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# Isomerization of hexane by zeolite HZSM-5 The effect of cyclic hydrocarbons

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## Abstract

The main products of hexane (H) isomerization on HZSM-5 at 160°C in liquid phase are the isomers 2-methylpentane (2MP) and 3-methylpentane (3MP), accompanied by cracking and disproportionation products, but no alkenes. 2MP and 3MP are not formed by a simple carbocationic isomerization of H, because the 2MP/3MP ratio, (6–7)/1 is higher than the equilibrium ratio of 2.1 and does not change with conversion between 1 and 10%. The same observation applies to the small amounts of 2,3-dimethylbutane formed. Methylcyclopentane (MCP) has a minor accelerating effect on the conversion of H only at ratios 1:1. No hydride transfer catalysis operates. At the same ratio (1:1), cyclopentane (CP) has a somewhat greater effect than MCP on the conversion of H. The redistribution of the label in the conversion of H-*u-d*<sub>4,3</sub> containing 4–5% MCP and of H containing 5% MCP-1-*d* showed that the products were formed from alkenes, which are the major intermediates of the reaction, even though none of them is found in the products desorbed. Each alkene exchanges hydrogen with the catalyst several times before being desorbed. The direct H/D exchange between the alkene (or its mechanistic equivalent) and the alkane, if it occurs, is less important. Thus, the usual mechanistic representation for alkane conversion, borrowed from reactions in superacid solutions, does not apply to the reaction with the zeolite catalyst. © 2000 Elsevier Science B.V. All rights reserved.

*Keywords:* Hexane; HZSM-5; Isomerization

## 1. Introduction

The mechanistic description of reactions of saturated hydrocarbons catalyzed by solid acids is generally based on models and concepts developed through studies of reactions in solution [1–4]. Thus, alkane reactions on aluminosilicates have been described by mechanisms established for reactions catalyzed by

the liquid superacids H<sub>2</sub>O-AlCl<sub>3</sub> [5], HF-BF<sub>3</sub> [6], and HF-SbF<sub>5</sub> [7]. We have noted that even in solution the traditional carbocationic mechanistic model is not always adequate. Thus, we found that the reaction of 3-methylpentane (3MP) [8] and hexane (H) [9] catalyzed by the weakly superacidic trifluoromethanesulfonic acid (TFMSA) can proceed by two pathways. Which pathway is taken depends upon the concentration of alkenyl cations, resulting from the oxidation of the reactant by the catalyst, at the interface between the acid and hydrocarbon layers. When the alkenyl cation concentration was

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maintained below a critical value by dispersion away from the interface, a clean isomerization was observed. Otherwise, a disproportionation to lighter (cracking) and heavier products, with the former predominating, was observed. The isomers were also formed mainly by disproportionation [8,9].

For both H and 3MP, the relative rates and product selectivities in the isomerization mode fulfilled the expectations for a traditional carbocationic mechanism. The reaction in the cracking mode did not exhibit, however, the features of the carbocationic mechanism. Thus, the reaction in the cracking mode was significantly faster than in the isomerization mode, especially for hexane, such that the conversion rate ratio of 3MP to H was reduced from three orders of magnitude in the isomerization mode to one order of magnitude in the cracking mode [9]. The reaction in the cracking mode showed an induction period, during which alkenyl cations accumulated, and had the features of a chain reaction. Formation of 2,2-dimethylbutane (2,2DMB) as a primary product from H was also incompatible with a carbocationic isomerization mechanism [9].

The induction period was shortened or eliminated by the addition of mild oxidizing agents, like ferric ions, indicating that the initiation involves a one-electron oxidation [9]. Other authors had reported that the very slow isomerization of butane catalyzed by TFMSA was accelerated by precursors of free-radicals and by electrochemical oxidation [10].

An appropriate comparison of results obtained for solid acid catalysts with data from reactions with acids in solutions is rendered difficult by the different reaction conditions: close to room temperature with liquid feed for the liquid acids and at high temperatures with gas-phase feed for the solid acids [11]. We have, therefore, initiated an investigation of reactions of saturated hydrocarbons on solid acid catalysts, particularly zeolites, at temperatures below 200°C and with the reactants both in the gas phase and in the liquid phase.

Considering the importance assigned to hydride transfers in the acid-catalyzed conversions of saturated hydrocarbons [2], especially on HZSM-5 [3], it was interesting to follow the pathway of hydrogen atoms from reactants to products, by using reactants labeled with deuterium. We report here the results of that investigation.

## 2. Experimental

### 2.1. Reactants

Commercial, reagent-grade, hexane contained 0.45% methylcyclopentane, MCP, by GLC. The reagent-grade MCP contained about 2% H. Cyclopentane (CP), 99.5%, contained  $\leq 0.5\%$  2,2DMB and  $< 0.05\%$  MCP. The high-purity hexane (no MCP and no olefins) [12], hexane- $u-d_4$  [12], and MCP-1- $d$  [13] were synthesized as previously described. The deuterated hexane contained an average of 4.3 deuterium atoms per molecule and was a mixture of all isotopomers, from  $d_0$  to  $d_{14}$ , with the distribution: 5.3, 9.8, 13.1, 14.8, 14.3, 12.8, 10.0, 7.4, 5.0, 3.2, 2.0, 1.2, 0.7, 0.3, and 0.2%, respectively (GC-MS).  $^2\text{H-NMR}$  analysis indicated that the isotope was statistically distributed among all methyl and methylene groups. The isotopic purity of MCP-1- $d$  was higher than 99% [13].

### 2.2. Catalyst

The zeolite HZSM-5 CBV-3020,  $\text{SiO}_2/\text{Al}_2\text{O}_3 = 31$ , 0.02% (wt.)  $\text{Na}_2\text{O}$ , of  $412 \text{ m}^2/\text{g}$ , was obtained from Conteka. It was heated in air to 480°C over a period of 8 h and maintained at this temperature for 10 h, for activation.

### 2.3. Reactant and product analyses

The GLC and GC-MS (70 eV) analyses were conducted as in our previous studies [8,9]. Three of the compounds of interest, CP, 2MP and 2,3-dimethylbutane (2,3DMB), were not separated by GLC at the lowest temperature accessible (25°C), but could be separated in the GC-MS instrument at a column temperature of 13°C or less. Thus, the sum of these compounds was obtained from the GC analysis and their ratios from the total ion current in GC-MS.

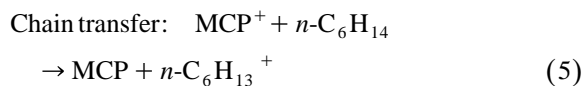
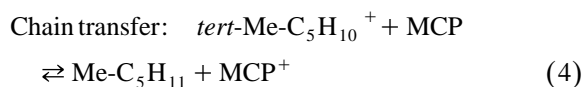
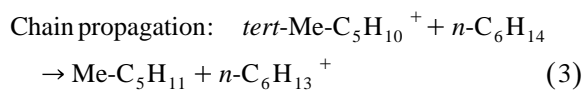
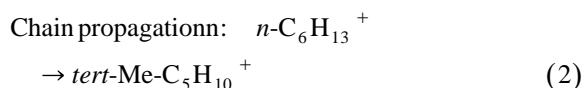
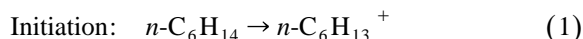
### 2.4. Catalytic reactions

For a reaction with liquid reactant, the catalyst (0.04–0.05 g), reagent (0.25 g), and a Teflon-coated stirring bar, were introduced in a dry 12 cm  $\times$  6 mm ID glass tube, which was then capped, cooled in

liquid nitrogen, and sealed under vacuum [14]. The tube was shaken for mixing and immersed vertically in an oil bath thermostated at 140–160°C, placed over a magnetic stirring plate, and allowed to react with stirring for a determined length of time. It was checked that the catalyst was fully covered with liquid throughout the experiment. The sample was then frozen in liquid nitrogen and the tube was cut open and capped with a rubber septum. Upon heating to room temperature, samples were taken through the septum from both the gas phase and liquid phase and analyzed by GLC and GC-MS.

### 3. Results and discussion

An effect of MCP upon the rate of reaction of H was thought of as a manifestation of hydride transfer catalysis [15] in HZSM-5. (The existence of hydride transfer catalysis for certain reactions in superacidic or strongly acidic solutions has been established [16].) In that case, the mechanistic pathway for isomerization, expressed by Eqs. (1)–(3), would be changed by the addition of Eqs. (4) and (5). By running the reactions at low conversions one can neglect the reversibility, except for the fast [17,18] tertiary–tertiary hydride transfer of Eq. (4). The catalysis would require that Eq. (5) be faster than Eq. (3) (Curtin–Hammett principle) [19].



The results of several experiments are shown in Fig. 1. Each point in Fig. 1 represents an individual experiment. The same symbol was assigned to experiments started at the same time, that is, which used the same batch of catalyst and reactant. It is seen that

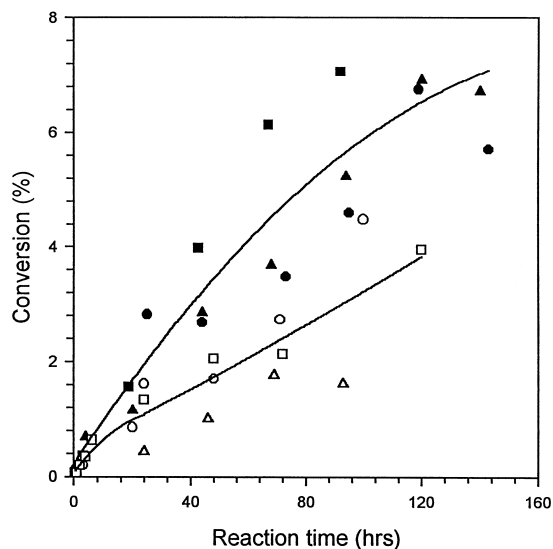


Fig. 1. Conversion of H and (H+MCP) mixtures on HZSM-5 at 160°C, in the liquid phase. (○) Synthetic (pure) H; (□, △), H: MCP = 99.55:0.45; (●, ■, ▲) H: MCP = 50:50 (±1).

the addition of a small amount of MCP (0.4–0.5%) did not affect the reaction rate of H. The commercial and the synthetic hexane reacted at the same rate. This result can be interpreted based on the known rates of the hydride transfer steps,  $k(3) = 2 \times 10^{-2} \text{ l mol}^{-1} \text{ s}^{-1}$  at 0°C for Eq. (3) [7] and  $k(4) \geq 200 \text{ l mol}^{-1} \text{ s}^{-1}$  at –50°C for Eq. (4) [20] and the ratio H/MCP of 221 (0.45% MCP in H):

$$\frac{r(4)}{r(3)} > (\text{or } \gg) 44.6, \quad \text{i.e.} \quad \frac{200}{(2 \times 10^{-2} \times 221)} \quad (6)$$

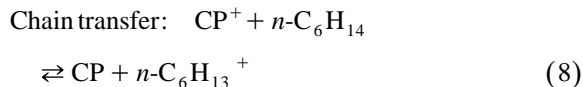
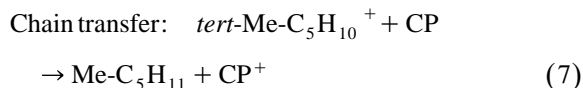
It is also known that the equilibrium of Eq. (4) is displaced to the right [21,22]. Therefore, the reaction should occur by Eq. (5), rather than by Eq. (3), even if the rate constants for the two steps were the same. If Eq. (5) was intrinsically faster than Eq. (3), a significant acceleration of the overall rate should be observed. The absence of *any* acceleration for the mixture containing 0.4–0.5% MCP eliminates the hydride transfer catalysis from consideration for the reaction of H on HZSM-5.

A minor rate effect was seen only in experiments with the MCP to H ratio of 1:1, also shown in Fig. 1. There is some spread of data, but at a given reaction

time the lowest point for the 1:1 mixtures is above the highest point of pure H in almost all cases. The overall difference is, however, similar to the uncertainty of the data. Certainly, the rate effect of an equimolar amount MCP on the rate of H is marginal. On the other hand, we observed that the reaction of MCP becomes slower upon mixing with H in a 1:1 ratio than it is for pure MCP.

We also examined the reaction of H mixed with an equal amount of cyclopentane (CP). The latter has no tertiary hydrogen and its reaction with tertiary hexyl cations Eq. (7) should not be faster than Eq. (3). Therefore, the chain transfer involving CP (Eqs. (7) and (8)) adds one step without any rate advantage and CP cannot act as a hydride transfer catalyst. Nonetheless, hexane reacts faster in the mixture with CP than in the mixture with MCP. The actual acceleration could not be determined precisely, because GLC separation of 2MP from CP was not achieved when the latter was in large excess. Therefore, the conversion was assessed from the amount of 3MP formed. The levels of 3MP formed in the reactions of H, (H + MCP) and (H + CP) are shown in Fig. 2. It appears that there is an induction period in the reaction of H in the presence of CP, during which

the rate is similar to that measured for the other systems, after which conversion of H in the mixture with CP becomes faster. The induction period indicates that the rate increase is not induced by CP itself, but by a product formed from it.



The rate effects reported above can be explained by the existence of steric hindrance for the hydride transfer from MCP [3]. This explanation is questionable, however, because carbocationic isomerization of MCP itself involves a hydride transfer from MCP to  $\text{CH}^+$ . Moreover, recent calculations have shown that the hydride transfer is not intrinsically more sterically demanding than  $\beta$ -cracking or its reverse reaction, alkylation [23]. Alternatively, the initiation step [14] or the initiation *and* propagation steps could occur not by the standard carbocationic mechanism, but by a pathway involving one-electron transfers (oxidation) and ion-radicals as intermediates [9,11,12,24–27]. Then, the cyclic alkanes may act upon the one-electron oxidation step. We observed that cycloalkanes inhibit the formation of allyl cations from H in the reaction catalyzed by TFMSA [12]. The induction period indicates that a reactive intermediate has to be generated first. Formation of a ‘reactive coke’ on the catalyst was suggested by previous workers [28].

The reaction products consisted of isomers, mostly 2MP and 3MP, together with cracking and disproportionation products ( $\text{C}_3\text{--C}_5$  and  $\geq \text{C}_7$ ). No alkenes were observed. A significant feature of the product distribution was the ratio 2MP/3MP (6–7/1), well over the equilibrium ratio (2.1/1) and not changing with the increase in conversion between 1 and 10%. These isomers cannot be formed, therefore, by the carbocationic isomerization of hexane, in which the 2MP–3MP interconversion is much faster than the isomerization of H. Likewise, small amounts of 2,3-dimethylbutane (2,3DMB) were observed in the GC-MS analyses in which the separation was performed at 10°C. The experiments with deuterated hexane (below) showed that 2,3DMB was formed from H.

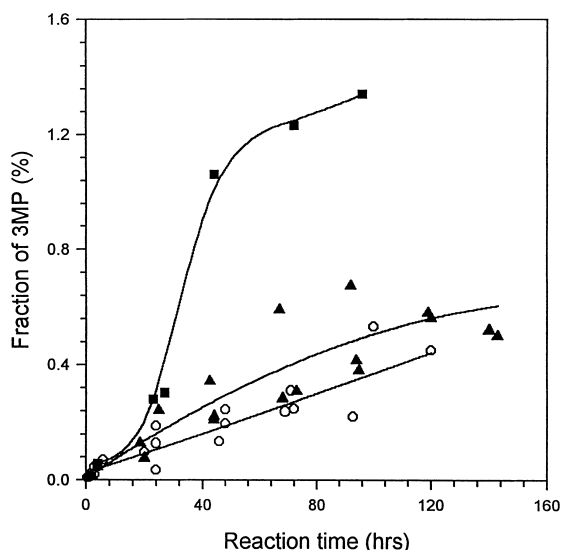


Fig. 2. Effect of CP on the reaction of H on HZSM-5 at 160°C, in the liquid phase, evidenced in the conversion to 3MP. (O) H (synthetic and commercial); (▲) H + MCP (50:50); (■) H + CP (55:45).

The carbocationic isomerization mechanism is, again, precluded, because 2,3DMB is formed in that mechanism only after 2MP and 3MP have reached equilibrium.

The product distribution obtained for the reactions of mixtures was changed in the same way for both reactants, that is, toward cleaner product slate than what was obtained for the pure reactants, H and MCP. As shown in Table 1, mixing with MCP reduces the extent of disproportionation and cracking of H. This effect is not seen, or is marginal, upon addition of 0.44% MCP, but it is apparent for the 1:1 mixture. The quantity of side-products did not change with conversion in the range studied by us (up to 10% overall). On the other hand, the only secondary product observed in the reaction of MCP was cyclopentane, which must be formed by a complex reaction pathway, because no methane was evidenced among products. Unlike the formation of

cracking products from H, which is more important in the early stages of reaction, the formation of CP from MCP exhibits an induction period (Fig. 3). Upon mixing with H, the formation of CP from MCP is inhibited (Fig. 3). In the presence of CP, however, the extent of disproportionation and cracking of H increased, as shown in the last column of Table 1. In this particular mixture, the amount of side-products was smaller during the induction period than later, but within each stage it did not change with conversion. No reaction to volatile products was observed for CP, alone or in the mixture with H.

The absence of hydride transfer catalysis in the reaction of H was also shown by the lack of retardation in the reaction of H conducted in the presence of 5% MCP-1-*d* in comparison with the reaction run with the same concentration of unlabeled MCP. At a conversion of 3–4%, the isomeric products 2MP and 3MP contained only 0.1–0.2 deuterium atoms per

Table 1  
Distribution of products from H on HZSM-5 in the absence or presence of cycloalkanes<sup>a</sup>

Product	Additive to H			
	None <sup>b</sup>	0.44% MCP <sup>c</sup>	49.3% MCP <sup>d</sup>	45.3% CP
2MP	80.3 <sup>e</sup>	80.6 <sup>f</sup>	86.8 ± 0.8 <sup>f</sup>	... <sup>g</sup>
3MP	12.0 (1.00)	12.0	11.3 ± 1.0	(1) <sup>h</sup>
2,2DMB <sup>i</sup>	0.0	0.0	? <sup>j</sup>	? <sup>j</sup>
<i>n</i> -C <sub>5</sub>	1.6 (0.13)	1.6	0.56 ± 0.20	(0.40 ± 0.03) <sup>k</sup> ; (0.66 ± 0.08) <sup>l</sup>
<i>i</i> -C <sub>5</sub>	1.3 (0.11)	1.1	0.25 ± 0.05	(0.22 ± 0.01) <sup>k</sup> ; (0.44 ± 0.05) <sup>l</sup>
<i>n</i> -C <sub>4</sub>	1.5 (0.13)	1.2	0.47 ± 0.05	(0.27 ± 0.03) <sup>k</sup> ; (0.60 ± 0.08) <sup>l</sup>
<i>i</i> -C <sub>4</sub>	1.1 (0.09)	0.8	0.22 ± 0.03	(0.16 ± 0.01) <sup>k</sup> ; (0.41 ± 0.06) <sup>l</sup>
C <sub>3</sub> <sup>m</sup>	0.7 (0.06)	0.7	0.35 ± 0.07	(0.16 ± 0.02) <sup>k</sup> ; (0.27 ± 0.04) <sup>l</sup>
≥ C <sub>7</sub>	1.4 (0.12)	1.8	(0) <sup>n</sup>	(0.24 ± 0.02) <sup>k</sup> ; (0.62 ± 0.04) <sup>l</sup>

<sup>a</sup> Reactants in liquid phase, at 160°C. For mixtures with MCP and CP, only the products from H are listed.

<sup>b</sup> At 4.5% conversion, reaction time, 100 h.

<sup>c</sup> At 4.0% conversion, reaction time 120 h.

<sup>d</sup> Average of six batches, at 5–11% conversion, reaction times, 68–140 h (standard deviations given).

<sup>e</sup> Separation in the GC-MS at 11°C indicated somewhat more 2,3-DMB than pentane.

<sup>f</sup> The 2,3DMB content was not determined.

<sup>g</sup> 2MP was not separated from the large excess of CP.

<sup>h</sup> The values in parentheses are normalized to the amount of 3MP in the mixture, taken as 1.00. They are compared with the values in parentheses in the second column.

<sup>i</sup> 2,2-Dimethylbutane.

<sup>j</sup> MCP contained 2,2DMB. The increase in the concentration of the latter, observed during the reaction, was most likely due to the loss of the other components by coking.

<sup>k</sup> Average of three batches, at low conversion (< 0.6% conversion to 3MP).

<sup>l</sup> Average of three batches, at higher conversion (2–2.5% conversion to 3MP).

<sup>m</sup> Evaporation losses of this product are possible, but they should be similar in all experiments.

<sup>n</sup> Some of the heavy products might have been covered in the GC analysis by MCP and CH.

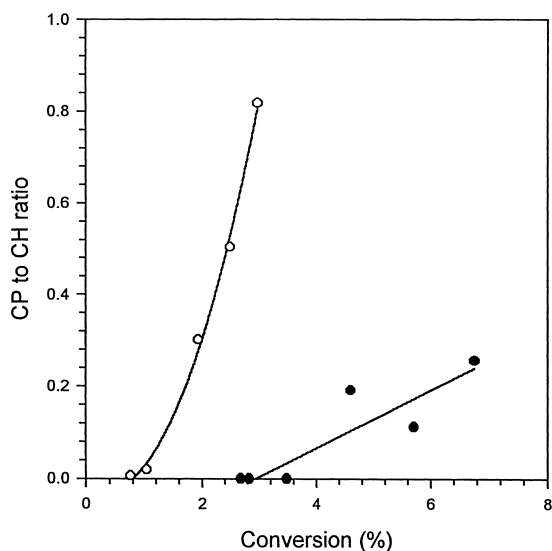


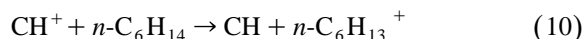
Fig. 3. Ratio of CP to CH (cracking to isomerization) in the reaction of MCP on HZSM-5 at 160°C, in the liquid phase; (○) MCP alone; (●) MCP+H (50:50).

molecule. CH formed (4.5–5.5%) from MCP-*d* had lost most (94%) but not all of its label and it contained a small amount (ca. 1%) of dilabeled molecules, whereas the deuterium loss from MCP was within the uncertainty of the measurements. Based on the amount of 3MP and 2MP formed, the mechanism including Eq. (5) should give a much greater deuterium incorporation in methylpentanes and a well measurable loss of label from MCP. The low level of deuteriation of methylpentanes indicates that the deuterium lost from CH was retained by the catalyst.

The same conclusions were reached, only more clearly, from the reaction of polydeuterated H and 4–5% MCP. Catalytic addition of deuterium to 1,4-hexadiene at ambient temperature and pressure and without a solvent gave hexane containing on the average 4.3 deuterium atoms per molecule (30.7% isotope enrichment), statistically distributed among the two methyl groups and four methylene groups [12]. Mixtures of this material with 4–5% MCP were reacted to a conversion of 1.2–2.3%, i.e. smaller than the amount of MCP added, and the products were analyzed by GLC and GC-MS.

The first observation from these experiments was a sizeable loss of deuterium from the isomerization

products of H. For the standard carbocationic mechanism Eqs. (1)–(5), the maximum loss of deuterium would be 0.3 atoms per molecule if the primary kinetic isotope effect (KIE) is disregarded and significantly lower if the KIE is considered, as it should [29]. To the extent that Eq. (3) operates, the loss of isotope should be even smaller. The deuterium content of the reaction products is shown in Table 2 and the deuterium distribution is presented in Table 3. It is seen in Table 2 that there is very little deuterium incorporation in MCP, which confirms that Eq. (5) does *not* intervene in the reaction mechanism. A possible explanation of this result would be that isomerization of MCP<sup>+</sup> is faster than the hydride transfer from H, in which case the sequence of Eqs. (9) and (10) would replace Eq. (5) in the mechanistic description of the reaction. This alternative pathway is at best minor, however, because the amount of CH formed in the reaction is about four times smaller than the amount of 2MP and 3MP.



The observation that CH acquires more than one deuterium atom per average molecule offers the al-

Table 2

Deuterium content in the reaction products from H-*u-d*<sub>4</sub> with MCP<sup>a</sup>

Product	Deuterium content <sup>b</sup>
H	4.20 ± 0.27
2MP	2.77 ± 0.13
3MP	2.68 ± 0.22
<i>n</i> -C <sub>5</sub>	2.80 ± 0.26
<i>i</i> -C <sub>5</sub> <sup>c</sup>	(≈ 2.3)
<i>n</i> -C <sub>4</sub> <sup>c</sup>	1.95 ± 0.06
<i>i</i> -C <sub>4</sub> <sup>c</sup>	1.77 ± 0.26
C <sub>3</sub> <sup>c</sup>	1.35 ± 0.05
MCP	0.04 ± 0.02
CH	2.01 ± 0.36

<sup>a</sup> Reactants in liquid phase, at 160°C; MCP content 4%, unless indicated otherwise.

<sup>b</sup> Average of four runs, with standard deviations indicated. The reaction times were 19, 19, 44, and 70h (conversions: 1.2, 1.3, 1.6, and 2.3%); the 70h-run contained 5% MCP. The relative intensity of each isotopomeric ions was integrated over the entire GC peak. The accuracy of the determination decreases as the quantity of material decreases, that is, in the order: H, MCP, 2MP > 3MP > CH > *n*-C<sub>5</sub> > *i*-C<sub>5</sub>, *n*-C<sub>4</sub>, *i*-C<sub>4</sub>, C<sub>3</sub>.

<sup>c</sup> Average of two runs, at 1.3 and 2.3% conversion.

Table 3  
Deuterium distribution in the reaction products from H-u- $d_4$  and MCP<sup>a</sup>

Product	Deuterium distribution (content of isotopomer, %) <sup>b</sup>												
	$d_0$	$d_1$	$d_2$	$d_3$	$d_4$	$d_5$	$d_6$	$d_7$	$d_8$	$d_9$	$d_{10}$	$d_{11}$	$d_{12}$
H <sup>c</sup>	4.9 ± 0.5	9.8 ± 0.7	13.5 ± 1.7	15.4 ± 1.8	14.9 ± 1.3	12.9 ± 0.4	10.1 ± 0.6	7.3 ± 1.1	4.8 ± 1.2	2.9 ± 1.0	1.7 ± 0.7	0.9 ± 0.4	0.5 ± 0.3
2MP	7.0 ± 1.5	13.5 ± 1.1	22.6 ± 1.9	24.1 ± 0.8	17.9 ± 1.5	9.5 ± 1.1	4.2 ± 0.7	1.3 ± 0.7	0.0	0.0	0.0	0.0	0.0
3MP	9.4 ± 1.4	14.3 ± 5.5	21.1 ± 6.8	24.2 ± 1.7	16.5 ± 0.4	10.0 ± 2.9	3.2 ± 2.8	1.2 ± 2.1	0.0	0.0	0.0	0.0	0.0
<i>n</i> -C <sub>5</sub>	7.1 ± 2.7	16.7 ± 1.1	18.8 ± 4.7	19.9 ± 3.8	15.9 ± 1.6	10.1 ± 2.9	5.2 ± 1.3	3.7 ± 0.3	0.0	0.0	0.0	0.0	0.0
MCP	97.7 ± 0.9	1.1 ± 0.5	0.7 ± 0.19	0.2 ± 0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
CH	24.8 ± 10.0	14.4 ± 0.2	20.9 ± 2.4	20.6 ± 3.6	12.6 ± 2.7	5.1 ± 2.0	1.4 ± 0.6	0.3 ± 0.3	0.0	0.0	0.0	0.0	0.0

<sup>a</sup> See footnote *a*, under Table 2.

<sup>b</sup> See footnote *b*, under Table 2.

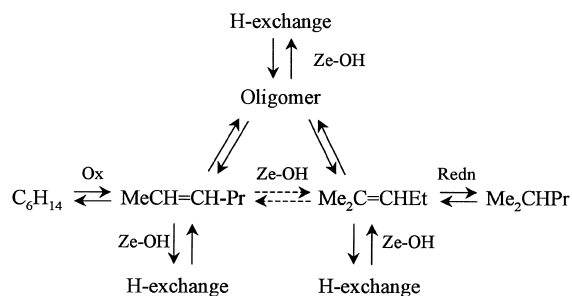
<sup>c</sup> To be compared with the isotope distribution in the starting material, given in Section 2.

ternative that the CH product replaces MCP as hydride donor in Eq. (4). That proposition is untenable, because the MCP to CH ratio at the end of an experiment was around 30 and the former is a much better hydride donor. In fact, CH is not much better than H as a hydride donor and the ratio H to CH at the end of an experiment was about 750. Moreover, at the total incorporation of 15–20%, the isotope distribution for the multiple reaction of a stable molecule should be  $d_1 > d_2 > d_3$ , instead of the observed  $(d_2 \approx d_3) > (d_1 \approx d_4)$ . The observed distribution indicates multiple exchanges in a reactive intermediate, before conversion to the stable product, here CH [30].

The distribution of deuterium can be rationalized by a mechanism in which the intermediates are alkenes, which exchange hydrogen with the catalyst several times before being converted to the saturated hydrocarbons and being desorbed. The isotopomer fractionation on the GC column allowed us to establish that even in MCP, for which the overall deuteration is barely detectable, there are molecules that contain as many as six deuterium atoms. The mechanism of alkene formation by a one-electron oxidation followed by the transfer of one hydron and one hydrogen atom to the catalyst has been discussed before [14]. Alternatively, the C–H bond may be cleaved by insertion of aluminum into it (metal ion catalysis). The formation of alkenes does not have to poison the catalyst, because alkene polymerizations in which the product (oligomer) was displaced from the catalyst by the reactant rather than poison it, was

reported for HZSM-5 at low temperatures [31]. In the reaction of alkanes, oligomers are also most likely formed. Their cleavage forms both hexane isomers and disproportionation products. The monomeric olefins and the oligomers, can exchange hydrogen with the OH (or possibly Al-H [32]) groups. The easy hydrogen transfer on zeolites was shown before by the formation of significant amounts of alkanes in the isomerization of alkenes [33].

The overall reaction is illustrated by Scheme 1, for the conversion of H to 2MP. In the Scheme, the mechanism of the critical step, the alkene formation, remains open. It may involve a one-electron oxidation as discussed above, or metal ion catalysis [32]. Burwell et al. have established long time ago that activation of paraffins on silica-alumina catalysts does not involve equilibrium formation of molecular hydrogen [34]. The hydrogen exchange may involve exchange of hydrons (protons or deuterons) with the



Scheme 1.

acid sites (addition to alkenes and elimination). A proposal of direct transfer of *two* hydrogens between alkanes and the radical-cations formed by alkene oxidation in strong liquid acids has also been advanced [20]. The multiple exchange indicates that the formation of alkenes is slower than their isotope exchange. Because the alkenes are not desorbed at the temperatures investigated, their total concentration is limited by their equilibrium ratio to the alkane, which is very low. This agrees with the results of an in situ IR spectroscopic study of HZSM-5 during hexane reaction, which showed that most of the OH groups stayed uncomplexed and available for reaction [35,36]. The IR study was conducted, however, at higher temperature than our experiments [35,36].

Isotope exchange between D<sub>2</sub>O-exchanged solid acids and saturated hydrocarbons has long been known [34,37–39] and was confirmed recently by NMR investigations [40]. The process was interpreted as occurring in parallel or in competition with skeletal rearrangement [40]. We find now that the elimination and addition which exchange hydrogen are steps of the rearrangement mechanism.

An intriguing observation was that the deuterium concentration of pentane, a cracking product, was higher than that of the isomerization products; this finding would suggest that cracking to this product had occurred before the precursor had time to exchange fully with the catalyst. The other cracking products do not show the same pattern of deuteration, but their small amounts in the mixture did not allow an accurate isotope count, so no conclusion can be reached on this account.

Finally, we note that the temperatures of our experiments were much lower than in most studies of hydrocarbon reactions over zeolites. Higher temperatures are known, however, to favor thermal-type, free-radical processes. We do not expect that there would be a higher carbocationic character of intermediates and transition structures under those conditions than under ours.

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