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Skeletal Isomerization of Hexenes on γ-Alumina

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After some preliminary experiments the influence of the choice of double-bond isomers on skeletal reactions on γ-alumina was investigated. Double-bond isomerization is not always fast compared with skeletal isomerization. Skeletal isomerization of hexenes was investigated using one double-bond isomer of each skeletal isomer as a feed. A complete reaction scheme was developed and discussed with respect to different reaction mechanisms. Together with results from 2,2,3-trimethylbutene isomerization it could be concluded that a nonclassical cyclopentyl mechanism alone may explain all the reactions.

1. INTRODUCTION

In some former papers (*1–4*) we discussed the reactivity of reforming catalysts (Pt/Al_2O_3) and of the carrier alone, more or less with respect to the catalyst. It could be shown that on alumina at least three types of reactive centers exist, which are connected to Lewis acid centers. The difference may be caused by different acidities as observed by Pines and Haag (*5*). These authors also claim to have observed a methyl shift mechanism for the isomerization reactions. Besides isomerization reactions cracking and cyclizations (*4*) are observed under the given conditions. The rates of these reactions are slow compared with those of isomerization. In this article we wish to discuss experimental results, which may be evaluated with respect to isomerization mechanisms. Besides the 1,2-methyl shift mechanism a number of other mechanisms shall be discussed: the 1,3-methyl shift, the ethyl shift, a dimerization-cracking mechanism (*6*), and a mechanism with cyclopropyl ions as intermediates (*7*).

2. EXPERIMENTAL

Reactions were investigated using a glass microreactor filled with 0.16 g of alumina (γ-Al_2O_3 from Merck, Darmstadt, activated by extraction with hot HNO_3). The oxide was pretreated for 2 h at 530°C in hydrogen or helium (60 ml/min). The gas stream was purified from O_2 with BTS-catalyst (Cu on silicagel) and dried with Siccapent (P_2O_5 on silicagel) first and then in an adsorption cold trap (filled with a molecular sieve of 3 Å) at −196°C. One part of the gas stream was saturated with alkene (4 mg/min). The reaction took place at 370°C with a hydrocarbon partial pressure of 10 Torr (1 Torr = 133.32 Pa) in helium. The reaction products were gently hydrogenated normally (at 200°C with Pt on alumina) to reduce the time necessary for analysis to 4 min (25 m squalene/fused silica) compared to at least 10 min for a complete separation of all alkenes (on 50 m 5% Carbowax 20 M/fused silica). The hexenes used were:

hexene-1	99.8% (Henkel)
cis-4-methyl-pentene-2	99.9% (Fluka)
3-methyl-pentene-1	99.9% (Fluka)
2,3-dimethyl-butene-1	99.9% (Fluka)
3,3-dimethyl-butene-1	98.1% (Fluka)
2,3,3-trimethyl-butene-1	99.6% (Aldrich)

The alkenes were dried over dry molecular sieve (3 Å) prior to use.

3. RESULTS AND DISCUSSION

3.1. Preliminary Experiments

According to the ideas of Pines and Haag (*5*) 1,2-methyl shift reactions of the alkenes

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should lead to isomerization. As a consequence isomerization of hexene should lead to 2-methyl-pentene in a primary reaction and 3-methyl-pentene should be formed in a secondary reaction. In contrast to these ideas 3-methyl-pentenes were observed—even after extrapolation to reaction time zero—in the product. If 3-methyl-pentene were really a secondary product, the second reaction should be extremely fast compared to the first one. To test this, hexene-1 and *cis*-4-methyl-pentene-2 were used as a feed with 50 mg γ-Al_2O_3 (chlorine free, pretreated at 530°C) at 370°C in helium (50 ml/min saturated with alkene at 0°C). The reaction of hexene-1 led to 2.01% 2-methyl-pentenes and 2.06% 3-methyl-pentenes; that of *cis*-4-methyl-pentene-2 led to 5.2% of 3-methyl-pentenes and 0.45% of hexenes. It must be concluded that 3-methyl-pentenes really are a primary product of hexene-1 because both steps of the hypothetical reaction sequence are of the same order of velocity. Though both 2- and 3-methyl-pentenes are formed as primary products, the following experiments show that they are not formed completely on the same centers of the catalyst (*4*).

(a) The ratio of both products depends on the pretreatment temperature.

(b) The ratio depends on the operation time of the catalyst.

In order to see whether the reactivities are different with different double-bond isomers of hexene, hexene-1, *cis*-hexene-2, and *trans*-hexene-3 were used as feed. Figure 1 gives the conversion to the single-branched isomers as a function of time of use of the catalyst. No difference can be seen, but the deviation from the curve is remarkable. So another system was investigated more thoroughly (Table 1). For the two double-bond isomers *cis*-4-methyl-pentene-2 and 2-methyl-pentene-1 conversions under the same conditions as for the first example were studied. This system was chosen because the double-bond isomers could be separated without hydrogenating the product on the column described. From Table 1 it follows that double-bond isomerization is not yet in thermodynamic equilibrium. Evidently the reactions of the first three isomers and those of the last two are both nearly in equilibrium, but the interconversion of alkenes of each group seems to be comparatively slow. Figure 2 shows the equilibrium concentrations of the different hexenes according to Kilpatrik *et al.* (*8*). The ratios between the values for the products found from 2-methyl-pentene-1 are in fairly good agreement with those calculated from Fig. 2, while from *cis*-4-methyl-pentene-2 the first group of products is in about

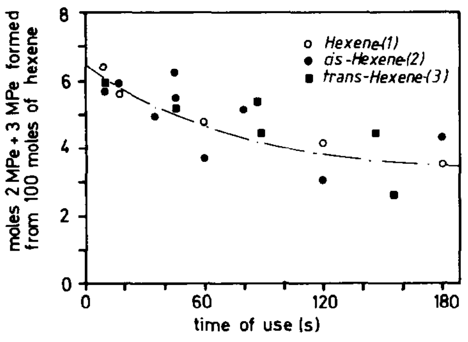


FIG. 1. Formation of 2- and 3-methyl-pentane from different *n*-hexenes as a function of time of use of the catalyst (γ-Al_2O_3 + 0.36% Cl).

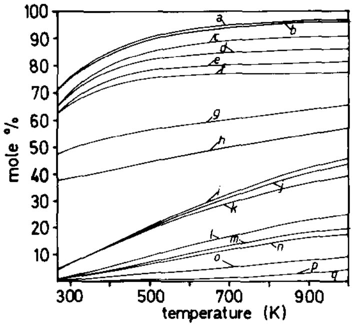


FIG. 2. Equilibrium concentrations of hexenes at different concentrations: (a) 2,3-dimethyl-butene-2, (b) 3,3-dimethyl-butene-1, (c) 2,3-dimethyl-butene-1, (d) 2-ethyl-butene-1, (e) *trans*-4-methyl-pentene-2, (f) *cis*-4-methyl-pentene-2, (g) *trans*-3-methyl-pentene-2, (h) *cis*-3-methyl-pentene-2, (i) 2-methyl-pentene-2, (j) 4-methyl-pentene-1, (k) 3-methyl-pentene-1, (l) 2-methyl-pentene-1, (m) *trans*-hexene-3, (n) *cis*-hexene-3, (o) *trans*-hexene-2, (p) *cis*-hexene-2, (q) hexene-1.

TABLE 1

Composition of the Isomeric Alkene Mixture Starting from Two Methyl-Pentenes Reacting under the Influence of 50 mg of Catalyst

Composition of the isomeric mixture of *cis–trans* and double-bonded compounds starting from			Conversion to skeletal isomers (in wt%) starting from		
Educts: Products	*cis*-4-Methyl-pentene-2	2-Methyl-pentene-1	Educts: Products	*cis*-4-Methyl-pentene-2	2-Methyl-pentene-1
4-Methyl-pentene-1	8.68	2.40	3,3-Dimethyl-butene-1	0.52	0.16
cis-4-Methyl-pentene-2	14.99	4.14	2,3-Dimethyl-butenes	8.83	2.89
trans-4-Methyl-pentene-2	34.02	6.43	3-Methyl-pentene	10.33	9.88
2-Methyl-pentene-1	13.35	29.10	Hexene	1.64	1.94
2-Methyl-pentene-2	28.96	57.93			

tenfold excess compared with equilibrium concentration. As could be expected the skeletal isomerization is affected under these conditions by the choice of the reactant.

3.2. Complete Reaction Scheme

One of each skeletal isomer hexene was used as a feed to investigate the complete scheme of skeletal isomerization of hexenes. In order to enable fast separation by GC, the products were hydrogenated gently before entering the chromatographic column. The experiments were executed in the standard way, with a partial pressure of 10 Torr of alkene, after a time on stream of 2 min each. Figures 3–7 give the mole percents of different isomers in the reacted product (without feed product) as a function of degree of conversion. The degree of conversion was influenced by changing the amount of catalyst because of the possible influence of gas velocity on deactivation (9). Deactivation was fastest with hexene and slowest with doubly branched compounds. Control measurements with hexene showed that, within the limits of error, deactivation in the first 2 min could be neglected for the isomerization reactions.

In the figures primary products show a finite intercept with the ordinate. Secondary products—if not formed in a reaction extremely fast compared with the primary reaction—should give curves without intercept. One curve increasing with another decreasing may indicate the formation of the substance causing the first curve from that causing the other.

Figure 3 again shows 2- and 3-methylpentenes to be primary products, with

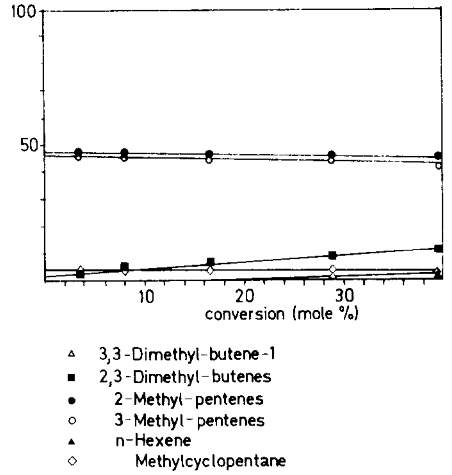


FIG. 3. Reaction of hexene-1: composition of reaction product at different conversions.

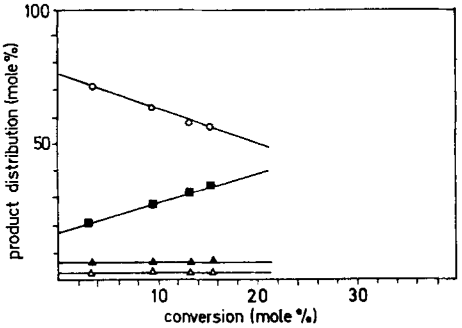


FIG. 4. Reaction of *cis*-4-methyl-pentene-2: composition of reaction product at different conversions (symbols as in Fig. 3).

about the same velocity of formation for both; methylcyclopentane is a primary product too, formed in smaller amount. The double-branched isomers are secondary products, and 2,3-dimethyl-butanes perhaps tertiary products. Figure 4 gives the reactions of *cis*-4-methyl-pentene-2. All products are formed directly, but the decrease of the curve for 3-methyl-pentenes and the increase of that for 2,3-dimethyl-butenes show that the latter is formed from the former too. As Figure 5 shows, 2-methyl-pentenes and hexenes are formed from 3-methyl-pentene directly, with 2,3-dimethyl-butene as a secondary and 2,2-dimethyl-butenes probably as tertiary products. 2,3-Dimethyl-butene-1 reacts forming primarily 2,2-dimethyl-butenes and 2-methyl-pentenes with a further interconversion of the former to the latter (Fig. 6). All others seem to be tertiary products. Finally, 3,3-dimethyl-butene-1, as Fig. 7 shows, forms but one primary product, the 2,3-dimethyl-butenes, which in further reactions give 2-methyl-pentenes.

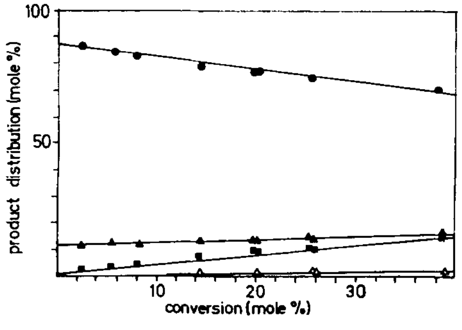


FIG. 5. Reaction of 3-methyl-pentene-1: composition of reaction product at different conversions (symbols as in Fig. 3).

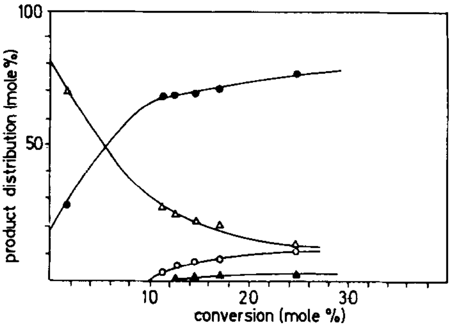


FIG. 6. Reaction of 2,3-dimethyl-butene-1: composition of reaction product at different conversions (symbols as in Fig. 3).

Taking into account the conversion rates of the reactants one may calculate a reaction scheme for the velocity constants (Fig. 8).

Because of the results about double-bond isomerization, described in the last chapter, which were obtained later than those about skeletal isomerization described here, the scheme shall be written as follows: the special isomer used as a feed is written on top and the alkane (skeletal isomer) found as a product after hydrogenation is written below.

Though there may be some doubt about the exact values of the velocity constants in the scheme, the scheme should be correct in general.

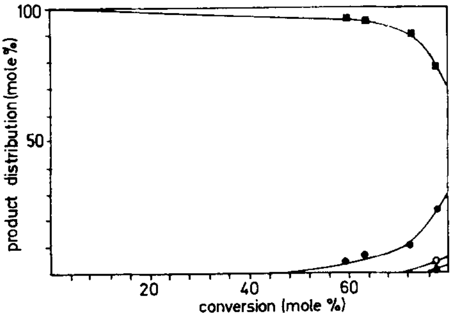


FIG. 7. Reaction of 3,3-dimethyl-butene-1: composition of reaction product at different conversions (symbols as in Fig. 3).

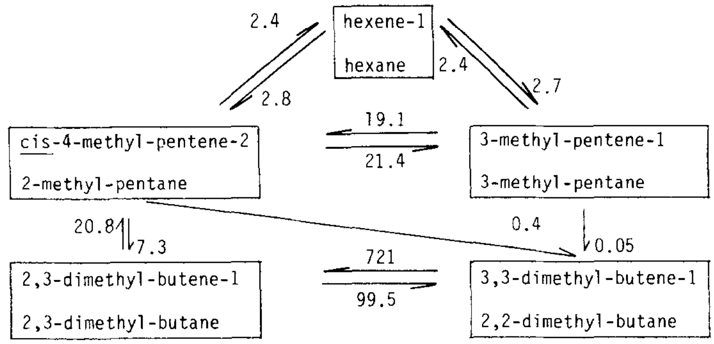


FIG. 8. Isomerization path and velocity constants (mole/liter-hr) for hexenes on alumina (reactant alkene on top, product after hydrogenation below).

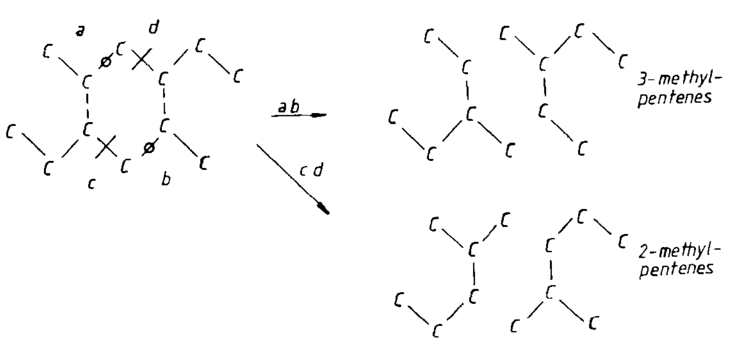
3.3. *Isomerization Mechanism*

As mentioned in the introduction, a number of different mechanisms shall be discussed for the isomerization reactions.

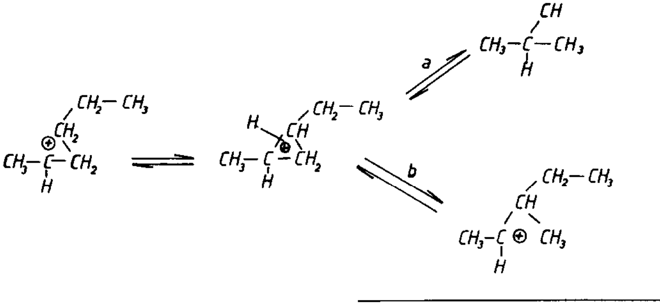
(1) 1,2-methyl shift,
(2) 1,3-methyl shift,
(3) 1,2-ethyl shift,
(4) dimer-cracking mechanism,
(5) cyclopropyl mechanism.

The first may easily be ruled out as the only mechanism, because 3-methyl-pentenes should be secondary products of hexene, but they were observed to be primary products, as described earlier. A 1,3-methyl shift should be possible only in a few reactions and could explain the reaction scheme only in combination with a 1,2-methyl shift. But in contrast to observations the reaction 3-methyl-pentene forming 2,3-dimethyl-butene should be possible too. So this mechanism doesn't seem to be of greater importance. If the 1,2-ethyl shift were important, the reaction 2-methyl-pentenes to 2,2-dimethyl-butenes should be faster than it was observed to be (comparable to 3-methyl-pentene → hexene).

The fourth mechanism described by Bolton and Lanewala (*6*) should proceed via dimers as

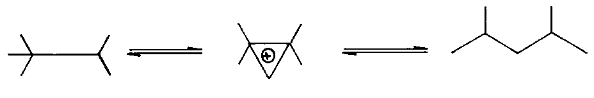


Under these conditions there are other possibilities for cracking the six-membered ring, which should lead to pentenes and heptenes. Heptenes were not formed on alumina in detectable amounts. The cyclopropyl mechanism finally may really explain all the existing reactions.



In Fig. 9 all cyclopropyl ions with six C atoms are compiled together with the alkenes into which each may be cracked (alkenes which may be reacted via a primary ion only are written in brackets). From these theoretical reflections one may construct a scheme of interconversion possibilities, which is given (with reaction via primary ions dotted) in the lower part of Fig. 9. Both schemes are identical with the exception of the possibility of a direct conversion of 2,2-dimethyl-butenes via an ion 2 to 2-methyl-pentenes, which was not observed in the experiments in contrast to the reverse reaction.

For a final test of the importance of this cyclic mechanism 2,2,3-trimethyl-butene-2 was chosen, which, according to analogous ideas, should only react directly to 2,4-dimethyl-pentenes, a reaction that could not be explained using one of the other mechanisms:



The composition of reaction products as a function of conversion for this experiment is given in Fig. 10. 2,4-Dimethyl-pentenes are really found as the only primary products of importance, with a very small amount (0.69%) of 2,2-dimethyl-pentenes, which may be formed according to this mechanism via a primary ion too. From temperature dependence the activation energies could be estimated to be 46 kJ/mole for the formation of 2,4-dimethyl-pentenes and 75 kJ/mole for 2,2-dimethyl-pentenes, where the latter reaction might even be a 1,2-methyl shift. A similar transformation of 2,2,3-trimethyl-pentane in concentrated H_2SO_4 was discussed by Stevenson *et al.* (*10*). Even reactions with a cyclobutyl cation as an intermediate were discussed (*10, 11*). This mechanism could not explain the hexene reactions at all, because hexene should not react to 2-methyl-pentenes but only to 3-methyl-pentenes and 2,3-dimethyl-butenes, and 2,2,3-trimethyl-butene might not from 2,4-dimethyl-pentenes but should react to 2-methyl-hexene and 2,3- and 3,3-dimethyl-pentenes. A cyclopentyl mechanism would not allow a reaction of 2,2,3-trimethyl-butene at all.

The results described demonstrate that only the 1,2-methyl shift might be of some importance besides the cyclic mechanism. From the hexene reactions it is difficult to decide whether this shift mechanism is important or not, because some reactions are possible by the cyclic but not by the shift mechanism (as described), but not the reverse. More informative again is the example of 2,2,3-trimethyl-butene, which should

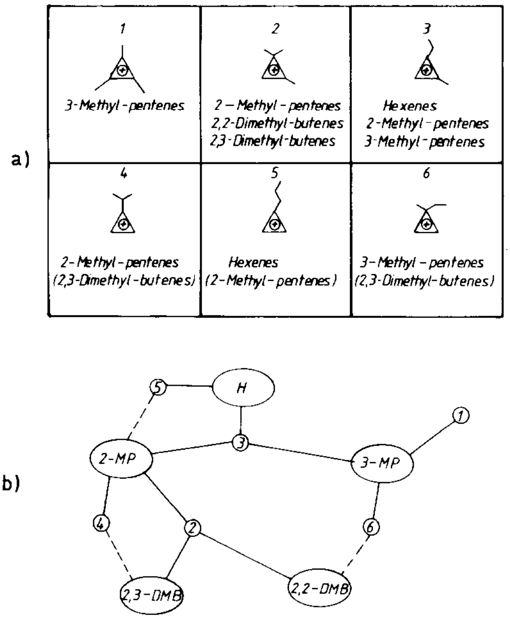


FIG. 9. (a) Possible types of substituted cyclopentyl ions as intermediates between the alkenes cites below (in brackets if reached via primary ionic state only). (b) Reaction scheme via cyclopentyl ions: small circles—cyclopentyl ions (number as in a); large circles—alkenes. H: hexenes, 2-MP: 2-methyl-pentenes, 3-MP: 3-methyl-pentenes, 2,2-MP: 2,2-dimethyl-butenes, 2,3-MP: 2,3-dimethyl-butenes.

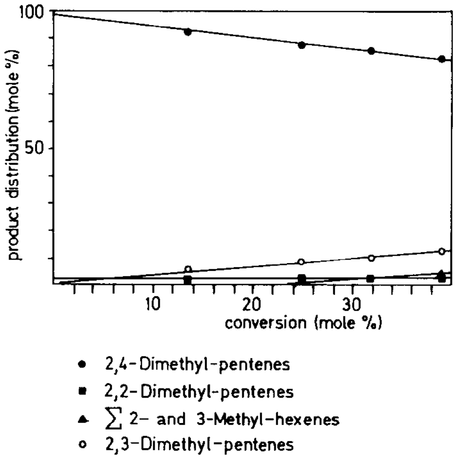


FIG. 10. Reaction of 2,2,3-trimethyl-butene-2: composition of reaction product at different conversions.

react to 2,2- and 2,3-dimethyl-pentenes following the shift mechanism only. As mentioned already 0.67% of the primary products are 2,2-dimethyl-pentenes, but no 2,3-compound was found. Even the small amount may have formed via a primary ion along the cyclic way. One may conclude that the shift mechanism has little or no importance for isomerization on alumina.

Generally one should expect to find constant ratios of reaction rates for products which are formed via a common intermediate ion provided there is no competing reaction path. It is not possible to test this from Figs. 3 to 7 because of the changing conversion allowing secondary reactions. One example of this type is the formation of 2-methyl-pentenes and 2,3-dimethyl-butenes

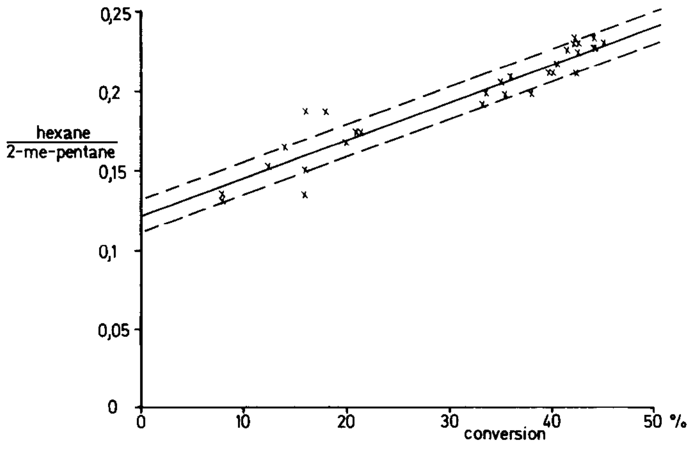


FIG. 11. Product ratio of hexane to 2-methyl-pentane as a function of conversion of 3-methyl-pentene-1.

from 3,3-dimethyl-butene via ion 2. Here a decision is impossible because practically no 2-methyl-pentene is formed. The other reaction of this type is formation of hexenes and 2-methyl-pentenes from 3-methyl-pentenes.

Figure 11 shows values of this ratio obtained with samples pretreated at different temperatures (450–900°C). In spite of the different activities of the catalyst, this ratio is only a function of conversion. Extrapolation to conversion zero gives—within the limits of error (ca. 10%)—a common intercept of 0.122 for all samples, showing that indeed the above-mentioned constancy of product ratio for substances formed from one common cyclopropyl ion is really observed.

The change of the ratio 2- to 3-methylpentenes during the reaction of hexene may partially be caused by a second pathway from hexene to 2-methyl-pentenes via ion 9 (Fig. 9) with the intermediate formation of a primary ion. This reaction should be favored on more reactive centers. Indeed the ratio is increasing with pretreatment temperature where centers of greater activity are formed, and decreases with time onstream, where the most active centers are poisoned first. The same, of course, would apply to a more energetic parallel reaction with another mechanism.

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