JOURNAL OF CATALYSIS **132**, 409–421 (1991)

# Primary Products in Catalytic Cracking of Alkanes: Quantitative Analysis

Y. V. KISSIN[1]

*Gulf Research and Development Company, Pittsburgh, Pennsylvania*

Received January 23, 1991; revised July 25, 1991

Catalytic cracking of several $C_8$ and $C_{10}$ isoalkanes over a zeolite-based catalyst at 250 and 350°C was studied and the distributions of primary cracked products (isomerized saturated hydrocarbons with the same carbon atom numbers as in the feed alkane) were analyzed. Comparison of relative yields of the primary products showed that not only the same products were formed in cracking of different isoalkanes but that their distributions did not depend on the structure of the feed molecules. The relative yields of different primary products were found to be generally proportional to the thermodynamic stabilities of corresponding isoalkanes. All isoalkane products with a methyl group in the second positions of alkyl chains represent an exception: their relative yields are uniformly 2–2.5 times higher than those expected from thermodynamics due to the additional stabilizing effect of the second methyl group on the concentration of respective carbocations.

## INTRODUCTION

The studies of catalytic cracking reactions of individual hydrocarbons over solid acidic catalysts continue to attract interest after over 50 years (*1, 2*), with respect to both their intimate mechanism (*3–5*) and the reaction kinetics (*6, 7*). When the cracking reactions are carried at sufficiently high temperatures, i.e., over 400°C, they generate numerous products; sometimes many dozens of products can be formed with broadly comparable yields from a single hydrocarbon. A need exists to classify the products into at least two groups, primary and secondary, according to a qualitative definition:

reactant molecule → primary products (stable and unstable)

unstable primary products → secondary products (stable and unstable)

Best and Wojchiechowski (*8*) developed a detailed kinetic technique for discriminating between these four categories of products. For example, in their study of cumene cracking in the 350–450°C range, they defined benzene, propylene and ethylbenzene as stable primary products, ethyltoluene and diisopropylbenzenes as unstable primary products, toluene as a stable secondary product, and diethylbenzene as an unstable secondary product (*8*). Such a classification is well suited for the description of vigorous cracking processes that involve numerous C–C-bond fission and formation steps. However, it is less convenient for a detailed mechanistic analysis of cracking reactions of aliphatic hydrocarbons under relatively mild conditions.

It is well known that catalytic cracking of a saturated hydrocarbon $C_nH_{2n+2}$ involves several distinct steps that can be separately studied by fine-tuning experimental conditions. The first reaction step includes the formation of a carbocation $C_nH_{2n+1}^+$ and its subsequent isomerization. This step does not involve any net fission of the C–C bonds and produces no changes in the carbon atom number of the reactant molecule, *n*. Despite the fact that no cracking as such (breaking of C–C bonds) occurs at this stage, isomerization of feed alkanes should not be re-

---

[1] Present address: Edison Research Lab., Mobil Chemical Co., P.O. Box 3029, Edison, NJ 08818-3029.

0021-9517/91 $3.00

garded as merely a side reaction accompanying cracking processes, but rather as the first intrinsic step in the cracking reaction sequence. The products of this step, isomerized saturated hydrocarbons iso-$C_nH_{2n+2}$, can be named the primary reaction products. The second reaction step includes the fission of one C–C bond in isomerized carbocations. The products of this reaction, saturated and unsaturated hydrocarbons $C_m$ with $1 < m < n$, can be called the secondary products of cracking reactions.

The present article discusses quantitative aspects of the formation of the primary cracking products. Numerous examples of hydrocarbon isomerization in catalytic cracking and hydroisomerization reactions under mild conditions were described in the literature (*4*, *11–14*). This article can be viewed as a continuation of these studies. Its main difference from the previous publications is in the scope of feed hydrocarbons. In total, 17 $C_8$ and $C_{10}$ alkanes as well as several normal and isoalkanes with higher carbon atom numbers were tested. Our ability to examine cracking reactions of numerous hydrocarbons, mostly mono- and dimethyl-substituted, is based on the application of a special microreactor technique described in detail in the previous article (*15*). With this technique, very small quantities of feeds, of the order of 0.1 $\mu$l, are sufficient for the analysis of cracking products.

## THEORY

The current theory of gas-phase catalytic cracking over solid acidic catalysts regards carbocations as the active species in hydrocarbon cracking reactions (*9*, *10*, *16*). According to the theory, the carbocations are formed in the interactions between adsorbed hydrocarbon molecules and acidic sites on the catalyst surface. The detailed mechanism of the carbocation formation in these reactions remains a disputed subject (*10*, *16–18*). Depending on reaction conditions, both Lewis and Brønsted sites can be apparently responsible for the formation of carbocations, with high temperatures favoring the Brønsted-site mechanism (*16–18*).

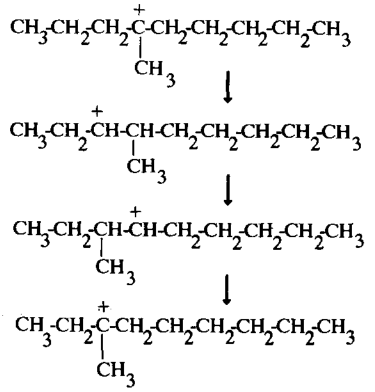


FIG. 1. Type A skeleton isomerization reactions of carbocations.

Regardless of the origin of the carbocations, once formed, they usually undergo a series of reactions including hydride transfer, chain skeleton isomerization, and breaking of C–C bonds (*9*, *10*, *16*). The theory of these carbocation reactions is based on numerous studies performed in solution at low temperatures (*9*, *10*, *19*). The experimental data presented in this article describe only one type of the carbocation reactions, the hydrocarbon chain isomerization. According to the classification of Poutsma (*9*), two different mechanisms are responsible for the skeletal isomerization of carbocations.

*Type A rearrangement.* This reaction involves three consecutive stages, the first hydride shift, the alkyl-group shift, and the second hydride shift. These steps are illustrated in Fig. 1 using 4-methylnonane as an example.

*Type B rearrangement.* This reaction proceeds via a cyclic intermediate. It usually results in the change in the degree of alkane branching. This rearrangement is illustrated in Fig. 2 using 2-methylnonane as an example.

## EXPERIMENTAL

As described in Ref. (*15*), a gas chromatograph (Hewlett–Packard 5880A) was used both as a cracking microreactor and as an

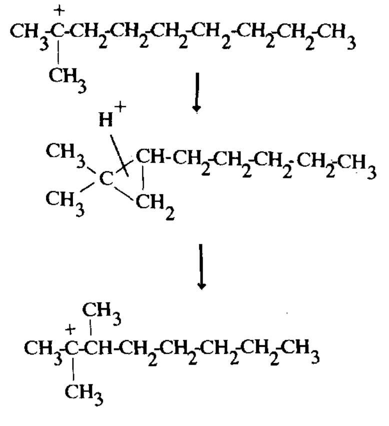


FIG. 2. Type B skeleton isomerization reactions of carbocations.

analytical tool. A small quantity (usually from 0.01 to 0.05 g) of a cracking catalyst was placed on the frit of the evaporator (a fritted glass tube in the injection assembly) and was overlaid with a small amount of an inert powder (10% OV-1 on SW/AW DMSC, ca. 0.03 g). The catalyst was subsequently dried in a helium flow at 200°C for 24 h.

To carry out a cracking reaction, the injection assembly was heated to a desired temperature, and 0.05 to 0.2 μl of a feed was injected with a microsyringe in the space above the catalyst layer. The feed vapor flowed with the helium stream and contacted the catalyst over a period of 1–2 s. The unreacted feed and reaction products immediately entered the chromatographic column and were analyzed. The column was 50 m, 0.2-mm-i.d. fused silica capillary-coated with the 0.5-μm film of cross-linked methyl silicone. Helium was used as a carrier gas at a flow rate of 1 ml/min. The column temperature was programmed to increase from 40 to 300°C at a rate of 5°C/min. Peak area calculations were carried out with a Hewlett–Packard lab automation system. The calibration factors for all peak areas were assumed equal.

Industrial catalyst FSS-1 (Filtrol), steam-equilibrated, was used for cracking of all hydrocarbons. Its active ingredient is the rare-earth-exchanged Y zeolite. The same load of the catalyst was usually used for cracking of several feed injections. All hydrocarbons were suppled by Wiley Organics Co. The previous article (*15*) contains information on catalyst aging and on the relative reactivities of various alkanes in catalytic cracking reactions.

## EXPERIMENTAL RESULTS

When the cracking reactions of isoalkanes are carried out under mild conditions, in the 250–350°C range, the reaction products, in addition to an unreacted feed hydrocarbon, contain two types of products, isoalkanes with the same carbon atom number (primary products) and isoalkanes with lower carbon atom numbers (secondary products). The structures of the secondary products will be discussed in a separate report. An increase in temperature always results in the decrease in the relative yields of the primary products. Figure 3 shows one example of primary products formed in the cracking of 2,3-dimethyloctane at 250°C. They include various mono- and dimethyl-substituted $C_{10}$

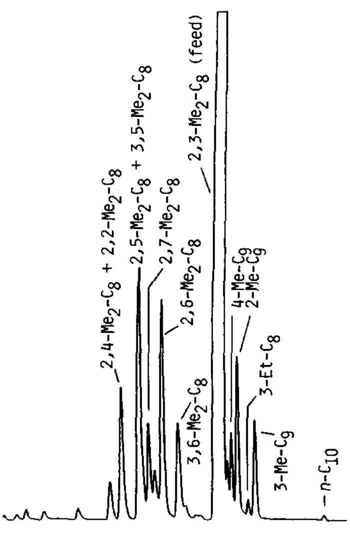


FIG. 3. Primary products formed in catalytic cracking of 2,3-dimethyl-octane at 250°C.

isoalkanes, *n*-decane, and several trimethyl-substituted heptanes (some of their peaks are seen to the left from the peaks of dimethyloctanes in Fig. 3).

Tables 1 and 2 list relative yields of the principal primary products formed in the cracking of various $C_{10}$ isoalkanes at 250 and 350°C. Two normalization procedures were used to calculate the relative yields. The first procedure uses 2-methylnonane as the reference compound, and the second procedure uses 2,6-dimethyloctane as the reference compound. Two reference compounds are required due to a strong overlap of the peaks of some products with the peaks of unreacted feeds (usually from 50 to 80% of the feed remains unconverted in these experiments (*15*)). For example, cracking of monomethyl-substituted nonanes usually prevents the use of 2-methylnonane as a reference compound. Similarly, when dimethyl-substituted isoalkanes are cracked, the peak of 2,6-dimethyloctane often overlaps with large feed peaks. Most feed isoalkanes contain, as impurities, small quantities of other isoalkanes, which prevented the measurement of some product yields.

In addition to the isodecanes listed in Tables 1 and 2, we studied several other $C_{10}$ alkanes. *N*-decane has much lower reactivity in catalytic cracking under mild conditions than most $C_{10}$ isoalkanes (*15*). It produces extremely low yields of primary cracking products. Other linear alkanes studied, *n*-$C_9H_{20}$, *n*-$C_{12}H_{26}$, *n*-$C_{14}H_{30}$, *n*-$C_{16}H_{34}$, and *n*-$C_{17}H_{36}$, also generate virtually no primary products while yielding large quantities of secondary products. 2,3-Dimethyloctane produces very low yields of the primary products, the most abundant of which are 2,5- and 2,6-dimethyloctanes. 3,4,5-Trimethylheptane at 250°C also produces primary products with very low relative yields compared to those of secondary products. They include, in approximately equal proportions, various di- and trimethyl-branched isoalkanes but very little monomethylnonanes.

Table 3 lists the distribution of the principal primary products formed in the catalytic cracking of several isooctanes at 350°C. Again, the main primary cracking products are mono- and dimethyl-substituted $C_8$ isoalkanes. The yields of *n*-octane, 2,2-, and 3,3-dimethylhexanes are very low. Similarly low are the yields of 2,3,4-, 2,2,3-, 2,2,4-, and 2,3,3-trimethyl-substituted pentanes (not reported in Table 3). Reactions carried out at 350 and 250°C gave generally similar results. For example, cracking of 2,4-dimethylhexane at 250°C gave the following primary products (with the yields normalized to the yield of 2-methylheptane): *n*-octane, 0.016; 3-methylheptane, 0.87; 4-methylheptane, 0.27; 2,3-dimethylhexane, 0.73; 3,4-dimethylhexane, 0.16; 3,3-dimethylhexane, 0.02; and 2,2-dimethylhexane, ca. 0.

Cracking of branched alkanes with higher carbon atom numbers also generates a variety of primary products, most abundant among them being mono- and dimethyl-substituted alkanes. Figure 4 shows one example of the distribution of these products, formed in the cracking of 2-methylundecane at 250°C.

## QUANTITATIVE INTERPRETATION OF PRODUCT DISTRIBUTIONS

Examination of Tables 1 and 2 shows not only that the same primary products are formed in the cracking of most examined $C_{10}$ isoalkanes, but also that their relative yields do not depend on the structures of the feed molecules. The same is true for the case of catalytic cracking of $C_8$ isoalkanes (Table 3). These data indicate that isomerization reactions of parent carbocations reach an equilibrium state under conditions employed, at least when the feed compounds are methyl-branched alkanes. These results are discussed from two points of view: the factors that determine the equilibrium and the reaction mechanisms that bring these isomerization reactions to equilibrium.

We assume that the equilibrium distribu-

TABLE 1

Distribution of Primary Products Formed in Catalytic Cracking of Various $C_{10}$ Isoalkanes at 250°C over FSS-1 Catalyst

A. Internal reference compound: 2-Methylnonane

| Feed: Product | 2,3-$Me_2C_8$ | 2,6-$Me_2C_8$ | 2,7-$Me_2C_8$ | 3,5-$Me_2C_8$ | 3,6-$Me_2C_8$ | Average |
|---|---|---|---|---|---|---|
| $n$-$C_{10}$ | 0.04 | 0.03 | 0.02 | 0.05 | 0.02 | 0.03(+33%) |
| 2-$MeC_9$ | 1 | 1 | 1 | 1 | 1 | 1 |
| 3-$MeC_9$ | 0.64 | 0.69 | 0.72 | 0.63 | 0.71 | 0.68(+5%) |
| 4-$MeC_9$ | 0.50 | 0.54 | 0.56 | 0.46 | 0.50 | 0.51(+6%) |
| 5-$MeC_9$ | 0.28 | 0.27 | 0.29 | 0.27 | 0.28 | 0.28(+4%) |
| 2,3-$Me_2C_8$ | [a] | 0.70 | 0.80 | 0.71 | 0.72 | 0.73(+4%) |
| 2,4-$Me_2C_8$ + 2,2-$Me_2C_8$[b] | 1.05 | 0.96 | 1.15 | 0.95 | 0.95 | 1.01(+7%) |
| 2,5-$Me_2C_8$[c] | 1.33 | 1.46 | 1.46 | [d] | 1.55 | 1.45(+4%) |
| 2,6-$Me_2C_8$ | 1.58 | [a] | [d] | 2.15 | 2.28 | 2.00(+14%) |
| 2,7-$Me_2C_8$ | 0.66 | 1.15 | [a] | [d] | 0.92 | 0.91(+19%) |
| 3,3-$Me_2C_8$ | 0.01 | [d] | [d] | 0 | [d] | ca. 0 |
| 3,5-$Me_2C_8$[c] | 0.72 | 0.79 | 0.79 | [a] | 0.83 | 0.78(+4%) |
| 3,6-$Me_2C_8$ | 0.82 | 1.06 | 1.10 | 1.22 | [a] | 1.05(+10%) |
| 4,5-$Me_2C_8$ | 0.05 | — | 0.08 | 0.07 | 0.08 | 0.07(+14%) |
| 3-$EtC_8$ | [d] | 0.08 | 0.08 | 0.07 | 0.08 | 0.08(+7%) |

B. Internal reference compound: 2,6-Dimethyloctane

| Feed: Product | 2-$MeC_9$ | 5-$MeC_9$ | 2,3-$Me_2C_8$ | 3,5-$Me_2C_8$ | 3,6-$Me_2C_8$ | 3-$EtC_8$ | Average |
|---|---|---|---|---|---|---|---|
| $n$-$C_{10}$ | 0.06 | 0.10 | 0.02 | 0.02 | 0.01 | — | ca. 0.04 |
| 2-$MeC_9$ | [a] | [d] | 0.63 | 0.46 | 0.43 | — | 0.51(+16%) |
| 3-$MeC_9$ | [d] | [d] | 0.40 | 0.46 | 0.31 | — | 0.39(+16%) |
| 4-$MeC_9$ | [d] | [d] | 0.31 | 0.21 | 0.22 | — | 0.25(+25%) |
| 5-$MeC_9$ | [d] | [a] | 0.18 | 0.12 | 0.12 | — | 0.14(+19%) |
| 2,3-$Me_2C_8$ | — | — | [a] | 0.33 | 0.32 | — | 0.32(+3%) |
| 2,4-$Me_2C_8$ + 2,2-$Me_2C_8$[b] | 0.55 | 0.59 | 0.66 | 0.44 | 0.42 | 0.49 | 0.52(+16%) |
| 2,5-$Me_2C_8$[c] | 0.79 | 0.83 | 0.84 | [d] | 0.68 | 0.77 | 0.78(+8%) |
| 2,6-$Me_2C_8$ | 1 | 1 | 1 | 1 | 1 | — | 1 |
| 2,7-$Me_2C_8$ | 0.44 | 0.44 | 0.42 | [d] | 0.40 | 0.50 | 0.44(+6%) |
| 3,3-$Me_2C_8$ | 0 | 0 | 0 | 0 | [d] | 0 | ca. 0 |
| 3,5-$Me_2C_8$[c] | 0.40 | 0.45 | 0.45 | [a] | 0.36 | 0.42 | 0.42(+6%) |
| 3,6-$Me_2C_8$ | 0.56 | 0.54 | 0.42 | 0.57 | [a] | 0.37 | 0.49(+16%) |
| 4,5-$Me_2C_8$ | 0.04 | — | 0.03 | 0.03 | 0.04 | — | 0.04(+14%) |
| 3-$EtC_8$ | [d] | — | 0.08 | 0.03 | 0.04 | [a] | 0.05(+48%) |

[a] Feed isoalkane.

[b] Peaks of these isomers overlap, the total area is measured.

[c] The peak of 2,5-dimethyloctane overlaps the peak of one of the stereoisomers of 3,6-dimethyloctanes. The separation of the products is carried out under assumption that both 3,6-dimethyloctane stereoisomers are present in equal amounts.

[d] Overlap with the feed peak prevents estimation.

TABLE 2

Distribution of Primary Products Formed in Catalytic Cracking of Various $C_{10}$ Isoalkanes at 350°C over FSS-1 Catalyst

A. Internal reference compound: 2-Methylnonane

| Feed: Product | 2,3-$MeC_8$ | 2,6-$Me_2C_8$ | 2,7-$Me_2C_8$ | 3,6-$Me_2C_8$ | Average |
|---|---|---|---|---|---|
| $n$-$C_{10}$ | 0.02 | ca. 0.10 | 0.04 | ca. 0.10 | ca. 0.06 |
| 2-$MeC_9$ | 1 | 1 | 1 | 1 | 1 |
| 3-$MeC_9$ | 0.72 | 0.59 | 0.75 | 0.73 | 0.70(+8%) |
| 4-$MeC_9$ | 0.50 | 0.60 | 0.59 | 0.58 | 0.57(+3%) |
| 5-$MeC_9$ | [a] | 0.27 | 0.38 | 0.32 | 0.32(+11%) |
| 2,3-$Me_2C_8$ | [b] | 0.61 | 0.77 | 0.70 | 0.69(+8%) |
| 2,4-$Me_2C_8$ + 2,2-$Me_2C_8$[c] | 0.86 | 0.70 | — | 0.65 | 0.74(+11%) |
| 2,5-$Me_2C_8$[d] | 0.98 | [a] | [a] | 1.13 | 1.05(+7%) |
| 2,6-$Me_2C_8$ | 1.58 | [a] | — | 1.61 | 1.60(+1%) |
| 2,7-$Me_2C_8$ | 0.52 | — | [a] | 0.57 | 0.55(+4%) |
| 3,3-$Me_2C_8$ | ca. 0 | [a] | [a] | ca. 0 | ca. 0 |
| 3,5-$Me_2C_8$[d] | 0.53 | [a] | [a] | 0.52 | 0.52(+1%) |
| 3,6-$Me_2C_8$ | 0.58 | — | — | [b] | 0.58 |
| 4,5-$Me_2C_8$ | 0.04 | — | — | [a] | 0.04 |
| 3-$EtC_8$ | [a] | 0.08 | ca. 0.20 | ca. 0.05 | ca. 0.11 |

B. Internal reference compound: 2,6-Dimethyloctane

| Feed: Product | 2-$MeC_9$ | 3-$MeC_9$ | 4-$MeC_9$ | 5-$MeC_9$ | 2,3-$Me_2C_8$ | 3,6-$Me_2C_8$ | Average |
|---|---|---|---|---|---|---|---|
| $n$-$C_{10}$ | 0.21 | — | — | 0.10 | — | ca. 0.05 | ca. 0.12 |
| 2,3-$Me_2C_8$ | 1.10 | 1.00 | — | — | [b] | — | 1.05(+5%) |
| 2,4-$Me_2C_8$ + 2,2-$Me_2C_8$ | 0.63 | 0.60 | 0.57 | 0.55 | 0.68 | 0.40 | 0.61(+6%) |
| 2,5-$Me_2C_8$[d] | 0.69 | 0.81 | 0.72 | 0.74 | 0.83 | 0.70 | 0.78(+7%) |
| 2,6-$Me_2C_8$ | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| 2,7-$Me_2C_8$ | 0.42 | 0.43 | 0.47 | 0.49 | 0.44 | 0.35 | 0.45(+5%) |
| 3,3-$Me_2C_8$ | 1 | 1 | 1 | 1 | 1 | 1 | ca. 0 |
| 3,5-$Me_2C_8$[d] | 0.37 | 0.43 | 0.39 | 0.40 | 0.44 | 0.33 | 0.39(+8%) |
| 3,6-$Me_2C_8$ | 0.47 | 0.55 | 0.44 | 0.49 | 0.49 | [b] | 0.49(+5%) |
| 4,5-$Me_2C_8$ | 0.18 | 0.21 | 0.17 | 0.26 | — | — | 0.20(+15%) |
| 3-$EtC_8$ | 0.29 | — | — | 0.23 | — | — | 0.26(+11%) |
| 4-$EtC_8$ | 0.16 | 0.12 | [a] | [a] | — | — | 0.14(+14%) |

[a] Overlap with the feed peak prevents estimation.

[b] Feed isoalkane.

[c] Peaks of these isomers overlap, the total area is measured.

[d] See footnote *c* of Table 1.

tions of the primary isoalkane products are determined by thermodynamic stabilities (formation energies) of corresponding adsorbed carbocations. While these parameters for high molecular weight cations adsorbed on the catalyst surface are not known, we assume that, in the first approximation, the formation energies of the ions are proportional to the formation energies of corresponding isoalkanes. Such proportionality appears to be especially justified when the charge positions in the cations under consideration are similar. For example, it seems reasonable to assume that

TABLE 3

Distribution of Primary Products Formed in Catalytic Cracking of Various $C_8$ Isoalkanes at 350°C over FSS-1 Catalyst

| Feed: Product | 2-$MeC_7$ | 3-$MeC_7$ | 2,4-$Me_2C_6$ | 2,5-$Me_2C_6$ | Average |
|---|---|---|---|---|---|
| $n$-$C_8$ | — | [c] | — | 0.04 | 0.04 |
| 2-$MeC_7$ + 3-$EtC_6$ | [a] | [c] | 1 | 1 | 1 |
| 3-$MeC_7$ | — | [a] | 0.96 | 0.89 | 0.92 |
| 4-$MeC_7$ | — | — | 0.30 | 0.28 | 0.29 |
| 2,2-$Me_2C_6$ | ca. 0 | ca. 0 | — | ca. 0 | ca. 0 |
| 2,3-$Me_2C_6$ | — | — | 0.53 | 0.49 | 0.51 |
| 2,4-$Me_2C_6$ | 0.74[b] | 0.92[b] | [a] | — | 0.83 |
| 2,5-$Me_2C_6$ | 0.88[b] | 1.00[b] | [c] | [a] | 0.94 |
| 3,3-$Me_2C_6$ | — | — | — | 0.06 | 0.06 |
| 3,4-$Me_2C_6$ | — | — | 0.19 | 0.12 | 0.16 |

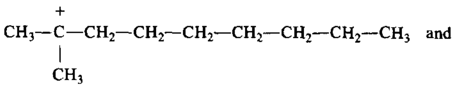
*Note.* Internal reference compound: 2-methylheptane.

[a] Feed isoalkane.

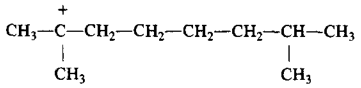
[b] Indirect estimations, from the [2,i-$Me_2C_6$] : [2,3-$Me_2C_6$] ratios and the [2,3-$Me_2C_6$] : [2-$MeC_7$] ratio in the products of 2,4-$Me_2C_6$ cracking.

[c] Overlap with the feed peak prevents estimation.

the formation energies of two carbocations,

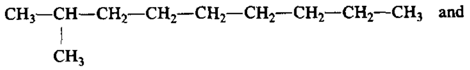


$$CH_3-\overset{+}{\underset{\displaystyle CH_3}{\underset{|}{C}}}-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3 \quad \text{and}$$

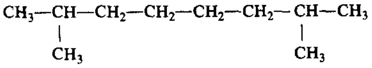


$$CH_3-\overset{+}{\underset{\displaystyle CH_3}{\underset{|}{C}}}-CH_2-CH_2-CH_2-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3$$

parallel the formation energies of respective isoalkanes



$$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3 \quad \text{and}$$



$$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-CH_2-CH_2-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3$$

because both ions are tertiary and the alkyl groups attached to their charge-carrying atoms have similar substitution arrangements.

Table 4 lists Gibbs formation energies for various $C_{10}$ isoalkanes. The $\Delta G_f$ values for 250 and 350°C were linearly extrapolated from the data at 500, 600, and 700 K tabulated in Ref. (*20*). The $\Delta\Delta G_f$ values (with respect to $\Delta G_f$ for particular methyl-substituted nonanes) were used to calculate thermodynamic equilibrium distributions of various $C_{10}$ alkanes at both temperatures, as $\exp(\Delta\Delta G_f)$ values. The equilibrium distribu-

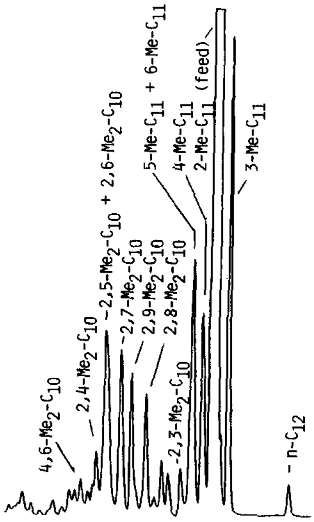


FIG. 4. Primary products formed in catalytic cracking of 2-methylundecane at 250°C.

TABLE 4

Gibbs Formation Energies (*20*) and Equilibrium Distributions of $C_{10}$ Alkanes

| Alkane | 250°C | | | 350°C | | |
|---|---|---|---|---|---|---|
| | $\Delta G_f$ (kJ/mol) | $\Delta\Delta G_f^a$ (kJ/mol) | exp($\Delta\Delta G_f$) normalized | $\Delta G_f$ (kJ/mol) | $\Delta\Delta G_f^a$ (kJ/mol) | exp($\Delta\Delta G_f$) normalized |
| $n$-$C_{10}$ | 256.61 | 2.93 | 0.51 | 360.06 | 2.01 | 0.68 |
| 2-$MeC_9$ | 253.67 | 0 | 1 | 358.05 | 0 | 1 |
| 3-$MeC_9$ | 252.74 | −0.93 | 1.24 | 356.36 | −1.70 | 1.39 |
| 4-$MeC_9$ | 253.38 | −0.29 | 1.07 | 357.17 | −0.88 | 1.19 |
| 5-$MeC_9$ | 256.24 | 2.59 | 0.55 | 360.64 | 3.47 | 0.61 |
| 2,2-$Me_2C_8$ | 257.05 | 5.18 | 0.46 | 363.74 | 5.69 | 0.33 |
| 2,3-$Me_2C_8$ | 257.14 | 3.47 | 0.45 | 362.05 | 4.00 | 0.46 |
| 2,4-$Me_2C_8$ | 254.98 | 1.31 | 0.74 | 360.03 | 1.98 | 0.68 |
| 2,5-$Me_2C_8$ | 252.34 | −1.33 | 1.36 | 357.65 | −0.40 | 1.08 |
| 2,6-$Me_2C_8$ | 251.74 | −1.93 | 1.56 | 356.56 | −1.49 | 1.33 |
| 2,7-$Me_2C_8$ | 255.56 | 1.89 | 0.65 | 361.24 | 3.29 | 0.53 |
| 3,3-$Me_2C_8$ | 258.31 | 4.64 | 0.34 | 364.24 | 6.18 | 0.30 |
| 3,4-$Me_2C_8$ | 257.51 | 3.84 | 0.41 | 362.19 | 4.14 | 0.45 |
| 3,5-$Me_2C_8$ | 254.07 | 0.40 | 0.91 | 358.63 | 0.58 | 0.89 |
| 3,6-$Me_2C_8$ | 253.68 | 0.19 | 0.96 | 358.69 | 0.64 | 0.88 |
| 4,5-$Me_2C_8$ | 261.53 | 7.86 | 0.16 | 367.72 | 9.66 | 0.15 |
| 3-$EtC_8$ | 258.74 | 5.07 | 0.31 | 363.14 | 5.08 | 0.37 |
| 4-$EtC_8$ | 256.40 | 2.73 | 0.54 | 360.55 | 2.59 | 0.62 |

[a] $\Delta\Delta G_f = \Delta G_f - \Delta G_f(2\text{-}MeC_9)$.

tions for $C_8$ isoalkanes were calculated using the same approach.

Tables 5 and 6 compare the experimental data on the distributions of $C_{10}$ and $C_8$ primary cracking products (averaged values from Tables 1–3) and their thermodynamic equilibrium distributions. Each table consists of two sections. In Section A, 2-methyl-substituted isoalkanes are used as the reference compounds, whereas in section B monomethyl-substituted isoalkanes with the methyl group in the central position in the chain, 5-methylnonane, and 4-methylheptane respectively, are used as the reference compounds.

The data in Tables 5 and 6 can be rationalized in the following way. All branched primary cracking products can be subdivided into two groups with respect to their relative abundance. The first group includes isoalkanes with a methyl group in the second position of the chain, i.e., 2-methyl-substituted isoalkanes and 2,$x$-dimethyl-substituted isoalkanes. The second group includes mono- and dimethyl-substituted isoalkanes with methyl groups in all positions in the chains other than the second one.

As follows from the Section B in Tables 5 and 6, the experimentally determined distributions of the isoalkanes belonging to the second group approximately reflect their thermodynamic stabilities. For example, the experimentally measured ratios between the yields of 3-methylheptane, 4-methylnonane, and 3,4-dimethylhexane at 350°C are 3.2 : 1.0 : 0.6, as compared to the calculated ratios 3.4 : 1.0 : 0.6 (Table 6B). Similarly, the experimentally measured ratios between the yields of 3-methylnonane, 4-methylnonane, 5-methylnonane, 3,5-dimethyloctane, 3,6-dimethyloctane, and 4,5-dimethyloctane at 350°C are 2.2 : 1.8 : 1.0 : 1.6 : 1.8 : 0.1, and the calculated ratios are 2.3 : 2.0 : 1.0 : 1.5 : 1.4 : 0.2 (Table 5B). These data, at least on a semiquantitative level,

TABLE 5

Comparison of Experimental Data on Distribution of Primary Products in Catalytic Cracking of $C_{10}$ Isoalkanes (Average Values) and Thermodynamic Equilibrium Data for $C_{10}$ Alkanes

| | 250°C | | 350°C | |
|---|---|---|---|---|
| | Cat. cracking | $\exp(\Delta\Delta G_f)$ | Cat. cracking | $\exp(\Delta\Delta G_f)$ |
| A. Reference compound: 2-Methylnonane | | | | |
| $n$-$C_{10}$ | 0.03 | 0.51 | ca. 0.06 | 0.68 |
| 2-$MeC_9$ | 1 | 1 | 1 | 1 |
| 3-$MeC_9$ | 0.68 | 1.24 | 0.70 | 1.39 |
| 4-$MeC_9$ | 0.51 | 1.07 | 0.57 | 1.19 |
| 5-$MeC_9$ | 0.28 | 0.55 | 0.32 | 0.61 |
| 2,3-$Me_2C_8$ | 0.73 | 0.45 | 0.69 | 0.46 |
| 2,4-$Me_2C_8$ | 1.01 | 0.75[a] | 0.92 | 0.68[a] |
| 2,5-$Me_2C_8$ | 1.45 | 1.36 | 1.05 | 1.08 |
| 2,6-$Me_2C_8$ | 2.00 | 1.56 | 1.60 | 1.33 |
| 2,7-$Me_2C_8$ | 0.91 | 0.65 | 0.55 | 0.53 |
| 3,3-$Me_2C_8$ | ca. 0 | 0.34 | ca. 0 | 0.30 |
| 3,5-$Me_2C_8$ | 0.78 | 0.91 | 0.52 | 0.89 |
| 3,6-$Me_2C_8$ | 1.05 | 0.96 | 0.58 | 0.88 |
| 4,5-$Me_2C_8$ | 0.07 | 0.16 | 0.04 | 0.15 |
| 3-$EtC_8$ | 0.08 | 0.31 | 0.11 | 0.37 |
| 4-$EtC_8$ | | | 0.22 | 0.62 |
| B. Reference compound: 5-Methylnonane | | | | |
| $n$-$C_{10}$ | 0.11 | 0.93 | 0.19 | 1.11 |
| 2-$MeC_9$ | 3.57 | 1.82 | 3.12 | 1.64 |
| 3-$MeC_9$ | 2.43 | 2.25 | 2.19 | 2.28 |
| 4-$MeC_9$ | 1.82 | 1.94 | 1.78 | 1.95 |
| 5-$MeC_9$ | 1 | 1 | 1 | 1 |
| 2,3-$Me_2C_8$ | 2.61 | 0.82 | 2.16 | 0.75 |
| 2,4-$Me_2C_8$ | 3.61 | 1.35[a] | 2.88 | 1.11[a] |
| 2,5-$Me_2C_8$ | 5.18 | 2.47 | 3.28 | 1.77 |
| 2,6-$Me_2C_8$ | 7.14 | 2.84 | 5.00 | 2.18 |
| 2,7-$Me_2C_8$ | 3.25 | 1.18 | 1.72 | 0.87 |
| 3,3-$Me_2C_8$ | ca. 0 | 0.62 | ca. 0 | 0.49 |
| 3,5-$Me_2C_8$ | 2.78 | 1.65 | 1.62 | 1.46 |
| 3,6-$Me_2C_8$ | 3.75 | 1.74 | 1.81 | 1.44 |
| 4,5-$Me_2C_8$ | 0.25 | 0.29 | 0.12 | 0.24 |
| 3-$EtC_8$ | 0.29 | 0.56 | 0.34 | 0.61 |
| 4-$EtC_8$ | | | 0.68 | 1.02 |

[a] Peaks of 2,2- and 2,4-dimethyloctanes overlap. The equilibrium data for 2,4-dimethyloctane are used because, judging by the data for 3,3-dimethyl-octane and $C_8$ alkanes in Table 6, all geminally substituted isoalkanes are present in the primary cracking products in very low concentrations.

agree with the above stated assumption that the formation energies of different tertiary carbocations parallel the formation energies of respective isoalkanes.

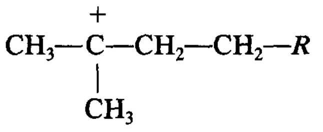
Sections B of Tables 5 and 6 show also that the experimentally measured fractions of the methyl-branched isoalkanes belonging to the first group (those with a methyl group in the second position of alkyl chains) are always higher than their respective thermodynamic stabilities by a factor of 2–2.5. A possible explanation for these increased yields is the hyperconjugation effect of methyl groups in carbocations

TABLE 6

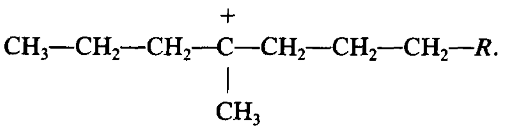
Comparison of Experimental Data on Distribution of Primary Products in Catalytic Cracking of $C_8$ Isoalkanes (Average Values) and Thermodynamic Equilibrium Data for $C_8$ Alkanes

| | 250°C | | 350°C | |
|---|---|---|---|---|
| | Cat. cracking | $\exp(\Delta\Delta G_f)$ | Cat. cracking | $\exp(\Delta\Delta G_f)$ |
| | A. Reference compound: 2-Methylheptane | | | |
| $n$-$C_8$ | ca. 0.02 | 0.53 | ca. 0.04 | 0.68 |
| 2-$MeC_7$ | 1 | 1 | 1 | 1 |
| 3-$MeC_7$ + 3-$EtC_6$ | 0.84 | 1.28 | 0.92 | 1.32 |
| 4-$MeC_7$ | 0.27 | 0.36 | 0.29 | 0.40 |
| 2,2-$Me_2C_6$ | ca. 0 | 0.34 | ca. 0 | 0.26 |
| 2,3-$Me_2C_6$ | 0.73 | 0.27 | 0.50 | 0.26 |
| 2,4-$Me_2C_6$ | 1.50 | 0.64 | 0.83 | 0.59 |
| 2,5-$Me_2C_6$ | 2.13 | 0.63 | 0.94 | 0.44 |
| 3,3-$Me_2C_6$ | 0.02 | 0.24 | 0.06 | 0.21 |
| 3,4-$Me_2C_6$ | 0.16 | 0.20 | 0.16 | 0.22 |
| | B. Reference compound: 4-Methylheptane | | | |
| $n$-$C_8$ | ca. 0.07 | 1.47 | ca. 0.14 | 1.70 |
| 2-$MeC_7$ | 3.70 | 2.78 | 3.45 | 2.50 |
| 3-$MeC_7$ + 3-$EtC_6$ | 3.11 | 3.55 | 3.17 | 3.40 |
| 4-$MeC_7$ | 1 | 1 | 1 | 1 |
| 2,2-$Me_2C_6$ | ca. 0 | 0.94 | ca. 0 | 0.65 |
| 2,3-$Me_2C_6$ | 2.70 | 0.75 | 1.72 | 0.65 |
| 2,4-$Me_2C_6$ | 5.55 | 1.78 | 2.86 | 1.48 |
| 2,5-$Me_2C_6$ | 7.89 | 1.75 | 3.14 | 1.10 |
| 3,3-$Me_2C_6$ | 0.07 | 0.67 | 0.21 | 0.52 |
| 3,4-$Me_2C_6$ | 0.59 | 0.56 | 0.55 | 0.55 |

(*19, 21*), which increases relative stabilities of methyl-substituted carbocations compared to those of other alkyl-branched carbocations. This effect, for example, explains high stability of the $(CH_3)_3C^+$ carbocation (*10, 19*). In the present case, we assume that all 2-methyl-branched alkanes are formed with relatively higher yields because two methyl groups are adjacent to the charged carbon atom in the respective carbocations, whereas all other methyl-branched carbocations have only one methyl group, i.e.,



$CH_3\text{—}\underset{\displaystyle CH_3}{\overset{+}{C}}\text{—}CH_2\text{—}CH_2\text{—}R$ vs

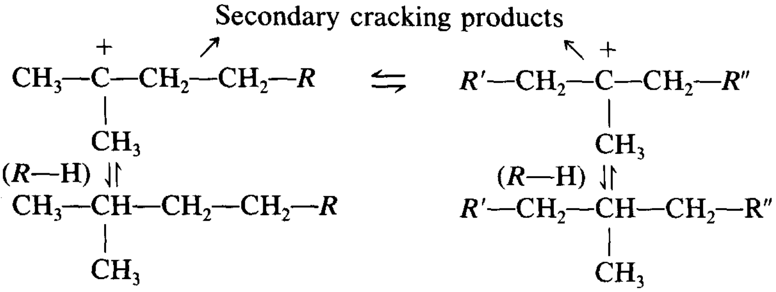


$CH_3\text{—}CH_2\text{—}CH_2\text{—}\underset{\displaystyle CH_3}{\overset{+}{C}}\text{—}CH_2\text{—}CH_2\text{—}CH_2\text{—}R.$

On the other hand, when the distributions of the 2-methyl-substituted isoalkanes are compared separately (Sections A in Tables 5 and 6), they again confirm the rule that the distributions of the primary cracking products reflect their relative thermodynamic stabilities. For example, the experimentally measured ratios between the yields of 2-methylnonane, 2,3-, 2,4-, 2,5-, 2,6-, and 2,7-dimethyloctanes at 350°C are 1.0 : 0.7 : 0.9 : 1.0 : 1.6 : 0.6, and the calculated ratios are 1.0 : 0.5 : 0.7 : 1.1 : 1.3 : 0.5 (Table 5A). This uniform enhancement in the relative yields of isoalkanes with a methyl group in the second position of alkyl chains may also explain why such isoalkanes are the principal primary products in the cracking of saturated hydrocarbons with higher carbon atom numbers (Fig. 4).

The situation is complicated by the fact that tertiary carbocations, in addition to skeleton-isomerization reactions shown in Figs. 1 and 2, also participate in two other reactions, irreversible formation of secondary cracking products (C–C bond fission) and reversible hydride abstraction reactions:

---



$$\begin{array}{ccc}
 & \text{Secondary cracking products} & \\
 \overset{+}{\underset{\substack{|\\ CH_3}}{CH_3-C}}-CH_2-CH_2-R \;\nearrow & \rightleftharpoons & \nwarrow\; R'-CH_2-\overset{+}{\underset{\substack{|\\ CH_3}}{C}}-CH_2-R'' \\
 (R-H)\ \downarrow\uparrow & & (R-H)\ \downarrow\uparrow \\
 \underset{\substack{|\\ CH_3}}{CH_3-CH}-CH_2-CH_2-R & & R'-CH_2-\underset{\substack{|\\ CH_3}}{CH}-CH_2-R''
\end{array}$$

---

In principle, the preferential formation of 2-methyl-branched primary products can be also attributed either to slower cracking rates of respective carbocations or to their higher hydride abstraction rates. However, such possible differences in reactivities cannot be readily attributed to any structural features of the carbocations, and hyperconjugation appears to be a more probable cause of the present experimental finding.

Thus, the basic rule describing quantitatively the distributions of the primary products formed in the catalytic cracking of isoalkanes can be formulated in the following way:

(a) the relative yields of different isoalkanes are proportional to their thermodynamic stabilities,

(b) the relative yields of all isoalkanes with a methyl group in the second position in the alkyl chain are, uniformly, 2–2.5 times higher than those expected on the basis of their thermodynamic stabilities alone. We attribute this yield enhancement to the additional stabilization effect of the second methyl group on the concentrations of respective carbocations.

Three types of alkanes represent exceptions from this rule (see Tables 5 and 6):

1. Judging by the data for 2,2- and 3,3-dimethylhexanes (Table 6) and for 3,3-dimethyloctane (Table 5), geminally substituted isoalkanes are formed with very low yields, well below the levels expected from their thermodynamic stabilities.
2. Normal alkanes are also formed with yields much lower than those expected from their thermodynamic stabilities (Tables 5B and 6B, Figs. 3 and 4).
3. Ethyl-substituted isoalkanes are formed with yields ca. 2 times lower than those expected from their thermodynamic stabilities (Table 5B).

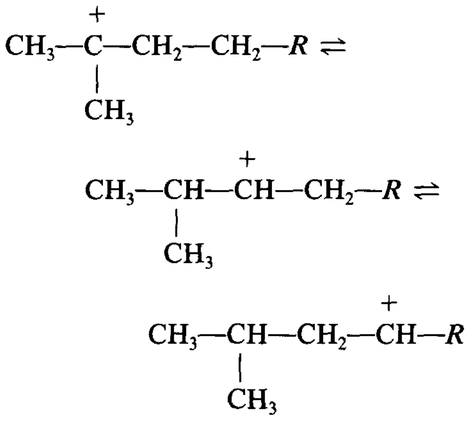
Analysis of possible reasons for these exceptions provides an additional insight into the cracking mechanism.

## DISCUSSION

The results of the present study are, in general, consistent with the mechanism of carbocation reactions, which includes type A and type B skeleton rearrangements of carbocations shown in Figs. 1 and 2. The data in Tables 1–3, 5, and 6 provide several quantitative details of these rearrangements.

Judging by the primary product distribution data in Table 1, all tertiary $C_{10}$ carbocations undergo complete randomization even at 250°C in a period of time not exceeding 1–2 s, the estimated contact time (*15*). The fact that the same equilibrium mixtures of mono- and polysubstituted isoalkanes are produced independently of the branching degree of feed isoalkanes (Tables 1–3) indicates that both the type A and type B rearrangements are fully operative under these conditions.

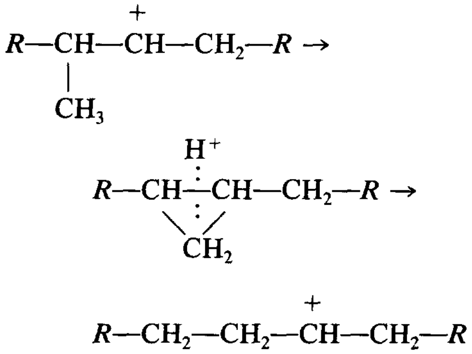
It is known that the skeleton isomerizations of carbocations are accompanied by very rapid 1–2 hydride shift reactions (*19, 22, 23*):



$$CH_3-\underset{\underset{CH_3}{|}}{\overset{+}{C}}-CH_2-CH_2-R \rightleftharpoons CH_3-\underset{\underset{CH_3}{|}}{CH}-\overset{+}{CH}-CH_2-R \rightleftharpoons CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2-\overset{+}{CH}-R$$

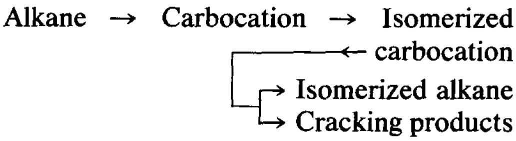
The conclusion that the equilibrium distributions of the methyl-branched primary cracking products reflect their thermodynamic stabilities (with additional effects due to the hyperconjugation effects of methyl groups) supports the notion that the positive charge, although it rapidly migrates along the chain, has different "residence times" at different carbon atoms and most frequently resides at tertiary carbon atoms.

Most dimethyl-substituted isoalkanes readily produce mixtures of monomethyl-substituted isoalkanes (Tables 1 and 2). This fact indicates that a particular B-type rearrangement reaction, which reduces the degree of alkane branching, proceeds quite readily, e.g.,



$$R-\underset{\underset{CH_3}{|}}{\overset{+}{CH}}-CH-CH_2-R \rightarrow R-\underset{\diagdown}{CH}\overset{\overset{H^+}{\vdots}}{-}\underset{\diagup}{CH}-CH_2-R \;(\text{bridged by } CH_2) \rightarrow R-CH_2-CH_2-\overset{+}{CH}-CH_2-R$$

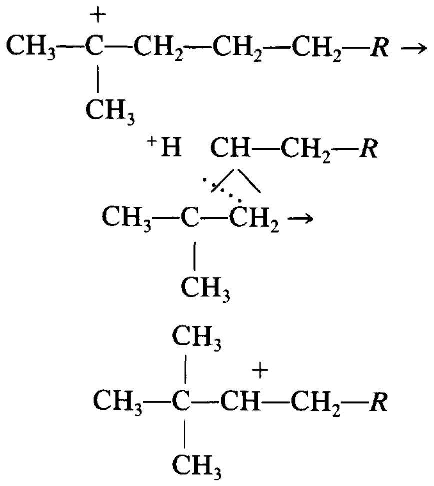
However, these reactions fail to produce *n*-alkanes with yields commensurable with their thermodynamic stabilities. A possible explanation of this anomaly can be proposed if one describes relative stabilities of different carbocations in kinetic terms:



Alkane → Carbocation → Isomerized carbocation
→ Isomerized alkane
→ Cracking products

Release of an isomerized alkane from the catalyst surface proceeds in parallel with cracking of a respective carbocation and requires the H-shift from the active center. One can propose that secondary carbocations, precursors of *n*-alkanes, are very unstable and undergo C–C fission reactions much more readily than tertiary carbocations. This assumption is partially supported by the fact that the relative yields of primary cracking products (isomerized alkanes of the same molecular weight) in relation to the yields of secondary cracking products are always substantially lower in *n*-alkane cracking compared to isoalkane cracking.

The same explanation can be applied to account for low yields of geminally substituted isoalkanes. Although the B-type isomerization apparently can produce carbocations with such skeletons



the resulting carbocations are secondary and hence may undergo C–C fission reactions more easily.

Finally, the decreased relative yields of ethyl-substituted isoalkanes can be attributed to the absence of the additional stabilizing effect exerted by a methyl group attached to the charge-bearing carbon atom.

## ACKNOWLEDGMENTS

Experimental assistance of Mr. W. B. Payne is greatly appreciated.

## REFERENCES

1. Greensfielder, B. S., and Voge, H. H., *Ind. Eng. Chem.* **37,** 514, 983, 1038 (1945).
2. Thomas, C. L., *Ind. Eng. Chem.* **41,** 2564 (1949).
3. Lombardo, E. A., Pierantozzi, R., and Hall, W. K., *J. Catal.* **110,** 171 (1988).
4. Abbot, J., and Wojciechowski, B. W., *J. Catal.* **113,** 353 (1988).
5. Dass, D. V., and Odell, A. L., *J. Catal.* **113,** 259 (1988).
6. Abbot, J., and Wojciechowski, B. W., *J. Catal.* **104,** 74, 80 (1987).
7. Mirodatos, C., and Barthomeuf, D., *J. Catal.* **114,** 121 (1988).
8. Best, D., and Wojchiechowski, B. W., *J. Catal.* **47,** 11 (1977).
9. Poutsma, M. L., *in* "Zeolite Chemistry and Catalysis" (J. Rabo, Ed.), Chap. 8. Am. Chem. Soc., Washington, DC, 1976.
10. Gates, B. C., Katzer, J. R., and Schuit, G. C. A., "Chemistry of Catalytic Processes." McGraw–Hill, New York, 1979.
11. Bolton, A. P., and Lanewala, M. A., *J. Catal.* **18,** 1 (1970).
12. Weitkamp, J., and Farag, H., *Acta Phys. Chem.* **24,** 327 (1978).
13. Steijns M., Froment, G., Jakobs, P., Uytterhoeven, J., and Weitkamp, J., *Ind. Eng. Chem., Prod. Res. Dev.* **20,** 654 (1981).
14. Abbot, J., and Wojciechowski, B. W., *J. Catal.* **108,** 347 (1987).
15. Kissin, Y. V., *J. Catal.* **126,** 600 (1990).
16. Wojciechowski, B. W., and Corma, A., "Catalytic Cracking: Catalysts, Chemistry, and Kinetics." Dekker, New York, 1986.
17. Haag, W. O., and Dessau, R. M., *in* "Proceedings, 8th International Congress on Catalysis, Berlin, 1984," Vol. II, p. 305. Dechema, Frankfurt-am-Main, 1984.
18. Haag, W. O., Lago, R. M., and Weisz, P. B., *Nature* **309,** 589 (1984).
19. March, J., "Advanced Organic Chemistry," 3rd ed. Wiley, New York, 1985.
20. "Selected Values of Properties of Hydrocarbons and Related Compounds," Vol. 9, API Project 44, A&M College of Texas.
21. Symons, M. C. R., *Tetrahedron* **18,** 333 (1962).
22. Millard, B. J., and Shaw, D. F., *J. Chem. Soc. B* 664 (1966).
23. Mayer, K. K., and Djerassi, C., *Organic Mass Spectrosc.* **5,** 817 (1971).