Mechanism of the paring reaction of naphtenes

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1-cyclohexyloctane is isomerized on the large pore, bifunctional zeolite catalyst Pt/H-Y. The detailed isomerization mechanism of this naphtene molecule is revealed through a thorough analysis of the numerous isomerization products. It is found that methyl side-chains are generated on the ring of the molecule via a ring contraction–expansion mechanism, which are subsequently transferred to the *n*-alkyl substituent via methyl shifts. Direct branching of the *n*-alkyl chain is a much slower process compared to the generation of methyl substituents on the ring.

Keywords: bifunctional catalysis; paring reaction; 1-cyclohexyloctane; naphtenes

1. Introduction

Hydrocracking is one of the large petrochemical processes [1,2]. To unravel and study reaction mechanisms involved in the conversions of such complex hydrocarbon mixtures usually the fate of pure compounds is followed on a typical catalyst, such as a bifunctional faujasite-type zeolite. With alkanes the reaction mechanism is rather well understood irrespective of their chain length [3,4], while with naphtenes studies have been restricted to the use of model molecules with 12 or less carbon atoms [5–9]. The conversion paths of heavier naphtenes in isomerization and hydrocracking processes remain unknown, although it is particularly relevant knowledge for understanding diesel and lube oil isodewaxing technologies [10].

A salient mechanistic feature of the hydrocracking of C_{10}–C_{12} naphtenes is the so-called "paring reaction" [5,6]. The name is derived from the apparent "paring" of alkyl groups in poly-alkyl substituted rings prior to their elimination from the ring as an isoalkane. For instance, hydrocracking of all C_{10} naphtenes selectively yields isobutane and methylcyclopentane, irrespective of the isomer that is converted, viz. butylcyclohexane, pentylcyclopentane, diethylcyclohexanes or tetramethylcyclohexanes [6]. The paring reaction, like any isomerization or hydrocracking reaction on a bifunctional catalyst, is rationalized using an ionic reaction mechanism, involving carbocation intermediates that are generated by dehydrogenation and protonation of the parent molecule [6,11]. The detailed mechanism of the paring reaction of tetramethylcyclohexane, proposed in the original paper, proceeds via a series of exocyclic and endocyclic alkyl shifts until a branched C_4 substituent is generated on the ring that can be eliminated through a fast type A β-scission reaction (scheme 1) [6]. Type A β-scission requires the presence of three branchings in the carbon skeleton, positioned in α, γ, γ with respect to the positively charged carbon. This configuration allows a tertiary alkylcarbenium ion to be cracked into a smaller tertiary carbenium ion and an olefin. Type A β-scission is much faster than other types of β-scission, in which

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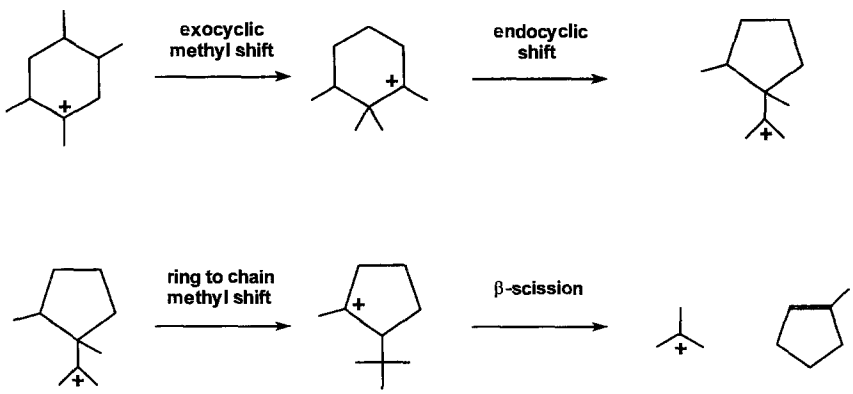


Scheme 1.

secondary alkylcarbenium ions are involved as parent or product ion [12].

An important feature of the paring rearrangement, illustrated in scheme 1, is that the degree of branching of the molecule remains unaltered. To calculate the branching degree, the occurrence of a quaternary and tertiary carbon is considered to introduce two and one branching, respectively. Isomerizations not involving a change in the degree of branching (type A) are orders of magnitude faster than isomerizations involving a change in branching (type B) [13]. Mechanistically, both transformations proceed over corner protonated cyclopropane intermediates (CPCP) [14]. In type B isomerizations, a corner to corner proton jump has to occur before ring reopening, a slow step not involved in type A isomerizations (scheme 2) [3]. Similar alkylcarbenium ion chemistry is involved in the isomerization of *n*-alkanes [3,4]. Monobranched, dibranched and tribranched isomers are obtained in consecutive reactions [15]. The distribution of isomers with the same branching degree is close to thermodynamic equilibrium. This should be the result of fast consecutive type A isomerizations. Equilibrium, however, is not attained among isomers of different degree of branching. The concentration of tribranched isomers in the reaction products is always low, since specific isomers from this group crack very rapidly through type A β-scission.

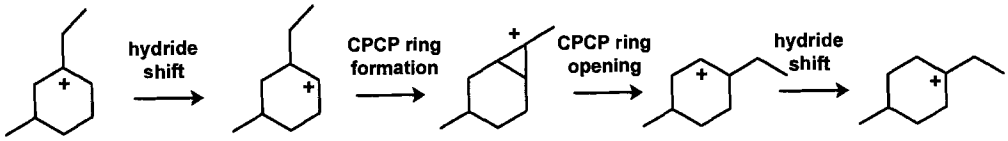
Naphtene molecules with less than three branchings must necessarily undergo further branching steps in order to reach a structure that is susceptible to type A β-scission. An intriguing feature of this catalytic chemistry, yet not addressed in literature, is whether these branchings are generated in the *n*-alkyl substituent, or in the ring.

In the present work, we reacted 1-cyclohexyloctane on a large pore bifunctional zeolite catalyst, Pt/H-Y, and analyzed the isomerization products in detail. Based on isomer product distributions obtained at increasing feed conversion degrees a more detailed mechanism for the paring reaction could be advanced.

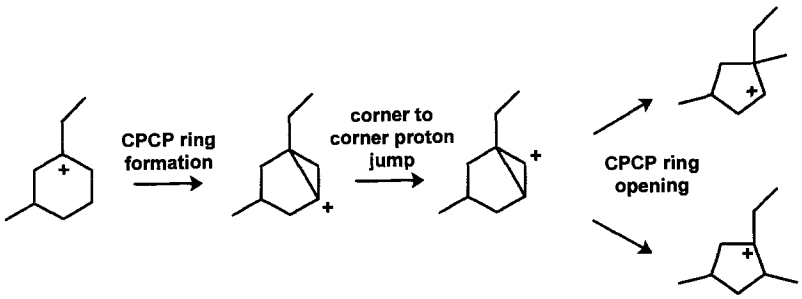
2. Experimental

Na-Y zeolite from Ventron was cation exchanged with ammonium for 30% of the exchange capacity, saturated with water and heated in a covered crucible in a muffle furnace, preheated at 973 K. After this self-steaming treatment, the framework Si/Al ratio was increased from 2.5 to 2.8. The steamed zeolite was exchanged with excess NH_4Cl under reflux conditions and subsequently with $Pt(NH_3)_4^{2+}$ complex in order to obtain a loading of 0.5% by weight of Pt metal. Thereupon, the zeolite powder was compressed, crushed and sieved. A 0.2 g sample of the 0.25–0.50 mm pellets was charged into a stainless steel microreactor with internal diameter of 1 cm. Catalyst activation consisted in heating from 300 to 673 K under a stream of oxygen keeping it at 673 K for 1 h. The catalyst bed was purged with nitrogen and contacted with hydrogen for another hour.

1-cyclohexyloctane obtained by batch hydrogenation of 1-phenyloctane (Janssen, 99%) on a Pd/carbon black catalyst, was used as feed in the catalytic experiments. The catalytic experiments were performed in a fixed-bed, continuous flow microreactor with on-line high-resolution GC and GC/MS analysis. The H_2 to 1-cyclohexyloctane molar ratio in the feed was 450 at a constant



type A isomerization



type B isomerization

Scheme 2.

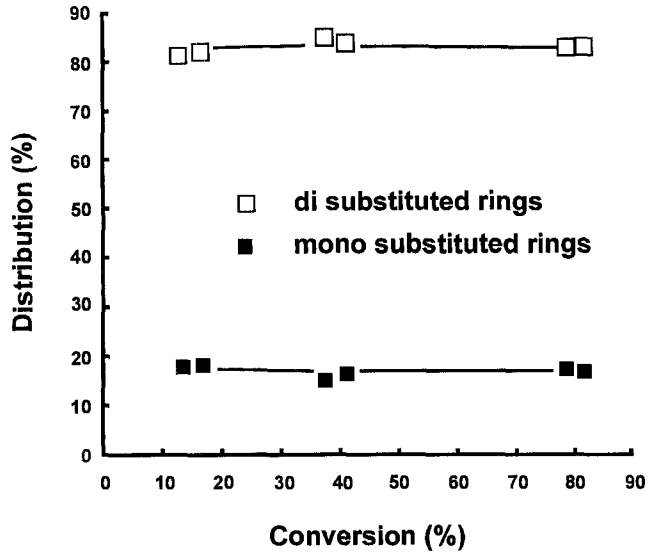


Fig. 1. Distribution of the isomers of the feed according to the number of ring substituents against 1-cyclohexyloctane conversion.

pressure of 0.45 MPa and a reactor temperature of 460 K. The space time at the entrance of the reactor on hydrocarbon basis, W/F_0, was varied from 0.06 to 4.0 kg h mol^{-1} in order to vary the reaction severity. The GC-FID (HP5880A) and GC-MS (HP5998A) instruments were equipped with capillary columns (Chrompack) with CP-Sil-5CB stationary phase (film thickness of 1.31 μm), an internal diameter of 0.32 mm, a length of 120 m and containing 300 000 theoretical plates. C_{14} naphtene isomers with different ring sizes and/or nature and number of alkyl substituents were determined by MS. *Positional* and *cis–trans* isomers of methyl,heptyl substituted cyclohexanes could be identified by analogy to the elution of smaller methyl,alkyl substituted cycloalkanes. The fraction of unidentified products is relatively small (typically 20%) and represents compounds with strongly overlapping or small chromatographic signals.

3. Results and discussion

Below 50% conversion of 1-cyclohexyloctane, isomerization was the only reaction observed. Alkanes with 14 carbons were not observed since ring opening is a very difficult reaction [13]. 1-cyclohexyloctane has only one isomer with the same branching degree, viz. 1-cyclopentylnonane. Its formation proceeds via an endocyclic alkyl shift and is expected to be fast. In the chromatograms, there was no peak that could be assigned to this compound. It cannot be ruled out that it elutes together with 1-cyclohexyloctane. All identified reaction products in the C_{14} fraction are dibranched alkylcycloalkanes, containing 5-rings or 6-rings. The selective formation of dibranched structures from a monobranched molecule is in agreement with branching being a stepwise mechanism, as previously observed with paraffins [15]. Introducing a third branching in the molecule results in tribranched structures that are susceptible to

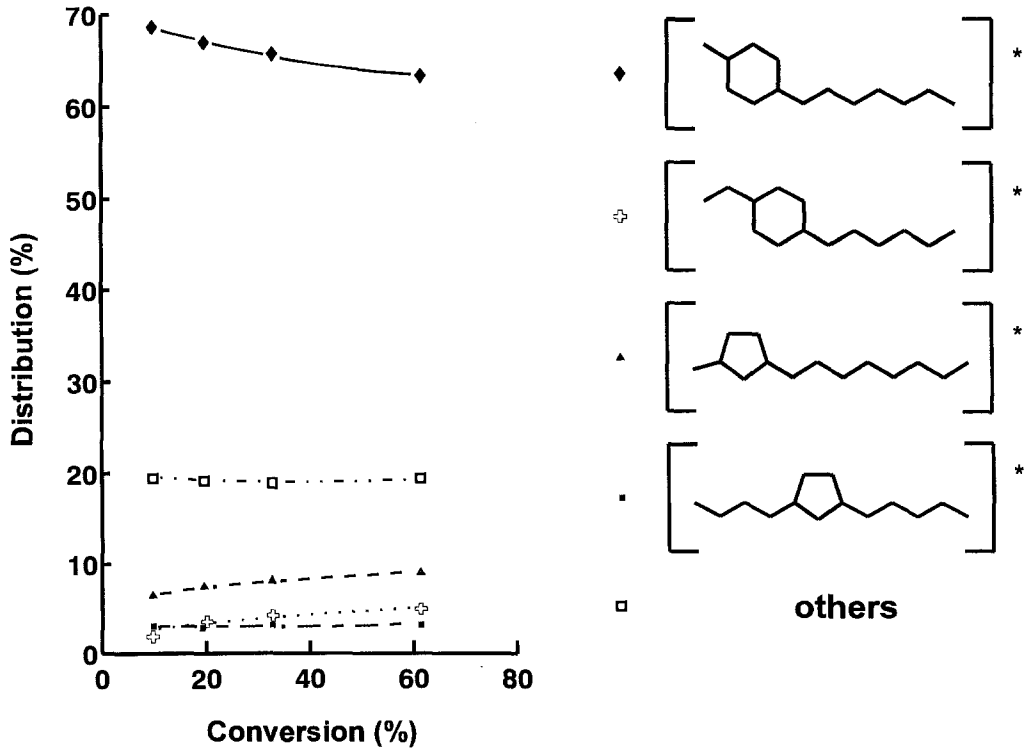


Fig. 2. Distribution of identified di-*n*-alkyl substituted cycloalkane feed isomers against conversion (* several *positional* and *cis–trans* isomers).

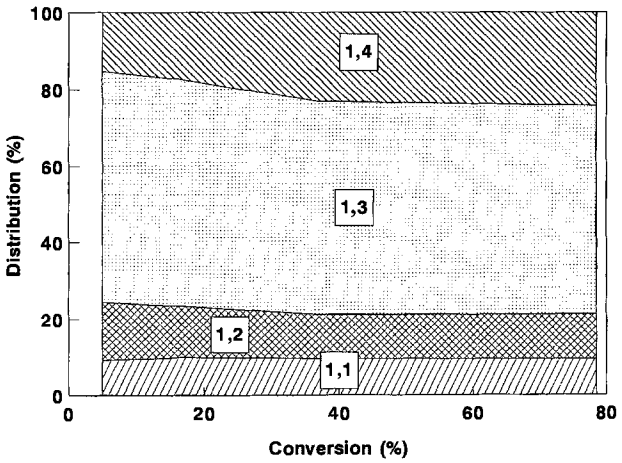


Fig. 3. Distribution of *positional* methyl,heptyl substituted cyclohexane feed isomers against conversion.

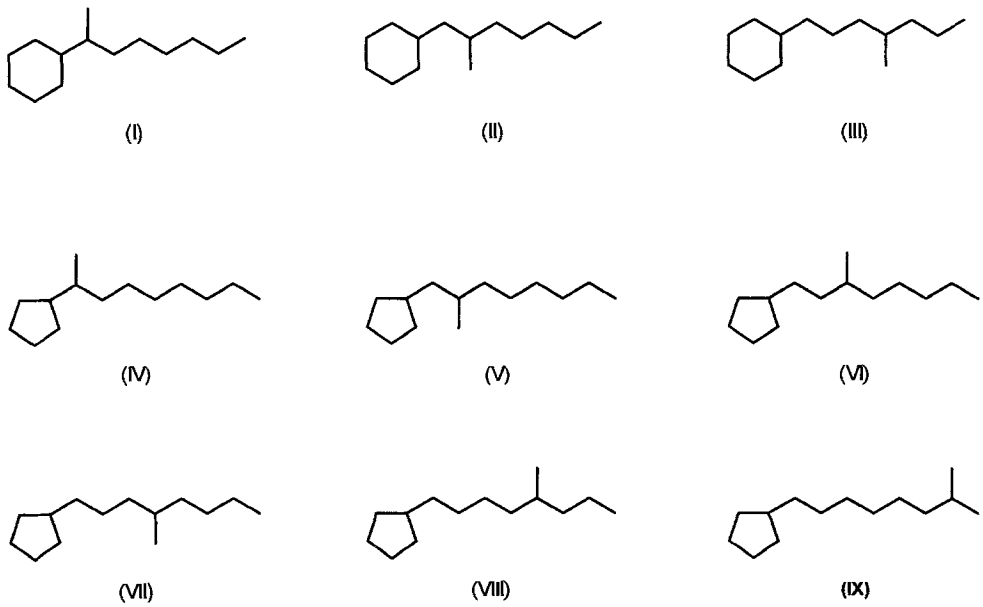
fast type A β-scissions, explaining the low concentration of such compounds in the reaction products at any level of conversion. When feed conversion is in the range from 10 to 60%, the di-alkyl substitued isomers represent 80 to 70% of the products. 20 to 30% of remaining identified products are compounds with one alkyl substituent on the ring (fig. 1).

The distribution of isomers with di-substituted rings is shown in fig. 2. Methyl,heptyl substituted cyclohexanes are most abundantly formed in this fraction, followed by methyl,octyl substituted cyclopentanes. For some isomers representing together some 20 wt% of this fraction, it has not been possible to determine unambiguously the exact nature of the two *n*-alkyl substituents. Elongation of one *n*-alkyl substituent at the expense of the other one occurs through endocyclic type A isomerizations that are expected to be fast rearrangements. The composition of this product fraction does not change significantly in the range from 10 to 60% conversion. Presumably, it reaches its equilibrium distribution.

The *positional* and *cis–trans* isomers of methyl,heptyl substituted cyclohexanes have been analyzed individually (fig. 3). All possible isomers are formed and their distribution hardly changes with conversion. The distribution of this fraction most probably reflects the thermodynamic equilibrium distribution, which is typically rich in 1,3-disubstituted rings as observed with smaller naphtenes [16,17].

Several dibranched isomers with a single alkyl substituent were present such as 2-cyclohexyloctane (I), 1-cyclohexyl-2-methylheptane (II) and 1-cyclohexyl-4-methylheptane (III) (scheme 3). Other positional isomers of the family of 1-cyclohexylmethylheptanes, if formed, could not be resolved. Among the isomers containing the cyclopentyl moiety, such as 2-cyclopentylnonane (IV), 1-cyclopentyl-2-methyloctane (V), 1-cyclopentyl-3-methyloctane (VI), 1-cyclopentyl-4-methyloctane (VII), 1-cyclopentyl-5-methyloctane (VIII) and 1-cyclopentyl-7-methyloctane (IX) (scheme 3), 1-cyclopentyl-6-methylnonane could not be separated.

The distributions of identified isomers with one alkyl substituent on the cyclohexyl or cyclopentyl moiety are given in figs. 4 and 5, respectively. The distribution of 6-ring containing isomers changes substantially with conversion indicating that the equilibration of the composition of this fraction proceeds slower than for the methyl,heptyl substituted cyclohexanes (fig. 3). The distribution in fig. 4 suggests that the equilibration of the dibranched mono alkyl substituted cyclohexanes occurs



Scheme 3.

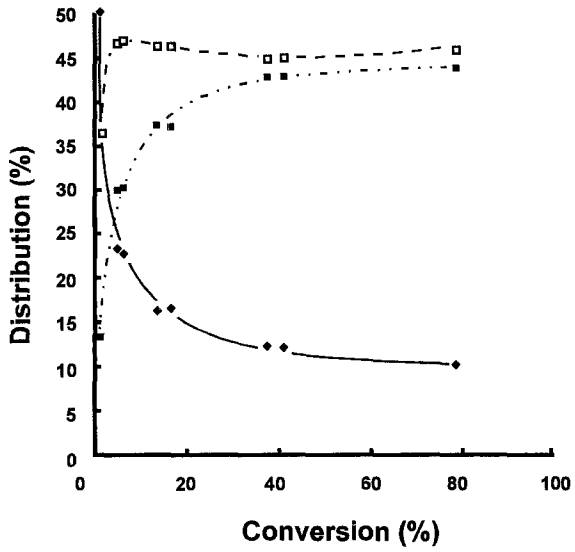


Fig. 4. Distribution of identified dibranched mono alkyl substituted cyclohexanes against conversion. (◆) 2- cyclohexyloctane (I), (□) 1-cyclohexyl-2-methylheptane (II), (■) 1-cyclohexyl-4-methylheptane (III).

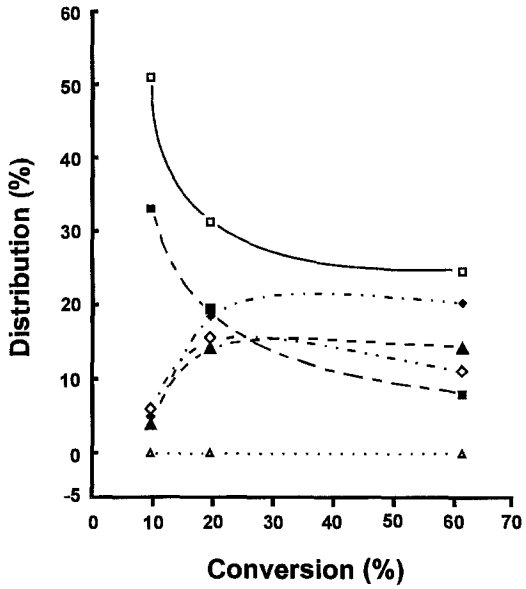
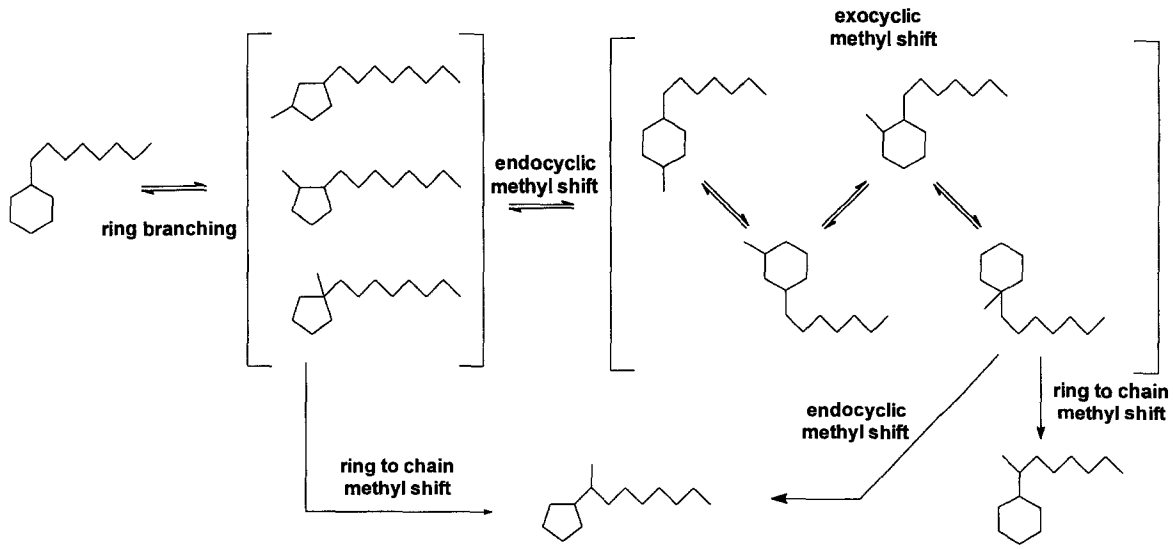


Fig. 5. Distribution of identified dibranched mono alkyl substituted cyclopentanes against conversion. (■) 2- cyclopentylnonane (IV), (□) 1-cyclopentyl-2-methyloctane (V), (◆) 1-cyclopentyl-3-methyloctane (VI), (◇) 1-cyclopentyl-4-methyloctane (VII), (▲) 1-cyclopentyl-5-methyloctane (VIII), (△) 1-cyclopentyl-7-methyloctane (IX).

through consecutive reactions, forming subsequently compound (I), (II), and (III). A similar pattern is observed for the 5-ring containing isomers: the formation of isomers with the methylbranching at chain positions close to the ring (IV and V) is kinetically favoured, and that of isomers with methylbranchings at remote positions from the ring (IV–IX) kinetically suppressed.

There exist two potential pathways rationalizing the formation of dibranched isomers with a 6-ring moiety and a single alkyl substituent from octylcyclohexane. A first possible mechanism could result in branching of the alkyl chain via formation of CPCP structures. Since the relative stability of the different CPCP structures is expected to be only slightly different [14], and the CPCP intermediates can give rise to the formation of all possible positional isomers, it is unlikely that chain branching is the dominating mechanism. The product distributions of figs. 4 and 5 suggest that branching occurs selectively in the ring, followed by a sequence of exo- and endocyclic type A isomerizations (scheme 4). Via the 1-methyl-1′-heptylcyclohexane and 1-methyl-1′-octylcyclopentane isomers the methylbranching is transferred from the ring to the chain. Since *positional*



Scheme 4.

methyl,heptyl substituted cyclohexane isomers are equilibrated at every level of conversion through exocyclic alkyl shifts (fig. 3), while the equilibration of the methyl-branching positions in the alkyl chain is much slower (figs. 4 and 5), it seems that type A isomerizations over the naphtenic ring are faster than in the alkyl chain.

4. Conclusions

The observed product distribution from 1-cyclohexyloctane on a Pt/H-Y bifunctional catalyst allowed to formulate more general conclusions concerning the reaction mechanisms at stake in the bifunctional catalytic conversion of naphtenes. Type A and B rearrangements involving carbon–carbon bonds in rings are shown to be much faster than those in the alkyl substituents of the rings. Consequently, methylbranching of alkyl substituents on naphtenic rings occurs via a fast transfer of methyl groups from the ring to the alkyl substituent. Mechanistically, methyl substituents are generated on the naphtenic ring via type B isomerizations. Fast exocyclic alkyl shifts form 1,1′-methylalkylcyclohexane (cyclopentane) key intermediates. Subsequently, methyl shifts transfer the methyl side-chain from the ring to the large alkyl substituent of the ring.

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