JOURNAL OF CATALYSIS 68, 291–311 (1981)

Reactions of Methylpropene-2-^{13}C on H–Mordenite

I. Reaction Mechanisms

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Received July 31, 1979; revised May 15, 1980

The reactions of isobutene on a freshly prepared and outgassed H–mordenite have been investigated at 120 and 170°C. Initially most of the reactant is retained on the surface and the gaseous products are mainly isopentane and isopentenes. Increasing reaction temperature increases the amounts of saturated hydrocarbons. After aging the catalyst, a stationary regime is reached where the formation of the hydrocarbon residues is no longer apparent. The products, mostly olefinic, include C_8 hydrocarbons with trimethylpentane or dimethylhexane structure and C_5–C_7 hydrocarbons, mostly with dimentylbutane and dimethylpentane skeletons. The use of methylpropene-2-^{13}C demonstrates the existence of two types of products. Trimethylpentenes and 2,5-dimethylhexenes are doubly labeled on carbons 2 and 4 or carbons 2 and 5, respectively. In the other gaseous products $C_{n+4}H_{2n+8}$ ($2 \leq n \leq 4$: 2,4-dimethylhexenes, 2,3-dimethylbutenes, 2,4-dimethylpentenes), four carbon atoms retain the structure and the label of the reacting isobutene while the n additional carbon atoms are randomly labeled, with an overall ^{13}C content of $n/4$. The specific labeling of these compounds is best explained by the complete randomization of all the carbon atoms in isobutene via transient formation of a cyclopropylcarbinyl–cyclobutyl cation. Addition of the resulting scrambled C_4 unit as α-methylallylic cation to isobutene yields partially scrambled 2,4-dimethylhexene-$^{13}C_2$. Attachment of the C_4 scrambled unit as a homoallylic cation or α-methylallylic cation to the zeolite framework provides an adsorbed intermediate species which yields, after protonation, olefin addition, possibly hydride and methyl shifts, and β-fission the expected C_5–C_7 hydrocarbons. It is suggested that two types of sites are involved in the reactions of isobutene on aged mordenite at 120°C. Weak Brønsted acid sites account for the formation of trimethylpentenes. Strong acid sites, resulting most probably from the conjunction of Brønsted and Lewis sites, are responsible for the generation of allylic cations by hydride abstraction, yielding the dimethylhexenes and the C_5–C_7 olefins.

INTRODUCTION

On account of the wide variety of active sites existing on the surface of a solid acidic catalyst, the mechanisms of skeletal rearrangement of olefins is still a matter of controversy. By using a ^{13}C-tracer technique, the behaviour of a typical Brønsted acidic catalyst, supported *para*-toluenesulfonic acid, has been investigated (*1*). The aim of the present work is to study the reaction mechanisms of olefins on a more complex acidic catalyst. Decationated H–mordenite has been chosen for this study since both Brønsted and Lewis sites coexist on the surface (*2*).

At low temperature, double-bond migration and polymerization are the two main reactions of olefins on decationated or rare-earth exchanged zeolites (*3, 4*). When temperature is increased, rearranged gaseous products, including alkanes and aromatics are obtained (*4*). These reaction products, except aromatics, are the same as the ones obtained on silica–alumina and could be accounted for by a sequence of polymerization, isomerization, cracking, and hydrogen transfer (*5*).

However, a recent investigation of but-1-ene-4-^{13}C reactions on HY zeolite showed that the reaction mechanisms were proba-

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0021-9517/81/040291-21$02.00/0

bly more complex (*6*). At 200°C, the main products, isobutane and isopentane, are enriched in carbon-13 relative to the starting material, indicating that part of the internal carbon atoms are left on the surface. Moreover, the rearrangements which occur lead only to a partial scrambling of the label, very far from a complete randomization, which could not be thoroughly investigated.

This complex behaviour of olefins is very different from that of saturated hydrocarbons: when exposing *n*-pentane-3-^{13}C (*7a*) or ^{13}C-labeled methylpentanes (*7b*) to H-zeolites, unimolecular rearrangements account for the isomerized molecules, while complete randomization of the carbon atoms is observed for the cracked products.

In this work, methylpropene-2-^{13}C has been used to investigate further the catalytic reactions of olefins on zeolites. The choice of this molecule was determined by symmetry considerations: double-bond shift does not change the position of the label, which should reduce the number of possible dimers and simplify the structure of the polymeric species and hence of the reaction products.

EXPERIMENTAL

Materials. 2-Methyl-2-propanol-2-^{13}C was prepared by Grignard synthesis from methylmagnesium iodide and propanone-2-^{13}C. The latter compound, obtained from Merck, Sharp & Dohme had an isotopic purity of ca. 90%. Catalytic dehydration of the labeled alcohol yielded methylpropene-2-^{13}C without any label scrambling (*8*).

The H–mordenite used in this study was obtained from Norton (zeolon–H) and had the following composition:

$Al_2O_3 = 9.1\%$; $SiO_2 = 74\%$;
$Na_2O = 0.3\%$; $NH_4 < 0.1\%$;
$H_2O = 16.5\%$; $SiO_2/Al_2O_3 = 8.1$.

It was activated at 550°C in a stream of dry air for 2 h and then stored at room temperature.

Apparatus and procedure. The catalytic reactions were carried out in an all-glass grease-free flow apparatus. Reactant was introduced at constant pressure (5 Torr) in a flow of purified hydrogen (1 atm, 40 ml/min) in the reactor where the catalytic bed (100 mg), isothermal, operated under differential conditions. Before each run, the catalyst was outgassed for 2 hr in hydrogen at the reaction temperature (120 or 170°C). Two calibrated katharometers were inserted in the flow line before and after the reactor in order to estimate the amounts of materials left on the catalyst.

Analysis. A complete glc analysis of the reaction mixture could be achieved by using two columns: DC 200 (15% on fire brick—$\frac{1}{8}$ in.—5 m long) at −17 to 20°C and SE 30 (15% on firebrick—$\frac{3}{16}$ in.—5 m long) at 20–40°C.

In the case of ^{13}C experiments, the major part of the reaction mixture was hydrogenated directly in the flow line on platinum black at 60°C and separated into three fractions by chromatography on a $\frac{1}{4}$-in., 5-m-long 15% SE 30 column at room temperature. These fractions included isobutane, isopentane and all the C_6–C_8 products.

All mass spectra were recorded on a Varian-Mat CH7 apparatus using 70-V electrons to ionize the molecules. Mass spectra of isobutane and isopentane were obtained by using the direct inlet system and a high resolution (ca. 3000) to resolve the multiplets at masses $m/e = 44, 28$, etc. The heavier molecules were analysed using the glc–ms coupling device, with a 5-m, $\frac{1}{8}$-in. DC 200 chromatographic column at −17–20°C and the same other operating conditions as already described (*9*).

The glc–ms coupling was also used in the case of ^{12}C experiments to resolve by deconvolution chromatographic peaks including several isomers: 2,3-dimethylpentane, 2-methylhexane; 2,2,3-trimethylpentane, 2,5-dimethylhexane, and 2,4-dimethylhexane. For the latter mixture, ions at masses $m/e = 99, 85, 71$ were used and the result is shown in Fig. 1.

Treatment of the mass spectra. The re-

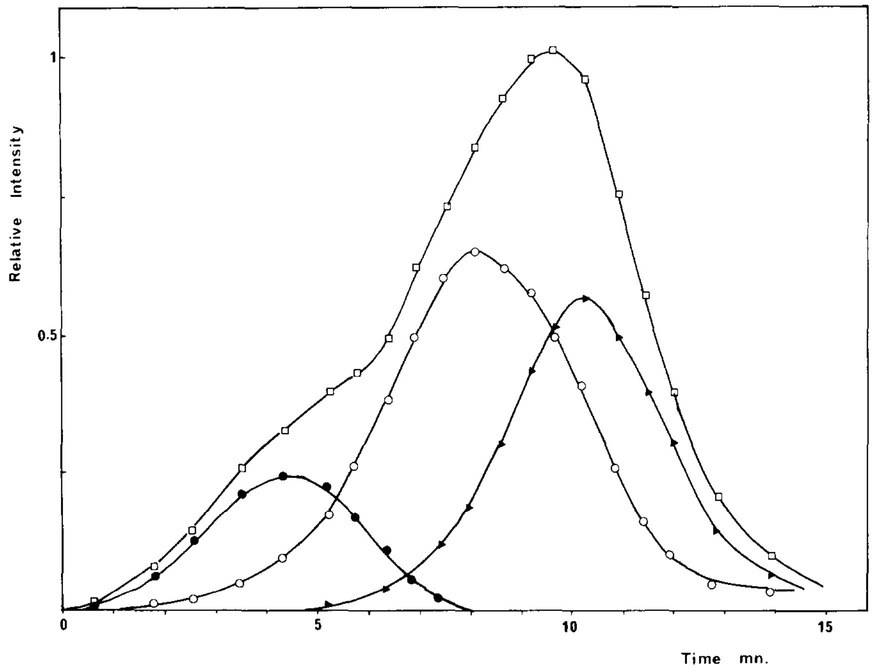


FIG. 1. Deconvolution of a chromatographic peak including: ●, 2,2,3-trimethylpentane; ▶, 2,4-dimethylhexane; ○, 2,5-dimethylhexane; □, total ionic current.

corded mass spectra were corrected for naturally occurring isotopes and C–H fragmentation in order to obtain the percentages of the various parent ions $^{13}C_a{}^{12}C_{n-a}H^{\oplus}_{2n+2}$ and main fragments $^{13}C_a{}^{12}C_{m-a}H^{\oplus}_{2m+1}$. For the C–H fragmentation corrections, isotopic effects in breaking C–C and C–H bonds were neglected and it was assumed that the $C_mH^{\oplus}_{2m}$ (−H) and $C_mH^{\oplus}_{2m-1}$ (−2H) ions had the same chance of losing a label as the main fragment ion $C_mH^{\oplus}_{2m+1}$—i.e., they were formed by the same mechanism. This assumption was checked by examining carefully the complete spectrum of many selectively labeled acyclic hydrocarbons (*10*). The error introduced was less than 5%, provided the dehydrogenated fragments $C_mH^{\oplus}_{2m}$, $C_mH^{\oplus}_{2m-1}$ were less than 50% of the main fragment ion $C_mH^{\oplus}_{2m+1}$.

Fragmentation patterns. Several reaction mechanisms will be assumed, under Results, resulting in a particular labeling of the reaction products. The labeling of the various fragments can then be calculated by using the fragmentation patterns of these molecules in the source of the mass spectrometer. Complete fragmentation patterns may only be obtained if one knows the mass spectrum of each isotopic species. This is the case for pentanes, hexanes (*8, 11*), and isobutane (this work). The mechanism of demethylation and deethylation under electron impact of methylpentanes, 2,3-dimethylbutane, isopentane, and isobutane are represented in Table 1. They correspond roughly to the rupture at the most highly branched carbon atom. This rule was thus extended to all the molecules, dimethylhexanes, dimethylpentanes, and trimethylpentanes, for which the fragmentation pattern was not accurately determined. The error introduced is certainly less than 5% and may be considered as negligible for the gemdisubstituted alkanes.

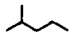
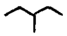
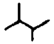
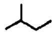
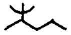
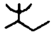
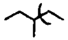
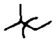
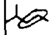
RESULTS

Catalyzed Reactions of Methylpropene

Several processes occur when isobutene

TABLE 1

Fragmentation of Alkanes

Molecule							C_7 - C_8 hydrocarbons
Demethylated ions	major fragm.	 100 %	 85 %	 100 %	 95 %	 100 %	
	minor fragm.		 15 %		 5 %		
Deethylated or depropylated ions	major fragm.	 88.5 %	 97 %	 91 %			
	rearranged ion	 3.5 %  5 %  5 %	 3 %	 5 %  4 %			

reacts on a freshly prepared and outgassed H-mordenite. Part of the molecule is retained on the surface to form strongly adsorbed residues, and part appears in the gas phase as C_4–C_8 hydrocarbons. The complexity of the gaseous reaction products has already been noted by Lapidus *et al.* on A, X, and Y zeolites (*12*).

Formation of strongly adsorbed residues. The hydrocarbon weight fractions at the entrance $p_i n_i$ and exit $\Sigma p_f n_f$ (where p and n are the partial pressure and the carbon number of the molecules, respectively) of the catalytic bed are recorded versus time by using two calibrated katharometers (Figs. 2a, 3a). The area between the two curves $p_i n_i(t)$ and $\Sigma p_f n_f(t)$ allows one to estimate the amounts of isobutene retained on the surface as hydrocarbonaceous residues. These amounts increase with the reaction temperature T_r (0.27 and 0.68 mmol/g of catalyst at 120 and 170°C, respectively) and do not depend upon the outgassing temperature T_d, provided T_d is less than 250°C.

Gaseous products. Analyses of the gaseous products after hydrogenation were made at various stages of aging, as represented by arrows in Figs. 2a and 3a. The product distributions obtained in two experiments at 120 and 170°C are reported in Tables 2 and 3. The total amounts of C_8 and C_5–C_7 hydrocarbons appearing in the gas phase are represented in Figs. 2b and 3b.

The product distribution changes continuously when increasing the amounts of retained materials (aging or deactivation). When a stationary state is achieved, where the hydrocarbon weight fractions are the same at the entrance and the exit of the catalyst bed ($p_i n_i = \Sigma p_f n_f$), the product distribution remains mostly unchanged and depends only upon the reaction temperature.

At 120°C, no C_1–C_3 hydrocarbons are formed and isomerization to *n*-butene does not take place. Initially, the major reaction products have the structure of isopentane and 2,3-dimethylbutane. After aging, the C_8 hydrocarbons become predominant. Be-

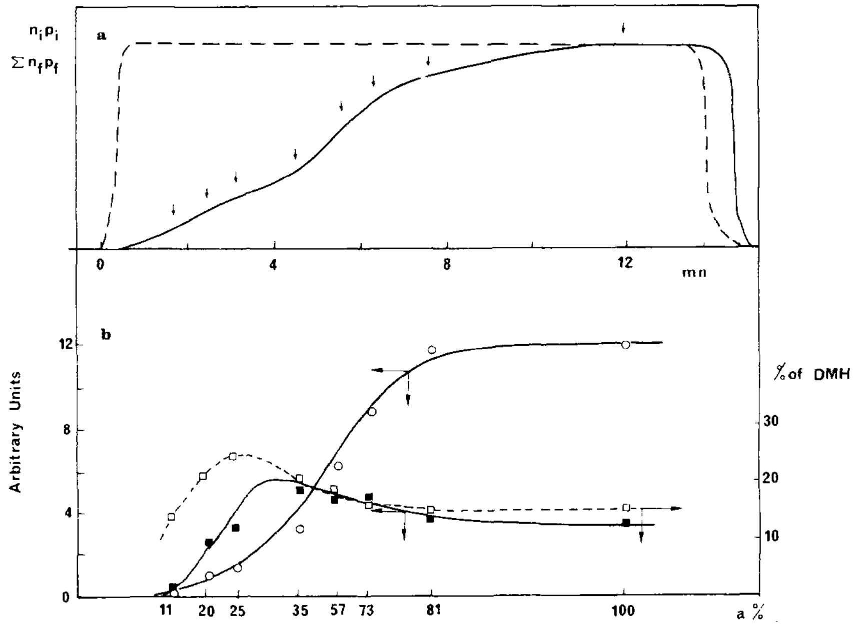


FIG. 2. (a) Adsorption of isobutene on H-mordenite at 120°C, (– – –) $p_i n_i$; (——) $\Sigma p_f n_f$. (b) Amounts of gaseous products (arbitrary units) after hydrogenation, ○, octanes; ■, C_5–C_7 hydrocarbons; □, percentage of dimethylhexanes (DMH) among the total octanes.

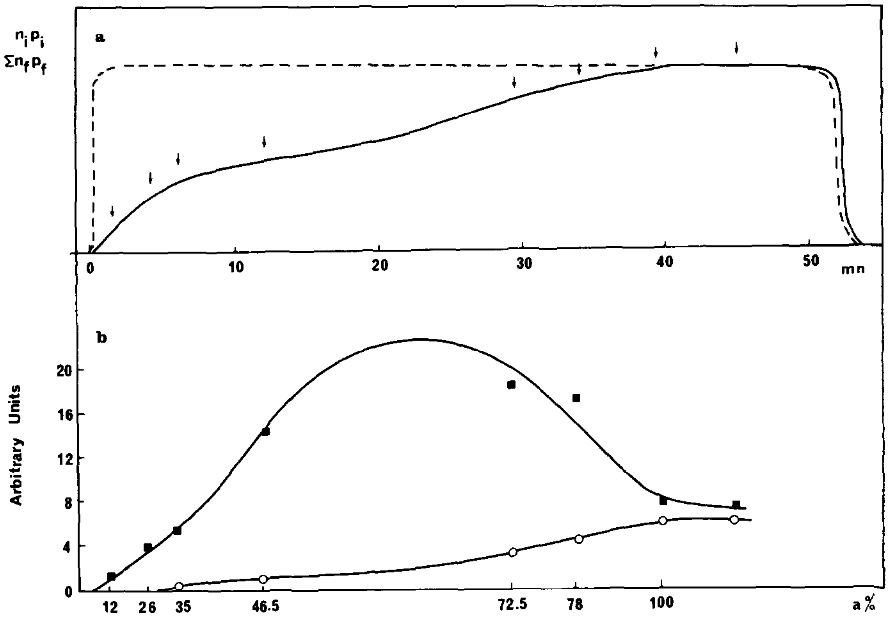


FIG. 3. (a) Adsorption of isobutene on H-mordenite at 170°C, (– – –) $p_i n_i$; (——) $\Sigma p_f n_f$. (b) Amounts of gaseous products (arbitrary units) after hydrogenation; ○, octanes; ■, C_5–C_7 hydrocarbons.

TABLE 2

Reaction of Isobutene on H-Mordenite at 120°C; Structure of the reaction products

Time (min):	1.50	2.50	3.25	4.50	5.50	6.50	8.0	13.0	17.0
Gaseous products (%)[a]:	11	20	25	35	57	73	81	100	100
Hydrocarbonaceous residues (%)[b]:	24	38.5	52	70	82	87.5	93	100	100
C_3	1.5	—	—	—	—	—	—	—	—
i-C_5	59	40.8	35.3	27.1	17.8	19.6	9.6	9.6	8.9
C_6	23.3	22.1	28.1	24.9	20.2	13.1	9.1	8.7*	7.6
C_7	3.3	6.5	7.6	7.2	6.3	4.5	3.8	3.1**	2.9
2,2,4-TMP	5.6	10.6	8.5	15.2	20.2	25	28	29	31
2,2-DMH	—	0.4	0.4	0.4	0.7	0.5	—	0.7	0.5
2,5-DMH, 2,4-DMH, 2,2,3-TMP	1.7	6.3	6.9	7.5	9.6	10.1	11.7	12.6***	12.8
2,3,4-TMP	5.1	13.1	12.6	16.8	24	26.5	37.6	33.7	34.5
2-M-3-EtP, 2,3,3-TMP, 2,3-DMH	—	—	0.3	0.7	1.1	0.7	0.2	2.5	1.8
Total conversion (%)	5.7	22.7	18.5	23.9	20	21	20.1	16	14
C_8 (%)	12.4	30.4	28.7	40.6	55.4	62.8	77.5	78.5	80.6

Note. (*) 2,3-DMB, 82.7%; 2-MP, 9%; 3-MP, 8%; (**) 2,4-DMP, 42%; 2,3-DMP, 29%; 2-MH, 22.5%; 3-MH, 6.5%; (***) 2,2,3-TMP, 15%; 2,5-DMH, 49%; 2,4-DMH, 36%. DMB = dimethylbutanes, DMP = dimethylpentanes, TMP = trimethylpentanes, MEtP = methylethylpentane, MP = methylpentanes, MH = methylhexanes, DMH = dimethylhexanes.

[a] Percentage of isobutene which has not been retained on the zeolite. $a = p_f/p_i \times 100$.

[b] Percentage of zeolite saturation (ratio between the amounts of hydrocarbonaceous residues at time t and after complete saturation).

TABLE 3

Reaction of Isobutene on H-Mordenite at 170°C; Structure of the reaction products

Time (min):	2	4	6	12	30	34	38	45
Gaseous products (%)[a]:	12	26	35	46.5	72.5	78	100	100
Hydrocarbonaceous residues (%)[b]:	8.2	18.2	27	48.7	93.4	98	100	100
C_3	8.3	4.2	4.7	6.7	2.4	2.6	1.5	1.2
n-C_4	12.4	27.1	15.2	11.4	8.1	10.3	6.7	6.6
i-C_5	74.2	55.8	65	44.5	36.7	37.3	21.3	21
n-C_5	0.5	1.6	3.9	2.1	2.7	2.2	1.4	1.2
C_6	4.1	10.9	9.5	21.7	22.3	19.6	17.5*	15.1
C_7	—	0.3	1.1	6.4	10.4	9.5	6.9	6.5
2,2,4-TMP	—	—	0.1	0.6	1.4	1.7	7.2	9.4
2,2-DMH	—	—	—	0.4	0.6	—	1.3	1.4
2,5-DMH; 2,4-DMH; 2,2,3-TMP	—	—	0.1	3	8.4**	8.7**	17.6***	18.1
2,3,4-TMP	—	—	0.1	0.6	2.4	2.6	16.1	17.5
2-M-3-EtP; 2,3,3-TMP; 2,3-DMH	—	—	—	2.1	4.5	5.1	2.3	2
Total conversion (%)	12.3	18	17	37.3	33.8	30.5	14.1	15
C_8 (%)	—	—	0.3	6.7	17.3	18.1	44.5	48.4

Note. (*) 2,3-DMB, 39.3%; 2-MP, 31.3%; 3-MP, 22.2%; n-H, 6.4%; (**) 2,2,3-TMP, 0.3%; 2,5-DMH, 46%; 2,4-DMH, 53.7%; (***) 2,2,3-TMP, 3.4%; 2,5-DMH, 44%; 2,4-DMH, 52.6%.

[a] See footnote a in Table 2.

[b] See footnote b in Table 2.

sides 2,2,4- and 2,3,4- trimethylpentanes, appreciable amounts of dimethylhexanes (mostly 2,5- and 2,4-) are obtained, the percentage of which among the octanes parallels closely the amounts of C_5–C_7 hydrocarbons (Fig. 2b).

More precise analyses of the C_4–C_6 olefinic and paraffinic hydrocarbons, obtained before and after having reached a stationary regime, have also been made and are reported in Table 4. In either case, the various olefin distributions are very close to equilibrium.

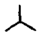
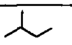
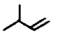
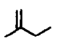
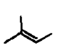
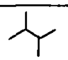
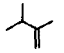
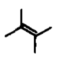
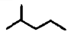
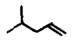
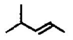
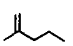
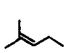
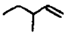
During aging, large amounts of saturated hydrocarbons are obtained, most probably related to the formation of highly dehydrogenated residues. After aging, saturated hydrocarbons are still present in the gas phase, but in much smaller amounts.

At 170°C, the same trends are observed for the variation with time of the product distributions (Tables 3 and 5). However, the percentages of saturated hydrocarbons in the early stage of the reaction are much higher than at 120°C, and so are the amounts of C_5–C_7 hydrocarbons. These always outpace the amounts of C_8 hydrocarbons and increase sharply with aging, going through a maximum. Dimethylhexenes are also favoured by an increase of temperature and represent 45% of the octenes in the final stage of the reaction. Lastly, one should also notice isomerization to $n - C_4$ hydrocarbons and the presence during aging of slight amounts of propane. In both experiments at 120 and 170°C, the maximum of C_5–C_7 hydrocarbons is related to a maximum of the total conversion in gaseous products, much more pronounced at higher temperature.

Complementary experiments. Since dimethylhexenes could have been formed by codimerization of n-butene and isobutene, a 60–40 mixture of these two molecules has been reacted on H-mordenite at 170°C. It is clear from Table 6 that the presence of n-butene in the reactant mixture did not change the distribution of the C_8 reaction mixture. The obtained distribution, exactly the same as the one obtained from isobu-

TABLE 4

Reaction of Isobutene on H-Mordenite at 120°C; Olefin-Paraffin Distributions in the C_4–C_6 Fractions

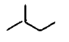
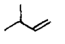
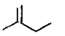
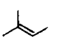
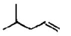
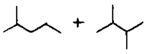
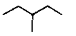
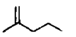
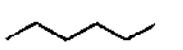
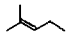
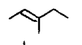
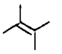
Gaseous products	a ranging from 0 to 100 %	a = 100 %
Hydrocarbonaceous residues	b ranging from 0 to 100 %	b = 100 %
	9.5	1.2
	90.5	98.8
	28	7
	0.4	0.9
	9.3	13.6
	62.2	78.3
	9.3	2.6
	17.3	20
	73.3	77.3
	20	8.4
	-	1.4
	2.1	4.5
	14.5	15.2
	63.4	70.3
	30	5.2
	-	-
	-	3.5
	70	91.2

tene, and the total conversion show that isobutene reacts much more rapidly than *n*-butene and that no codimerization takes place.

Contact reactions of isooctene and 2,5-dimethylhex-2-ene have also been effected at 170°C. Isooctene yields mostly isobutene by cracking (61.5%) and 2,3,4-trimethylpentenes by methyl shift (28.5%). The amounts of dimethylhexenes (5.5%) correspond closely to what could have been expected by readsorption and reaction of isobutene. Methyl shifts are the preeminent reactions of 2,5-dimethylhexenes, yielding 2,4-DMH (60%), 2,3- and 3,4-DMH (15%), and 2,2-DMH (2%). The remainder of the reaction products consists mostly of methylheptenes (10%) and C_2–C_7 hydrocarbons (13%). No linear C_4 hydrocarbons were detected in both experiments. The contact reactions of octenes show that dimethylhexenes and trimethylpentenes scarcely interconvert into each other and do not yield *n*-butene by cracking.

TABLE 5

Reaction of Isobutene on H-Mordenite at 170°C; Olefin–Paraffin Distributions in the C_4–C_6 Fractions

Gaseous products	a ranging from 0 to 43 %	a ranging from 43 to 100 %	a = 100 %
Hydrocarbonaceous residues	b ranging from 0 to 53 %	b ranging from 53 to 100 %	b = 100 %
	97	32	4
	3	68	96
	95.6	42	8.2
	-	0.6	1
	0.7	11.2	15.2
	3.6	46.2	75.5
	-	0.3	1
	64.7	38.8	33
	21.9	5.7	1
	-	2.4	5.9
	4.8	1.4	1.9
	3.9	19.2	25.4
	1	8.2	8.9
	3.6	24	23

From these complementary experiments we can therefore conclude that in the reaction of isobutene, dimethylhexenes cannot be formed by codimerization of *n*-butene and isobutene or by readsorption and further isomerization of trimethylpentenes.

Catalyzed Reactions of Methylpropene-2-^{13}C

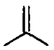
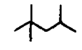
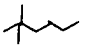
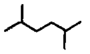
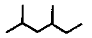
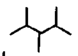
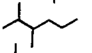
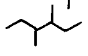
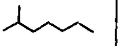
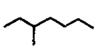
In order to investigate the mechanisms of formation of the various reaction products, experiments were effected with methylpropene-2-^{13}C at 120 and 170°C and at various stages of catalyst aging. The gaseous products in each fraction were collected, hydrogenated, separated by gas–liquid chromatography, and analysed for their isotopic content and the location of the label in the molecules. For the sake of simplicity, the only results presented here will be the ones concerning the labeling of the products obtained at 120°C on an aged (or deactivated) catalyst.

Octenes. Five octanes (2,2,4-trimethylpentane, 2,3,4-trimethylpentane, 2,2-dimethylhexane, 2,4-dimethylhexane, and 2,5-dimethylhexane) have been analysed for their isotopic content. While the three former molecules are completely separated by chromatography, the two latter are eluted together with 2,2,3-trimethylpentane in the same chromatographic peak. However, the major fragments for 2,4-DMH, 2,5-DMH, and 2,2,3-TMP appear at masses $m/e = 85,99$ and 57, respectively, and, for these characteristic ions, there are very small contributions of the two other molecules, making possible a complete ^{13}C analysis of each molecule.

The distributions of the $C_8H_{18}^{\oplus}$ ions of

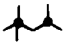
TABLE 6

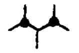
Codimerization of Isobutene and But-2-ene on H–Mordenite at 170°C; Comparison with Isobutene Dimerization; Distribution of the C_8 Hydrocarbons

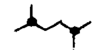
Reactant Skeleton of the products	 60 %  40 %	
	6.5	8.1
	2.8	3.5
 + 	49.5	48.2
	8.8	13.8
	8.6	9
 + 	15.9	11.6
	7.8	5.8
$^{\alpha}$Total /C_4	24 %	34 %
Total C_8 %	14.1	17.3

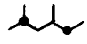
The analyses have been effected after 30 minutes of reaction (a = 70 %)

2,3,4-trimethylpentane, of the $C_7H_{15}^{\oplus}$ fragments of 2,2,4-trimethylpentane, 2,2-dimethylhexane, and 2,5-dimethylhexane and of the $C_6H_{13}^{\oplus}$ fragments of 2,4-dimethylhexane are reported in the first part of Table 7, together with the mass spectra of the labeled isobutenes collected at the same reaction time. This isobutene contains some amount of doubly labeled molecules due to prior rearrangement of the starting material which includes only light and monolabeled species. In the last columns of Table 7 are reported the expected distributions of the parent, demethylated, and deethylated fragment ions of the C_8 hydrocarbons, calculated by assuming a simple dimerization reaction of the isobutenes present in the reaction mixture in which only carbons-2 and -4 are labeled in trimethylpentanes and carbons-2 and -5 in dimethylhexanes.







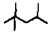
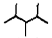
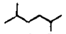
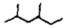
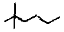


These distributions reproduce extremely well the $C_8H_{18}^{\oplus}$ pattern of 2,3,4-trimethylpentane and the $C_7H_{15}^{\oplus}$ patterns of 2,2,4-trimethylpentane and 2,5-dimethylhexane, which shows that in these molecules the labeling atom retains its location during the dimerization–isomerization process. On the contrary, the $C_7H_{15}^{\oplus}$ distribution of 2,2-dimethylhexane and the $C_6H_{13}^{\oplus}$ distribution of 2,4-dimethylhexane are substantially different from the ones expected, which shows that these molecules are obtained by a more complicated mechanism.

C_5–C_7 hydrocarbons. In the same experi-

TABLE 7

Labeling of Octenes

Reacting Hydrocarbons	 2,2,4-TMP	 2,3,4-TMP	 2,5-DMH	 2,4-DMH	 2,2-DMH	 2-MP	Simple Dimerization		Hypothesis 2
Ions	$C_7H_{15}^{\oplus}$	$C_8H_{18}^{\oplus}$	$C_7H_{15}^{\oplus}$	$C_6H_{13}^{\oplus}$	$C_7H_{15}^{\oplus}$	$C_4H_8^{\oplus}$	$C_8H_{18}^{\oplus}$ $C_7H_{15}^{\oplus}$	$C_6H_{13}^{\oplus}$	$C_6H_{13}^{\oplus}$
$^{13}C_3$	1.5	1.0	2.4	1.2	4.9	-	1.3	-	-
$^{13}C_2$	72.3	71.3	69.7	36.0	65.1	0.8	71.8	0.6	36.1
$^{13}C_1$	24.1	25.4	24.7	53.3	26.3	84.6	24.5	84.6	55.2
$^{13}C_0$	2.0	2.3	3.1	9.5	3.6	14.5	2.1	14.3	8.7
Δ	0.5	1.2	6.5	1730	63.2				(5.7)

$$\Delta \text{ (Mean square deviation)} = \sum_{i=0}^{i=3} \left({}^{13}C_{i\ \text{obs.}} - {}^{13}C_{i\ \text{calc.}} \right)^2$$

TABLE 8

Labeling of 2,3-Dimethylbutenes and 2,4-Dimethylpentenes

	2,4-Dimethylpentanes					2,3-Dimethylbutanes			
	Observed	Hypoth. 1	Hypoth. 2	Hypoth. 3 ($m = 2$)		Observed	Hypoth. 1	Hypoth. 2	Hypoth. 3 ($m = 2$)
		Parent ions $C_7H_{16}^{\oplus}$					Parent ions $C_6H_{14}^{\oplus}$		
$^{13}C_3$	1.6	0.8	—	6.6	$^{13}C_3$	1.9	0.5	—	2.2
$^{13}C_2$	52.4	54.3	54.2	42.2	$^{13}C_2$	34.8	39.1	36.1	32.1
$^{13}C_1$	38.5	39.4	40.4	44.6	$^{13}C_1$	54.5	49.3	55.2	56.7
$^{13}C_0$	7.5	5.2	5.4	6.6	$^{13}C_0$	8.7	10.8	8.6	9.0
Δ		11	11	170	Δ		50	5.6	12
^{13}C content	0.211	0.214	0.212	0.212	^{13}C content	0.216	0.215	0.213	0.212
		Depropylated fragments $C_4H_9^{\oplus}$					Demethylated fragments $C_5H_{11}^{\oplus}$		
					$^{13}C_3$	—	—	—	1.1
$^{13}C_2$	5.2	15.9	—	3.9	$^{13}C_2$	29.3	26.3	27.3	24.9
$^{13}C_1$	71.2	54.3	74.4	66.6	$^{13}C_1$	58.2	54.1	62.3	63.1
$^{13}C_0$	23.6	29.7	25.6	29.5	$^{13}C_0$	11.8	19.0	10.2	10.9
Δ		437	41	61	Δ		78	23.4	44.3
^{13}C content	0.204	0.215	0.186	0.186	^{13}C content	0.238	0.213	0.234	0.232

ment, the C_5–C_7 hydrocarbons have been hydrogenated and the mass spectra of the major products (2,4-dimethylpentane, 2,3-dimethylbutane, and 2-methylbutane) have been recorded. The distribution of the parent ions $C_nH_{2n+2}^{\oplus}$ and those of the more characteristic fragment ($C_4H_9^{\oplus}$ for 2,4-DMP, $C_5H_{11}^{\oplus}$ for 2,3-DMB, $C_4H_9^{\oplus}$ and $C_3H_7^{\oplus}$ for 2-MB) are tabulated in the first columns of Tables 8 and 9. These hydrocarbons contain mainly doubly, mono- and nonlabeled molecules and have the same ^{13}C content as the starting isobutene (21.6% per carbon atom).

In a first attempt to account for the observed distributions (*hypothesis 1*), it was assumed that the C_5, C_6, and C_7 hydrocarbons were obtained by removing three, two, or one carbon atom, respectively, randomly labeled or not labeled, from a dimer. Figure 4 shows as an example of how the distributions of the C_7 and C_6 parent or fragment ions may be derived from that of an octene dimer $^{13}C_2{}^{12}C_6H_{16}$. The distributions calculated in this way are tabulated in the second columns of Tables 8 and 9. The agreement between the observed and calculated distributions is excellent for the parent peaks of 2,4-DMP and 2-MB, satisfactory for the parent peaks of 2,3-DMB, but very bad for all fragment ions. The very high values of the mean square deviation Δ between the observed and calculated ^{13}C distributions show that a scheme involving the degradation of a completely scrambled dimer accounts for the *number* of carbon-13 atoms present in the molecules, but not for their *position*.

As shown in Tables 8 and 9, the label content of the demethylated fragments of 2,3-DMB and 2-MB is 15–20% higher than the label content of the parent ions, which shows that randomization of the label is not complete and does not spread over all methyl groups. On the other hand, the ^{13}C content of the depropylated $C_4H_9^{\oplus}$ fragments of 2,4-DMP is smaller than that of the parent ions which suggests that in 2,4-

TABLE 9

Labeling of Isopentenes

	Observed	Hypoth. 1	Hypoth. 2 (Mech. D)	Mech. D′ $\dot{C}-\dot{C}-\dot{C}+\dot{C}-\dot{C}$	Mech. D (30%) and Mech. D′ (70%)
		Parent ions $C_5H_{12}^{\oplus}$			
$^{13}C_3$	2.1	0.2	—	—	—
$^{13}C_2$	23.4	26.3	18.1	27.1	24.4
$^{13}C_1$	55.1	54.2	70	52.1	57.4
$^{13}C_0$	19.3	19.0	11.8	20.8	18.1
Δ		13	310	18	8
^{13}C content	0.216	0.215	0.213	0.213	0.213
		Demethylated fragment $C_4H_9^{\oplus}$			
$^{13}C_2$	21.6	15.9	18.1	21.7	20.6
$^{13}C_1$	55.8	54.3	70	47.1	54
$^{13}C_0$	21.8	29.7	11.8	31.2	25.4
Δ		115	314	164	17
^{13}C content	0.247	0.215	0.265	0.226	0.238
		Deethylated fragment $C_3H_7^{\oplus}$			
$^{13}C_2$	3.6	7.9	0.7	6.3	4.6
$^{13}C_1$	56.2	48.7	81.9	46.8	57.3
$^{13}C_0$	40.2	43.3	17.4	46.6	38
Δ		84	1185	137	7

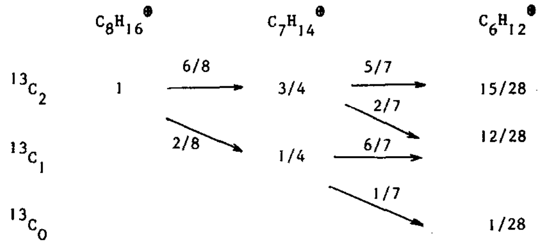


FIG. 4. Distributions of C_7 and C_6 parent or fragment ions derivable from octene dimer.

dimethylpentane one of the propyl groups or both retain more label than the remainder of the molecule.

Both results are consistent with a formal mechanism of formation of the C_5–C_7 hydrocarbons (*hypothesis 2*) adding to the methylpropene-2-^{13}C, mono- or nonlabeled groups of one, two, or three carbon atoms with the label randomly distributed and the same overall ^{13}C content as in the starting material.

Such a mechanism may be represented by the succession of three consecutive steps:

(1) complete scrambling of the four carbon atoms in a molecule of labeled isobutene;

(2) statistical removal of one, two, or three carbon atoms from the rearranged molecule to form a C_n unit;

(3) addition of the n carbon atoms of this unit on the same carbon atom of a second isobutene molecule to form $(CH_3)_2{}^{13}CH\ CH\ C^{\cdot}_x H_{2x+1} C^{\cdot}_y H_{2y+1}$, where $x + y = n$ and $C^{\cdot}$ represents a carbon atom of the scrambled C_n unit.

According to this mechanism, the following molecules represented in Table 10 would be formed from an isotopically pure monolabeled isobutene. The ^{13}C distributions of the various fragments may then be calculated easily if one assumes a simple fragmentation pattern in the source of the mass spectrometer. Since the starting material is not isotopically pure, but contains also some light isobutene, the distributions of the parent and fragment ions are not exactly the same as the ones presented in Table 10: simple calculations yield the distributions listed in the third columns of Tables 8 and 9.

For 2,4-DMP and 2,3-DMB the agreement between the observed and calculated distributions is good, much more satisfactory than when using hypothesis 1 of dimer degradation. In the case of isopentanes, however, none of the proposed mechanisms accounts for the observed distributions.

Since small but definite amounts of triply labeled 2,4-DMP and 2,3-DMB are formed, a more general mechanism (*hypothesis 3*) was derived and is given in the Appendix, assuming:

(1) formation of a polymer $(C_4H_8)_m$ and complete scrambling of the 4 m carbon atoms;

(2) statistical removal of one, two, or three carbon atoms, as in the previous mechanism, from the rearranged polymer to form C_n units; and

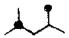
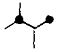
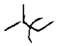
(3) addition of the n carbon atoms to a second molecule of labeled isobutene.

The distributions, calculated with $m = 2$, are reported in column 4 of Table 8. The calculated distributions do not fit the observed ones. The same is true of any combination of distributions using several values of m.

2,4-Dimethylhexenes and 2,3-dimethylpentenes. Since 2,4-dimethylhexenes are not formed by simple dimerization of isobutene or codimerization of isobutene and n-butene, an attempt was made to account for the distributions of the hexyl ions by assuming addition to a labeled isobutene of a

TABLE 10

^{13}C Distribution of the Fragment Ions According to Hypothesis 2

Molecules	 1/2	 1/4	 1/4	 1/2	 1/2	 1/4	 3/4	
Ions	$C_7H_{16}^{\oplus}$	$C_6H_{13}^{\oplus}$	$C_4H_9^{\oplus}$	$C_6H_{14}^{\oplus}$	$C_5H_{11}^{\oplus}$	$C_5H_{12}^{\oplus}$	$C_4H_9^{\oplus}$	$C_3H_7^{\oplus}$
Fragmentation pattern								
$^{13}C_2$	3/4	5/8	-	1/2	3/8	1/4	1/4	—
$^{13}C_1$	1/4	3/8	7/8	1/2	5/8	3/4	3/4	1
$^{13}C_0$	-	-	1/8	-	-	-	-	-
^{13}C content	0.25	0.27	0.22	0.25	0.275	0.25	0.31	0.33

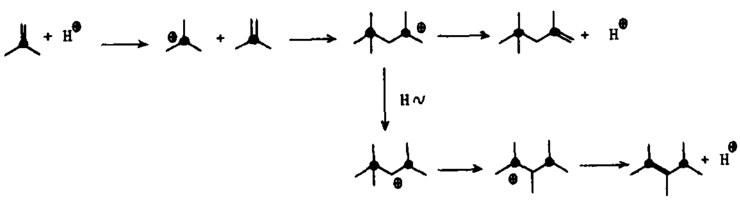
scrambled C_4 unit (hypothesis 2). The calculated distribution reported in the last column of Table 7 nicely fits the observed one.

Distribution of the parent ions of 2,3-dimethylpentenes, the second major C_7 reaction product, is better explained by combining equally two distributions, namely, one associated with a partial scrambling of the label according to hypothesis 2 and the other corresponding to a comlete randomization of all carbon atoms.

INTERPRETATION OF THE LABELING. REACTION MECHANISMS

Three types of reaction products are formed on a stabilized H–mordenite at 120°C:

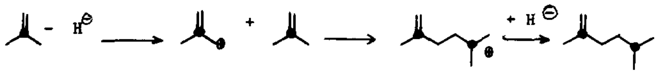
1. *Trimethylpentenes* result from the simple dimerization of isobutene, according to Markownikoff's rule, followed possibly by methyl shifts. The classical carbenium ion mechanism, involving protonation, addition of the *t*-butyl cation to isobutene, and deprotonation, accounts for their formation (*13*):



SCHEME 1. Mechanism A.

Note that according to Scheme 1, both carbon-13 atoms are retained in tertiary positions, which explains the labeling of the demethylated fragments.

2. *2,5-Dimethylhexenes* are also formed by dimerization, but the orientation of the molecules during addition is anti-Markownikoff. Dimerization is best represented then by the addition of an allylic cation to isobutene according to Scheme 2.

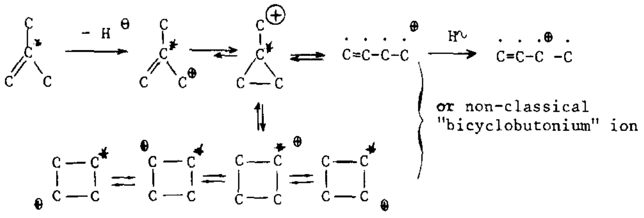


SCHEME 2. Mechanism B.

A similar mechanism has been proposed to explain the formation of dimethylhexanes in isobutane–isobutene alkylation (*14, 15*).

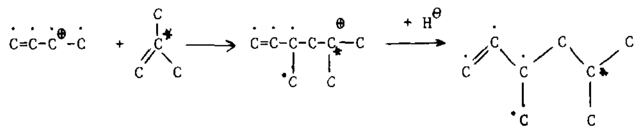
3. *2,4-Dimethylhexenes, 2,4-dimethylpentenes,* and *2,3-dimethylbutenes* are formed according to a complex mechanism involving two and *only two* molecules of reactant. This mechanism, differing from the polymerization–depolymerization mechanism proposed by Shephard *et al.* (*5*), Weeks and Bolton (*6*), and McIver *et al.* (*16*), consists formally of the addition to methylpropene-2-^{13}C of four, three, or two carbon atoms obtained from a completely rearranged monolabeled C_4 unit.

Mechanism of scrambling. Partial or complete randomization of three carbon atoms occurs in a C_4 unit when forming a cyclopropylcarbinyl cation (*17–19*). In order to achieve a complete scrambling of all four carbon atoms in a cyclopropylcarbinyl cation, hydride shifts are required occurring either by interconversion between classical cyclobutyl cations or via nonclassical side or corner protonated bicyclobutanes (*18*) (Scheme 3a).



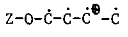
Scheme 3a. Mechanism of scrambling.

2,4-Dimethylhexene. We believe that on H-mordenite some of the β-methylallylic cations rearrange into the more stable cyclopropylcarbinyl cation (*20*), yielding completely rearranged C_4 units. Addition of one of these C_4 units as α-methylallylic cation to labeled isobutene would produce a 2,4-dimethylhexene molecule where one tertiary carbon atom is normally labeled ($\overset{*}{C}$ in Schemes 3a and b) while four carbon atoms, equivalent, retain one-fourth of the label ($\dot{C}$ in the schemes) (Scheme 3b).

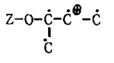


Scheme 3b. Formation of 2,4-dimethylhexene (mechanism C).

C_5–C_7 olefins. The same mechanism which accounts for the partially scrambled 2,4-dimethylhexenes could also explain the formation of the C_5–C_7 hydrocarbons, provided that, before addition to isobutene, the scrambled C_4 unit is incorporated in some way into the zeolitic framework, yielding carbenium-like species *A* and *B*

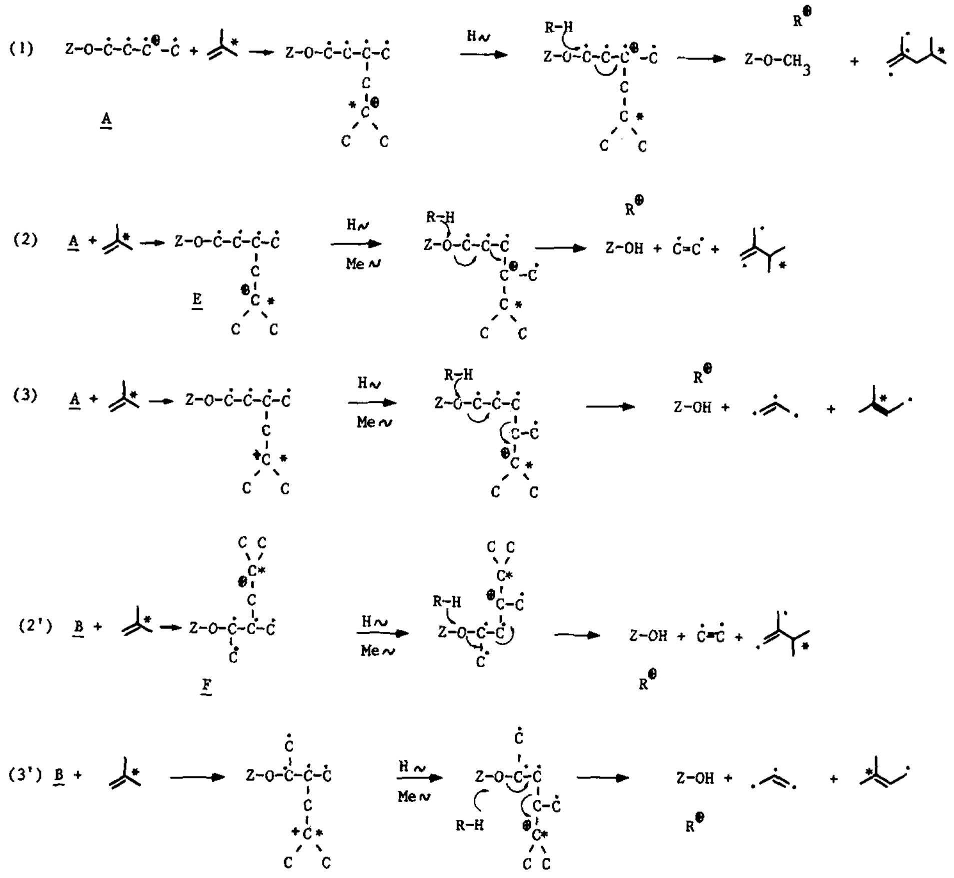

$Z{-}O{-}\dot{C}{-}\dot{C}{-}\dot{C}^{\oplus}{-}\dot{C}$

A

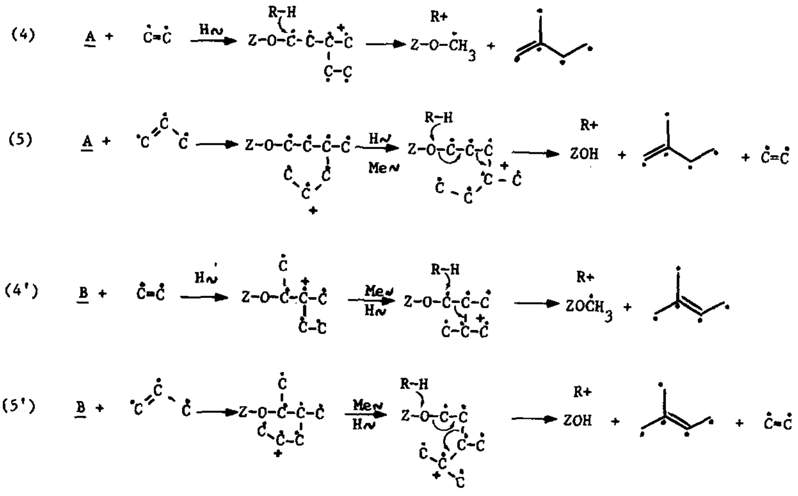

$Z{-}O{-}\underset{\underset{\displaystyle C}{|}}{C}{-}\dot{C}^{\oplus}{-}\dot{C}$

B

A second molecule of isobutene could then be added to cation *A* or *B*, yielding after hydride shift, possibly methyl shift, and β-fission, partially scrambled 2,4-dimethylpentenes, 2,3-dimethylbutenes, and isopentenes (Scheme 4). Following Scheme 4, ethylene and propylene should also be formed, retaining one-half or three-quarters of one label, respectively. These molecules, which do not appear in the gas phase, are immediately readsorbed on species *A* or *B* yielding heavier molecules (Scheme 5), or they polymerize on the surface. Isopentenes in reactions (4) and (5) are formed by adding C_3 and C_2 scrambled units (mechanism D′). The corresponding ^{13}C distribution is reported in column 4 of Table 8. Since the isopentene distributions could not be reproduced by mechanism D, an attempt of simulation was made by combining mechanisms D and D′. The agreement is excellent between the observed distribution and the calculated one when combining 30% D and 70% D′ (last column of Table 8). According to the proposed mechanism, olefins in reactions (1)–(5) would be obtained by a β-fission, which either regenerates a hydroxyl group (Z–OH), or leaves on the surface methoxy groups attached to the zeolitic framework (Z-O-CH_3). These groups would block the active sites and may therefore be responsible for the slight deactivation of the aged catalyst observed at 120°C (last two columns of Table 2).



SCHEME 4. Formation of C_5–C_7 olefins (mechanism D).



SCHEME 5. Formation of isopentene (mechanism D′).

DISCUSSION

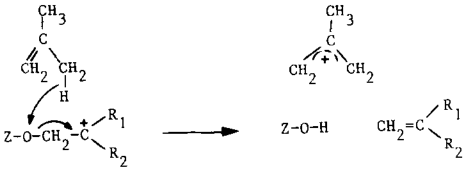
Reactions of Isobutene Considered as Chain Reactions

In a formal way, the formation of dimethylhexenes and C_5–C_7 hydrocarbons could be considered as a chain reaction represented in Scheme 6.

$$\begin{array}{llcll}
(6\text{-}1) & ZO^{\ominus} + C_4H_7^{\oplus} & \rightarrow & ZOC_4H_7 & (\underline{C} \text{ or } \underline{D}) \\
(6\text{-}2) & ZOH + ZOC_4H_7 & \rightarrow & ZO^{\ominus} + ZOC_4H_8^{\oplus} & (\underline{A} \text{ or } \underline{B}) \\
(6\text{-}3) & ZOC_4H_8^{\oplus} + C_4H_8 & \rightarrow & ZOC_8H_{16}^{\oplus} & (\underline{E} \text{ or } \underline{F}) \\
(6\text{-}4) & ZOC_8H_{16}^{\oplus} + C_4H_8 & \rightarrow & C_4H_7^{\oplus} + \left\{\begin{array}{l} C_2H_4 + C_6H_{12} \\ \text{or } C_8H_{16} \\ \text{or } C_3H_6 + C_5H_{10} \end{array}\right\} & + ZOH
\end{array}$$

SCHEME 6

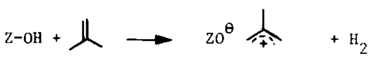
In order to achieve a catalytic cycle, the final step should be a concerted reaction where a new isobutene molecule is activated and olefinic products are formed (Scheme 7).



SCHEME 7

The initiation step in this chain, not represented in Scheme 6, is the formation of an allylic cation. This could be obtained in two different ways:

(a) By direct protonation of an allylic carbon–hydrogen bond in isobutene, resulting in the formation of molecular hydrogen

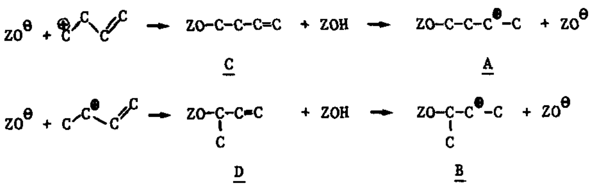


A similar protonic attack has been assumed by Minachev and co-workers to explain the hydrogen pressure dependence of the rate in the isomerization of saturated hydrocarbons (*21*).

(b) Via a tertiobutyl cation, according to a bimolecular process:

The latter scheme could account for some of the saturated hydrocarbons which always accompany the olefinic products.

In the two first propagation steps ((6-1) (6-2)), the $C_4H_7^{\ominus}$ unit, after scrambling, could add to the $ZO^{\ominus}$ counteranion as α-methylallylic or homoallylic cation. Formation of the active centers *A* or *B* would result then from the protonation of the resulting adsorbed olefins *C* or *D* (Scheme 8).



SCHEME 8

General Discussion

The existence of a hydrocarbon chain attached to the zeolitic framework has been invoked several times (*2, 6, 22*). In this work it receives good support from the mass spectrometric analysis of the hydrocarbon residues (*25*) left after reaction and dissolution of the zeolitic support, and also from the product distribution. It is very difficult to account by classical carbonium ion chemistry for C_5–C_7 olefins that retain partly the original label. A polymerization–depolymerization process would yield completely scrambled molecules, with a statistical distribution of ^{13}C and ^{12}C over all the carbon atoms of the molecules. That is the type of distribution which is indeed observed in the cracking products obtained from saturated hydrocarbons (*7, 23*). In the above discussion we did not define the nature, silicon or aluminum, of the atom to which the alkoxy groups are attached. Recent theoretical investigation suggests that in mordenite there is no preferential attachment of the proton to any particular framework oxygen (*24*). It is therefore very risky to define Z precisely.

That two types of products, differently labeled, are obtained on H–mordenite suggests the existence of two types of acidity. A very strong acidity, responsible for the generation of allylic cations by hydride abstraction, most probably results from the conjunction of Brønsted and Lewis sites (superacidity). This acidity explains the formation of dimethylhexenes and C_5–C_7 olefins, which run in parallel when changing reaction temperature and zeolite pretreatment. A weaker acidity is connected with the simple protonation of isobutene and formation of trimethylpentenes. This acidity is also involved during the production of dimethylhexenes and C_5–C_7 olefins, when forming an active positive center (*A*) from an adsorbed olefin (*C*).

In this paper we have only discussed the mechanism of formation of the C_5–C_8 hydrocarbons obtained at 120°C on a stabilized H–mordenite. The product distributions during the aging of the catalyst and at 170°C differ widely by the structure of the C_8 hydrocarbons (DMH rather than TMP) and the amounts of C_5–C_7 hydrocarbons. Moreover, the presence of saturated hydrocarbons during the first stages of the reaction at 120 and 170°C should also be emphasized. It is therefore quite likely that some other mechanisms take place under these conditions. A careful analysis of the reaction products obtained from labeled isobutene at 170°C and when aging the catalysts seems highly desirable and will be presented in Part II (*25*).

APPENDIX

Suppose that m molecules of isotopically pure methylpropene-2-^{13}C polymerize with complete scrambling of the 4 m carbon atoms. The probability of removing randomly p ^{13}C and q ^{12}C atoms to form a particular C_n configuration is

$$\mathcal{P}_n{}^p = \mathrm{C}_n{}^q \frac{m(m-1)\ .\ .\ .\ (m-p+1)\ 3m(3m-1)\ .\ .\ .\ (3m-q+1)}{4m(4m-1)\ .\ .\ .\ (4m-p-q+1)}$$

$$= \mathrm{C}_n{}^p \frac{m!}{(m-p)!} \frac{3m!}{(3m-q)!} \frac{(4m-n)!}{4m!}, \qquad (1)$$

with $n = p + q < 4m$ and $p < m$.

By adding all the possible C_n configurations to a second molecule of isobutene, a set of molecules $(\mathrm{CH}_2)_{n+4}$ is obtained, with a ^{13}C distribution defined by the relationship

$$^{13}\mathrm{C}_j = \mathcal{P}_n^{j-1}. \qquad (2)$$

This distribution extends from $j = n - 3m + 1$ to $j = m + 1$ when $3m < n < 4m$, from $j = 1$ to $j = m + 1$ when $m < n < 3m$, and from $j = 1$ to $j = n + 1$ when $n < m$.

Suppose now that only a fraction a of the reacting isobutene is labeled. The probability of selecting p ^{13}C atoms and q ^{12}C atoms from the polymer is then

$$Q_n{}^p = \mathcal{P}_n{}^p a^p + \mathcal{P}_n^{p+1}\mathrm{C}^1_{p+1}a^p(1-a) + \mathcal{P}_n^{p+2}\mathrm{C}^2_{p+2}a^p(1-a) + \cdots \qquad (3)$$

and the ^{13}C distribution of the $(\mathrm{CH}_2)_{n+4}$ products is

$$^{13}\mathrm{C}_j = (1-a)Q_n{}^j + a\ Q_n^{j-1} \qquad (4)$$

The number of terms in Eq. (3) equals $n - p + 1$ if $n < m$ and $m - p + 1$ if $n > m$. The carbon-13 distribution of the product extends from $^{13}\mathrm{C}_0$ to $^{13}\mathrm{C}_{n+1}$ if $n < m$, and from $^{13}\mathrm{C}_0$ to $^{13}\mathrm{C}_{m+1}$ if $n > m$.

Note that Eqs. (1) to (4), with $m = 1$, account also for the distributions of products obtained according to hypothesis 2.

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