RESEARCH NOTE

Primary Products in Hydrocarbon Cracking over Solid Acidic Catalysts under Very Mild Conditions: Relation to Cracking Mechanism

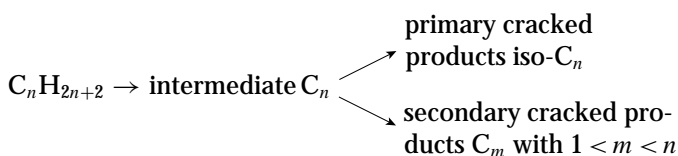Yury V. Kissin[1]

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This note analyzes primary products (reaction products with the same carbon atom numbers as in feeds) produced in cracking reactions of several C_7–C_9 isoalkanes over zeolite-based catalysts under very mild conditions, at 150–250°C and at high [feed] : [catalyst] ratios, and discusses formation mechanisms of these products. Primary products from methyl-substituted alkanes at low temperatures are predominantly isoolefins with the same skeleton structures as in feed alkanes. A chemical mechanism which was earlier proposed to describe formation of light cracked products from isoalkanes [*J. Catal.* **163**, 50–62 (1996)] is well suited to describe the formation of the primary cracked products as well. This mechanism includes a reaction between an isoalkane and the Brønsted center on the catalyst surface with the formation of a transient hydrosiloxonium ion $\gg$Si–O$^+$(H)–C$\ll$. The ion undergoes a hydrogen atom abstraction from the C–H bond in the β-position to O$^+$ with the formation of an olefin molecule which, in turn, rapidly isomerizes via the carbocationic mechanism. © 1998 Academic Press

When catalytic cracking reactions of individual alkanes over solid acidic catalysts are carried at sufficiently high temperatures, i.e., over 400°C, they generate numerous products; usually, many dozens of products are formed with broadly comparable yields from a single hydrocarbon. It is generally accepted that catalytic cracking of a saturated hydrocarbon involves several distinct steps which can be studied separately by fine-tuning experimental conditions. The first reaction step of cracking a C_nH_{2n+2} alkane includes the formation of reactive species C_n with the same carbon atom number and their subsequent isomerization. This step does not involve any net fission of C–C bonds. The products of this step, isomerized saturated or unsaturated hydrocarbons iso-C_n, are named the primary reaction products. The second reaction step includes the fission of at least one C–C bond. The products of this reaction, saturated and unsaturated hydrocarbons C_m with $1 < m < n$, are called secondary

products of cracking reactions (1):

$$C_nH_{2n+2} \rightarrow \text{intermediate } C_n \underset{\text{secondary cracked products } C_m \text{ with } 1 < m < n}{\overset{\text{primary cracked products iso-}C_n}{\Huge{\diagup}}}$$

The previous article (2) described secondary cracked products formed in reactions of isoalkanes and isoolefins over zeolite-based catalysts under very mild conditions. Analysis of cracking patterns of numerous methyl- and ethyl-branched isoalkanes showed that the compositions of the light products can be described by three empirical rules:

(1) A reaction site is formed at the tertiary carbon atom in an isoalkane molecule.
(2) The predominant C–C bond fission reaction involves the weakest C–C bond in the α-position to the reaction site.
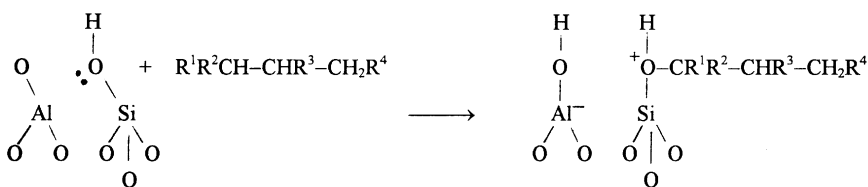(3) Main light products are olefins.

None of the cracking mechanisms described in the literature and involving reactions of carbenium and carbonium ions could adequately predict the observed product structures. Therefore, a new cracking mechanism of isoalkanes was proposed. It is shown in Scheme 1. The mechanism includes a reaction between an isoalkane and the Brønsted center on the catalyst surface with the formation of a transient hydrosiloxonium ion $\gg$Si–O$^+$(H)–C$\ll$. Secondary products are generated when the hydrosiloxonium ion undergoes scission of one of the C–C bonds in its alkyl groups in the β-position to O$^+$ with the formation of an olefin molecule (which rapidly isomerizes) and a smaller hydrosiloxonium ion.

Apparently, olefins and alkanes crack via different mechanistic routes. Comparisons of light cracked products from isoolefins and isoalkanes with the same skeletons in Ref. (2) showed that the respective products are drastically different
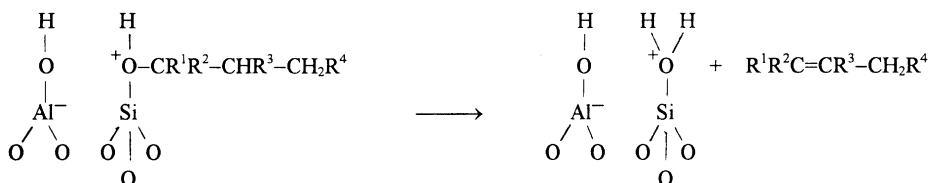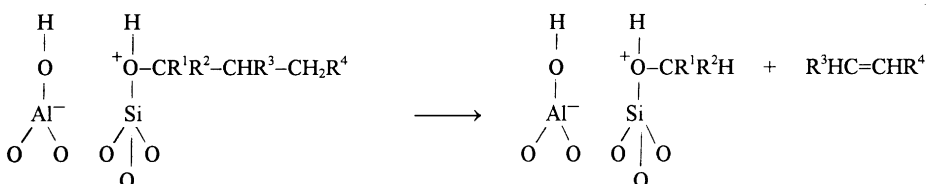
[1] Current address: Mobil Chemical Co., P.O. Box 3029, Edison, NJ 08818-3029.

Scheme 1

Formation of hydrosiloxonium ion:

$$H \qquad\qquad H \qquad\qquad H$$

O •O   +   R^{1}R^{2}CH–CHR^3–CH$_2$R^4 $\longrightarrow$ O $^+$O–CR^{1}R^2–CHR^3–CH$_2$R^4

Al   Si   Al$^-$ Si

O O O | O   O O O | O

O   O

Formation of primary products:

$$H \qquad H$$

O $^+$O–CR^{1}R^2–CHR^3–CH$_2$R^4 $\longrightarrow$ O $^+$O   +   R^{1}R^{2}C=CR^3–CH$_2$R^4

Al$^-$ Si   Al$^-$ Si

O O O | O   O O O | O

O   O

Formation of secondary products via β-C–C bond scission:

$$H \qquad H$$

O $^+$O–CR^{1}R^2–CHR^3–CH$_2$R^4 $\longrightarrow$ O $^+$O–CR^{1}R^{2}H   +   R^{3}HC=CHR^4

Al$^-$ Si   Al$^-$ Si

O O O | O   O O O | O

O   O

SCHEME 1

even when they are formed under very mild conditions. Studies of olefins with a low oligomerization ability (to prevent scrambling of product structures) showed that the olefin cracking could indeed be explained by fragmentation of carbenium ions via the standard β-C–C bond scission mechanism.

The present note discusses structures of primary products, isomerized C_n hydrocarbons, which are formed in small quantities from C_nH_{2n+2} isoalkanes in parallel with the secondary products.

EXPERIMENTAL

The experimental procedure was described earlier (1–4). It affords a study of various feeds over the same relatively fresh load of a catalyst at low feed concentrations in the gas phase. 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 hydrocarbon 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 column with a 0.5-μm film of crosslinked methyl silicone. The He flow rate was 1cc/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.

Cracking reactions of isoalkanes were carried out at 150–250°C at two different [feed]:[catalyst] ratios, one relatively high (0.4–0.5 μl feed per 0.010–0.015 g catalyst) and the second one low (~0.1 μl feed per 0.05 g catalyst). In both cases, feed conversions were very low, usually below 2–3%. Olefins have much higher reactivities than alkanes. To avoid olefin overcracking, they were diluted with linear alkanes, n-nonane or n-decane, in the 1 : 10 ratio (n-alkanes are completely inert under these conditions).

All hydrocarbons were supplied by Wiley Organics Co. The cracking experiments were carried out with a commercial steam-equilibrated cracking catalyst, Filtrol FSS-1, which contains the rare earth-exchanged Y zeolite.

RESULTS AND DISCUSSION

GC studies of primary cracked products formed under mild conditions (at very low conversions) suffer from one significant drawback. Small peaks of primary products in gas chromatograms of such reaction mixtures (hydrocarbons with the same carbon atom numbers as in feed molecules) are positioned relatively close to very large broad peaks of unreacted feeds. Some of the product peaks are completely overlapped by the feed peaks; positions of others can be noticeably shifted compared to those of the same peaks in chromatograms of calibration mixtures. Two general rules of thumb can be applied to the GC studies of such primary products: (a) product identification is most reliable when their peaks are removed as far as possible from the feed peak; and (b) product identification is more reliable if several of them are present—although their absolute peak positions can be shifted, their relative positions remain mostly unaffected by proximity to a very large feed peak.

We found that the nature of the primary reaction products from isoalkanes greatly differs depending on reaction temperature and the [feed] : [catalyst] ratio. The data on the primary products generated at 250–350°C from a large variety of C_9-C_{17} isoalkanes over a commercial cracking catalyst at relatively low [feed] : [catalyst] ratios were discussed previously (1). The results of that study can be summarized in the following way:

1. The same primary products, overwhelmingly, mixtures of monomethyl- and dimethyl-substituted alkanes iso-C_nH_{2n+2}, are formed in the cracking of any given isoalkane. For example, cracking of a series of C_{10} alkanes including n-decane, 2- and 5-methylnonanes, 2,3-, 2,6-, 2,7-, 3,5-, 3,6-dimethyloctanes, and 3-ethyloctane produces the same primary products, mostly all possible isomers of methylnonanes and dimethyloctanes.

2. Not only are the types of the products from different feeds the same, but their relative yields do not depend on the structures of the feed molecules.

In other words, these primary products are completely degenerate: there exists no discernible correlation between their structures and yields and those of the feed hydrocarbons. These data suggest that isomerization reactions of primary intermediates C_n reach an equilibrium state under the conditions employed, at least when the feed compounds are methyl-branched alkanes. A comparison of the experimentally measured yields of the primary products and thermodynamic stabilities of the respective isoalkanes (1) showed that relative yields of all branched primary cracking products reflect their thermodynamic stability.

However, when the cracking reactions of the same isoalkanes over solid acidic catalysts are carried out at lower temperatures, i.e., at 150°C, and at higher [feed] : [catalyst] ratios, the nature of the primary products is very different. Due to the above-mentioned difficulty in identifying primary products under these conditions (very small product GC peaks in the vicinity of large feed peeks), the number of isoalkanes suitable for the study of the primary products is significantly lower than the number of hydrocarbons examined earlier at higher temperatures (1).

Table 1 lists several examples of feed isoalkanes and the main primary products derived from them. GC peak identification of olefinic products in Table 1 was carried out with two different techniques, by recording gas chromatograms of isoolefin mixtures and by recording gas chromatograms of cationically isomerized olefins. For example, C=C bond isomerization in both 2-ethyl-1-hexene and 5-methyl-3-heptene produces mixtures of *cis*- and *trans*-3-methyl-2-hexene and 3-methyl-3-hexene, isomerization of 2,4-dimethyl-1-hexene produces a mixture of 2,4-dimethyl-2-hexene and *cis*- and *trans*-2,4-dimethyl-3-hexene, etc. (see below).

As Table 1 shows, the primary products from isoalkanes formed under very mild conditions are, in effect, dehydrogenation products which retain their skeletons and which contain C=C bonds (predominantly internal) next to tertiary carbon atoms in the feed isoalkanes. This finding can be easily reconciled with the previously published data on the structure of secondary cracking products in the same reactions. The cracking mechanism under very mild conditions described earlier (2) is based on the fact that the cracking pattern (C–C bond scission) of numerous isoalkanes can be reduced, with some simplifications, to a general
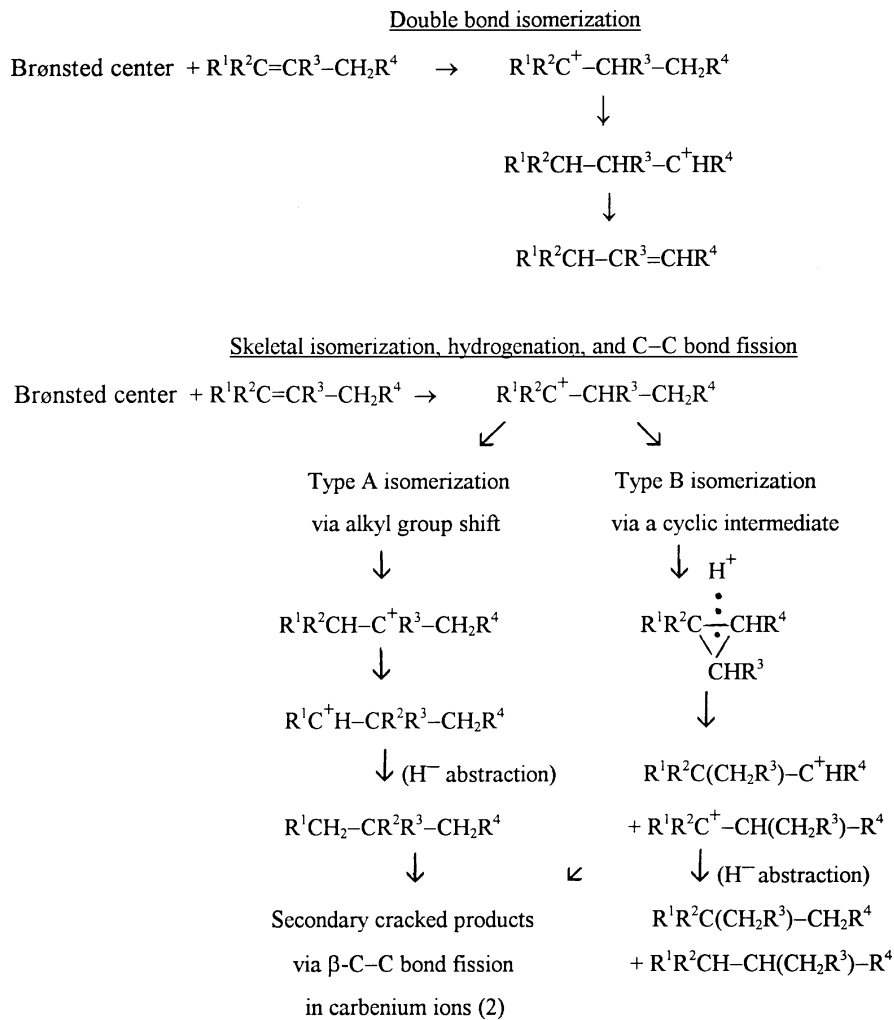
TABLE 1

Primary Products from Isoalkanes Produced over Y-Zeolite-Based Cracking Catalyst

Feed	Temperature	Conversion	Identified primary products
2-Methylhexane	150°C	0.3%	2-Methyl-2-hexene (minor quantities of 2-methyl-1-hexene and 3-methylhexane)
3-Methylheptane	150, 250°C	~0.2%	3-Methyl-2-heptene, 3-methyl-3-heptene
2,4-Dimethylhexane	150, 250°C	0.04, 0.11%	2,4-Dimethyl-2-hexene or 2,4-dimethyl-3-hexene
3,4-Dimethylhexane	150, 250°C	0.11, 0.065%	3,4-Dimethyl-3-hexene
2,6-Dimethylheptane	150, 250°C	0.42, 0.26%	2,6-Dimethyl-2-heptene, 2,6-dimethyl-1-heptene

Note. [feed] : [catalyst] ratios ca. 0.4–0.5 μl per 0.01 g catalyst.

Scheme 2. Carbocationic reactions of olefins

Double bond isomerization

$$\text{Brønsted center} + R^1R^2C=CR^3-CH_2R^4 \quad \rightarrow \quad R^1R^2C^+-CHR^3-CH_2R^4$$

$$\downarrow$$

$$R^1R^2CH-CHR^3-C^+HR^4$$

$$\downarrow$$

$$R^1R^2CH-CR^3=CHR^4$$

Skeletal isomerization, hydrogenation, and C–C bond fission

$$\text{Brønsted center} + R^1R^2C=CR^3-CH_2R^4 \rightarrow \quad R^1R^2C^+-CHR^3-CH_2R^4$$

$$\swarrow \qquad\qquad \searrow$$

Type A isomerization	Type B isomerization
via alkyl group shift	via a cyclic intermediate

$$\downarrow \qquad\qquad\qquad \downarrow\ H^+$$

$$R^1R^2CH-C^+R^3-CH_2R^4 \qquad R^1R^2C\overset{\cdot\cdot}{-\!\!|}CHR^4$$

$$\qquad\qquad\qquad\qquad\qquad\qquad \backslash/$$

$$\downarrow \qquad\qquad\qquad\qquad CHR^3$$

$$R^1C^+H-CR^2R^3-CH_2R^4 \qquad\qquad \downarrow$$

$$\downarrow\ (H^- \text{ abstraction}) \qquad R^1R^2C(CH_2R^3)-C^+HR^4$$

$$R^1CH_2-CR^2R^3-CH_2R^4 \qquad + R^1R^2C^+-CH(CH_2R^3)-R^4$$

$$\downarrow \qquad\qquad \nwarrow \qquad \downarrow\ (H^- \text{ abstraction})$$

Secondary cracked products $\qquad\qquad R^1R^2C(CH_2R^3)-CH_2R^4$

via β-C–C bond fission $\qquad\qquad\qquad + R^1R^2CH-CH(CH_2R^3)-R^4$

in carbenium ions (2)

SCHEME 2

rule: the C–C bonds undergoing fission are predominantly the weakest CH–CH$_2$ or CH–CH bonds adjacent to a tertiary carbon atom in a feed isoalkane.

The mechanism in Scheme 1 accommodates the data by Haag *et al.* about the crucial role of Brønsted acidic centers in zeolites containing adjacent Al and Si atoms (5–8) and uses the proposed structure of the Brønsted site described in the literature (5, 8, 9). The mechanism builds on the concept of oxonium ions R_3O^+ (and hydroxonium ions R_2HO^+) which are often generated in acid-catalyzed reactions (10). Scheme 1 presents the expanded version of the alkane cracking mechanism under very mild conditions which encompasses both the earlier findings (2) and the data on the primary cracked products in Table 1. According to the mechanism, an isoalkane $R^1R^2CHCHR^3CH_2R^4$ first reacts with a Brønsted center and forms a transient hy-

drosiloxonium ion $\geqslant$Si–O$^+$(H)–C$<$. As is typical for most proposed 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 a negative counter-charge in the vicinity of a tetra-coordinated Al atom (8, 9). The stage of the oxonium ion formation in Scheme 1 is probably reversible and represents alkane chemisorption by a zeolite (its kinetics was recently described (11)).

The hydrosiloxonium ion can undergo two parallel reactions, either the scission of a C–C bond in the β-position to O$^+$ with the formation of light olefinic products (shown in the bottom part of Scheme 1) or a hydrogen abstraction reaction from a C–H bond in the β-position to O$^+$ (the central part of Scheme 1). The latter reaction produces the primary product, an $R^1R^2C=CR^3CH_2R^4$ olefin (predominantly an

internal olefin). Similar decomposition reactions of alkyloxonium ions in the gas phase with the olefin formation are well known (12–14). The probability of the reaction is determined by the energetics of the $\geqslant$Si–O$^+$H$_2$ ion formation and by the thermodynamic stability of a leaving $R^1R^2C{=}CR^3$–CHR^4 olefin. The ratio between the secondary and the primary products depends on temperature: higher temperatures may favor the formation of smaller secondary products at the expense of heavier primary products: see the data for 3,4-dimethylhexane and 2,6-dimethylheptane in Table 1.

When the cracking reactions are carried out at higher temperatures or at lower [feed] : [catalyst] ratios, isomerization reactions in the oxonium ions and reactions of olefinic products via the carbenium ion mechanism can completely scramble their structures (15). These reactions are shown in Scheme 2. Validity of this olefin conversion mechanism can be easily demonstrated when isoolefins are reacted with the same cracking catalyst. For example, 2,4-dimethyl-1-hexene diluted with n-nonane in 1 : 10 ratio reacts with the catalyst at 150°C at the [olefin] : [catalyst] ratio of 0.02 μl/0.01 g quite extensively (the total feed conversion is 87%). It predominantly produces 2,4-dimethyl-2-hexene and 2,4-dimethyl-3-hexene with a total conversion of ca. 30%, as well as a variety of light secondary products described earlier (2), mostly 2-methyl-branched internal olefins. Under these conditions, the olefin produces only a small amount of 2,4-dimethylhexane, 2.8% of all primary C$_8$ products. At 250°C and at the same feed dilution, the total conversion of 2,4-dimethyl-1-hexene increases to 91%, and the primary isoalkanes (mostly 2,x-dimethylhexanes and methylheptanes) become more prominent and now account for nearly 25% of all C$_8$ products. Finally, when the same reaction is carried at 250°C with an undiluted olefin, con-

version of the feed olefin becomes nearly complete, and monomethyl- and dimethyl-substituted alkanes dominate the C$_8$ product region (86% of all primary products). A similar shift from primary isoolefins to isoalkanes at increased reaction severity was also observed in cracking of other branched olefins. If the olefins are capable of oligomerization (olefins with vinyl and vinylidene double bonds), the structure of the reaction products becomes even more complex due to the formation of olefin dimers (in cationic oligomerization reactions) and their subsequent fragmentation (2).

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