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Chemical Mechanism of Hydrocarbon Cracking over Solid Acidic Catalysts

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The article analyzes cracking reactions of isoalkanes and isoolefins over zeolite-based catalysts and discusses formation mechanisms of light reaction products under very mild conditions, at 150–250°C. Cracking patterns of 28 methyl- and ethyl-branched isoalkanes show that the compositions of light products can be described by an empirical rule: (1) the reaction site is formed at the tertiary carbon atom in an isoalkane molecule, (2) the predominant fission reaction involves the weakest C–C bond in the α-position to the reaction site, (3) the primary fission products are olefins. None of the cracking mechanisms described in the literature and involving reactions of carbenium and carbonium ions can adequately predict the observed product structures. A new cracking mechanism of isoalkanes which includes reactions between isoalkanes and Brønsted centers on the catalyst surface with the formation of transient hydrosiloxonium ions $>$Si–O$^+$(H)–C$<$ is proposed. The ions undergo the scission of the C–C bond in their alkyl groups in the β-position to O$^+$ with the formation of olefin molecules (which rapidly isomerize) and smaller hydrosiloxonium ions. Comparison of cracked products from olefins and alkanes with the same skeletons and the same expected carbocations shows that the respective products are drastically different when they are formed under very mild conditions, i.e., that the cracking mechanisms of olefins and alkanes are also different. Studies of olefins with low oligomerization abilities (to prevent scrambling of the product structures) show that the olefin cracking can indeed be explained by fragmentation of carbenium ions via the β–C–C bond scission mechanism.

INTRODUCTION

The mechanism of catalytic cracking of alkanes and olefins over solid acidic catalysts continues to generate a vigorous discussion even after 50 years of extensive research in this field (1–3). Three main questions remain unresolved: the nature of active sites on the catalyst surface, the nature of transient reaction intermediates formed in the reactions between the sites and substrates (linear and branched alkanes), and the chemical mechanism of the cracking reaction, the C–C bond fission.

Active Centers and Reaction Intermediates

Two types of acidic sites were proposed:

1. Lewis centers, very strong aprotic acidic species with vacant orbitals, which are capable of removing H$^-$ from alkane molecules and converting them into carbenium ions $C_nH_{2n+1}^+$ (1–4).

2. Brønsted centers, strong protic acidic species which either protonate alkane molecules to nonclassical carbonium ions $C_nH_{2n+3}^+$ with pentacoordinated carbon atoms (5–7) or directly protolyze C–C bonds in alkanes and produce smaller alkanes and carbenium ions (7–13). Brønsted acids are usually regarded as the active species in olefin cracking (14, 15); even relatively weak acids can protonate olefin molecules (16).

In the case of isoalkanes, both Lewis and Brønsted centers are believed to attack primarily tertiary C–H bonds in isoalkanes; the structures of respective carbocations of branched alkanes are (1–12) $R–CH_2–C^+(R'')–CH^2–R'$ (carbenium ion) and $R–CH_2–CH_2^+(R'')–CH^2–R'$ (carbonium ion).

The Mechanism of C–C Bond Fission

The main outcome of a catalytic cracking reaction is the formation of smaller alkanes and olefins from heavier alkanes. Under usual cracking conditions (temperatures over 400°C), any alkane or olefin produces a large number of various light products. The complexity of the product mixtures greatly hinders elucidation of the cracking mechanism. A number of reactions were proposed to explain the formation of small alkanes and olefins.

Monomolecular β–C–C bond scission in carbenium ions (1–3). Reaction 1 uses the carbenium ion of 2,4-dimethylpentane as an example:

$$(CH_3)_2C^+–CH_2–CH(CH_3)_2 \rightarrow (CH_3)_2C{=}CH_2 + {}^+CH(CH_3)_2. \quad [1]$$

In this particular case, the reaction produces an olefin molecule (isobutene) and a small secondary carbenium

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ion which eventually abstracts H^- either from a conjugated base on the catalyst surface or from another alkane molecule and is converted into an alkane (propane). The β-scission reaction was regarded as the principal feature of alkane and olefin cracking reactions for nearly 40 years (17). The main reason for such a wide acceptance is the fact that the β–C–C bond scission is a detailed kinetic equilibrium analog of the olefin cationic polymerization reaction:

$$CH_3-CH^+-R + CH_2{=}CH-R \rightarrow CH_3-CH(R)-CH_2-CH^+-R. \qquad [2]$$

The mechanism of the last reaction has a firm experimental confirmation (16, 18, 19). In addition, a low-temperature analog of the β–C–C bond scission reaction in $CR_3-CH_2-CR_2^+$ carbenium ions derived from alcohols in acidic solutions is described in the literature (16, 20, 21). However, the carbenium-ion mechanism has difficulties in explaining cracking of linear and monobranched alkanes. For example, the β–C–C bond scission in a monobranched carbenium ion (compare to Reaction [1]),

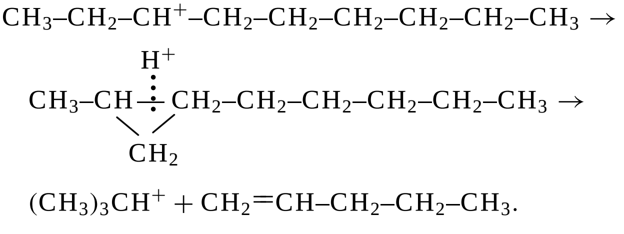
$$(CH_3)_2C^+-CH_2-CH_2-CH_3 \rightarrow (CH_3)_2C{=}CH_2 + {}^+CH_2-CH_3, \qquad [3]$$

produces a primary carbenium ion, a highly endothermic reaction (22). To avoid this difficulty, an alternative cracking route for such carbenium ions was proposed (23). It includes a charge shift and the formation of a secondary carbenium ion prior to the C–C bond scission:

$$(CH_3)_2C^+-CH_2-CH_2-CH_3 \leftrightarrow (CH_3)_2CH-CH_2-C^+H-CH_3 \rightarrow (CH_3)_2C^+H + CH_2{=}CH-CH_3. \qquad [4]$$

Although the formation of a small secondary carbenium ion in Reaction [4] is less endothermic than that of the primary carbenium ion in Reaction [3], the equilibrium concentration of the secondary ion in Reaction [4] is many orders of magnitude lower than that of the tertiary ion, which should make the cracking route in Reaction [4] extremely slow (22).

Monomolecular cracking through the formation of a nonclassical cyclic carbocation (24, 25). In the case of a secondary carbenium ion, this reaction can be represented as:



$$CH_3-CH_2-CH^+-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3 \rightarrow$$
$$CH_3-\underset{\diagdown\;\diagup \atop CH_2}{CH\overset{H^+}{\vdots}CH_2}-CH_2-CH_2-CH_2-CH_2-CH_3 \rightarrow$$
$$(CH_3)_3CH^+ + CH_2{=}CH-CH_2-CH_2-CH_3. \qquad [5]$$

In terms of the product structure, Reaction [5] yields the same olefins as Reactions [1] and [3] but, in general, it should generate more highly branched products.

Monomolecular α-scission in carbonium ions. The following example from Ref. 6 demonstrates the expected reaction products from the carbonium ion formed from 3-methylpentane:

$$CH_3-CH_2-CH_2^+(CH_3)-CH_2-CH_3 \longrightarrow \left\{\begin{array}{l} CH_4 + CH_3-CH{=}CH-CH_2-CH_3 + H^+ \\ C_2H_6 + CH_3-CH{=}CH-CH_3 + H^+ \\ H_2 + CH_3-CH_2-C(CH_3){=}CH-CH_3 + H^+. \end{array}\right. \qquad [6]$$

This mechanism predicts parallel formation of a large number of small alkanes and olefins.

Bimolecular reactions of carbenium ions. Small carbenium ions, e.g., those formed in Reactions [1], [3], and [4], can abstract either H^- (8–13 16, 26) or even alkyl anions (11, 12, 16, 26) from feed molecules with the formation of various small alkanes.

This article describes cracking reactions of isoalkanes and isoolefins over a zeolite-based cracking catalyst and discusses the formation mechanisms of light reaction products under very mild conditions, at 150–250°C. From the perspective of this study, the above brief review of the existing reaction mechanisms shows their main disadvantage: a lack of the precise predictive power. If applied with ingenuity, the combination of Reactions [1–6] can explain formation of virtually any light product from any feed alkane or olefin. On the other hand, as shown below, none of the proposed mechanisms could predict the exact nature of initial products from branched alkanes which are discussed in this paper.

EXPERIMENTAL

Experimental procedures were described earlier (27–29). A gas chromatograph (Hewlett–Packard 5880A) with a flame ionization detector was used both as a cracking reactor and as an analytical tool. A small quantity of a cracking catalyst, usually 0.01–0.02 g, was placed on the frit of the injection glass tube, overlaid with inert powder (10% OV-1 on SW/AW DMSC, ca. 0.03 g), and dried in a He flow at 200°C. To carry out a cracking reaction, the injection assembly of the chromatograph was heated to a desired temperature and 0.05–0.2 μl of a liquid feed was injected in the space above the catalyst layer. The injected feed evaporated and contacted the catalyst, and then the mixture of the unreacted feed and reaction products immediately entered the chromatographic column. The column was, a 50-m, 0.2-mm capillary coated with the 0.5 μm film of cross-linked methyl silicone. The He flow rate was 1 cc/min, and the column temperature was increased from 40 to 300°C at a rate of

5°C/min. All FID response coefficients for light hydrocarbons were assumed equal. Reaction conversions reported below correspond to combined weight yields of all light cracked products.

The following reaction conditions were adopted:

1. Cracking reactions were carried out at 150–250°C, at relatively high [catalyst] : [feed] ratios and, consequently, at very low conversions, usually below 2–3%. Olefins have much higher reactivities compared to alkanes. To avoid olefin overcracking, they were diluted with linear alkanes, *n*-nonane or *n*-decane, in the 1 : 10 ratio. The *n*-alkanes are completely inert under these conditions.
2. The structures of isoalkanes and olefins were selected in such a way that they either provided a possibility of only one cracking pathway or afforded several different, clearly distinguishable pathways within a given molecule.
3. In several instances, alkanes and olefins with the same skeletons were cracked under similar conditions. These experiments provided an opportunity by which to compare directly the reaction products from the same expected carbocations.
4. Formation of light olefins is predicted by all existing reaction mechanisms. The reaction conditions were selected to avoid skeletal isomerization of olefinic products. However, double bond migration reactions in olefins could not be suppressed even under these mild conditions.

The adopted experimental conditions have several drawbacks:

1. Because a flame ionization detector was used, hydrogen could not be detected.
2. The long capillary column is well suited for the identification of relatively heavy reaction products. However, due to poor resolution, the GC analysis could not distinguish between propane and propylene and could barely separate ethane and ethylene.

All olefins and alkanes were supplied by Wiley Organics Co. Most experiments were carried out with a commercial steam-equilibrated cracking catalyst Filtrol FSS-1 which contains the rare earth-exchanged Y zeolite. Several experiments were also carried out with delaminated laponite (DL), an amorphous, weakly catalytic porous solid with S_0 of 380 m^2/g.

Calculations of steric effects in active center models were carried out with the semiempirical steric simulation program Cerius^2 (the Mopac method).

RESULTS

Experimental conditions employed in this study correspond to a short-duration plug flow of a dilute gas stream over a porous solid catalyst. This arrangement allows the study of a large number of different feeds over the same relatively fresh load of catalyst at low feed concentrations in the gas phase, of the order of 0.1–0.2 mmol/liter (27–29). The effective catalyst/substrate ratios in the experiments were ca. 50–100; e.g., a 250–500 A^2 area on the catalyst surface was available for each feed molecule (27). This ratio allows one to neglect competition between a substrate and product molecules for reaction sites. The overall kinetics of alkane cracking under these conditions approximately follows the first-order law (27).

CATALYTIC CRACKING OF ISOALKANES

Cracking of Isoalkanes with One Preferred Reaction Point and One Preferred Reaction Pathway

Several of the tested isoalkanes have symmetric structures with two identical tertiary carbon atoms. The underlying assumption in the subsequent discussion is that the reaction point in the cracking reactions is positioned at one of the tertiary atoms. Therefore, cracking of symmetrically branched isoalkanes was expected to produce degenerate products, a condition which greatly simplifies product analysis.

3,4-Dimethylhexane. Cracking of 3,4-dimethylhexane over FSS-1 catalyst at l50°C proceeds with a very low conversion, ca. 0.5%. Table 1 gives all experimentally found light reaction products. In addition to them, a number of C_8 alkanes with isomerized structures were formed, as described in Ref. 28.

Several conclusions from the data in Table 1 are immediately obvious:

1. Over 90% of reaction products are olefins.
2. The largest fraction of the reaction products, nearly 80 mol%, are linear butenes which are formed in the fission of the C(3)–C(4) bond between two tertiary CH groups. The literature data on olefin reactions over solid acidic catalysts (30–35) and our earlier data (29) show that double-bond

TABLE 1

Cracking of 3,4-Dimethylhexane

		Relative yields (mol.%)	
	Catalyst:	FSS-1, 150°C	DL, 200°C
Product	Conversion (wt%):	0.46	0.55
C_2 products		2.8	4.8
C_4 products			
1-Butane		13.5	20.0
trans-2-Butene		22.7	32.2
cis-2-Butene		39.3	37.8
n-Butane		4.0	2.7
C_6 products			
trans-3-Methyl-2-pentene		2.6	1.2
cis-3-Methyl-2-pentene		2.0	0.6
3-Methyl-1-pentene		0.7	0.3
3-Methylpentane		5.5	0.4

isomerization in linear olefins as well as their hydrogenation over commercial cracking catalysts occur very easily. It is thus reasonable to assume that all initial C_4 products formed in the C(3)–C(4) bond fission were 2-butenes and that they produced 1-butene and *n*-butane as secondary products.

3. The yield of *cis*-2-butene is noticeably higher than that of *trans*-2-butene. *Trans*-2-butene is more stable thermodynamically than its *cis*-isomer, and catalytic cracking of isoalkanes under more severe conditions always produces 2-butenes with the [*trans*] : [*cis*] ratio of ca. 1.3. The predominance of *cis*-2-butene in low-temperature experiments is an indication of a particular steric arrangement during the C–C bond fission.

4. Minor cracked products are C_2 and C_6 olefins and alkanes formed in the fission of the C(2)–C(3) bond. The molar yield of the C_2 products is much smaller than the combined yield of the C_6 olefins.

The cracking pattern of 3,4-dimethylhexane can be represented by a simple *empirical rule*:

1. The reaction site is formed at the tertiary carbon atom in an alkane molecule.
2. The predominant fission reaction involves the weakest C–C bond in the α-position to the site.
3. The primary fission products are olefins.

This is illustrated in the case of 3,4-dimethylhexane in

$$\begin{aligned}&CH_3\text{–}CH_2\text{–}C^{*}H(CH_3)\text{–}CH(CH_3)\text{–}CH_2\text{–}CH_3 \rightarrow\\ &\quad CH_3\text{–}CH{=}CH\text{–}CH_3 + CH_3\text{–}CH{=}CH\text{–}CH_3(+2H).\end{aligned} \qquad [7]$$

Alkanes with two isopropyl groups: 2,5-dimethylhexane and 2,6-dimethylheptane. Cracking of two skeletally similar molecules, 2,5-dimethylhexane over DL at 200°C and 2,6-dimethylheptane over FSS-1 catalyst at 150°C, also proceed with low conversions (Tables 2 and 3). The cracking patterns in both cases are quite similar to that for 3,4-dimethylhexane:

TABLE 2

Cracking of 2,5-Dimethylhexane (200°C, DL, 0.3% Conversion)

Products	Relative yields (mol%)
C_1 product (methane)	0.9
C_2 products (etane + ethylene)	11.3
C_3 products	2.5
C_4 products	
Isobutene	4.4
Isobutane	0.6
C_5 products	
3-Methyl-1-butene	6.0
2-Methyl-2-butene	57.6
2-Methyl-l-butene	4.4
trans-2-Pentene	5.0
2-Methylbutane	7.3

TABLE 3

Cracking of 2,6-Dimethylheptane (150°C, FSS-1, 2.3% Conversion)

Products	Relative yields (mol%)
C_3 products	19.1
C_4 products	
Isobutene	17.6
Isobutane	6.2
C_5 products	13.7
C_6 products	
4-Methyl-1-pentene	7.8
4-methyl-2-pentene	22.8
2-methyl-1-pentene	3.2
2-methyl-2-pentene	9.5

1. Olefins again represent the largest fractions of all reaction products.
2. The main products are formed in the fission of the C(2)–C(3) bonds. It appears reasonable to assume that the initial cracked products in both cases were 1-olefins, 3-methyl-1-butene from 2,5-dimethylhexane, and 4-methyl-1-pentene from 2,6-dimethylhexane. However, the double-bond migration in the respective molecules produced all possible olefins with the same skeletons, with 2-methyl-2-butene and 4-methyl-2-pentene as the most abundant products.
3. Molar yields of C_3 products, which are also expected in the C(2)–C(3) bond fission, are again quite low, especially in the case of 2,5-dimethylhexane.

It is easy to see that the empirical cracking rule formulated above still holds: the reaction point is positioned at the tertiary carbon atom and the weakest α–C–C bond is broken (compare to Reaction [7]).

2-Methyl-substituted isoalkanes. These alkanes represent one more case of molecules with one preferred reaction site, the tertiary carbon atom. Due to a relatively high thermodynamic stability of the CH–CH_3 bond, only one cracking pathway can be expected, the fission of the –CH–CH_2– bond. Tables 4 and 5 give the product distributions for two 2-methyl-substituted alkanes. In general, these results are similar to those produced in the cracking of symmetrically branched dimethyl-substituted alkanes (compare to Tables 2 and 3). Olefins are the largest fractions of all reaction products, and most heavy products are formed in the fission of the C(2)–C(3) bonds: linear C_5 olefins from 2-methylheptane and linear C_7 olefins from 2-methylnonane. As before, we can assume that the initial products are 1-olefins, 1-pentene, and 1-heptene, respectively, but the subsequent double-bond migration produces linear olefins with internal double bonds. Molar yields of C_3 products, which are also expected in the C(2)–C(3) bond fission, are adequately high in the cracking of 2-methylheptane but are again low in the case of 2-methylnonane.

TABLE 4

Cracking of 2-Methylheptane (200°C, DL, 0.03% Conversion)

Products	Relative yields (mol%)
C_3 products	40.2
C_4 products	
Isobutene	9.9
2-Butanes (*trans* + *cis*)	1.5
C_5 products	77.3
1-Pentene	11.4
trans-2-Pentene	27.1
cis-2-Pentene	16.7
n-Pentane	11.6

Cracking of two other 2-methyl-substituted alkanes, 2-methyldecane and 2-methylundecane, was studied with FSS-1 catalyst at 250°C. In both cases, linear C_{n-3} olefins again constituted the major fractions of the products, 40 to 60 wt%. However, smaller linear olefins, C_{n-4}, C_{n-5}, etc., also became noticeable among the reaction products. Their formation suggests parallel cracking pathways involving reaction sites at other carbon atoms in the alkane chains in addition to the tertiary carbon atom.

Cracking of Isoalkanes with One Preferred Reaction Point and Several Possible Reaction Pathways

3-Ethyloctane. According to the above empirical rule, cracking of this isoalkane should produce two families of products:

1. The fission of the C(3)–C(4) bond should form linear pentenes, both 1-pentene and its isomers with internal double bonds. In this case, both cracking fragments should have the same carbon atom numbers and the same skeleton structures. Indeed, as Table 6 shows, these C_5 olefins account for over 40 mol% of all cracked products.
2. The second possible pathway is the fission of two identical C(2)–C(3) bonds. In this case, C_2 and linear C_8 olefins are expected. This route also has the experimental confirmation. However, octenes formed in these reactions are apparently quite reactive and produce secondary products. This may explain higher ethylene yields compared to the combined yields of C_8 products. Cracking of 3-ethylnonane over FSS-1 catalyst at 250°C produces similar results: the fission of the C(3)–C(4) bond results in the formation of linear pentenes and linear hexenes, and the fission of the C(2)–C(3) bonds gives ethylene and linear C_9 olefins.

TABLE 5

Cracking of 2-Methylnonane (250°C, FSS-1, 0.50% Conversion)

Products	Relative yields (mol%)
C_3 products	7.4
C_4 products	
Isobutene	7.2
C_5 product	25.5
C_7 products	
1-Heptene	10.0
trans-2-Heptene	17.5
cis-2-Heptene	11.5
trans-3-Heptene	8.7
cis-3-Heptene	6.4
n-Heptane	5.6

TABLE 6

Cracking of 3-Ethyloctane

		Relative yields (mol%)	
	Catalyst:	FSS-1, 250°C	DL, 200°C
Products	Conversion (wt%):	1.4	~1.0
C_2 products		39.0	~33
C_5 products			
1-Pentene		10.9	~15
trans-2-Pentene		15.9	~21
cis-2-Pentene		14.5	~19
n-Pentane			~5
C_8 products			
1-Octene		0.7	
4-Octene (*cis* + *trans*)		3.7	
trans-3-Octene		3.9	
cis-3-Octene		4.0	~7
trans-2-Octene		3.9	
cis-2-Octene		3.7	

Monomethyl-substituted alkanes. In the case of all monomethyl-substituted alkanes except for 2-methylalkanes, the reaction site is positioned at the tertiary carbon atom and two cracking pathways are possible. Both these pathways are usually realized in low-temperature experiments. For example, cracking of 3-methylheptane (FSS-1, 250°C, conversion 0.4%) produces two groups of products: the fission of the C(2)–C(3) bond generates C_2 and the mixture of linear hexenes, and when the C(3)–C(4) bond is broken, 1- and 2-butenes are formed. The second pathway gives three times more products than the first one. Similar reaction patterns were observed in the cracking of 3-, 4-, and 5-methylnonanes at 200–250°C.

Cracking of Isoalkanes with Several Reaction Points

All asymmetrically disubstituted isoalkanes belong to this category. Tables 7 and 8 list cracked products from two vicinally dimethyl-substituted alkanes, 2,3-dimethylheptane and 2,3-dimethyloctane. In both cases, the existence of two different reaction sites (at each CH group) is possible. However, the weakest bond in both molecules, the C(2)–C(3) bond, should have the highest fission probability irrespective of the position of the reaction site. The results in Tables 7 and 8 confirm this assertion: the majority of all early cracking products are formed as a result of the scission of this bond. The fission of the C(3)–C(4) bond is also

TABLE 7

Cracking of 2,3-Dimethyloctane

Products		Relative yields (mol%)
	Catalyst:	DL, 200°C
	Conversion:	0.80%
C_1 product (methane)		1.2
C_2 product		
Ethane + ethylene		0.6
C_3 products		28.1
C_4 products		
1-Butene		0.9
trans-2-Butene		0.6
cis-2-Butene		0.9
n-Butane		0.4
C_5 products		
2-Methyl-1-butene		0.2
2-Methylbutane		0.2
C_6 products		
1-Hexene		8.3
trans-3-Hexene		6.6
trans-2 + *cis*-3-Hexene		26.8
cis-2-Hexene		23.7

observable, especially in the case of the 2,3-dimethyloctane cracking over FSS-1 catalyst: it produces a mixture of linear and branched C_5 products.

The final example of a complex reaction pattern is cracking of 2,6-dimethyloctane over FSS-1 catalyst at 250°C. This reaction produces a large variety of light cracked products in each carbon atom range from C_2 to C_8. Table 9 classifies the products as a function of the reaction site position (mostly on each of the tertiary carbon atoms) and the position of the broken C–C bond. This consistent interpretation of a complex product mixture became possible only because the previous examples described reaction products formed in each individual cracking pathway.

TABLE 8

Cracking of 2,3-Dimethylheptane

Product		Relative yields (mol.%)	
	Catalyst:	FSS-1, 250°C	DL, 200°C
	Conversion	0.23%	0.17%
C_2 products		2.1	~0
C_3 products		29.7	35.8
C_4 products		2.1	5.7
C_5 products		27.5	7.1
1-Pentene		3.6	0.3
trans-2-Pentene		3.0	1.9
cis-2-Pentene		1.9	1.8
2-Methyl-l-butene		0.7	1.5
2-Methyl-2-butene		3.9	1.5
n-Pentane		0.2	0.4
2-Methylbutane		12.6	~0.2
2,3-Dimethylbutane		0.6	
C_7 products		37.4	51.4
1-Heptene		6.0	6.1
trans-3-Heptene		7.4	9.6
cis-3-Heptene		3.4	—
trans-2-Heptene		12.8	18.8
cis-2-Heptene		10.6	13.4
n-Haptane		1.2	3.5

TABLE 9

Cracking of 2,6-Dimethyloctane (FSS-1, 250°C, 0.33% Conversion)

Carbon atom numeration

$$\mathrm{C(1)H_3{-}\underset{C(2')H_3}{C(2)H}{-}C(3)H_2{-}C(4)H_2{-}C(5)H_2{-}\underset{C(6')H_3}{C(6)H}{-}C(7)H_2{-}C(8)H_3}$$

Products	Relative yields (mol%)
A: Position of reaction site: C(2) atom; fission of C(2)–C(3) bond	
Propylene + propane	5.9
C_7 products with 3-methyl-branched skeleton (4-methyl-1-hexene, 3-methyl-2-hexenes, 3-methyl-3-hexenes, 3-methylhexane)	34.6
B: Position of reaction site: C(6) atom; fission of C(5)–C(6) bond	
Linear C_4 products (1-butene, 2-butenes)	14.0
C_6 products with 2-methyl-branched skeleton (2-methyl-1-pentene, 2-methyl-2-pentene, 4-methyl-2-pentenes, 4-methyl-1-pentene)	18.0
C: Position of reaction site: C(6) atom; fission of C(6)–C(7) bond	
Ethylene + ethane	9.6
C_8 products with 2-methyl-branched skeleton	5.8
D: Position of reaction site: C(3) atom; fission of C(2)–C(3) bond —the same products as from C(2) site, C(2)–C_3) bond fission	
E: Position of reaction site: C(3) atom; fission of C(3)–C(4) bond	
Isobutene + isobutane	~6
C_6 products with 3-methyl-branched skeleton (3-methyl-2-pentenes)	~3
F: Position of reaction site: C(4) atom; fission of C(3)–C(4) bond —the same products as from C(3) site, C(3)–C(4) bond fission	
G: Position of reaction site: C(4) atom; fission of C(4)–C(5) bond	
C_5 products with 2-methyl-branched skeleton (2-methyl-1-butene, 2-methyl-2-butene)	9.0

Effect of Reaction Severity on the Product Distribution

Reaction conditions employed in the previous examples correspond to very early stages of alkane cracking, the condition required for the analysis of primary reaction products. Any increase in the reaction severity, either a temperature increase or a decrease of the feed/catalyst ratio, results in the formation of more complex mixtures of reaction products. Table 10 demonstrates this effect using 3,6-dimethyloctane as an example. The first column lists products generated under very mild conditions. The reaction produces cracked products with structures which are easily discernible based on the same empirical rule. 3,6-Dimethyloctane has two identical preferential reaction sites, C(3) and C(6) CH groups. Therefore, two cracking patterns are possible. The fission of the C(2)–C(3) bond

TABLE 10

Cracking of 3,6-Dimethyloctane over FSS-1 Catalyst under Different Conditions

		Relative yields (mol%)			
	Temperature (°C):	200	350	250	350
	Feed/cat. ratio (g/g):	0.029	0.029	0.0014	0.0014
Product	Conversion (%)	0.11	0.86	52.6	33.7[a]
Methane		0	7.5		
Ethane + ethylene		13.7	10.0	0.2	0.5
Propane + propylene		0	8.9	4.0	9.8
C_4 products					
Isobutane		0	3.9	17.5	15.1
Isobutene		0	5.0	4.9	8.1
1-Butene		6.2	2.8		
2-Butenes		2.8	6.2	7.9	8.4
C_5 products					
2-Methylbutane		2.8	5.3	1.1	17.9
3-Methyl-1-butene		0.3	0.8	0	0.3
2-Methyl-1-butene		0.9	3.5		1.7
2-Methyl-2-butene		4.8	8.6	7.6	6.5
1-Pentene		0	0.8		0.5
2-Pentenes		0	2.9	3.2	3.2
n-Pentane		0	0		0.9
C_6 products					
2-Methylpentane		0	3.9	13.9	11.5
2-Methyl-1-pentene		0	2.0	0	0.7
2-Methyl-2-pentene		0.9	2.2	1.1	1.2
2-Ethyl-1-butene		1.8	0.7	0.4	0.7
3-Methylpentane		24.7	4.4	6.3	4.1
3-Methyl-1-pentene		0.9	1.4	0	0.2
3-Methyl-2-pentene		12.7	4.5	1.2	0.7
n-Hexane		0	0.6	0	0.7
2-Hexenes		0	1.4	—	0.4
Methylcyclopentane		0	0.6	1.3	1.7
C_7 products					
2-Methylhexane		0	2.0	3.5	1.8
2-Methyl-1-hexene		0	0.4	0.2	0.1
2-Methyl-2-hexene		0	0	0.1	0.1
2-Methyl-3-hexene		0	0.1	0	0.1
3-Methylhexane		0	0.8	1.7	0.9
3-Methyl-1-hexene		0	0	0	0.1
3-Methyl-3-hexene		0	0.7	0.2	0.3
2,3-Dimethylpentane		0	1.0	—	0.4
C_8 products					
2-Methylheptane		0	0	0.6	0.1
2-Methyl-1-heptene		0	0	0.1	0.1
3-Methylheptane		27.8	3.8	0.5	0.2
3-Methyl-2-heptene		0	0.6	0	0
3-Methyl-3-heptene		0	0	0	0.3
2,3-Dimethylhexane		0	0	0.1	0.4
2,4-Dimethylhexane		0	0	0.3	0.1
2,5-Dimethylhexane		0	0	0.3	0.1

[a] Aged catalyst.

gives C_2 products and C_8 products with the methyl group in the third position in the chain (mostly 3-methyl-heptane in this experiment) with a combined yield of over 40%. The fission of the C(3)–C(4) bond produces a mixture of linear C_4 olefins and 3-methyl-branched C_6 products, 3-methylpentenes, and 3-methylpentane (see Fig. 1), with a total yield of 50%. Another, less energetically favorable reaction position, at the CH_2(4) group, generates two C_5 products with the 2-methyl-branched skeleton (combined yield of ca. 9%).

Both an increase in the reaction temperature (column 2 in Table 10) and a decrease in the feed/catalyst ratio (columns 3 and 4) result in the formation of numerous products, either through skeletal isomerization of the initial products (linear C_5 products in addition to 2-methyl-branched C_5 products, linear and 2-methyl-branched C_6 and C_8 products in addition to 3-methyl-branched products with the same carbon atom number) or through numerous secondary reactions which produce hydrocarbons with all other possible carbon atom numbers. The final outcome of all these reactions is the formation of completely scrambled hydrocarbon mixtures with a predominance of monomethyl- and dimethyl-branched alkanes in all carbon atom numbers, as well as the formation of a few olefins with the highest thermodynamic stabilities, such as isobutene, 2-methyl-2-butene, 2-methyl-2-pentene, etc. As was shown earlier, at this increased severity level the compositions of the product mixtures practically do not depend on the skeletal structures of feed alkanes (29). The results in Table 10 demonstrate once again that in order to investigate the chemical mechanism of alkane cracking over solid acidic catalysts one has to limit reaction conditions to temperatures not exceeding 200°C and to relatively high feed/catalyst ratios.

A New Class of Cracked Products, Unconjugated Dienes

Analysis of reaction products from various isoalkanes at 250–350°C showed the presence of a new class of reaction

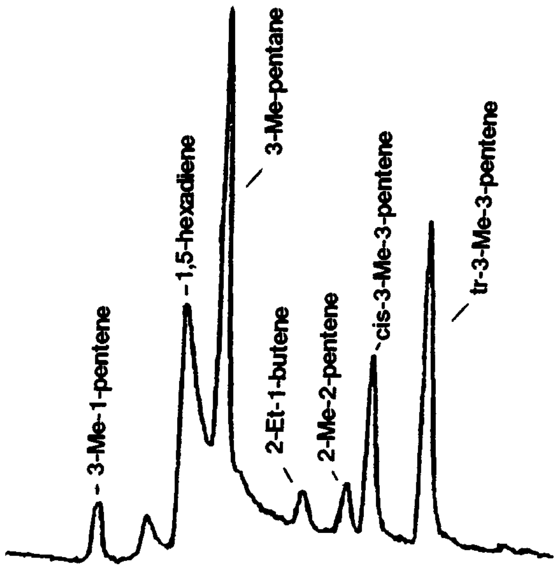


FIG. 1. Gas chromatogram of reaction products from 3,6-dimethyloctane (FSS-1, 250°C).

products which has not been reported in detail in the past, linear unconjugated α,ω-dienes. The positions of the diene peaks in gas chromatograms and their relative positions with respect to the peaks of n-alkanes and linear α-olefins were determined from two sources, GC data for several individual dienes and by analyzing thermocracked products from 1-tetradecene and 1,7-octadiene (over quartz, at 515°C, 2–3 sec).

Analysis of the diene products in cracking of 28 different isoalkanes showed the following consistent pattern:

1. All isoalkanes with methyl groups in the second position in the chain (13 compounds), such as all studied 2-monomethyl-branched C_{10}–C_{17} alkanes and dimethyl-branched alkanes with one or both of their methyl groups in the second position (e.g., 2,4- and 2,6-dimethylheptanes, 2,3-, 2,6- and 2,7-dimethyloctanes, etc.) produced 1,4-pentadiene as the principal diene product.
2. All compounds with methyl groups in the third position in the chain (7 compounds), such as 3-methylheptane and 3-methylnonane, and dimethyl-branched alkanes with one of the methyl groups in the third position in the chain (2,4- and 3,4-dimethylhexanes, 2,6- and 3,6-dimethyloctanes) produced 1,5-hexadiene as a prominent product.
3. Both studied 3-ethyl-branched alkanes, 3-ethyloctane and 3-ethylnonane, produced 1,6-heptadiene.
4. Linear alkanes appear to not generate any dienes; however, very low reaction yields, even at 250–350°C, preclude a definite conclusion.

The peaks of the dienes have a distinct appearance in the gas chromatograms of the reaction products recorded under our experimental conditions (Fig. 1): whereas the peaks of light alkanes and olefins are relatively narrow and symmetric, the diene peaks are always broad and trailing. This peak shape suggests that the dienes are either strongly adsorbed on the catalyst surface or formed at rates much lower than those of other reaction products.

CATALYTIC CRACKING OF OLEFINS UNDER MILD CONDITIONS

Olefin reactions over solid catalysts at 250–350°C were described in detail earlier (29). The main results of the present study are consistent with the literature data (32–37) and can be summarized as follows. All cracked products from olefins can be separated into two groups, products with the same carbon atom numbers as the feeds and products with other carbon atom numbers.

Olefin Transformations with the Preservation of the Carbon Atom Number

1. Double-bond shift in olefins occurs very easily in the 150–250°C range and usually results in the formation of equilibrium mixtures of all possible olefins with a given skeleton. This reaction is the main obstacle to stereochemical studies of alkane cracking, as shown above.

TABLE 11

Light Reaction Products from C_7 Olefins with Different Skeletons (150–200°C, FSS-1)

	Relative yields (mol%)			
Olefins:	2-Methyl-1-hexene	2-Methyl-2-hexene	3-Methyl-1-hexene	3-Methyl-2-hexene
Products Conversion (wt%):	2.9	3.9	4.1	3.4
C_4 products				
Isobutene	21.2	23.0	~5	20.5
Isobutane	<1	1.9		2.7
2-Butenes	~0	~0		8.8
C_5 products				
2-Methyl-1-butene	1.8	1.1	1.6	5.5
2-Methyl-2-butene	10.5	11.1	9.1	24.4
2-Methylbutane	~0	0.4	0.6	1.3
C_6 products				
2-Methyl-1-pentene	13.3	11.0	2.2	4.9
2-Methyl-2-pentene	48.1	41.1	31.6	11.2
4-Methyl-2-pentene + 2-Methylpentane	5.1	10.4	2.9	4.2
3-Methyl-1-pentene	0	0		<0.3
3-Methyl-2-pentene	0	0	27.8	13.7
2-Ethyl-1-butene	0	0	16.9	1.0
3-Methylpentane	0	0		0.6

2. Skeleton isomerization in olefins proceeds at lower rates and becomes significant only at temperatures of 250°C and above.
3. Olefin hydrogenation with the skeleton preservation also becomes significant at temperatures exceeding 200–250°C. Under more severe conditions, alkanes with isomerized skeletons are also formed.

Formation of Lighter and Heavier Products

1. Judging by the data in Ref. 29, most lighter and all heavier cracked products from olefins, especially from linear olefins, are formed in a sequence of reactions including oligomerization as the first step followed by cracking of the oligomers.
2. These products are highly degenerated: within each carbon atom number, the structure of the cracked products bears no resemblance to and cannot be deduced from the structure of the feeds.

In the current investigation of olefin cracking, we limited the scope to one subject: analysis of light products from isoolefins with the same or similar skeletons as those of the isoalkanes described above. This choice had a rationale: the evaluation of a possibility that olefins, if cracked under very mild conditions, would exhibit reaction patterns similar to those of analogous isoalkanes.

In agreement with the previous conclusions, the reaction products from isoolefins at 150–200°C also consist of the same two principal components. The first group

TABLE 12

Light Reaction Products from C_8 Olefins with Different Skeletons (FSS-1)

Olefins:	Relative yields (mol%)					
	5-Methyl-3-heptene	2,4-Dimethyl-1-hexene	3,4-dimethyl-3-hexene			
Temperature (°C):	150	200	150	250	350	350[a]
Products Conversion (wt%):	2.9	9.4	1.4	12.6	16.8	39.0
Methane	0	0	0	0	3.1	~0
Ethane + ethylene	0	0	0	1.4	2.7	1.5
Propane + propylene	0	0	0	8.1	17.9	20.6
C_4 products						
Isobutene	3.7	22.1	4.1	17.9	23.4	31.6
Isobutane	0.6	1.6	0.8	1.3	1.5	7.0
2-Butenes	4.6	3.4	0	4.9	9.4	10.7
C_5 products						
2-Methyl-1-butene	3.1	9.2	6.5	5.7	5.0	5.3
2-Methyl-2-butene	13.6	52.4	36.1	20.0	13.5	15.2
2-Methylbutane	2.7	2.4	8.7	1.6	1.2	6.2
3-Methyl-1-butene	0	0	0	0	0.8	0.5
1-Pentene	0	0	0	0	0.2	0.2
2-Pentenes	0	0	0	0	1.3	1.9
C_6 products						
2-Methyl-1-pentene	3.6	0	0	1.6	0.6	1.0
2-Methyl-2-pentene	5.1	0	0	3.9	1.0	1.8
4-Methyl-2-pentene + 2-Methylpentane	3.4	0	0	6.0	1.0	3.2
3-Methyl-1-pentene	0.7	0	0	0	1.4	0.1
3-Methyl-2-pentene	12.2	2.7	29.4	6.6	1.7	3.0
2-Ethyl-1-butene	0	0	0	0	0.4	0.2
3-Methylpentane	2.2	0	2.8	0	0	1.1
C_7 products (total)			11.6	26.6	13.4	8.0
2-Methyl-1-hexene	1.8	0.3				
2-Methyl-2-hexene	2.3	1.8				
2-Methyl-3-hexene	6.3	0				
2-Methylhexane	9.5					
3-Methyl-2-hexene	22.3	0	3.3			
3-Methyl-3-hexene	0	0	2.6			
3-Methylhexane	2.3	0	3.1			
2,4-Dimethyl-1-pentene	0	3.3	0			
2,4-Dimethyl-2-pentene	0	0.7	0			

[a] Undiluted olefin feed, fresh catalyst.

includes olefins with the same carbon atom numbers and the same skeleton structures. For example, cracking of *trans*-3-methyl-2-pentene at 150°C produces a mixture of 3-methyl-1-pentene, 2-ethyl-1-butene, and *cis*- and *trans*-3-methyl-2-pentenes in the 0.0053 : 0.0073 : 0.52 : 1 ratio, as well as a small amount of a hydrogenated primary product, 3-methylpentane. No skeleton isomerization occurs under these conditions. The second group includes a large variety of light products with different carbon atom numbers and skeleton structures. As before, any attempt of rationalization of the product structures defies a simple single pattern. The products from several C_7 and C_8 isoolefins are given in Tables 11 and 12. Table 12 also lists the products from one C_8 olefin, 3,4-dimethyl-3-hexene, formed in experiments at 150, 250, and 350°C. Several general conclusions can be drawn:

1. The overwhelming fractions of all products are olefins.

2. Each C_n olefin produces light products in the range from C_4 to C_{n-1}. No C_1, C_2, or C_3 products were observed under mild conditions while they became quite prominent at higher temperatures (Table 12).

3. Irrespective of skeleton structures of the feeds, all monomethyl-substituted olefins produce the same three olefinic products with quite high yields, isobutene, 2-methyl-2-butene, and 2-methyl-2-pentene. Olefins with the same skeletons and with differently positioned double bonds (2-methyl-1-butene, 2-methyl-1-pentene, and 4-methyl-2-pentene), as well as isoalkanes (isobutane, 2-methylbutane, and 2-methylpentane), are also usually formed.

4. Olefins with the same skeletons but with different positions of double bonds produce the same light products

but with different yields: compare the data for 2-methyl-1-hexene vs 2-methyl-2-hexene and for 3-methyl-1-hexene vs 3-methyl-2-hexene in Table 11.

5. No similarities were found in the structures of cracked products from alkanes and olefins with the same skeletons. Compare, for example, reaction products from 3,4-dimethylhexane (Table 1) vs those from 3,4-dimethyl-3-hexene (Table 12) or 3-methylheptane (discussed above) vs 5-methyl-3-heptene (Table 12).

6. A temperature increase above 200°C rapidly brings a complete degeneration in the product distributions. Table 12 shows that whatever specificity one can discern in the types of products formed at 150°C, such as the high yield of 3-methyl-2-pentene and the low yield of isobutene from 3,4-dimethyl-3-hexene, rapidly disappears at higher temperatures, and the reaction products from practically all olefins at 350–400°C became indistinguishable, irrespective of the feed structure.

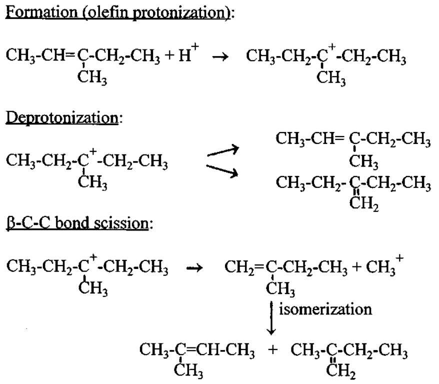
DISCUSSION

The present studies of olefin cracking under mild conditions were carried out in an expectation that they could aid in understanding of the alkane cracking mechanism. This supposition has a long history in the literature on catalytic cracking (1–3, 6, 17) and is based on the hypothesis that, in both cases, the actual reactive species responsible for most C–C fission reactions are the same carbenium ions. The results presented above show that this hypothesis is not correct: the products from olefins and alkanes with the same skeletons and the same expected carbocations are drastically different even when they are formed under very mild conditions. These differences suggest that the cracking mechanisms of olefins and alkanes are also different.

Mechanism of Olefin Cracking

Ability of olefins to react with Brønsted acidic sites with the formation of carbenium ions is one of the least disputed subjects in the literature on catalytic cracking. It is supported by a large body of studies of olefin reactions in acidic solutions (16) and by a direct observation of olefin protonization by zeolites (38). A tendency of olefins to form oligomeric products over solid catalysts (17), and the fact that these light oligomers, mostly dimers and trimers, have the same structures as those produced in cationic polymerization reactions (29, 35), represent another convincing proof that carbenium ions from olefins are indeed formed on the catalyst surface.

However, ability of carbocations to initiate oligomerization reactions depends on the olefin structure. Olefins with vinyl and vinylidene bonds have much higher reactivities in cationic polymerization reactions than olefins with internal vinylene (R–CH=CH–R), trisubstituted and tetrasubstituted double bonds. Therefore, only catalytic reactions of olefins with a lower oligomerization ability can be used for the analysis of true fragmentation patterns of carbenium ions.



SCHEME I. Reactions of carbenium ion derived from 3-methyl-2-pentene.

In the case of the lightest olefin of this type we examined, *trans*-3-methyl-2-pentene, the expected β–C–C bond scission reactions in the respective tertiary carbenium ion are shown in Scheme I. Our experimental results (cracking at 150°C, total conversion to light products 6.2 wt%) generally agree with this scheme:

1. Over 92 mol% of the carbenium ions deprotonize and form both the original olefin (54.6 mol%) and the expected isomerization products, *cis*-3-methyl-2-pentene (28.3 mol%), 2-ethyl-1-butene (3.8 mol%), and 3-methyl-1-pentene (0.3 mol%), the balance being 3-methylpentane.

2. Because the β–C–C bond fission reaction in this carbocation, the breaking of the CH_3–CH_2 bond, requires a significant energy, the respective products constitute merely 5.8 mol% of the total product mixture (but still 76 mol% of all light products). As expected, these products have the 2-methyl-branched C_5 skeleton: 2-methyl-2-butene (4.5 mol%), 2-methyl-1-butene (0.8 mol%), as well as 2-methylbutane (0.5 mol%).

Cracking of another symmetrically branched olefin, 3,4-dimethyl-3-hexene, can be explained in a similar way. The expected cracked products are given in Scheme II (part A). Experimental data on the light products formed at 150°C (Table 12) are, in general terms, consistent with the scheme:

1. The heaviest of the expected products, the C_7 olefins formed in the scission of the CH–CH_3 bond in the tertiary carbenium ion, should have the 3-methyl-branched skeletons. They are indeed generated with the yield of 9.0 mol%.

2. The C_6 products formed in the CH–CH_2 bond scission in the tertiary ion also should have the 3-methyl-branched skeleton. Their combined experimental yield is higher (32.2 mol%) because the fission of this bond is less energetically demanding.

3. No evidence was found of the C–C bond fission in the secondary carbenium ion [it may be formed in a charge shift

Part A
Reactions of carbenium ion derived from 3,4-dimethyl-3-hexene

Formation (olefin protonization):

$$CH_3-CH_2-C(CH_3)=C(CH_3)-CH_2-CH_3 + H^+ \rightarrow CH_3-CH_2-C^+(CH_3)-CH(CH_3)-CH_2-CH_3$$

β-C-C bond scission in tertiary carbenium ion:

$$CH_3-CH_2-C^+(CH_3)-CH(CH_3)-CH_2-CH_3 \rightarrow CH_3-CH_2-C(CH_3)=CH-CH_3 + C^+H_2-CH_3$$

Charge shift and β-C-C bond scission in secondary carbenium ion:

$$CH_3-CH_2-C^+(CH_3)-CH(CH_3)-CH_2-CH_3 \rightarrow CH_3-CH_2-CH(CH_3)-CH(CH_3)-C^+H-CH_3$$
$$\downarrow$$
$$CH_3-CH=CH-CH_3 + CH_3-CH_2-C^+H-CH_3$$

Methyl shift and β-C-C bond scission:

$$CH_3-CH_2-C^+(CH_3)-CH(CH_3)-CH_2-CH_3 \rightarrow CH_3-CH(CH_3)-CH_2-C^+(CH_3)-CH_2-CH_3$$
$$\downarrow$$
$$(CH_3)_2C=CH-CH_3 + CH_3-C^+H-CH_3$$

Part B
Expected cracked products from 3,4-dimethylhexane according to different C-C bond scission mechanisms

Carbenium ion: $CH_3-CH_2-C^+(CH_3)-CH(CH_3)-CH_2-CH_3$
(the same as from 3,4-dimethyl-3-hexene)

β-C-C bond scission: $CH_3-CH=C(CH_3)-CH_2-CH_3 + C_2H_5^+$
or $CH_3-CH_2-CH=C(CH_3)-CH_2-CH_3 +$
$(CH_3)_2C=C(CH_3)-CH_2-CH_3 + CH_3^+$

Cyclic intermediate: Cracking is impossible with this mechanism.

Carbonium ion: $CH_3-CH_2-CH_2^+(CH_3)-CH(CH_3)-CH_2-CH_3$

α-C-C bond scission: $CH_3-CH_2-C(CH_3)=C(CH_3)-CH_2-CH_3 + H_2$
$CH_3-CH_2-CH=C(CH_3)-CH_2-CH_3 + CH_4$
$CH_3-CH=C(CH_3)-CH_2-CH_3 + C_2H_6$
$CH_3-CH=CH-CH_3 + n\text{-}C_4H_{10}$

SCHEME II. Cracking of isoalkanes and isoolefins with 3,4-dimethyl-branched skeleton.

reaction (22)]. Such a reaction should have produced linear butenes (see Scheme II, part A). On the other hand, the experimentally observed C_5 products (Table 12) can be satisfactorily explained by the methyl group-shift reaction expected in the carbenium ion chemistry (22). The possibility of this cracking path is supported by the presence of C_8 olefins with the 2,4-dimethyl-branched skeleton (2,4-dimethyl-2-hexene, 2,4,-dimethyl-1-hexene, etc.) in the reaction products.

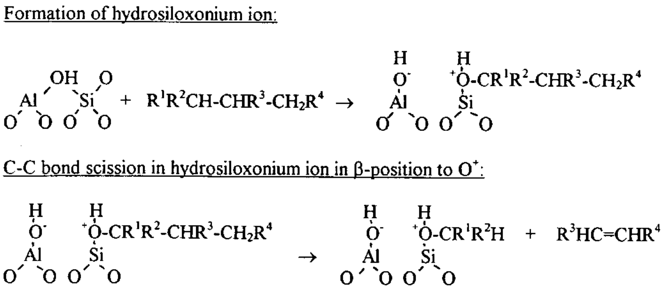
In conclusion, these low-temperature data and the structures of cracked products diven in Tables 11 and 12 support the β–C–C bond fission in carbenium ions as the olefin cracking mechanism.

Mechanism of Alkane Cracking

Comparison of isoalkanes and isoolefins with the same skeletons (3,4-dimethylhexane vs 3,4-dimethyl-3-hexene, 3-methylheptane vs 5-methyl-3-heptene, etc.) rules out any significant role of carbenium ions and the β–C–C bond scission mechanism in alkane cracking under mild conditions. Scheme II compares proposed cracking reactions of an olefin (part A) and an alkane (part B) with the same 3,4-dimethyl-branched skeleton. If the β–C–C bond scission mechanism in tertiary carbenium ions is operative in both cases, one would expect the formation of the same cracked products from the alkane and the olefin. The experimental data contradict this prediction (compare Tables 1 and 12). Similarly, these data do not support the carbenium ion isomerization mechanism and β–C–C bond scission in secondary carbenium ions (23) which also should be operative in both examples.

As far as the participation of pentacoordinated carbonium ions in the alkane cracking reactions is concerned (part B in Scheme II), the only existing experimental analogies can be drawn with low-temperature decomposition reactions of isoalkanes in superacids (13). In the latter case, protolysis of alkanes containing tertiary carbon atoms and $CH–CH_3$ bonds (the bonds present in most alkanes discussed in this paper) is usually dominated by the release of H_2 and CH_4 as well as by dissociation of the weakest $CH–CH_2$ bonds. Even at low temperatures, these reactions usually produce numerous light alkanes from any single feed. These reactions are expected to be even less structure-specific under the regular alkane cracking conditions, in contrast to the experimental results.

As shown above, cracking of isoalkanes over solid acidic catalysts under mild conditions can be reduced, with some simplifications, to a general rule: the C–C bonds undergoing fission are, predominantly, the weakest $CH–CH_2$ or CH–CH bonds adjacent to tertiary carbon atoms (see Reaction [7] as an example). When one attempts to propose a mechanism of alkane cracking, this empirical rule should find a clear explanation. Another experimental finding that should be accommodated is the data by Haag *et al.* about a crucial role of Brønsted acidic centers containing adjacent Al and Si atoms in the cracking activity of zeolites (5, 6, 37, 38). Our mechanism is described in Scheme III. It borrows from organic chemistry the concept of oxonium ions R_3O^+ which are often generated in chemical reactions under acidic conditions (13). The mechanism also uses the structure of Brønsted sites in zeolites described in the literature (5, 17, 38). According to the proposed mech-



SCHEME III. Proposed mechanism of alkane cracking.

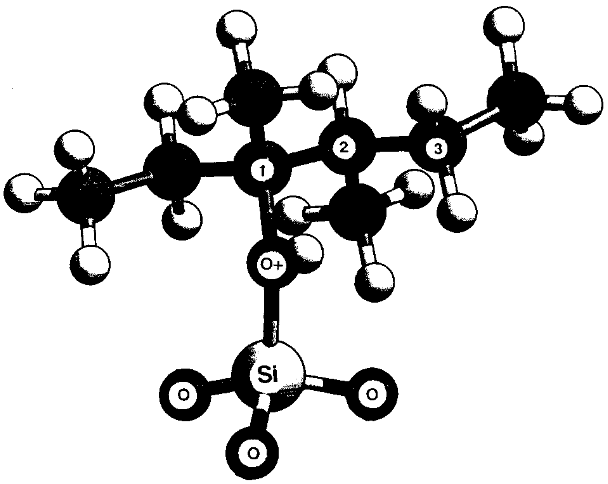


FIG. 2. Steric model of the proposed active center bearing the (*R*, *S*)-3,4-dimethylhexane moiety.

anism, an isoalkane $R^1R^2CHCHR^3CH_2R^4$ reacts with a Brønsted center and forms a transient hydrosiloxonium ion $>$Si–O$^+$(H)–C$<$. As in the case of most mechanisms of heterogeneous catalysis, the structures of immediate neighboring groups at the ion are mostly speculative; their only generally accepted feature is the position of the negative countercharge in the vicinity of the tetracoordinated Al atom (17, 38). The stage of the oxonium ion formation in Scheme III can be reversible and can represent alkane chemisorption by a zeolite.

We propose that the hydrosiloxonium ion undergoes the scission of the C–C bond in its alkyl group in the β-position to O^+ (Scheme III). The probability of this reaction is determined by the energetics: it is higher when the remaining $>$Si–O$^+$(H)–CR^1R^2H ion is stabilized due to the nucleophilic properties of R^1 and R^2 groups and when the leaving $R^3HC{=}CHR^4$ olefin has a higher thermodynamic stability. Similar C–C scission reactions in the gas phase are known for hydroxonium ions ROH_2^+ and hydroaminium ions RNH_3^+ (39, 40). At higher temperatures, isomerization reactions in the oxonium ions and secondary reactions of the primary olefinic products via the carbenium ion mechanism completely scramble the structures of the reaction products (27, 28).

Figure 2 shows a model of the proposed active center, the hydrosiloxonium ion bearing the (R, S)-3,4-dimethylhexane moiety. The structure was sterically relaxed by using the Cerius^2 program (Mopac method). Data in Table 1 (see discussion above) can be visualized as due to the scission of the C–C bond in the β-position to O^+ (carbon atoms marked 1 and 2). The scission reaction is accompanied by a transfer of one of the hydrogen atoms attached to the C(3) atom to the C(1) atom (distances 2.68 and 2.89 Å). Two C–C bonds in the transition complex, C(2)H–CH_3 and C(3)H_2–CH_3, are in the *gauche* conformation, the arrangement that favors the *cis*-structure of the leaving 2-butene molecule. This conclusion is supported by the data on the thermodynamically unfavorable [*cis*] : [*trans*] ratio in the butene products (Table 1).

When an alkane cracking reaction is carried out at low temperatures, the hydrosiloxonium ions with small CHR^1R^2 groups, such as methyl, ethyl, or isopropyl, can be relatively stable. This may explain often observed disbalances in the molar yields of complimentary light and heavy reaction products, such as lower yields of C_2 vs C_6 products from 3,4-dimethylhexane (Table 1), lower yields of C_3 vs C_5 products from 2,5-dimethylhexane (Table 2), lower yields of C_3 vs C_6 products from 2,5-dimethyiheptane (Table 3), C_3 vs : C_7 products from 2,6-dimethyloctane (Table 9), etc.

At higher temperatures, siloxonium ions can react with feed alkanes with the formation of small alkanes, e.g.:

$$\begin{aligned} &{>}\mathrm{Si{-}O^+(H){-}CR^1R^2H + CH\,R'R''{-}CH_2R''' \rightarrow} \\ &\qquad {>}\mathrm{Si{-}O^+(H){-}CR'R''{-}CH_2R''' + CH_2R^1R^2.} \end{aligned}$$

This reaction is in many respects similar to the bimolecular reactions of carbenium ions proposed in the literature (see Introduction).

Finally, the question of the predominance of alkanes vs olefins in cracking reactions at high temperatures should be addressed. Two arguments can be put forward. First, primary olefins formed in the decomposition of oxonium ions are usually very reactive (29); they easily oligomerize and crack via the carbenium ion intermediates. Second, linear unconjugated dienes formed from isoalkanes at low temperatures (see above) can represent a possible hydrogen source in the course of their conversion into aromatics and coke.

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