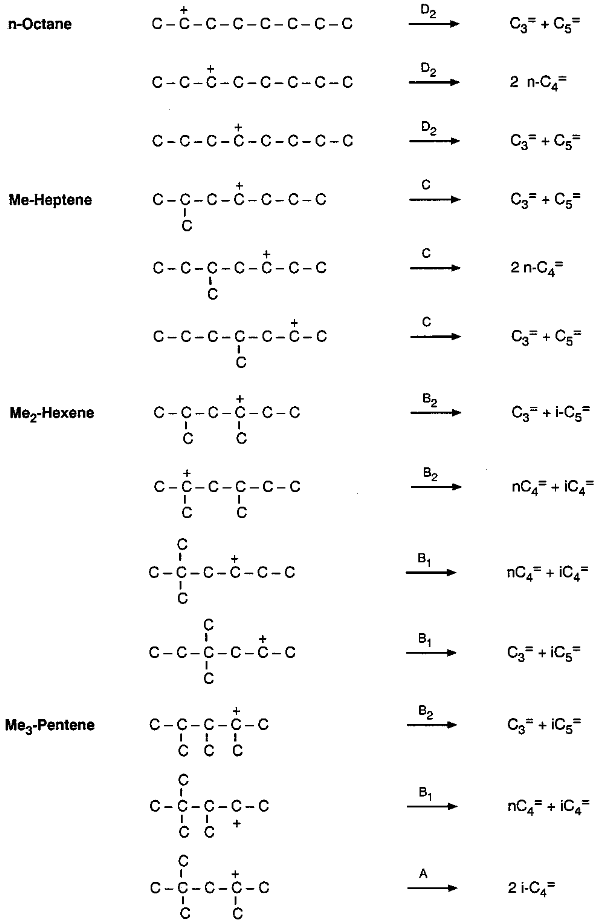

FIG. 6. Predominant β-scission structures and cracking types and resulting products for octene cracking.

TABLE 3

Hexene Cracking over HZSM-5 at 510°C

Cracking rate type	Rate per type	No. of structures	Rel. rate	Relative rates of formation (moles) $C_2^=$	$C_3^=$	n-$C_4^=$	i-$C_4^=$
E 2/i-4	1	2	2	2	—	—	2
D 2/n-4	2	3	6	6	—	6	—
D 3/3	2	1	2	—	4	—	—
C 3/3	40	1	40	—	80	—	—
Rate totals:			**50**	**8**	**84**	**6**	**2**
Distribution, mol%			Calculated	8.0	84.0	6.0	2.0
			Observed	7.5	84.4	5.8	2.3

produces one linear olefin and one branched olefin, and A-type scission gives two branched olefins.

If the A-type scission were dominant, the products would be mostly isobutene, since that is the exclusive product of the A-type scission. However, for 1-octene cracking over ZSM-5 at 510°C (Table 2), the selectivity to propylene plus pentene exceeds the selectivity to total butenes, and the percent isobutene in butenes is only 44%. Either the A-type cracking is not appreciably faster than B-type cracking, or the octyl cations crack before they isomerize to the one tribranched isomer involved in A-type scission. The latter explanation is more likely. Abbot and Wojchiechowski (8) noted that the rate of cracking of olefins increased dramatically with carbon number in going from pentene to octene, but the rate of skeletal isomerization hardly changes. Moreover, the formation of the highly branched 2,4,4,-trimethylpentyl cation may be greatly restricted within the ZSM-5 pores. Weitkamp *et al.* (15) present this constraint on formation of highly branched carbenium ion precursors to A-type cracking in ZSM-5 as an explanation for selectivity differences found in hydrocracking of large paraffins in ZSM-5 versus large pore catalysts. For ZSM-5, we neglect A-type cracking of 1-octene in our analysis of the relative contributions of different cracking modes.

Prediction of Cracking Selectivities and Rates from Cracking Rates of Individual Carbenium Ions

It is possible to describe the overall rate of cracking of an olefin as the sum of the various cracking rates of individual carbenium ions

$$r \text{ total} = k[\text{olef}] = (\nu_B k_B + \nu_C k_C + \nu_D k_D + \nu_E k_E)\,[\text{olef}]$$

where ν_i = number of carbenium ion structures cracking via a particular scission mode, and k_i = relative cracking rate constant of ith mode.

By the procedure outlined above, relative k_i values for E-, D-, and C-type cracking have been obtained from hexene cracking. From heptene cracking, we obtain an additional value for k_B. These relative rates of cracking are as follows:

Cracking type	Relative rate constant for ZSM-5 at 510°C
E	1
D	2
C	40
B	120

Using these values for k_i, and the corresponding abundance factors ν_i obtained from the detailed listing of all the relevant carbenium ion structures (e.g. Figs. 3–4), one can calculate an expected product distribution for cracking of C_6–C_8 olefins. The procedure and the results are listed in Tables 3–5. The relative rates of reaction given in Tables 3–5 are scaled to a hexene cracking rate of 50 mol per unit time. For example, the sum of the relative rates of the

TABLE 4

Heptene Cracking over HZSM-5 at 510°C

Cracking type	Rate per type	No. of structures	Rel. rate	Relative rates of formation (moles)				
				$C_2^=$	$C_3^=$	n-$C_4^=$	i-$C_4^=$	$C_5^=$
E 2/5	1	3	3	3	—	—	—	3
E 3/i4	1	1	1	—	1	—	1	—
D 2/5	2	3	6	6	—	—	—	6
D 3/n4	2	3	6	—	6	6	—	—
C 3/n4	40	2	80	—	80	80	—	—
B 3/i4	120	2	240	—	240	—	240	—
	Rate totals:		**336**	**9**	**327**	**86**	**241**	**9**
	Distribution, mol%:		Calculated	1.3	48.7	12.8	35.9	1.3
			Observed	0.9	48.8	12.7	36.6	0.9

various hexene cracking modes listed in Table 3 sum to 50 moles hexene cracked per unit time, while the relative rate of products formed from hexene cracking sum to 100 mol per unit time. The product distributions for Tables 3–5 were renormalized to take into account only C_2–C_5 olefins. It is apparent that a satisfactory agreement between the calculated and the observed product distribution exists. It is noteworthy that the calculated product distribution for 1-octene cracking in Table 5 is not based on data from octene cracking (other than the insight that A-type cracking can be neglected for 1-octene feed), but is predicted from the relative rates of B- and C-type beta-scissions as determined using the *heptene* feed.

In Table 6 are summarized the contributions of the various cracking types to the overall cracking rate for C_6–C_8 olefins. About 70–80% of the cracking process follows the easiest cracking path available. The values for 1-octene apply to essentially all octene isomers as feed except for 2,4,4-trimethylpentene. With ZSM-5 at 510°C, this isomer cracks at low conversion almost exclusively by the tertiary–tertiary A-type scission, as evidenced by nearly 100% selectivity to isobutene; however, at conversions higher than about 10%, isomerization to other skeletal isomers with B- and C-type cracking begins to contribute. Since A-type cracking is intrinsically faster than other types, the rate of cracking with 2,4,4-trimethyl-2-pentene feed ought to be appreciably faster than the rate of 1-octene cracking, in the absence of diffusional limitations. However, 1-octene cracked more than 50 times faster than 2,4,4-trimethyl-2-pentene, due to the severely limited transport of the tribranched isomer in the ZSM-5 channels. Preliminary results with cracking n-octene over ultrastable Y (USY) catalyst at about 500°C show product distributions similar to those seen with ZSM-5, indicating that, even for the large-pore USY, B-type and C-type cracking largely drain away the C_8 species before they can isomerize to the 2,4,4-isomer and crack via A-type cracking. Restriction on the formation or transport of the tribranched species cannot be invoked as the reason for this cracking pattern in USY, since a 2,4,4-trimethyl-2-pentene feed cracked much faster than n-octene over USY. Thus, at high temperature over solid acids, cracking of monobranched and dibranched C_8 species can compete effectively with isomerization to the

TABLE 5

Octene Cracking over HZSM-5 at 510°C

Cracking type	Rate per type	No. of structures	Rel. rate	Relative rates of formation (moles)			
				$C_3^=$	n-$C_4^=$	i-$C_4^=$	$C_5^=$
C 3/5	40	6	240	240	—	—	240
C n4/n4	40	2	80	—	160	—	—
B 3/5	120	3	360	360	—	—	360
B n4/i4	120	3	360	—	360	360	—
Rate totals:			**1040**	**600**	**520**	**360**	**600**
Distribution, mol%:			Calculated	28.8	25.0	17.3	28.9
			Observed	27.5	24.9	19.5	28.0

TABLE 6

Percent Cracking by Cracking Type 510°C, HZSM-5

Cracking type	Feed			
	1-$C_6^=$	1-$C_7^=$	1-$C_8^=$	2,2,4-$TMP^=$
A	—	—	—	100
B	—	71	69	—
C	80	24	31	—
D	16	4	—	—
E	4	1	—	—
Totals:	**100**	**100**	**100**	**100**

TABLE 7

Relative Rates of Olefin Cracking over HZSM-5 at 510°C

Olefin feed	Cracking type	Relative rate constant, k_i	No. of structures, n_i	Relative rate
$C_6^=$	C	40	1	40
	D	2	4	8
	E	1	2	2
				50
$C_7^=$	B	120	2	240
	C	40	2	80
	D	2	6	12
	E	1	4	4
				336
$C_8^=$	B	120	6	720
	C	40	8	320
				1040

2,4,4-trimethylpentyl isomer which cracks by the energetically favorable tertiary–tertiary (A-type) β-scission.

Using the same rate parameters (obtained from analysis of C_6–C_7 cracking selectivities) which were used above to match the product distribution, relative rates of the overall cracking of the parent C_6–C_8 olefins have been obtained, as shown in Table 7. The calculated rates of overall cracking increase in the ratios 1 : 7 : 21 for hexene, heptene and octene, respectively, as compared to the observed ratios of 1 : 8 : 25. The agreement between calculated and observed relative reaction rates is satisfactory, considering that the calculated octene rate is based solely on carbenium ion scission rates estimated from hexene and heptene cracking.

The results of this study at 510°C involving pure olefins as feeds and products show similarities to the study of Martens *et al.* (16, 17) involving hydrocracking of C_8–C_{10} paraffins to light paraffins at 200°C or less with a dual-functional catalyst containing an active metal (Pt), where olefins are believed to be reaction intermediates. In both cases, isomerization of linear feed molecules to branched isomers precedes cracking. The nature of the products and their relative abundance can be accounted for by applying the rules of carbenium ion chemistry. However, some differences are apparent. In contrast to paraffin cracking, it was found necessary, with light olefin cracking at 510°C, to invoke the participation of cracking paths involving primary carbenium ions (D- and E-type cracking). The fraction of cracking occurring by these paths ranges from over 60% for C_5, to 20% for C_6, and 5% for C_7. Also, the ratios of cracking by the most energetically favored paths are different. For C_7, hydrocracking proceeded 99% by path B, and only 1% by path C (16); for olefin cracking, B-type cracking accounted for only about 70% of the total cracking. With linear C_8 feed, isomerization to the 2,4,4-trimethylpentyl isomer with subsequent A-type cracking accounted for 35% of the octane cracking (17), whereas with 1-octene cracking, essentially all the cracking was via B- and C-type beta scission. Since the slower cracking modes are expected to have higher activation energies, the greater contribution by these cracking modes observed in the present study is likely due, in large part, to the higher reaction temperature employed.

CONCLUSIONS

The relative rates of cracking and resultant product distributions for cracking C_5–C_8 olefins over ZSM-5 catalyst were quantified and rationalized in terms of carbenium ion mechanisms. Cracking rates increase more dramatically with carbon number for olefins than for paraffins, as more energetically favorable modes become available for β-scission of the carbenium ion formed by proton donation to the olefin. For instance, cracking of pentene involves formation at some point of a primary carbenium ion, whereas octene cracking can proceed via tertiary carbenium ion intermediates. The appearance of isomers in abundance prior to appreciable cracking of olefin feeds indicates that an olefin typically undergoes numerous chemisorption and desorption events before cracking.

The product distribution from cracking of C_6–C_7 olefins was used to estimate the relative contributions of various modes of β-scission, as classified by the types of carbenium ions involved. From these results, it was possible to estimate both the overall rate and product distribution for cracking of 1-octene, by summing the expected contributions of the different types of β-scission involved in octene cracking. For hexene and heptene feeds, the most-favorable β-scission mode available (involving just secondary ions for hexene, and secondary plus tertiary for heptene) accounted for 70–80% of the cracking. For 1-octene feed, however, the olefin was nearly all cracked via secondary–tertiary and tertiary–secondary β-scission before it isomerized to the 2,4,4-trimethylpentene isomer required to undergo the most energetically favored (tertiary–tertiary) form of cracking.

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