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Degenerate Non-primary Products in Catalytic Cracking of Isoalkanes

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Product distributions in catalytic cracking of a series of C_{10}–C_{17} isoalkanes over two acidic catalysts, a Y-zeolite-based commercial catalyst and SiO_2–Al_2O_3, were studied at 250 and 350°C. The cracked products from a C_n alkane belong to two distinct groups, primary products (isomerized C_n alkanes), and degenerate non-primary products, isoalkanes ranging from C_3 to C_{n-1}. Degeneration of the non-primary products is expressed in two ways:

1. In each carbon number range, the non-primary products from alkanes are the mixtures of isoalkanes containing mostly monomethyl- and dimethyl-branched alkanes. The compositions of the mixtures are practically independent of the structures of feed alkanes, and the relative yields of isoalkanes with different skeletons are mostly determined by the thermodynamic stabilities of respective isomers.

2. The distributions of the non-primary products with respect to their carbon numbers have the inverted-U shapes with the maxima at C_4–C_5. These distributions also do not depend on the skeleton structure of the feeds.

The main reason for the cracked product degeneration is high reactivity of a part of the reaction products, light olefins, in reactions over acidic catalysts. This conclusion is based on the experimental cracking study of a series of C_3–C_{14} olefins with the same catalysts under mild conditions (100–250°C). © 1994 Academic Press, Inc.

INTRODUCTION

Catalytic cracking of individual alkanes is a complex multistage process (1–11). According to the carbocation theory (8, 9, 11), cracking of heavy alkanes proceeds through highly reactive carbocation intermediates. The formation mechanism of the carbocations in the reactions between acidic centers on the catalyst surface and saturated hydrocarbon molecules remains a disputed subject. Both Lewis and Brønsted sites have been proposed as participants in the carbocation formation step (7–10, 12): the Lewis centers can directly produce carbenium ions while the Brønsted centers initially produce carbonium ions which subsequently form carbenium ions (7, 10, 11, 12).

Heavy carbocations undergo a series of reactions including chain skeleton isomerication and the C–C bond fission (8, 9, 11). A generalized scheme of these reactions, based on the published data, is shown in Fig. 1. When a cracking reaction of a single alkane is carried out at temperatures over 300°C, nuemrous light products are always formed with broadly comparable yields. Several approaches to classification of these products are possible. Wojchiechowski (13, 14) proposed a kinetic classification procedure:

reactant molecule → primary products
(stable and unstable)

unstable primary products → secondary products
(stable and unstable), etc.

Attribution of a particular cracked product as a primary or a secondary one according to this approach is based on the shapes of kinetic curves which describe product yields as a function of time on stream (13, 14). Such a classification is well suited for the description of vigorous cracking processes that involve numerous C–C bond fission steps. However, it is less convenient for a detailed mechanistic analysis of cracking reactions under relatively mild conditions.

Earlier we proposed an alternative classification of cracked products (4) which was based on the carbocation theory of catalytic cracking. Within this classification, the first reaction step in the cracking reaction of a C_n alkane involves isomerization of its carbocation and a release of a large number of primary cracking products, C_n isoalkanes (Fig. 1). This step does not involve any net fission of the C–C bonds. Quantitative analysis of the distributions of the primary products derived from a number of C_8 and C_{10} isoalkanes was presented earlier (4).

A single C–C bond fission in the isomerized C_n^+ carbocations (Reaction 2 in Fig. 1) results in the formation of two secondary products, lighter olefins C_m and lighter alkanes C_{n-m}. Formation of olefins greatly complicates the detailed analysis of catalytic cracking. Olefins can be easily converted to carbocations by Brønsted sites (8,

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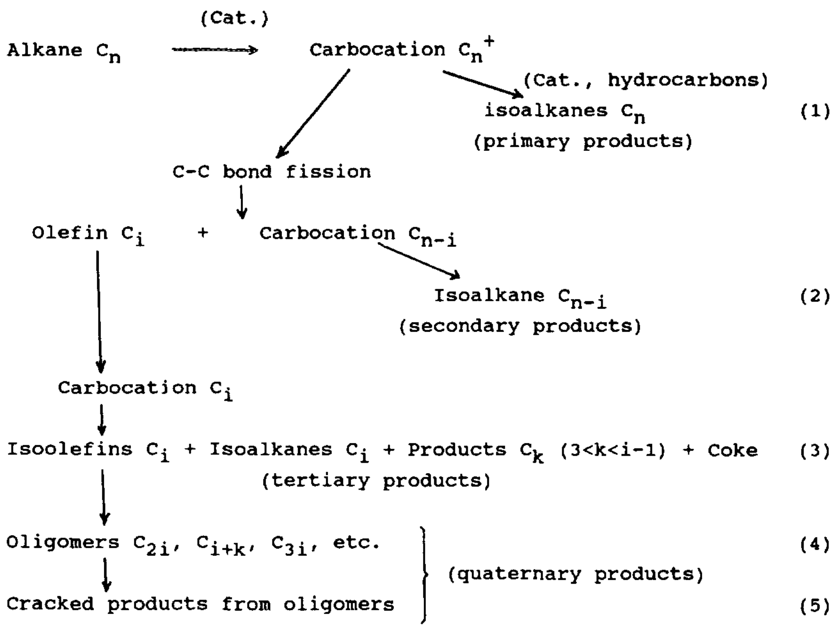


FIG. 1. General scheme of catalytic alkane cracking.

9, 11). For this reason, they have a very high reactivity over acidic catalysts and can form a large variety of products (Fig. 1), including isoalkanes with the same carbon number, C_m, (Reaction 3) as well as a variety of isoalkanes C_i with $3 < i < 2m$ which are generated from olefin oligomers (Reactions 5 (Fig. 1)). All these reactions involve active centers of different acidities and possibly a different nature. The chemical structures of the products derived from olefins C_m are practically indistinguishable from those of the secondary alkanes C_{n-m} formed in Reaction 2. As a result, a separate quantitative analysis of the secondary, tertiary, and quaternary products in alkane cracking apparently becomes impossible. Rather, all non-primary products of a C_n alkane cracking, i.e., all alkanes and olefins with carbon numbers different from n should be regarded as degenerate in the sense that their structures cannot be traced to the structures of feed alkanes.

This article addresses three subjects related to the degree of degeneration of the non-primary cracked products:

1. An experimental study of olefin reactions over acidic catalysts under mild conditions. This study was necessary to provide a direct comparison of olefin and alkane reactions with the same catalysts and in the same apparatus.
2. The chemical structures of the non-primary products derived from alkanes with different skeletons.
3. The distributions of the non-primary products with respect to their carbon atom numbers.

EXPERIMENTAL

As described earlier (4, 15), a gas chromatograph (Hewlett–Packard 5880A) was used both as a cracking reactor and as an analytical tool. A small quantity of a cracking catalyst, 0.01–0.05 g, was placed on the frit of the injection tube, overlaid with a small amount of an 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 the cracking reaction, the injection assembly was heated to a desired temperature, and 0.05 to 0.2 μl of a liquid feed or 1–2 ml of a gas feed was injected in the space above the catalyst layer. The 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 cm^3/min, and the column temperature was increased from 40 to 300°C at a rate of 5°C/min.

All olefins and alkanes were supplied by Wiley Organics Co. Most experiments were carried out with commercial steam-equilibrated cracking catalyst FSS-1 (Filtrol) which contained ca. 20% of the rare earth-exchanged Y zeolite with S_0 of 400–500 m^2/g. A few experiments also were carried out with two other catalysts, amorphous silica–alumina AAA (calcined for 12 h at 540°C) and delaminated laponite.

RESULTS AND DISCUSSION

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 for the study of a large number of different feeds over relatively fresh catalysts at low feed concentrations. The average concentration of a feed in the gas flow is of the order of 0.1–0.2 mmol/liter. Cracking of olefins (described below) showed that this experimental setup did not cause any feed-stream slip between catalyst particles. The effective catalyst/substrate weight ratios in the experiments were in the 50–200 range. Under these conditions, a 500–1000 Å^2 area on the catalyst surface is available for each feed molecule (15), i.e., competition between the substrate and product molecules for adsorption centers can be neglected. The overall kinetics of alkane cracking under these conditions approximately follows the first-order law (15).

1. Olefin Reactions over Acidic Catalysts

Cracking of a number of linear and branched C_5–C_9 α-olefins over acidic catalysts was thoroughly investigated in the literature (16–24). When a C_m olefin is cracked at 200–250°C, the dominant reaction is the double-bond shift resulting in the formation of olefin mixtures. Under more severe conditions, two other reactions become prominent, skeletal isomerization of olefin molecules and formation of lighter and heavier products (20–23). Two mechanisms for the latter process are usually considered:

Monomolecular cracking:

$$C_mH_{2m} \rightarrow \text{alkanes } C_iH_{2i+2} + \text{olefins } C_iH_{2i} \text{ with } 3 < i < m.$$

Stoichiometry of this reaction requires an external source of hydrogen, most probably due to the formation of polyaromatic coke.

Bimolecular cracking via dimer formation:

$$C_mH_{2m} \rightarrow [C_{2m}H_{4m}] \rightarrow \text{alkanes } C_iH_{2i+2} \\ \text{and olefins } C_iH_{2i} \text{ with } 3 < i < 2m.$$

The ability of an olefin to form dimers is thought to greatly decrease with the increase of its molecular weight. For example, when cracking with the ZSM-5 zeolite was carried out at 400°C (22), the fraction of the products formed via bimolecular cracking decreased as

$$\begin{array}{ccccc} 1\text{-}C_5H_{10} & 1\text{-}C_6H_{12} & 1\text{-}C_7H_{14} & 1\text{-}C_8H_{16} & 1\text{-}C_9H_{18} \\ \sim 100\% & 81\% & 13\% & \sim 0 & \sim 0 \end{array}.$$

The primary goal of our olefin cracking study reported below was to compare olefin and alkane reactions under similar conditions in order to evaluate the contribution of olefin reactions to the overall process of alkane cracking. Low-conversion olefin reactions with a commercial catalyst under our experimental conditions could be carried out only at 150–250°C. Although the results presented below do not suggest a need for a significant departure from the previously established mechanisms of olefin cracking, the quantitative data provide a necessary framework for a better understanding of alkane cracking.

Double bond isomerization. Double bond shift with the preservation of the molecular skeleton is the fastest reaction among other olefin reactions. It can be investigated separately from other processes only with aged catalysts at very low temperatures, 150–200°C, or with delaminated laponite (a very poor cracking catalyst) at 300–350°C. Nearly equilibrium mixtures were produced from all studied olefins. Several examples are given in Table 1.

Skeleton isomerization. Skeleton isomerization in olefins also proceeds relatively easily, starting at 200°C with active catalysts and at 350°C with delaminated laponite. For example, reaction of 4-Me-1-$C_5^=$ over delaminated laponite at 350°C produced both the double bond shift products (the same as those from 2-Me-1-$C_5^=$ in Table 1) and 3-Me-2-$C_5^=$ as the principal products.

Olefin hydrogenation. Two different types of saturated products must be distinguished. The first one is an alkane with the same skeleton as that of the feed olefin. Such alkanes are produced relatively easily, e.g., at temperatures as low as 200°C in the presence of FSS-1 catalyst. The normalized yields of respective *n*-alkanes from linear α-olefins at 250°C were, for 1-octene, 12.7%; for 1-decene, 17.7%; for 1-undecene, 10.8%; and for 1-dodecene, 12.8%. The same catalyst also hydrogenizes isoolefins: even at 150°C *trans*-Me-2-$C_5^=$ gives 3-Me-C_5, both 2-Me-1-$C_6^=$ and *trans*-2-Me-2-$C_6^=$ produce 2-Me-C_6, 2,4-Me_2-1-$C_6^=$ forms 2,4-Me_2-C_6, etc.

Formation of alkanes with isomerized skeletons. When temperatures approach 250°C, alkanes with isomerized skeletons become the most abundant products of olefin reactions. In addition to *n*-octane, all linear octenes at 250°C also produce 2-, 3-, and 4-methylheptanes, 2,2-, 2,3-, 2,4-, 2,5-, 3,3-, and 3,4-dimethylhexanes. Similarly, in addition to *n*-decane, cracking of 1- and 5-decenes under the same conditions also generates all pos-

TABLE 1

Compositions of Isomerized Olefin Mixtures over FSS-1 Catalyst at 150–200°C

Feed	Product distribution (normalized yields)
1-$C_8H_{16}^=$	1- 6.2%, *trans*-2- 29.6%, *cis*-2- 10.1%, *trans*-3- 23.4%, *trans*-4- 11.4%, *cis*-3 + *cis*-4- 19.2%
cis-2-$C_8H_{16}^=$ [a]	1- 4.3%, *trans*-2- 19.4%, *cis*-2- 10.8%, *trans*-3- 24.5%, *trans*-4- 14.9%, *cis*-3 + *cis*-4- + *n*-C_8H_{18} 26.2%
trans-3-Me-2-$C_5^=$	3-Me-1-$C_5^=$ 2.1%, *trans*-3-Me-2-$C_5^=$ 50.8%, *cis*-3-Me-2-$C_5^=$ 30.3%, 2-Et-1-$C_4^=$ 16.7%
2-Me-1-$C_5^=$	2-Me-1-$C_5^=$ 25.8%, 2-Me-2-$C_5^=$ 72.3%, 4-Me-1-$C_5^=$ <0.5%, *trans* + *cis*-4-Me-2-$C_5^=$ 1.8%

[a] Reaction at 350°C, accompanied by extensive oligomerization and hydrogenation.

sible isomers of methylnonanes and dimethyloctanes. The same isoalkanes are formed from branched olefins. For example, *trans*-5-Me-3-$C_7^=$, in addition to the isoalkane with the same skeleton, 3-methylheptane, produces 2- and 4-methylheptanes and various dimethylhexanes; 2,6-Me_2-2-$C_7^=$ forms, in addition to 2,6-dimethylheptane, all other isomeric dimethylheptanes and methyloctanes, etc.

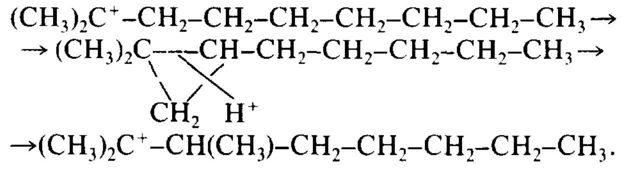
Table 2 lists relative yields of isooctanes produced in the cracking of several octenes at 250 and 350°C. When linear octenes were used as feeds, monomethyl-substituted alkanes were the dominant products. However, when dimethyl-branched hexenes were used as feeds, various dimethyl-substituted alkanes were much more abundant. Cracking linear decenes gave similar results: monomethyl-substituted alkanes were the dominant products, while dimethyl-substituted alkanes were formed with much lower yields. These experiments also showed that the distributions of isodecanes in such reactions, in a broad sense, did not depend on the type of the catalysts, whether they were zeolite based or silica–alumina.

These results can be rationalized in terms of the standard carbocation rearrangement scheme (8, 9, 11):

Type A skeleton rearrangement (*methyl shift*):

$$CH_3\text{–}CH_2\text{–}CH_2\text{–}C^+(CH_3)\text{–}CH_2\text{–}CH_2\text{–}CH_2\text{–}CH_2\text{–}CH_3 \rightarrow$$
$$\rightarrow CH_3\text{–}CH_2\text{–}C^+(CH_3)\text{–}CH_2\text{–}CH_2\text{–}CH_2\text{–}CH_2\text{–}CH_2\text{–}CH_3.$$

Type B skeleton rearrangement (*change of branching degree*):



$$(CH_3)_2C^+\text{–}CH_2\text{–}CH_2\text{–}CH_2\text{–}CH_2\text{–}CH_2\text{–}CH_2\text{–}CH_3 \rightarrow$$
$$\rightarrow (CH_3)_2C\text{---}CH\text{–}CH_2\text{–}CH_2\text{–}CH_2\text{–}CH_2\text{–}CH_3 \rightarrow$$
$$CH_2 \quad H^+$$
$$\rightarrow (CH_3)_2C^+\text{–}CH(CH_3)\text{–}CH_2\text{–}CH_2\text{–}CH_2\text{–}CH_2\text{–}CH_3.$$

Formation of monomethyl-substituted alkanes from linear olefins (Table 2) requires only one B-type rearrangement followed by several A-type rearrangements. On the other hand, formation of dimethyl-substituted alkanes requires

TABLE 2

Relative Yields of C_8 Isoalkanes Formed from Various Octenes over FSS-1 Catalyst at 250 and 350°C.

Alkane product	Feed						Primary C_8 isoalk. (average) (Ref. 4)
	1-$C_8^=$	*cis*-2-$C_8^=$	*cis*-4-$C_8^=$	*trans*-5-Me-3-$C_7^=$	2,4-Me_2-1-$C_6^=$	3,4-Me_2-3-$C_6^=$	
				250°C			
n-C_8	[a, b]	[a, b]	[a, b]	—	~0	~0	~0.02
2-Me-C_7	1.0	1.0	1.0	1.0	1.0	1.0	1.0
3-Me-C_7; 3-Et-C_6	1.25	1.25	1.28	[a]	1.39	5.79	0.84
4-Me-C_7	0.38	0.40	0.59	0.71	0.55	2.10	0.27
2,2-Me_2-C_6	~0	~0	~0	~0	—	~0	~0
2,3-Me_2-C_6	0.10	0.11	0.05	0.10	[c]	2.67	0.73
2,4-Me_2-C_6	0.18	0.18	~0.04	0.12	[a]	3.33	1.50
2,5-Me_2-C_6	0.09	0.08	~0.04	0.07	3.40	0.69	2.13
3,3-Me_2-C_6	0.03	0.04	—	—	0.73	0.50	0.02
3,4-Me_2-C_6	0.03	0.05	0.07	~0.06	0.79	[a]	0.16
				350°C			
n-C_8		[a, b]		~0	~0	—	~0.04
2-Me-C_7		1.0		1.0	1.0	1.0	1.0
3-Me-C_7; 3-Et-C_6		1.08		(1.51)[a]	1.25	1.69	0.92
4-Me-C_7		0.31		0.39	0.39	0.56	0.29
2,2-Me_2-C_6		~0		~0	~0	~0	~0
2,3-Me_2-C_6		0.20		0.21	2.24	2.00	0.50
2,4-Me_2-C_6		0.20		0.23	(3.90)[a]	2.32	0.83
2,5-Me_2-C_6		0.17		0.19	2.01	1.30	0.94
3,3-Me_2-C_6		0.05		0.10	—	1.29	0.06
3,4-Me_2-C_6		0.08		0.10	0.46	(0.95)[a]	0.16

Note. Reference compound: 2-Me-C_7.

[a] Formed in hydrogenation of feed olefin.

[b] Peak overlapped by peaks of *cis*-3- and *cis*-4-octenes.

[c] Peak overlapped by peak of 2,4-dimethyl-2-hexene.

at least two B-type rearrangements, a more energetically demanding process. Similarly, when the feed olefins already have strongly branched skeletons, formation of less branches isoalkanes via a reversed B-rearrangement is a slower process compared to the methyl shift via an A-type rearrangement.

The last column in Table 2 contains the averaged data on the distributions of linear and branched primary saturated products formed in Reaction 1 (Fig. 1) from various octanes at 250 and 350°C (from Ref. 4). The difference between the product distributions from olefins and alkanes is very significant. All alkanes, independently of their skeleton structures, produce virtually the same combinations of primary products with practically the same relative yields. These yields reflect thermodynamic stabilities of respective carbocations (4). On the other hand, olefins, when they react with the same catalysts and under the same conditions, never reach the same equilibrium product distributions.

These differences can be explained by the existence of active centers with drastically different properties. Cracking reactions of alkanes are relatively slow. For example, conversions of isooctanes over fresh catalysts vary from 2 to 7% at 250°C and from 5 to 15% at 350°C, and the *n*-octane conversions are, respectively, 0.5% and 1%. On the other hand, all octenes are completely converted to the mixtures of isomerized olefins and alkanes starting at 150°C. These differences are most probably caused by the relative rates of carbocation formations. At low temperatures, only the most acidic sites on the catalyst surface are capable of ionizing alkanes. Their carbocations are strongly coordinated to the sites and have relatively long lifetimes. As a result, the skeleton isomerization processes in them are usually brought to an equilibrium. On the other hand, olefins can be converted to carbocations by a much higher number of less acidic centers. These centers retain the carbocations for a short time only, and the B-type rearrangements do not come to completion.

Olefin oligomerization. Formation of olefin dimers is usually proposed to explain formation of heavy products in olefin reactions over acidic catalysts (16–23). However, many details of these reactions are poorly understood, mostly due to the very complex nature of generated oligomer mixtures (23). The experimental technique used in this study is very convenient for the selective examination of oligomerization reactions because it affords easy detection of heavy products even if they are formed with very low yields.

The original structures of olefin dimers could be discerned only in the case of propylene reaction at 100–150°C, when conversions do not exceed 0.2%. The structures of the dimers could be rationalized based on a simple cationic dimerization scheme:

$$\begin{aligned}
&CH_2{=}CH\text{–}CH_3 + H^+ \rightarrow CH_3\text{–}CH^+\text{–}CH_3\\
&\qquad CH_3\text{–}CH^+\text{–}CH_3 + CH_2{=}CH\text{–}CH_3 \rightarrow + CH_3\text{–}CH(CH_3)\text{–}CH_2\text{–}CH^+\text{–}CH_3 \rightarrow\\
&\qquad\qquad \rightarrow CH_3\text{–}CH(CH_3)\text{–}CH{=}CH\text{–}CH_3\ (67\%) + CH_3\text{–}CH(CH_3)\text{–}CH_2\text{–}CH{=}CH_2\ (23\%)\\
&CH_3\text{–}CH(CH_3)\text{–}CH_2\text{–}CH^+\text{–}CH_3 \rightarrow CH_3\text{–}C^+(CH_3)\text{–}CH_2\text{–}CH_2\text{–}CH_3 \rightarrow CH_3\text{–}C(CH_3){=}CH\text{–}CH_2\text{–}CH_3\ (7\%)\\
&CH_3\text{–}CH^+\text{–}CH_3 + CH_3\text{–}CH{=}CH_2 \rightarrow CH_3\text{–}CH(CH_3)\text{–}C^+(CH_3)\text{–}CH_3 \rightarrow CH_3\text{–}C(CH_3){=}C(CH_3)\text{–}CH_3\ ({\sim}3\%).
\end{aligned}$$

When the temperature is increased to 200°C and the propylene conversion increases to 2%, numerous products in every carbon number from C_4 to C_{15} are formed. Their relative yields, normalized to the C_6 yield, are:

C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	C_{11}
0.22	0.43	1.0	0.39	0.33	1.01	0.22	0.08·

Only enhanced yields of the C_6 and C_9 products indicate now that the original source of all these products are propylene oligomers. A similar phenomenon was described earlier for propylene oligomerization over ZSM-5 catalyst (23). A further temperature increase brings a gradual redistribution of the products in favor of lower carbon numbers, and at 400°C propylene trimers are barely observable.

Dimerization of 1-butene is always preceded by the double bond scrambling and produces complex mixtures of C_8 olefins and alkanes (Fig. 2). When *cis*- or *trans*-2-butenes react under similar conditions, their dimers contain the same compounds as those from 1-butene but with higher yields of unisomerized dimers, *trans*- and *cis*-3,4-Me_2-2-$C_6^=$ and 3,4-Me_2-2-$C_6^=$. Extensive hydrogenation of olefin dimers takes place even at 100°C, resulting in the formation of 3,4-Me_2–C_6. The latter isomerizes at increased temperatures into mixtures of all possible methylheptanes and dimethylhexanes.

Isoalkanes with carbon numbers $i < m$ and $m < i < 2m$. Oligomerization of olefins and subsequent cracking of the oligomers generates hundreds of compounds of various molecular weights and structures. Structural identification of the dimers, which is difficult even for 1-butene

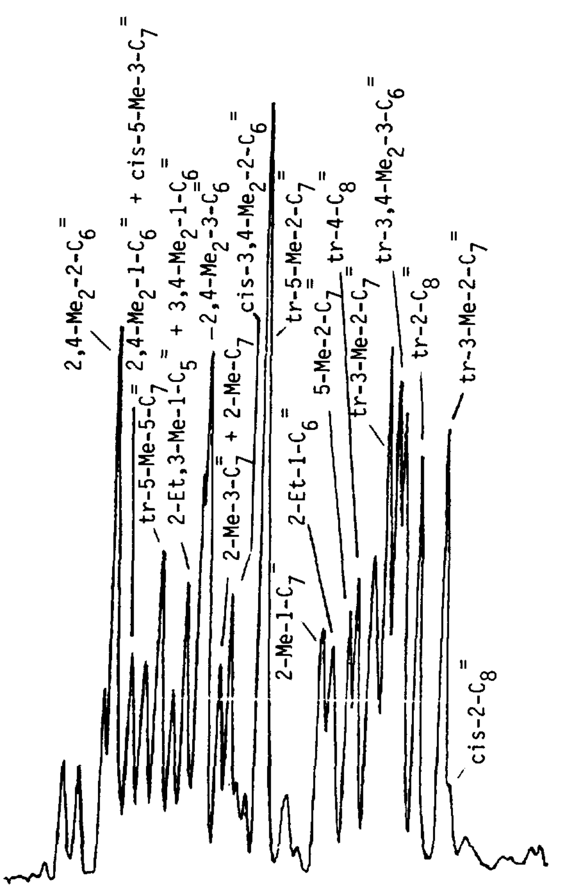


FIG. 2. 1-butene dimers formed over delaminated laponite at 350°C.

(Fig. 2), becomes impossible when oligomerization of higher olefins occurs. Instead, two more general subjects can be addressed:

1. The distributions and the sources of lighter C_i isoalkanes, with $i < m$, and heavier isoalkanes, with $m < i < 2m$, in olefin reactions.
2. The role of dimers in the cracking reactions of higher olefins.

Product distributions with respect to their carbon numbers were analyzed for 1-octene, 2- , 3- , and 4-octenes (separately for *cis* and *trans* isomers), 1-decene, 1-dodecene, and 1-tetradecene in the 200–400°C range. Absolute yields of the lighter and the heavier products at 250°C were:

Feed olefin C_m:	$1\text{-}C_8^=$	$1\text{-}C_{10}^=$	$1\text{-}C_{12}^=$
Lighter products, C_3–C_{m-1}:	1.4%	7.5%	17.2%
Heavier products, C_{m+1} and higher:	4.9%	14.7%	12.1%

Figure 3 gives two examples of such distributions, C_3–C_{17} products formed from 1-decene. The ordinate in Fig. 3 gives, in semi-logarithmic coordinates, relative molar yields of all products in each C_i range. The product distribution curve at 250°C is quite smooth. It has a flat maximum in the C_9–C_{11} range and shows no significant discontinuity between $i < m$ and $m < i < 2m$ ranges. When the temperature is increased to 350°C, the distribution curve, while retaining its shape, becomes more narrow and its maximum shifts to $i \sim 5$. Similar maximum shifts were observed at 350–400°C for the cracked products from 1-dodecene and 1-tetradecene. These data indicate that olefin oligomers rather than olefins themselves are the immediate source of all cracked products.

The product distributions from six linear octenes at 250°C were identical in shape and were similar to that in Fig. 3, with the distribution maximums in the C_7–C_9 range. The similarity suggests that the C = C bond positions in all octenes are completely randomized prior to oligomerization. The yields of C_{16} products from octenes are noticeably higher than those one would expect from the overall trend in the C_{11}–C_{15} range. This finding provides additional support to the hypothesis that dimers are intermediate products in most olefin cracking reactions rather than only in the case of the lightest olefins, as proposed in Ref. (22).

A complex shape of the curves in Fig. 3 suggests that numerous oligomer cracking and subsequent olefin oligomerization steps take place. The steadily decreasing yields of heavy cracked products (the right sides of the curves) can be explained in the following way: An earlier study (15) showed that cracking reactivities of isoalkanes

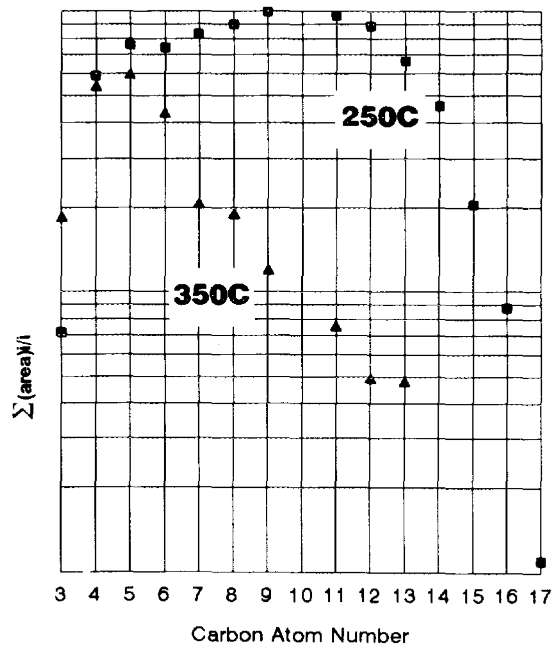


FIG. 3. Product distributions from 1-decene at 250 and 350°C. The ordinate gives the relative molar yields of the respective products.

greatly increase with an increase of their carbon numbers. For example, the reactivities of 2-Me-C_6, 2-Me-C_7, 2-Me-C_8, 2-Me-C_9, 2-Me-C_{11}, and 2-Me-C_{12} at 250°C increase as 1 : 3.3 : 7.6 : 15 : 46 : 72. These large differences suggest that oligomers of C_m olefins, branched iso-olefins and isoalkanes C_{2m}, C_{3m}, etc., rapidly and repeatedly crack to smaller molecules. This reaction is much more vigorous at increased temperatures, which explains the more narrow shape of the distribution curve at 350°C in Fig. 3 and the shift in its maximum. On the other hand, a gradual increase in the relative yields of lighter products (the left sides of the curves in Fig. 3), which is independent of the type of feed, is possibly caused by thermodynamic differences in product stabilities and by higher oligomerization rates of the lightest olefins.

Nature of cracked products with $i \neq m$. Saturated compounds dominate among these products. As an example, the C_8 products formed in the cracking of 1-dodecene at 300°C contains more than 60% of identified saturated compounds (mostly n-C_8, Me-C_7, Me_2-C_6, and Me_3-C_5) while only 17% are olefins (mostly linear octenes). Similarly, high contents of isoalkanes were observed in cracked products from all heavy olefins. Because the combined yields of light aromatic compounds under these mild conditions are relatively low, ca. 2–5%, coke formation via conjugated polyenes remains the most probable source of hydrogen required for alkane formation from olefins.

2. *Chemical Structures of Degenerate Non-primary Products in Alkane Cracking*

The cracking of any C_n alkane in the 250–400°C range produces primary products, C_n isoalkanes, and numerous light hydrocarbons C_i with i ranging mostly from 3 to $n - 1$ (1–6, 8, 9, 11). Heavier products, with $i > n$, are formed with very low yields. In addition, aromatic compounds, methyl- and ethyl-substituted benzenes, are formed at 350–400°C. For example, the cracking of 2-methylnonane (0.2 μl) over FSS-1 catalyst (0.025 g) at 350°C proceeds with a total conversion of 36%. Primary cracked products, various C_{10} alkanes, constitute 22.5% of all products; lighter isoalkanes, C_3–C_9, constitute over 75%; whereas heavier isoalkanes (mostly C_{11}) account merely for 0.4% of the total product yield, the balance being aromatics.

Most light cracked products formed under mild conditions are monomethyl- and dimethyl-substituted isoalkanes. Olefins are preserved in the cracked products in relatively low amounts. The most abundant among them are the lightest: propylene, linear butenes, isobutene, 2-methyl-2-butene, and 2-methyl-2-pentene. Relative yields of these olefins are much lower than those in olefin cracking.

Before examining the subject of the non-primary product distributions, a possible effect of reaction conversion on the distributions must be addressed. A series of cracking experiments was carried out using the same feed alkane, 2-methylnonane, and the same cracking catalyst, FSS-1. Reaction conversions in the experiments were varied by changing the amount of the feed and the amount of the catalyst, and by using an aged catalyst (the last effect was discussed earlier (15)). These experiments showed that the relative yields of different non-primary cracked products at 350°C do not depend on conversion. Table 3 gives one example of this independence—the distributions of various C_7 products at conversions ranging from 10 to ca. 60%.

We carried out a detailed cracking study of ca. 20 different isoalkanes over FSS-1 catalyst at 350°C and calculated the relative yields of the non-primary products in each of the C_6–C_{10} ranges. This analysis demonstrated marked similarities both in the structures of light products and in their relative yields, virtually without regard for the structures of feed alkanes. This means that most nonprimary products formed in alkane cracking are structurally degenerate. Tables 4 and 5 give two examples of these product distributions. The tables list the relative yields of various C_7 products (Table 4) and C_8 products (Table 5) from 15 different C_{10}–C_{16} alkanes. These data, as well as similar data for the C_{10} products formed from several heavy alkane feeds, show that the yields of branched alkanes within each particular carbon range, to the first approximation, are independent of the type of feed. Similar analysis for amorphous SiO_2–Al_2O_3 at 300°C gave analogous results: relative yields of most non-primary products were independent of the feed structure.

TABLE 3

Effect of Conversion on Relative Yields of C_7 Products Formed in Catalytic Cracking of 2-methylnonane over FSS-1 Catalyst at 350°C

	Conversion		
Product	60.5%	36.0%	9.4%
n-C_7	0.06	0.07	~0.10
2-Me-C_6	1.0	1.0	1.0
3-Me-C_6	0.72	0.69	0.67
2,2-Me_2C_5	<0.01	0.01	[a]
2,3-Me_2C_5	0.26	0.23	0.23
2,4-Me_2C_5	0.45	0.44	0.46
3,3-Me_2C_5	0.04	0.05	[a]
3-Et-C_5	0.07	0.06	0.08
2,2,3-Me_3-C_5	0.02	~0.02	[a]

Note. Standard: 2-methylhexane.

[a] Due to low conversion, yields of these products were too low to estimate dependably.

TABLE 4

Relative Yields of C_7 Products Formed in Catalytic Cracking of Isoalkanes over FSS-1 Catalyst at 350°C

Product							
Feed:	2-Me- -C_9	3-Me- -C_9	4-Me- -C_9	5-Me- -C_9	2,3-Me_2- -C_8	2,6-Me_2- -C_8	2,7-Me_2- -C_8
Conversion:	36.0%	33.6%	17.9%	27.8%	7.8%	14.4%	12.0%
n-C_7	0.07	0.08	0.07	0.04	0.27	—	—
2-Me-C_6	1.0	1.0	1.0	1.0	1.0	1.0	1.0
3-Me-C_6	0.72	0.59	0.57	0.59	0.55	0.64	0.54
2,2-Me_2C_5	<0.01	0.01	—	—	—	—	—
2,3-Me_2C_5	0.23	0.24	0.27	0.22	0.20	0.24	0.20
2,4-Me_2C_5	0.44	0.42	0.47	0.52	0.48	0.46	0.44
3,3-Me_2C_5	0.05	0.04	—	0.04	—	~0.05	0.06
3-Et-C_5	0.06	0.06	—	0.07	0.11	0.09	0.08
2,2,3-Me_3-C_4	0.02	0.02	—	0.01	—	<0.01	—

Feed:	3,5-Me_2- -C_8	3,6-Me_2- -C_8	2-Me- -C_{10}	3-Me- -C_{10}	4-Me- -C_{10}	2-Me- -C_{11}	2,6-Me_2- -C_{10}	2,6-Me_2- -C_{11}
Conversion:	17.0%	33.7%	49.5%	25.4%	15.6%	44.2%	58.9%	68.8%
n-C_7	—	—	0.06	0.06	—	0.09	0.03	0.04
2-Me-C_6	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
3-Me-C_6	0.57	0.58	0.69	0.64	0.60	0.76	0.66	0.72
2,2-Me_2C_5	—	—	—	—	—	—	—	—
2,3-Me_2C_5	0.26	0.20	0.24	0.22	0.22	0.25	0.24	0.28
2,4-Me_2C_5	—	0.52	0.35	0.35	0.43	0.30	0.32	0.35
3,3-Me_2C_5	—	~0.04	0.04	~0.06	—	0.04	0.04	0.05
3-Et-C_5	—	—	—	—	—	0.07	0.07	0.09
2,2,3-Me_3-C_4	—	—	~0.01	—	—	0.01	~0.02	—

Note. Standard: 2-methylhexane.

Table 6 lists average relative yields for each of the C_8 products derived from various heavy feed isoalkanes over FSS-1 catalyst (from Table 5) and SiO_2–Al_2O_3, and compares them with the thermodynamic equilibrium calculations based on Gibbs' formation energies (4). It is evident that the relative yields of most non-primary C_8 isoalkanes produced with two catalysts approximately reflect their thermodynamic stabilities. Three kinds of deviations from this simple picture were detected:

1. The relative yields of light linear alkanes vary in a much wider range than those of isoalkanes, and strongly depend on the structure of feed compounds. For example, the n-C_7 : 2-Me-C_6 ratio varies from 0.03 in the cracking of 2,6-dimethyldecane to 0.4–0.5 in the cracking of n-dodecane and n-tetradecane. Similarly, the n-C_8 : 2-Me-C_7 ratio varies from 0.11–0.13 in the cracking of 2-methylnonane and 2,6-dimethyldecane to 0.7–0.8 in the cracking of n-dodecane and n-hexadecane. Equally large variations were found in the relative yields of n-decane and n-dodecane produced from heavy isoalkanes.

2. The relative yields of geminally branched isoalkanes (2,2- and 3,3-dimethyl isomers in Tables 4 and 5) are usually much lower than can be expected from their thermodynamic stabilities.

3. Analysis of the C_{10} non-primary products from heavy isoalkanes shows that although the relative distributions of monomethyl-branched alkanes also approximately reflect their thermodynamic stabilities, the yields of dimethyl-substituted isoalkanes are usually lower by a factor of 2–3.

These deviations from thermodynamic equilibrium signify that kinetic factors play some role in the makeup of the light products. Transformation of monomethyl-branched alkanes into linear alkanes or into geminally branched dimethyl-substituted alkanes both proceed via the B-skeleton rearrangement mechanism discussed above. Apparently the particular reactions in carbocations leading to n-alkanes and geminally branched alkanes have higher activation energies than the B-type rearrangements leading to all other dimethyl-branched alkanes. As a result, formation reactions of linear and geminally branched alkanes do not reach equilibrium under mild conditions. The enhanced yields of light n-alkanes in the cracking of heavy n-alkanes is the principal evidence of the existence of linear carbocations with secondary CH^+ charges. Apparently these species have sufficient lifetimes at 350°C and form n-alkanes prior to their isomerization into more stable tertiary carbocations.

TABLE 5

Relative Yields of C_8 Products Formed in Catalytic Cracking of Isoalkanes over FSS-1 Catalyst at 350°C

Product	Feed					
	2-Me-C_9	3-Me-C_9	2,6-Me_2-C_8	2-Me-C_{10}	3-Me-C_{10}	n-C_{12}
n-C_8	0.11	0.19	0.20	0.26	0.14	0.81
2-Me-C_7	1.0	1.0	1.0	1.0	1.0	1.0
3-Me-C_7 +3-EtC_6	0.98	0.86	0.77	1.00	0.89	1.19
4-Me-C_7	0.36	0.30	0.24	0.38	0.30	0.41
2,3-Me_2C_6	0.29	0.31	0.24	0.36	0.28	0.41
2,4-Me_2C_6	0.58	0.56	0.56	0.52	0.48	0.40
2,5-Me_2C_6	0.48	0.53	0.60	0.46	0.44	0.36
3,3-Me_2C_6	0.23	0.07	—	—	—	—
3,4-Me_2C_6	0.09	0.13	—	—	—	—
	Feed					
	2-Me-C_{11}	2,6-Me_2-C_{10}	2,6-Me_2-C_{11}	n-C_{14}	2-Me-C_{14}	n-C_{16}
n-C_8	0.15	0.13	0.15	0.48	0.42	0.73
2-Me-C_7	1.0	1.0	1.0	1.0	1.0	1.0
3-Me-C_7 +3-EtC_6	1.03	0.94	0.96	0.87	0.98	1.37
4-Me-C7	0.33	0.29	0.30	^{a}	0.37	0.53
2,3-Me_2C_6	0.23	0.24	0.31	0.30	^{a}	0.43
2,4-Me_2C_6	0.39	0.41	0.56	0.39	0.32	0.70
2,5-Me_2C_6	0.34	0.40	0.53	0.21	0.35	0.41
3,3-Me_2C_6	0.02	0.03	0.07	—	0.05	—
3,4-Me_2C_6	0.07	0.06	0.07	^{a}	0.09	0.17

Note. Standard: 2-methylheptane. Reaction conversions are given in Table 4.

[a] The ratio cannot be measured due to peak broadening.

TABLE 6

Averaged Distributions of Non-primary C_8 Products Formed in Catalytic Cracking of Various Isoalkanes over FSS-1 and Amorphous SiO_2–Al_2O_3 at 350°C

Isoalkane	Non-primary products FSS-1	Non-primary products SiO_2–Al_2O_3	Thermodynamic equilibrium data (4)
2-Me-C_7	1.0	1.0	1.0
3-Me-C_7 +3-EtC_6	0.99	0.91	1.32
4-Me-C_7	0.35	0.33	0.40
2,3-Me_2C_6	0.31	0.31	0.26
2,4-Me_2C_6	0.49	0.40	0.59
2,5-Me_2C_6	0.43	0.50	0.44
3,3-Me_2C_6	0.05	—	0.21
3,4-Me_2C_6	0.10	0.10	0.22

Note. Standard: 2-methylheptane.

3. *Alkane Product Distributions with Respect to Carbon Number*

Figure 4 gives relative molar yields of C_i products as a function of i for the cracked products from eleven C_{10} isoalkanes at 350°C. The yields are calculated as $\Sigma(\text{area}_i)/i$ where the term $\Sigma(\text{area}_i)$ corresponds to the sum of the peak areas of linear, monomethyl- and dimethyl-branched C_i alkanes. The yields are normalized to the molar yields of C_5 products and are plotted in the logarithmic scale. All product distributions have a characteristic inverted-U shape with maximums at $i = 4$–5. Very similar product distribution curves were obtained at 250°C.

The principal conclusion from Fig. 4 is that the product distributions with respect to their carbon numbers, in a first approximation, do not depend on the skeleton structure of a feed, i.e., most non-primary products are degenerate in this sense also. Of course, the exact shapes of the distributions in Fig. 4 are, to a degree, affected by the feed structure. However, most of the differences,

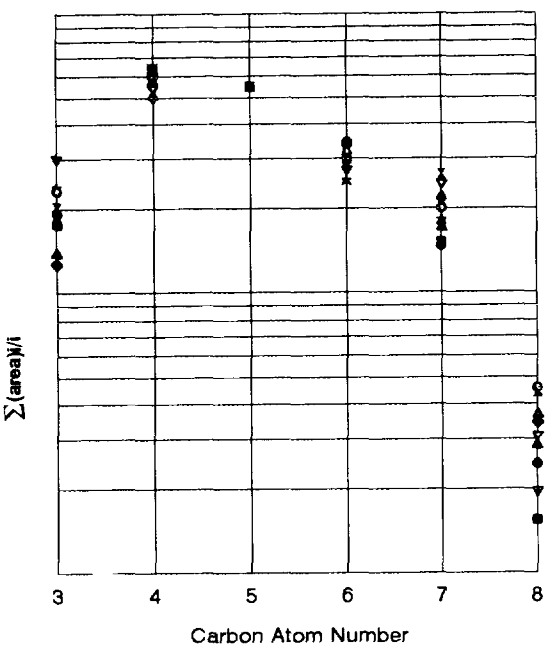


FIG. 4. Cracked product distributions from various C_{10} alkanes at 350°C: ⊗, n-C_{10}; ●, 2-Me-C_9; ○, 3-Me-C_9; ⧗, 4-Me-C_9; △, 5-Me-C_9; ▽, 2,3-Me_2-C_8; ▲, 2,6-Me_2-C_8; ◆, 2,7-Me_2-C_8; ▼, 3,5-Me_2-C_8; ■, 3,6-Me_2-C_8; ★, 3-Et-C_8.

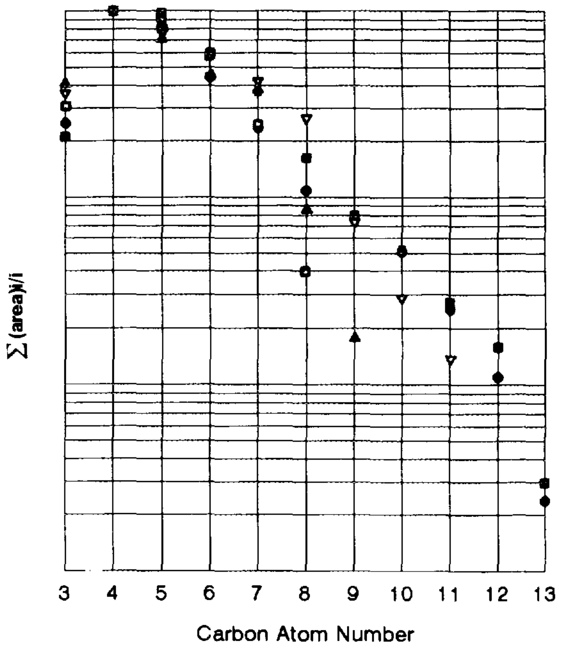


FIG. 5. Cracked product distributions from various 2-Me-C_n alkanes at 350°C: □, 2-Me-C_9; ▲, 2-Me-C_{10}; ▽, 2-Me-C_{11}; ●, 2-Me-C_{14}; ■, 2-Me-C_{16}.

especially in the C_8 range, are artifacts caused by difficulties in measuring very low product yields. For example, the yields of C_4–C_5 products are higher than those of C_8 products by ca. 30 times.

Figure 5 compares the product distributions at 350°C from five alkanes with the same skeleton, 2-methyl-branched chains. Although all curves in Fig. 5 have the same shape with maxima at $i = 4$–5, a clear trend exists: the distributions become broader with an increase in the feed carbon number. These differences merely reflect the fact that the cracked products from a C_n alkane usually cover the whole C_i range from 3 to $n - 1$ (2, 5, 6).

The data in Fig. 5 provide additional information on the contribution of secondary reaction products (Reaction 2) to all non-primary products. The tertiary C–H bond in 2-methyl-branched alkanes is especially susceptible to carbocation formation (8, 9, 11). A single fission of the β-C–C bond in the respective carbocation should give isobutene and n–C_{n-4} alkanes:

$$\begin{aligned} &CH_3\text{–}C^+(CH_3)\text{–}CH_2\text{–}C_{n-4} \rightarrow (CH_3)_2C{=}CH_2 \\ &\quad + n\text{–}C^+_{n-4}\,(+RH) \rightarrow n\text{–}C_{n-4}H_{2n-6} + R^+. \end{aligned} \qquad [6]$$

This reaction can indeed be traced: the yields of all C_{n-4} products (C_6 from 2-Me-C_9, C_7 from 2-Me-C_{10}, C_8 from 2-Me-C_{11}) are 30–60% higher than the yields expected from linear interpolations between the C_{n-3} and C_{n-5} products. These excess yields are not very large if one considers very significant differences in the ionization abilities of tertiary and secondary C–H bonds. In addition, the nature of both C_4 and C_{n-4} products is quite different from that expected from Reaction 6. For example, when 2-methylnonane is cracked over FSS-1 catalyst, isobutane is dominant (80%) among the C_4 products rather than isobutene, and n-hexane amounts to merely 4% of the combined C_6 yield, the major C_6 products being, as in all other C_i ranges, 2-methylpentane (ca. 50%) and 3-methylpentane (30%). These data show that even in this most obvious case the observation of the secondary products is very difficult even at 350°C due to their very strong contamination with the products of subsequent reactions.

Distribution plots similar to those shown in Figs. 4 and 5 were also observed in the cracking of other heavy alkanes. The same distribution shapes are also typical for cracked products derived from olefins (Fig. 3). Therefore, the distributions in Figs. 4 and 5 can be regarded as universal for all alkane-cracking reactions over acidic catalysts under mild conditions. These distributions can be rationalized based on a combination of thermodynamic and kinetic factors. If a single C–C fission reaction in a C_n carbocation occurs (Reaction 2) and if both cracked fragments, C_i and C_{n-i}, are immediately isomerized to the equilibrium mixtures of C_i ($i > 3$) and C_{n-i} skeletal isomers, the sums of the Gibbs' formation energies for C_i and C_{n-i},

$$\Delta\Delta G_f^0 = \Sigma(\Delta G_f^0)_i + \Sigma(\Delta G_f^0)_{n-i},$$

are nearly independent of the *i* value. For example, if the cracking of the equilibrium mixture of the C_{13} skeletal isomers is considered and the $(\Delta G_f^0)_i$ values for each *i* range are calculated as the ΔG_f^0 averages of all possible monomethyl-branched alkanes (25), the $\Delta\Delta G_f^0$ values for the various product pairs are:

Products from C_{13}:	$C_3 + C_{10}$	$C_4 + C_9$	$C_5 + C_8$	$C_6 + C_7$
$\Delta\Delta G_f^0$ (kJ/mol):	397.6	395.4	394.5	395.1

These differences are not large enough to account for distribution curves with relatively steep slopes, as those in Figs. 4 and 5.

A simple reaction model was used to explain the experimentally observed distributions. The model is based on the following assumptions:

1. Light olefins formed in Reaction 2 ($C_3^=$, $C_4^=$, and $C_5^=$) undergo rapid oligomerization reactions and produce dimers, trimers, co-dimers, and co-trimers (Reaction 4). Olefin oligomerization reactivities decrease with the C_m increase, as is typical for the cationic polymerization of olefins.
2. All heavy secondary and tertiary products, and all olefin oligomers (Reactions 2, 3, and 4) undergo further cracking. Their reactivities in these reactions rapidly increase with their carbon numbers (15).

Approximate cracking patterns of the equilibrium mixture of C_{13} carbocations were calculated using these assumptions (Fig. 6). In the calculations, the reactivities of light olefins in oligomerization reactions, $R(C_3^=) : R(C_4^=) : R(C_5^=)$, were assumed to decrease in the order 5 : 2.5 : 1, and the cracking reactivities of the heavy products were varied proportionally to the reactivities of 2-methyl-branched alkanes (15):

2-Me-C_{n-1}:
Cracking reactivity:

C_{12}	C_{11}	C_{10}	C_9	C_8	C_7	C_6
2.8	2.0	1.0	0.49	0.18	0.054	0.016.

The variables in the calculations were conversions in the olefin oligomerization reactions and in the cracking reactions, as well as the numbers of successive oligomerization and cracking steps. The calculated distributions (Fig. 6) have the same inverted-U shapes as the experimental distributions. Diminishing yields of the heavy products are due to their increasing reactivities in cracking reactions, while decreased C_3 yields are mostly due to high propylene reactivity in oligomerization reactions. Of course, the described cracking model is quite simplistic. Nevertheless, it provides a reasonably adequate explanation of the common distribution patterns of cracked products under mild conditions, as those shown in Figs. 4 and 5.

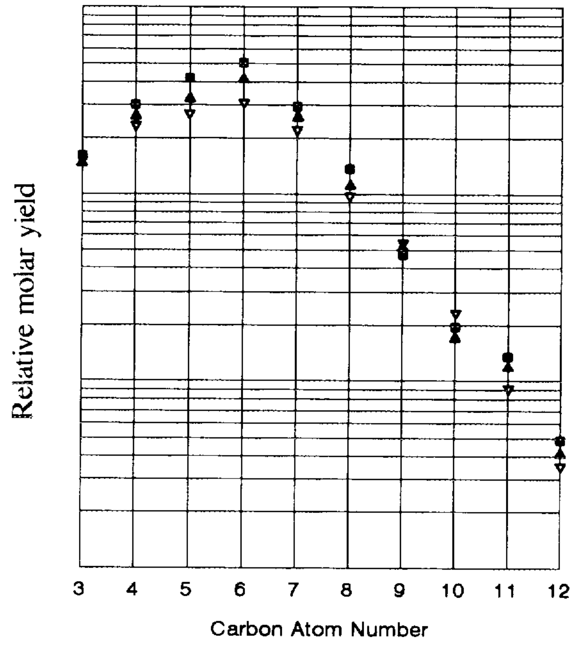


FIG. 6. Simulated cracked product distributions from the equilibrium mixture of C_{13} alkanes.

CONCLUSIONS

1. The study of the cracked product distributions from a series of C_{10}–C_{17} alkanes and C_3–C_{14} olefins over acidic catalysts at 250 and 350°C shows that all cracked products from nearly any C_n alkane, apart from the primary products (isomerized C_n alkanes), can be regarded as degenerate non-primary products, isoalkanes and iso-olefins C_i with *i* ranging from 3 to $n - 1$.
2. The non-primary products in each carbon number range are mostly the mixtures of isoalkanes with monomethyl- and dimethyl-branched skeletons. Relative yields of various isoalkanes, on a semi-quantitative level, are determined by the thermodynamic stabilities of respective isomers. Normal alkanes and geminally branched isoalkanes are the only two apparent exceptions to this rule, possibly because the equilibria between various skeleton structures are not always reached.
3. The distributions of non-primary C_i products with respect to their carbon numbers *i* have the inverted-U shapes with maxima at $i = 4$–5 (Figs. 4 and 5). The shapes of these distributions also do not depend on the skeleton structures of feed alkanes.
4. A semi-quantitative model describing the alkane product distributions is proposed. The model is based on the reaction scheme in Fig. 1 and accounts for the

dependence of all cracking and oligomerization reaction rates on the carbon numbers of the reactants.

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