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Evidence for Branching of Long-Chain *n*-Alkanes via Protonated Cycloalkanes Larger than Cyclopropane

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The formation of monobranched isomers from *n*-alkanes over bifunctional faujasite-type catalysts is explained by proposing the occurrence of alkylcarbenium ions as reaction intermediates and by using the general rules of alkylcarbenium ion chemistry. Methyl branching of *n*-alkanes occurs mainly via substituted corner-protonated cyclopropane intermediates. Protonated cycloalkanes with larger rings must be invoked in order to explain the primary nature of isomers with side chains larger than methyl groups and to rationalize the observed methyl-, ethyl-, propyl-, and butyl-branching selectivities. © 1990 Academic Press, Inc.

INTRODUCTION

The complexity of the reaction product mixture formed over bifunctional catalysts depends mainly on the carbon number of the feed molecules, as in bifunctional catalysis the carbon number of the product molecules generally does not exceed that of the feed. In spite of this restriction to the carbon number of the reaction products, the number of different products that are formed is very large when a long-chain *n*-alkane, containing more than seven carbon atoms, is converted. The elucidation of the bifunctional reaction scheme of long-chain *n*-alkanes progressed in parallel with improvements in high-resolution GLC separation techniques. The first studies were performed with single *n*-alkane reagents with carbon number up to 16 using Pt/CaY zeolite catalyst (*1–7*). This material was considered to be the prototype bifunctional catalyst. Later it was shown that the composition of the products obtained from the same long-chain *n*-alkanes with a Pt-containing ultrastable zeolite Y (Pt/USY) was very similar to that obtained with Pt/CaY (*8, 9*) and representative of a conversion in the absence of molecular shape-selectivity (*10*).

These bifunctional conversions can be explained by the classical bifunctional reaction scheme (*9–12*), proposed by Weisz (*13*) and Coonradt and Garwood (*14*). According to this scheme, the noble metal function of the catalyst rapidly establishes an equilibrium between alkanes and alkenes through dehydrogenation–hydrogenation. The alkenes become alkylcarbenium ions after protonation at the Brønsted acid sites. The rearrangements of chemisorbed alkylcarbenium ions are the rate-limiting steps in such a reaction network.

Over Pt/CaY and Pt/USY catalysts, long-chain *n*-alkanes are isomerized with a selectivity of 100% up to moderate levels of conversion (*7, 9*). The product distributions are unique functions of the degree of conversion over a wide range of reaction conditions (*9*). Branching isomerization of long-chain *n*-alkanes over Pt/USY and Pt/CaY catalysts is a step-by-step process (*7, 9, 12*). Mono-, di-, and tri-branched isomers are obtained in consecutive reactions. The rate of formation of side chains decreases in the following order (*7*):

methyl > ethyl > propyl > butyl branching.

The isomer distributions found at low degrees of conversion are kinetically con-

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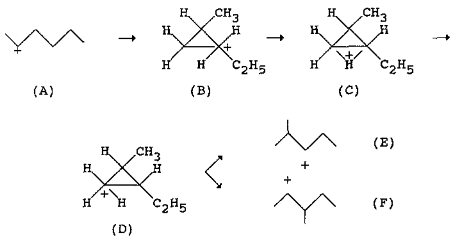


FIG. 1. CPCP methyl-branching mechanism of 2-hexyl cation.

trolled, thus revealing the selectivity of the branching mechanism (*7, 9, 12*).

In this paper a branching mechanism is proposed which rationalizes the initial product selectivities among the monobranched isomerization products from long-chain *n*-alkanes.

THEORY

Branching Mechanism of Short-Chain n-Alkylcarbenium Ions

The branching rearrangements of small alkylcarbenium ions ranging from $C_3H_7^+$ to $C_8H_{17}^+$ in superacid solutions are well known from ^{13}C and ^1H NMR studies (*15*). The branching mechanism of alkylcarbenium ions currently accepted involves the formation of cyclic alkylcarbonium ion intermediates. Figure 1 illustrates this mechanism for the branching of 2-hexyl cation (A) into 2-methyl-3-pentyl cation (E) and 3-methyl-2-pentyl cation (F). The first step is the cyclization of 2-hexyl cation (A) into a substituted corner-protonated cyclopropane (CPCP), viz., 1-protonated-1-ethyl-2-methylcyclopropane (B). Subsequently, a proton which is bound to the pentacoordinated ring carbon atom jumps toward the corner carbon atom of the cyclopropane ring free of alkyl substituents. The concomitant formation of 1-protonated-2-ethyl-3-methylcyclopropane (D) is likely to proceed over an edge-protonated methyl-ethyl-substituted cyclopropane (C) intermediate. Two alternative ring opening modes of 1-protonated-2-ethyl-3-methylcyclopropane (D) are available, resulting in the formation of 2-methyl-3-pentyl cation (E), and 3-methyl-2-pentyl cation (F). Finally, the more stable tertiary 2-methyl-2-pentyl cation and 3-methyl-3-pentyl cation can be obtained after a hydride shift. In the scheme of Fig. 1, the corner-to-corner proton jump (B to D) is slow (*16*). It has been shown that the branching of light alkanes over heterogeneous bifunctional catalysts can be explained perfectly by the occurrence of the CPCP mechanism (*17*).

Branching of Long-Chain n-Alkylcarbenium Ions via PCP

Mechanistic data on the branching of alkylcarbenium ions larger than $C_7H_{13}^+$ in superacid solutions are lacking in the literature. Weitkamp developed reaction schemes for methyl branching of long-chain *n*-alkylcarbenium ions, based on the chemistry of short-chain alkylcarbenium ions (*7, 18*). This methyl-branching scheme involves substituted protonated cyclopropane intermediates (PCP). It is illustrated in Fig. 2 for methyl branching of the secondary decyl cations. In this figure, the nature of the PCP intermediates G, H, and I is not specified and these letters stand for a whole set of substituted corner-, edge-, and face-protonated cyclopropanes (*18*). Two reaction steps are considered, viz., PCP ring closure and PCP ring opening (Fig. 2).

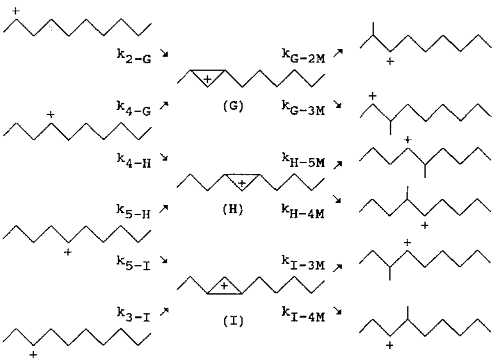


FIG. 2. Methyl branching of secondary decyl cations via PCP intermediates according to Refs. (*7*) and (*18*). G, H, and I stand for a set of edge-, corner-, and face-protonated cyclopropanes.

Prediction of the Initial Distribution of Methyl-branched Isomers from Long-Chain n-Alkanes via Weitkamp's PCP Branching Mechanism

In a kinetic treatment of the PCP methyl-branching schemes of *n*-alkanes, proposed by Weitkamp, the following assumptions were made (*7, 18*):

1. The surface coverages, θ, of all secondary *n*-alkylcarbenium ions derived from a *n*-alkane with an even carbon number are the same. For *n*-alkylcarbenium ions with odd carbon numbers, the θ value of the secondary ion with the positive charge on its central carbon atom is considered to be only half of that of its isomers. For the secondary nonyl cations, for example, the surface coverages are assumed to be

$$\theta_{2\text{-nonyl}} = \theta_{3\text{-nonyl}} = \theta_{4\text{-nonyl}} = 2\theta_{5\text{-nonyl}}. \quad (1)$$

The reason for introducing such a difference between even and odd carbon numbers is based on a statistical consideration (*18*). In a carbon chain with even carbon number, all potential positions for the positive charge occur twice. In carbon chains with odd carbon number the central position appears only once, while the other positions occur twice.

2. The rate constants for ring closure and ring opening are the same for all PCP intermediates. For the reaction scheme of Fig. 2, for example, this gives:

$$k_{2\text{-}G} = k_{3\text{-}I} = k_{4\text{-}G} = k_{4\text{-}H} = k_{5\text{-}I} = k_{5\text{-}H} \quad (2)$$

$$k_{G\text{-}2M} = k_{G\text{-}3M} = k_{I\text{-}3M} = k_{I\text{-}4M} = k_{H\text{-}4M} = k_{H\text{-}5M}. \quad (3)$$

Based on these assumptions, expressions for the steady-state catalyst surface coverages of the PCP intermediates can be derived. For the PCP intermediates G, H, and I of the methyl-branching scheme of the secondary decyl cations (Fig. 2), it can be verified that

$$\theta_G = \theta_H = \theta_I. \quad (4)$$

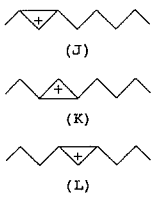


FIG. 3. PCP intermediates involved in the PCP methyl branching of secondary nonyl cations.

For the PCP branching of nonyl cations, the PCP intermediates J, K, and L, shown in Fig. 3, must be considered.

If the adequate rate equations are written, it can be verified that the surface coverage of the PCP intermediate with the centrally positioned cyclopropane ring, L, amounts only to half of that of the other intermediates J and K:

$$\theta_J = \theta_K = 2\theta_L. \quad (5)$$

Based on the reaction scheme of Fig. 2 and on Eq. (4), the relative rates of formation of the methylnonyl cations are

$$r_{2MC9} = 1; \quad r_{3MC9} = 2; \quad r_{4MC9} = 2; \quad r_{5MC9} = 1, \quad (6)$$

and the expected product distribution from decane is 16.7% for 2-methylnonane and 5-methylnonane and 33.3% for 3-methylnonane and 4-methylnonane.

For the PCP branching of nonyl cations it follows that

$$r_{2MC8} = 1; \quad r_{3MC8} = 2; \quad r_{4MC8} = 2. \quad (7)$$

The expected reaction product mixture from nonane contains 20% of 2-methyloctane and 40% of 3-methyloctane and 4-methyloctane.

Systematic application of the PCP methyl-branching model was made to the branching of *n*-alkanes with carbon numbers from 6 to 15. Calculated and experimentally obtained initial distributions of the methyl-branched isomers from *n*-alkanes are compared in Fig. 4. For nonane, decane, undecane, and dodecane, a satisfactory agreement between the predicted and experimental data, obtained with Pt/CaY and Pt/USY catalysts, is found. This was considered by

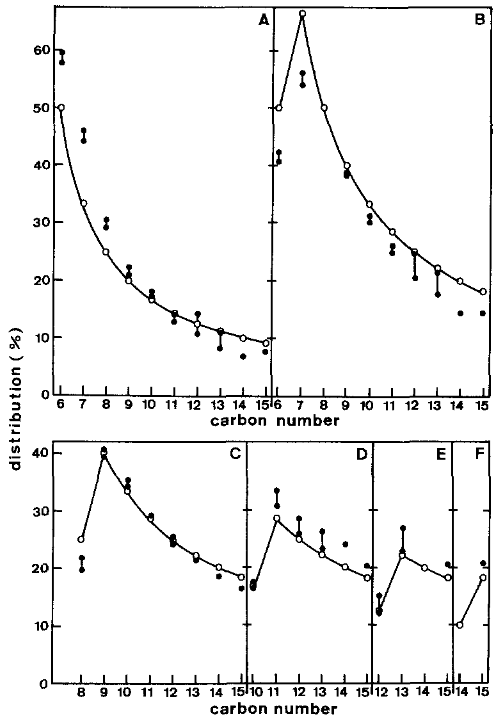


FIG. 4. Predicted and experimental distributions of monomethyl-branched isomers from *n*-alkanes. The open symbols represent the values, predicted by Weitkamp's PCP branching model. The full symbols are experimental points, obtained with Pt/CaY (after Ref. (*7*)) and Pt/USY catalysts. (A) 2-methyl-branched, (B) 3-methyl-branched, (C) 4-methyl-branched, (D) 5-methyl-branched, (E) 6-methyl-branched, and (F) 7-methyl-branched isomer.

Weitkamp as a strong argument in favor of the occurrence of a branching mechanism via PCP intermediates (*7*, *18*). Nevertheless, systematic deviations between the two sets of data were encountered with the other feed molecules.

Figure 4 shows that when hexane and heptane are converted over Pt/USY and Pt/CaY, the amount of the 2-methyl-branched isomer is always in excess of that predicted by the PCP mechanism. With octane as feedstock, an excess of 2-methylheptane is formed at the expense of the 3-methyl- and 4-methyl-branched isomers (Fig. 4).

For *n*-alkanes with carbon numbers higher than 12, an opposite effect is encountered. The formation of 2-methyl-branched isomers is now lower than predicted. Whereas equal amounts of the other methyl-branched isomers are expected, it is experimentally found that branching at centrally located carbon atoms is favored.

Branching Mechanism Involving CPCP Intermediates

In the kinetic treatment of the methyl-branching mechanism proposed in the previous section, it was assumed that the surface coverage of all secondary *n*-alkylcarbenium ions with the same carbon number is the same, except for the centrally charged ion in the case of an odd carbon number. However, it is known from the behavior of alkylcarbenium ions in superacids that hydride shifts are very fast when they transform a secondary into another secondary ion (*19*). The secondary *n*-alkylcarbenium ions should, therefore, be equilibrated rapidly and the values of their surface coverages should reflect their relative stabilities. There is no evidence from the literature that the centrally charged cation is less stable. In the case of secondary heptyl cations, for example, the 4-heptyl cation, which is the centrally charged cation, is even the most stable. The standard enthalpy of formation of 4-heptyl cation is 2.5 and 6.3 kJ mol^{-1} lower than those for 3-heptyl and 2-heptyl cation, respectively (*20*). Generally, the secondary *n*-alkyl cations are very close in energy, except for the 2-alkyl cation, which is slightly less stable (*21*).

A more detailed reaction scheme for methyl-branching of the secondary nonyl cations via CPCP intermediates is shown in Fig. 5. A simplified representation of the CPCP structures, in which the formal representation of the C-H bonds is omitted, has been used. The CPCP intermediates obtained after ring closure are denoted with asterisks. Corner-to-corner proton jumps rearrange the primarily obtained $CPCP_i^*$ ions into $CPCP_i$ ions in which the positive charge is now located on a ring carbon atom, free of alkyl side chains. $CPCP_2$ can thus be

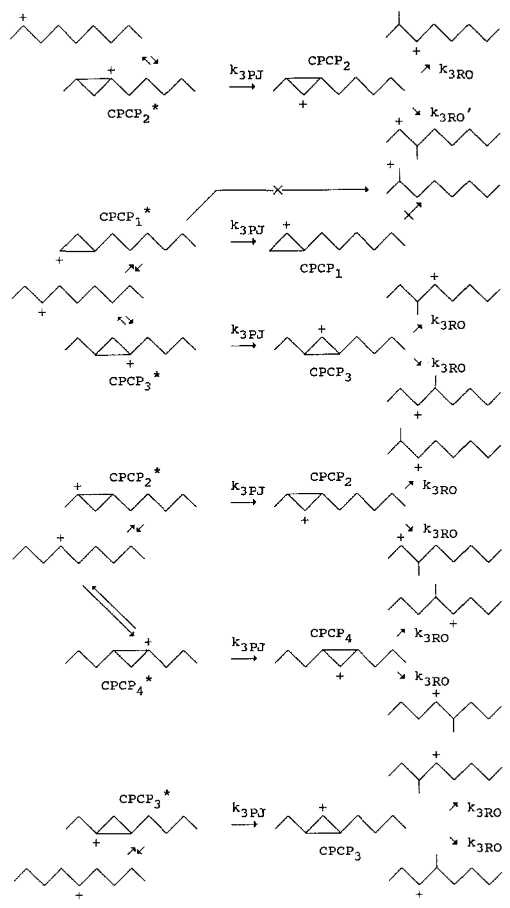


FIG. 5. CPCP branching scheme of secondary nonyl cations.

obtained from 2-nonyl cation, CPCP$_1$ and CPCP$_3$ from 3-nonyl cation, CPCP$_2$ and CPCP$_4$ from 4-nonyl cation, and CPCP$_3$ from 5-nonyl cation. The formation of CPCP$_1$ does not lead to the formation of a methyl branching upon opening of the cyclopropane ring unless a primary cation is formed. Therefore, this reaction path is considered to be very unlikely. Upon ring opening of CPCP$_2$, CPCP$_3$, or CPCP$_4$ a secondary methyloctyl cation is obtained. In each case one supplementary hydride shift is sufficient to obtain a tertiary methyloctyl cation. Figure 5 shows that upon ring opening of CPCP$_2$ and CPCP$_3$ two different positions for the methyl branching can be obtained.

As CPCP formation can be assumed to be fast with respect to the corner-to-corner proton jumps, the CPCP$_i^*$ structures should be equilibrated through ring opening and closure reactions and hydride shifts on the secondary alkylcarbenium ions. The distribution of the CPCP$_i^*$ ions obtained after cyclization should, therefore, reflect their relative stabilities. As the stabilities of cyclic alkylcarbonium ions with the same carbon number are very close (*22*), it is reasonable to assume that the surface coverages of the CPCP$_i^*$ intermediates are identical.

Therefore, in CPCP branching schemes it is sufficient to consider all the different CPCP$_i^*$ ions which can be formed by ring closure and to assume that their surface coverages are the same. If, subsequently, one corner-to-corner proton jump is allowed, CPCP$_i$ intermediates are obtained which upon ring opening result in a branched cation. The relative surface coverages of the CPCP$_i$ intermediates can be retrieved from the numbers of adequate corner-to-corner proton jumps. The final step to be considered is ring opening. This simplified scheme is shown in Fig. 6 for CPCP isomerization of nonyl cations. From the scheme of Fig. 6 it appears that

$$\theta_{\mathrm{CPCP}_2} = \theta_{\mathrm{CPCP}_3} = 2\theta_{\mathrm{CPCP}_4}. \qquad (8)$$

This is the same relation as that found for the surface coverages of the PCP intermediates J, K, and L in Weitkamp's model (see Eq. (5)). The present deduction avoids making the assumption that the surface coverage

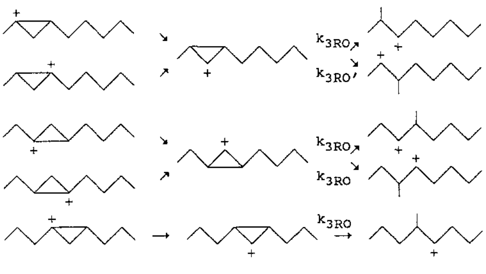


FIG. 6. Simplified CPCP branching scheme of nonyl cations.

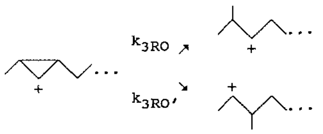


FIG. 7. Rival ring opening modes of $CPCP_2$ intermediates.

of 5-nonyl cation is only half that of 2-, 3-, and 4-nonyl cation, which is questionable.

In one of the ring-opening modes of $CPCP_2$ intermediates, a 3-methyl-2-*n*-alkylcarbenium ion is formed. This is illustrated in Fig. 7. The opening of the $CPCP_2$ ring gives either a 3-methyl-2-*n*-alkyl cation, leading to a methyl branching at position 3, or a 2-methyl-3-*n*-alkyl cation, resulting in a methyl branching at position 2. As explained above, the stability of a cation charged at carbon atom 2 is lower than that charged at carbon atom 3. Therefore, the formation of the 3-methyl-branched isomer could proceed at a lower rate. Its rate constant is denoted with a "prime." This difference in rate between the two ring opening modes of $CPCP_2$ can account for the discrepancy between the experimental methyl-branching selectivity of hexane and heptane and the one predicted according to the PCP mechanism (Fig. 4).

Branching Mechanism Involving Substituted Protonated Cycloalkanes with Larger Rings

For the branching rearrangements of short-chain alkylcarbenium ions in superacids at low temperatures, there is no need to invoke mechanisms via cyclic alkylcarbonium ions with larger rings. Protonated cyclobutane (PCB) is 130 kJ mol^{-1} less stable than protonated methylcyclopropane (*23*). However, this does not preclude that at elevated temperatures on heterogeneous catalysts, CPCB and cyclic alkylcarbonium ions with other ring sizes can play an important role.

A branching mechanism via cyclic alkylcarbonium ions with larger rings, CPC*X*, can be conceived analogous to the CPCP mechanism. Branching via substituted corner-protonated cyclopentane (CPCPe) intermediates, for instance, is illustrated in Fig. 8 with a 3-decyl cation. The reaction steps are ring closure, resulting in the formation of a $CPCX_i^*$ intermediate, corner-to-corner proton jump, giving a $CPCX_i$ intermediate, and ring opening of the latter. In principle, the largest substituted protonated ring that can be formed for an *n*-alkane with carbon number *n*, and which gives rise to the formation of a side chain upon ring opening is an (*n*-2)-membered ring. The rate-determining step in branching isomerization via CPC*X* is assumed to be the corner-to-corner proton jump. In the model it is assumed that the rate constant for corner-to-corner proton jump is the same for all $CPCX_i^*$ intermediates with the same ring size. The catalyst surface coverages of all $CPCX_i^*$ intermediates are assumed to be the same. Unlike the case of the surface coverage of $CPCP_i$ intermediates, where differences can occur depending on the position of the cyclopropane ring in the chain, it can be easily verified that the surface coverage of all $CPCX_i$ intermediates with the same ring size is always the same. Furthermore, in contrast to the CPCP intermediates, for which often two rival ring opening modes are available, the ring in $CPCX_i$ isomers can be opened only according to one single mode.

The reaction schemes for branching via CPC*X* intermediates are very simple as it is sufficient to consider the ring opening reactions of all possible $CPCX_i$ intermediates. The ring opening modes of the different

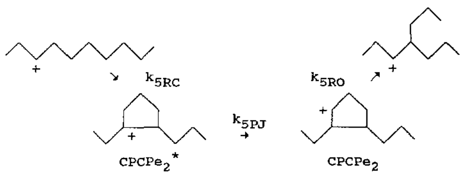
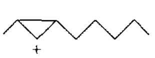
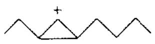
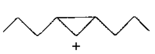
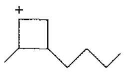
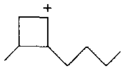
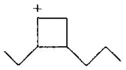
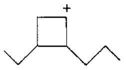
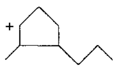
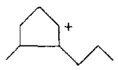
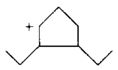
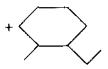
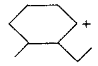
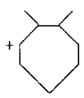


FIG. 8. Branching of 3-decyl cation via CPCPe.

TABLE 1

Simplified Scheme for Branching of Nonane via CPC*X* Intermediates

CPCX_i Intermediate	f_i^a	Ring opening reaction
	0.40	$\overset{k_{3RO}}{\nearrow}$ 2-methyl-3-octyl cation $\underset{k_{3RO'}}{\searrow}$ 3-methyl-2-octyl cation
	0.40	$\overset{k_{3RO}}{\nearrow}$ 3-methyl-4-octyl cation $\underset{k_{3RO}}{\searrow}$ 4-methyl-3-octyl cation
	0.20	$\overset{k_{3RO}}{\nearrow}$ 4-methyl-5-octyl cation $\underset{k_{3RO}}{\searrow}$ 4-methyl-5-octyl cation
	0.25	$\xrightarrow{k_{4RO'}}$ 3-ethyl-2-heptyl cation
	0.25	$\xrightarrow{k_{4RO}}$ 3-methyl-4-octyl cation
	0.25	$\xrightarrow{k_{4RO}}$ 4-ethyl-3-heptyl cation
	0.25	$\xrightarrow{k_{4RO}}$ 3-ethyl-4-heptyl cation
	0.33	$\xrightarrow{k_{5RO'}}$ 3-propyl-2-hexyl cation
	0.33	$\xrightarrow{k_{5RO}}$ 4-methyl-5-octyl cation
	0.33	$\xrightarrow{k_{5RO}}$ 4-ethyl-3-heptyl cation
	0.50	$\xrightarrow{k_{6RO'}}$ 3-ethyl-2-heptyl cation
	0.50	$\xrightarrow{k_{6RO}}$ 4-methyl-3-octyl cation
	1.00	$\xrightarrow{k_{7RO'}}$ 3-methyl-2-octyl cation

[a] Fraction of total coverage of CPC*X*.

CPC*X* intermediates are assumed to occur at the same rate, except for the opening of CPCX_2 when it results in the formation of a secondary alkylcarbenium ion, charged at carbon atom 2.

The branching scheme of nonane via CPCP and CPC*X* intermediates is outlined in Table 1. The surface coverages of the CPCX_i intermediates can be considered fractions, f_i, of the total coverage of CPC*X*:

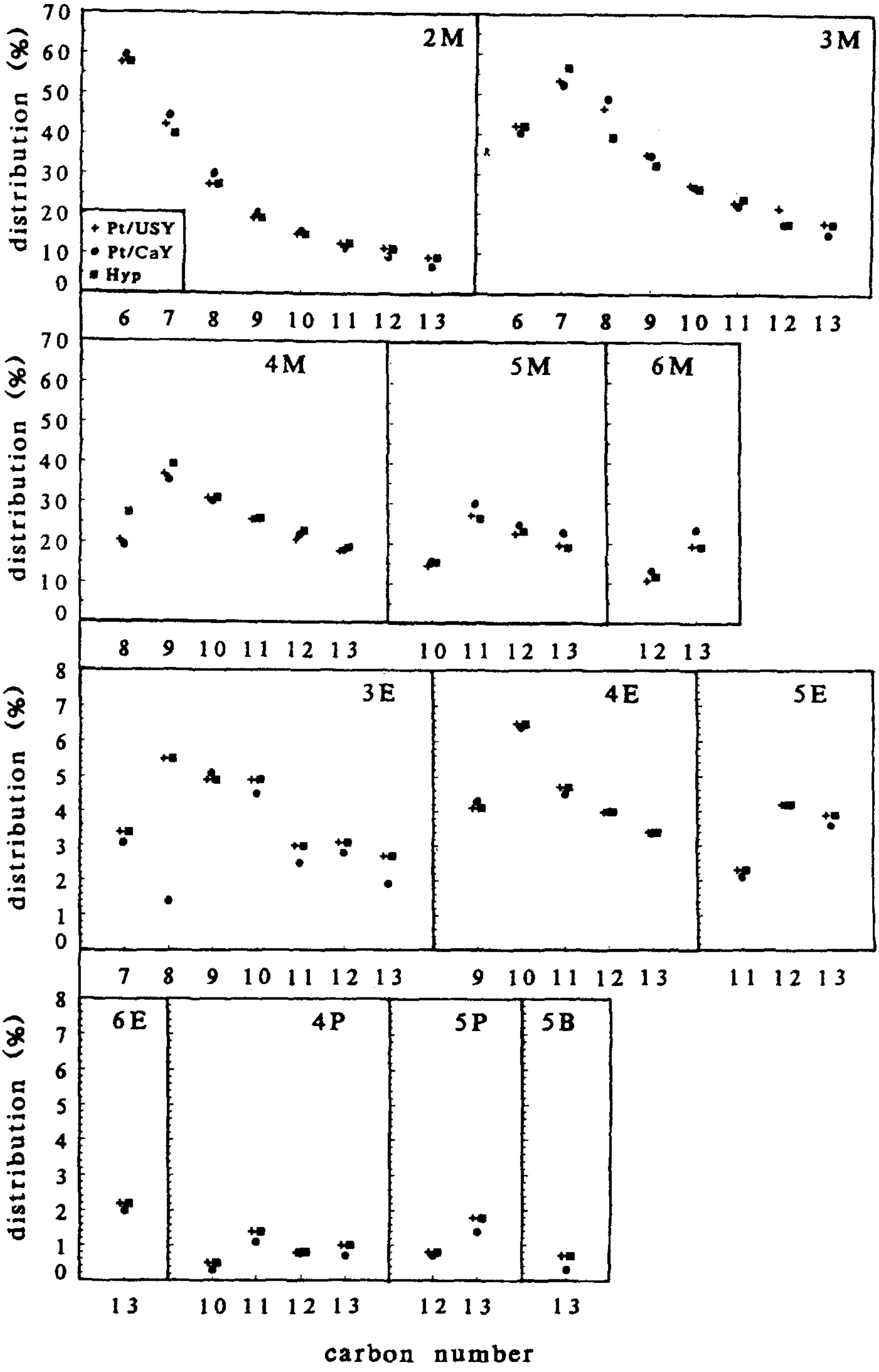


FIG. 9. Initial distribution of the monobranched isomers from *n*-alkanes with carbon numbers from 6 to 13. Hyp represents the hypothetical values used in the CPCX branching model (see text). The data obtained with Pt/CaY are from Ref. (7).

$$\theta_{\mathrm{CPC}X} = \sum_i \theta_{\mathrm{CPC}X_i}$$

$$\text{and } \theta_{\mathrm{CPC}X_i} = f_i\, \theta_{\mathrm{CPC}X}. \quad (9)$$

Relative rates, $R_{\mathrm{CPC}X}$, of the branching modes via the different CPCX intermediates are defined in the following way:

$$R_{\mathrm{CPC}X} = k_{XR\mathrm{O}}\, \theta_{\mathrm{CPC}X} \quad (10)$$

$$R_{\mathrm{CPC}X}{}' = k_{XR\mathrm{O}}{}' \theta_{\mathrm{CPC}X}. \quad (11)$$

For the branching scheme of the nonyl cations (Table 1), for example, it follows that

$$r_{2\text{-}MC8} = 0.40\, R_{\mathrm{CPCP}} \quad (12)$$

$$r_{3\text{-}MC8} = 0.40\, R_{\mathrm{CPCP}} + 0.40\, R_{\mathrm{CPCP'}} + 0.25\, R_{\mathrm{CPCB}} + 1.0\, R_{\mathrm{CPCHe'}} \quad (13)$$

$$r_{4\text{-}MC8} = 0.80\, R_{\mathrm{CPCP}} + 0.33\, R_{\mathrm{CPCPe}} + 0.50\, R_{\mathrm{CPCH}} \quad (14)$$

$$r_{3\text{-}EC7} = 0.25\, R_{\mathrm{CPCB}} + 0.25\, R_{\mathrm{CPCB'}} + 0.50\, R_{\mathrm{CPCH'}} \quad (15)$$

$$r_{4\text{-}EC7} = 0.25\, R_{\mathrm{CPCB}} + 0.33\, \mathrm{R}_{\mathrm{CPCPe'}} + 0.33\, R_{\mathrm{CPCPe}}. \quad (16)$$

In the same way, sets of rate equations were derived for the branching of n-alkanes with carbon numbers from 6 to 13. Generally, the number of $R_{\mathrm{CPC}X}$ parameters is larger than the number of equations. As the number of $R_{\mathrm{CPC}X}$ values which could be determined directly using the experimental data was always restricted, those with smallest ring sizes were preferentially retained in the equations. For those with largest ring sizes, it was assumed that $R_{\mathrm{CPC}X}$ equals zero. It will later become clear why this is a reasonable assumption.

The use of the experimental initial distributions of the monobranched isomers led to negative values for some of the R values. A hypothetical initial composition of the isomerization products was therefore derived as follows. The concentration of the isomers with ethyl or bulkier side chain, the ratio of the isomers with bulky side chains to those with methyl branching, as well as the ratio of the 2-methyl-branched isomers to those with side chains bulkier than methyl, were taken from experiments over the Pt/USY catalyst. The composition of the other methyl-branched isomers was then derived from a best fit with the kinetic equations. The hypothetical compositions of the monobranched isomerization products are compared with the experimental data in Fig. 9. The two sets of data are in fair agreement.

The $R_{\mathrm{CPC}X}$ values obtained for the n-alkanes in the range from hexane to tridecane are shown in Fig. 10. The following relations between the rates of the different type B isomerization pathways were found for n-alkanes ranging from hexane through tridecane. Most probably they are also valid for larger n-alkanes.

$$R_{\mathrm{CPCP}} > R_{\mathrm{CPCP'}};\quad R_{\mathrm{CPCB}} > R_{\mathrm{CPCB'}};\quad R_{\mathrm{CPCPe}} > R_{\mathrm{CPCPe'}} \quad (17)$$

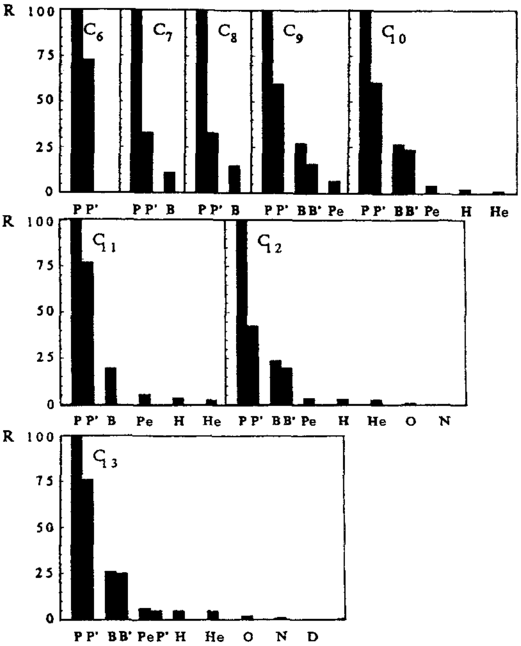


FIG. 10. Relative rates (R) of branching pathways of n-alkanes with carbon number from 6 to 13 via CPCX intermediates. The ring size, X, is denoted with P (cyclopropane), B (cyclobutane), Pe (cyclopentane), H (cyclohexane), He (cycloheptane), O (cyclooctane), N (cyclononane), and D (cyclodecane).

$$R_{\mathrm{CPCP}} > R_{\mathrm{CPCB}} > R_{\mathrm{CPCPe}} > R_{\mathrm{CPCH}} > \dots \quad (18)$$

The relative rates of the different reactions seem to be independent of carbon number (Fig. 10). As the number of rings that can be formed increases with increasing carbon number, the contribution of larger than cyclopropane rings in the branching event increases.

The agreement between the calculated and experimental monobranched isomer distributions (Fig. 9) and the systematics in the rate data (Fig. 10) indicate that the proposed mechanism is essentially correct and that next to substituted protonated cyclopropanes, to a lower extent substituted protonated cyclobutanes, cyclopentanes, etc., contribute to the formation of the first branching in a linear hydrocarbon skeleton.

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