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

II. Influence of Aging and Reaction Temperature

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Catalyzed reactions of methylpropene-2-^{13}C on H–mordenite have been carried out at 50, 120, 170 (before and after catalyst aging), and 400°C. At low temperature (50°C) no hydrocarbon residues are formed, and simple protonation takes place leading to trimethylpentenes. At 120°C during aging, and at 170°C the carbon-13 distribution shows that the gaseous C_5–C_7 products are deeply rearranged. The distributions cannot be accounted for by the same mechanism of partial scrambling—i.e., addition of scrambled monolabeled C_1, C_2, and C_3 units to an isobutene molecule (mechanism D)—observed on aged mordenite at 120°C (Part I) and are best explained by combining linearly a distribution associated with mechanism D and a distribution involving complete redistribution of all carbon atoms (statistical). At 400°C isobutene yields saturated hydrocarbons and aromatics, all of which have a statistical distribution of the carbon-13. These results and the mass spectrometric analysis of the hydrocarbon residues allowed us to propose the following sequence of reactions. At 120°C, during aging, and at 170°C polymeric cations attached to the zeolite framework are deactivated by β-fission producing carbenium ions and adsorbed olefin radicals. These radicals may then act as hydride and proton donors leading to saturated hydrocarbons and adsorbed alkadiene radicals. Such adsorbed olefinic and dienic radicals, which represent the strongly adsorbed residues left on the zeolite at 120 and 170°C, yield at 400°C paraffins by hydride transfer and triene precursors of the aromatics by β-fission. In this reaction scheme, the formation of deeply rearranged hydrocarbons is explained by successive adsorption–desorption steps of the primary olefins and cations.

INTRODUCTION

In the reaction at 120°C of methylpropene-2-^{13}C on an aged zeolite, some of the reaction products were partially scrambled. The C_5–C_7 products contained an isobutyl radical labeled like the reactant and additional carbon atoms resulting from a completely scrambled monolabeled C_4 unit. To explain the formation of such hydrocarbons, we suggested in Part I (*1*) that the intermediate species were short hydrocarbon chains, four to eight carbon atoms long, positively charged, and attached to the zeolite framework.

On the other hand, a study of the catalyzed reactions of isobutene on H–mordenite at various temperatures showed that the product distributions depended upon experimental conditions. Different distributions were obtained during the aging of the catalyst—when hydrocarbon residues were deposited on the surface—and on stabilized mordenites.

In this paper we present the carbon-13 distributions of the molecules obtained at 170 and 400°C from methylpropene-2-^{13}C on a stabilized H–mordenite and also those obtained during the deposition of hydrocarbon residues at 120 and 170°C. To interpret the results we assume three proposals made in earlier publications:

(1) hydrocarbon residues may be considered to be the result of a cationic polymerization (*2*);

(2) these residues are hydrogen-deficient species, and their formation is linked to the appearance of saturated hydrocarbons (*3*);

(3) during the formation of the gaseous products at 200°C, the organic moiety is

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[1] Deceased, August 4, 1979.

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bound in some way to the zeolite framework, and carbon atoms are left on the surface (*4*).

EXPERIMENTAL

The apparatus, the experimental and analytical procedures, and the methods for calculating the ^{13}C distributions have been described in Part I (*1*). In an experiment made at 120°C, the hydrocarbon residues were separated by dissolving an aged mordenite in 42% hydrofluoric acid and extracting the organic material with chloroform. The mass spectrum of these residues was recorded on an LKB 9000 S mass spectrometer. In other experiment, a mordenite aged at 120°C was heated at 280°C in the source of a Thomson THN 208 mass spectrometer and the desorbed materials were analysed directly.

RESULTS AND INTERPRETATIONS

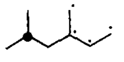
1. Reactions of Methylpropene-2-^{13}C at 170°C

The gaseous products formed at various stages of aging were condensed, hydrogenated, separated by gas–liquid chromatography (glc) and analysed for their ^{13}C content. Three fractions were collected: the first was obtained during the first 15 min, when the major part of the hydrocarbon material (85%) was deposited on the zeolite; the second was obtained during the following 25 min, just before the catalyst became completely saturated by the polymers, and the third was collected after the stationary regime had been reached, i.e., when the hydrocarbon pressure was the same at the entrance to and the exit from the catalytic bed.

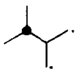
Isobutenes (and isobutanes). The isobutanes obtained after hydrogenation and glc separation of fractions II and III were analysed by mass spectrometry. The distributions of the parent ions are reported in Table 1. Appreciable amounts of doubly and triply labeled molecules were formed, in amounts that decreased from fraction II to fraction III, which shows that a deep rearrangement of the reacting hydrocarbon took place.

Octenes (and octanes). In Table 1 are reported the distributions of the demethylated fragment ions $C_7H_{15}^{\oplus}$ of trimethyl-2,2,4-pentanes and dimethyl-2,5-hexanes, and the distributions of the parent ions of trimethyl-2,3,4-pentanes, all of which were obtained after hydrogenation of fractions II and III. These distributions are very close to the ones calculated by assuming simple dimerization of the isobutenes present in the reaction mixtures. As in the case of the experiments made at 120°C on an aged mordenite (*1*), the agreement between the observed and the calculated distributions for both the $C_7H_{15}^{\oplus}$ and $C_8H_{18}^{\oplus}$ ions is good, demonstrating clearly the occurrence of a simple dimerization process that retains the original location of the label in isobutene.

In contrast, the deethylated fragment of 2,4-dimethylhexane cannot be accounted for by simple dimerization. Again, as in the case of the experiments made at 120°C, the ^{13}C distribution of the $C_6H_{13}^{\oplus}$ ions was the same as that expected according to mechanism C in which half of the molecule retains the original label of isobutene and half is a completely scrambled (^{13}C–^{12}C$_3$) unit.



Mechanism C

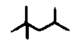
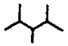
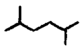
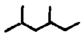


Mechanism D

2,3-Dimethylbutenes (and butanes). The 2,3-dimethylbutenes (and butanes) (2,3-DMB) present in all three fractions were analysed after hydrogenation of the reaction mixtures. The distributions of the $C_6H_{14}^{\oplus}$ and $C_5H_{11}^{\oplus}$ ions are reported in Table 2. Triply and quadruply labeled species are obtained, especially in the first fraction. They are not accounted for by the same mechanism of partial scrambling, mechanism D, that accounts for the distributions of 2,3-dimethylbutenes in the experiments made at 120°C (*1*). On the other hand,

TABLE 1

Reactions of Isobutene at 170°C; Distributions of the Octenes and of Isobutene

	octenes					calculated [1]		Mechanism C	 observed
	ions	$C_7H_{15}^{\oplus}$	$C_8H_{18}^{\oplus}$	$C_7H_{15}^{\oplus}$	$C_6H_{13}^{\oplus}$	$C_7H_{15}^{\oplus}$	$C_8H_{18}^{\oplus}$	$C_6H_{13}^{\oplus}$	$C_4H_{10}^{\oplus}$
	$\%^2$	2	4.8	6.6	7.5				
FRACTION II	$^{13}C_4$	1.3	2.6	1.6	0.4	0.7		0.4	-
	$^{13}C_3$	9.1	10.6	11	5.7	9.8		4.5	0.5
	ions % $^{13}C_2$	55.2	52.5	49.7	34.1	53.4		32.9	6.7
	$^{13}C_1$	29.6	28.3	31	47.6	30.8		49.9	71.3
	$^{13}C_0$	4.8	5.9	6.7	12.2	4.3		12.3	21.3
(M S D) △		5.5	12.7	20	8.4				
	$\%^2$	8.5	17.9	8.4	10				
FRACTION III	$^{13}C_4$	0.5	0.6	0.9	0.1	0.4		0.1	-
	ions % $^{13}C_3$	6.5	7.9	8.5	4.4	6.7		3	0.3
	$^{13}C_2$	62.4	62.3	57.5	35.8	61.2		34.6	4.3
	$^{13}C_1$	27	25.4	28.1	49.2	28.1		51.9	77.2
	$^{13}C_0$	3.6	3.6	5	10.4	3.3		10.4	18.2
(M S D) △		2.8	10	20	10.7				

[1] Calculated by assuming simple dimerization of the isobutene products.

[2] Percentage in the gaseous products.

distribution E, assuming a complete redistribution of all ^{13}C and ^{12}C atoms in 2,3-DMB, is also very different from the observed distribution, in spite of the presence of highly labeled species.

An attempt was made then to reproduce the observed distributions by combining linearly distributions D and E (reported in columns 2 and 3 of Table 2). The low values found for the mean square deviations (MSD) between the observed and the calculated distributions show the validity of such a treatment, whose physical meaning will be discussed later on. The contribution of the statistical mechanism E decreased steadily from 65% in fraction I at the beginning of aging to 30% in fraction III on a saturated mordenite.

C_4–C_7 products. Similar computations combining mechanisms D and E were made to account for the ^{13}C distributions in the hydrocarbons which have the same carbon skeleton as isopentane, 3-methylhexane, and 2,4-dimethylpentane (Table 3). The contribution of mechanism E, involving complete redistributions of all the carbon atoms, decreased during aging as in the case of 2,3-DMB. However, the scrambling of the label seemed more pronounced in the C_7 hydrocarbons which appeared as minor reaction products than in isopentanes and 2,3-DMB.

In the case of *n*-butane, the distributions of the isotopic varieties obtained in each fraction were very close to random. They may be accounted for by a combination of mechanism E (85–90%) with a true isomerization process producing *n*-butane-2-^{13}C and light *n*-butane (15–10%). Lastly, the isobutane distributions are best reproduced if it is assumed that a large fraction of these molecules are completely scrambled, namely, 80% during the first stages of aging and 20% on the stabilized zeolite.

Paraffins and olefins. Since a large fraction of the C_5–C_7 products appeared as saturated hydrocarbons, especially during the first stages of the reaction, some characteristic paraffins and olefins obtained during the aging of the zeolite were separated, and the extent of scrambling was estimated as in the previous sections. As shown in Table 4, the contribution of mechanism E involving a complete redistribution of all carbon atoms was always much larger in the paraffins than in the corresponding olefins. In fact, isopentane, 2,3-dimethylbutane, and 2-methylpentane were almost completely randomized.

II. Reactions of Methylpropene-2-^{13}C at 120°C

The major C_5–C_7 hydrocarbons formed at 120°C during the final stage of the reaction, on an aged mordenite, were formed exclusively according to mechanism D, which involves the addition of partially scrambled C_1, C_2, and C_3 units to an isobutene molecule (*1*). In contrast, for the first 12 min of reaction, when hydrocarbon residues are being deposited on the surface, mechanism D does not account for the distributions of the labeled gaseous products; as in the experiments made at 170°C, the observed distributions may be considered linear combinations of Type D and statistical Type E distributions corresponding to a complete redistribution of all carbon atoms. In Table 5 we report for various molecules the contributions of mechanism E and for different ions the MSD between the observed and the calculated distributions.

The ^{13}C distributions in several minor products obtained during the final stage of the reaction on an aged mordenite are also reported in Table 5. Unlike the major C_5–C_7 products, these molecules were extensively scrambled. However, for one of them (3-methylpentane) the observed distribution could not be reproduced by a combination of *X* and *Y*.

III. Reactions at 400°C

Methylpropene-2-^{13}C was reacted at 400°C on H-mordenite samples previously degassed at 400°C for 2 h. The product distributions are shown in Table 6 and the distributions of the parent and fragment

TABLE 2

Reaction of Isobutene at 170°C; Distributions of the 2,3-Dimethylbutenes

Distributions		Mechanisms		Fraction I 3.7[a]		Fraction II 5.7[a]		Fraction III 6.4[a]	
		D	E	Observed	$0.35X + 0.65Y$	Observed	$0.6X + 0.4Y$	Observed	$0.7X + 0.3Y$
		X	Y						
Parent ions	$^{13}C_6$	—	0.01	—	—	—	—	—	—
	$^{13}C_5$	—	0.3	0.1	0.17	—	0.1	—	0.1
	$^{13}C_4$	—	2.3	1.3	1.5	0.7	0.9	0.7	0.7
	$^{13}C_3$	—	10.6	8.4	6.9	6.4	4.2	6	3.2
	$^{13}C_2$	37.5	27.4	29.5	30.9	32	33.5	33.9	34.5
	$^{13}C_1$	54.7	37.7	43.6	43.7	47.4	47.9	48.1	49.6
	$^{13}C_0$	7.6	21.7	17.1	16.8	13.5	13.3	11.2	11.8
	(MSD) = Δ			4.4		7		10.6	
	m/e								
Demethylated fragments	76	—	0.05	—	—	—	—	—	—
	75	—	0.9	0.4	0.6	0.3	0.4	0.2	0.3
	74	—	6.4	5.2	4.2	3.9	2.6	2.9	1.9
	73	26.2	22.2	24.2	23.6	25.7	24.6	26	25
	72	59.2	38.8	44.4	45.9	48.3	51	51.1	53.1
	71	11.8	28.3	22.9	22.5	18.8	18.4	16.6	16.8
	70	2.1	2.3	2.45	2.5	2.2	2.2	2.6	2.2
	69	0.2	0.7	0.3	0.6	0.7	0.5	0.6	0.4
	(MSD) Δ			4		10		6.5	

[a] Percentages in the gaseous products.

TABLE 3

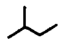
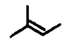
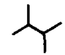
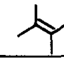
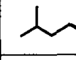
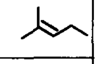
Reaction at 170°C; Distributions of the C_4–C_7 Products

Fraction	Hydrocarbon	2,4-Dimethylpentane	3-Methylhexane	2,3-Dimethylbutane	Isopentane	Isobutane	*n*-butane
I	Precentage[a]			3.7	62.7		5.5
	Distributions			$0.65Y + 0.35X$	$0.8Y + 0.2X$	$0.8Y + 0.2R$	$0.9Y + 0.1I$
	Δ						
	Parent ions	—	—	4.4	0.7	0.4	4
	Demethyl. frag.			4	1.9	3.5	—
	Deethyl. frag.			—	0.7	—	—
II	Percentage[a]	5	1	5.7	35.6		2.3
	Distributions	$0.7Y + 0.3X$	$0.7Y + 0.3X$	$0.4Y + 0.6X$	$0.5Y + 0.5X$	$0.35Y + 0.65R$	$0.85Y + 0.15I$
	Δ						
	Parent ions	4	7	7	7	2	9
	Demethyl frag.	14	12	10	12	4	—
	Deethyl. frag.	—	—	—	2.1	—	—
III	Percentage[a]	3.5	0.5	6.4	20.1		1
	Distributions	$0.5Y + 0.5X$	$0.7Y + 0.3X$	$0.3Y + 0.7X$	$0.4Y + 0.6X$	$0.2Y + 0.8R$	$0.85Y + 0.15I$
	Δ						
	Parent ions	5	11	10.6	5.6	1.5	10
	Demethyl. frag.	11	8	6.5	13	4.7	—
	Deethyl. frag.	—	—	—	4.8	—	—

[a] Percentage in the gaseous reaction products. R: same distribution as in the reactant; X: distribution according to mechanism D; I: distribution assuming simple bond shift; Y: distribution according to E.

TABLE 4

Reaction on a Nonstabilized Mordenite[1] at 170°C; Comparison between the Distributions of the Olefinic and Saturated Hydrocarbons

Hydrocarbon								
%[2]	68	32	42	58	30	70	51	49
distributions	0.65Y + 0.35R	0.35Y + 0.65R	0.9Y + 0.1X	0.6Y + 0.4X	0.8Y + 0.2X	0.5Y + 0.5X	1Y	0.7Y + 0.3X
(MSD) Δ parent ion	0.7	2.3	1.2	8	3	5.4	1	8
demethylated fragm.	1.5	4	4	7	6	-	3	-

[1] gaseous reaction products collected in the second fraction

[2] percentages in the gaseous reaction mixture

X, Y and R have the same meaning as in Table 3. MSD - mean square deviation.

ions obtained for some characteristic reaction products are reported in Tables 7 and 8. In many respects, the reaction products of isobutene differed greatly from the ones obtained at lower temperatures. Thus, (1) very few hydrocarbon residues were left on the surface; (2) the product distributions included large amounts of C_2–C_3 hydrocarbons (44%), C_7 and C_8 hydrocarbons being negligible (Table 6); (3) in the two major paraffinic products (isobutane and isopentane) and in the major aromatics (benzene and toluene) the carbon atoms were completely randomized, and the ^{13}C content of all these molecules, except isobutane, was slightly higher than that of the reacting isobutene (21.5%).

IV. *Reactions of Ethylene and Propylene*

At 170°C, ethylene and propylene formed strongly adsorbed residues (24 and 62 mg adsorbed per g, respectively). Gaseous products were also obtained during the first stages of the reaction. They consisted mainly of isobutane and isopentane, formed in exactly the same ratio (85/15) as in the experiments made with isobutene. However, the amounts of gaseous products rapidly decreased with the aging of the catalyst and became negligible on a stabilized mordenite: during the stationary regime, only 0.6% of the propylene and 1.3% of the ethylene were converted, yielding hydrocarbons up to C_6. Note that olefins were also obtained from propylene but not from ethylene (Table 9). In order to investigate further the lack of reactivity of ethylene and propylene on stabilized catalysts, isobutene was reacted at 120°C on a sample of zeolite previously aged at 170°C with propylene. The total conversion and the distribution of the gaseous products, similar to those obtained on a mordenite aged with isobutene, show that the catalyst aged with propylene still retained some activity.

At 400°C, the major reaction products were C_3–C_5 hydrocarbons, mainly saturated, and aromatics were also formed. The product distribution closely resembled that obtained from isobutene except that more coke was formed (Table 6).

TABLE 5

Reactions of Isobutene at 120°C; Distributions of the C_5–C_7 Products

Hydrocarbons products obtained	During aging		On a stabilized mordenite		
	2,3-Dimethylbutane	Isopentane	2,3-Dimethylpentane	2-Methylpentane	3-Methylpentane
Percentage[a]	16.5	25	0.9	0.8	0.7
Distributions	$0.7X + 0.3Y$	$0.6X + 0.4Y$	$0.5X + 0.5Y$	$0.55X + 0.45Y$	$0.5X + 0.5Y$
Δ					
Parent ion	1.4	2.5	11	7	50[b]
Demethylated frag.	1.4	3.5	—	4	1780[b]
Deethylated frag.	—	3.2	—	16	2031[b]

[a] Percentages in the gaseous reaction products.

[b] MSD for the best fit; X and Y have the same meaning as in Table 3.

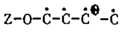
V. Mass Spectrometric Analysis of the Hydrocarbon Residues

The residues left on the zeolite after reaction at 120°C were extracted with chloroform after destruction of the zeolite by 42% hydrofluoric acid according to the method of Bierenbaum *et al.* (*5*). The mass spectrum of the hydrocarbons includes in decreasing amounts: paraffinic $C_nH_{2n+1}^{\oplus}$, olefinic $C_nH_{2n-1}^{\oplus}$, dienic $C_nH_{2n-3}^{\oplus}$, and trienic $C_nH_{2n-5}^{\oplus}$ fragment ions (Fig. 1). The presence of $C_nH_{2n-7}^{\oplus}$ and $C_nH_{2n-11}^{\oplus}$ ions showed that mononuclear and binuclear aromatics were also formed. Fragments at m/e 73, 147, 221, 295, and 369, and 133, 207, 281, 355, and 429 were also detected: they all resulted from silicon derivatives.

In order to simulate the reactions of isobutene at a higher temperature, a sample of zeolite aged at 120°C was heated in the source of a mass spectrometer at 280°C and the mass spectrum of the outgassed molecules was recorded (Fig. 2). The major fragment ions, $C_nH_{2n-3}^{\oplus}$, $C_nH_{2n-5}^{\oplus}$, and $C_nH_{2n-7}^{\oplus}$, correspond to dienes, trienes, and aromatics, respectively.

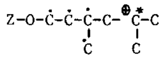
DISCUSSION

In the reactions of 2-methylpropene-2-^{13}C carried out at 120°C on a stabilized mordenite, the location of the labels in the C_5–C_7 products led us in Part I to envisage hydrocarbon radicals attached to the zeolitic framework (*1*).



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

A



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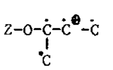

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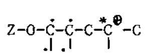


D

On the other hand, as shown in Table 10, there is a close relationship between the amount of hydrocarbon residues left on the surface under various experimental conditions and the percentage of C_5–C_7 hydro-

TABLE 6

Reactions of Isobutene, Propylene, and Ethylene on H–Mordenite at 400°C; Distribution of the Gaseous Products

products / reactants	C_1											C_6H_{14}	C_6H_{12}				Coke %
	–	–	7.2	11.6	21.6	36.2	4.3	4.8	1.6	2.8	0.5	0.3	0.2	3.2	4.1	0.9	5.5
	–	–	5.2	19.3	26.6	23.8	3.7	6.7	2.2	4.7	0.7	1	0.1	1.3	2.6	1.7	10
	0.2	2.2	28.2	33.9	5.8	14.9	–	6.3	0.2	4.9	0.4	0.4	0.1	0.6	1.1	0.7	13

carbons in the gaseous products. This phenomenon and the fact that the formation of hydrocarbon residues at 120 and 170°C is obviously related to the evolution of saturated hydrocarbons suggest that these residues consist of hydrogen-deficient entities linked, like species *A* or *C*, to the zeolitic framework. The mechanism of formation of these residues is best understood in the light of the various activity regimes of the zeolite, four of which may be considered, depending on temperature. At 50°C, there is no evidence whatsoever for an attachment of hydrocarbon chains to the zeolitic framework: simple protonation of isobutene takes place, leading to trimethylpentenes. At 120°C, on a *stabilized* zeolite a carbon–hydrogen bond of isobutene is also

TABLE 7

Reaction at 400°C: ^{13}C Distribution of Isopentane and Isobutane

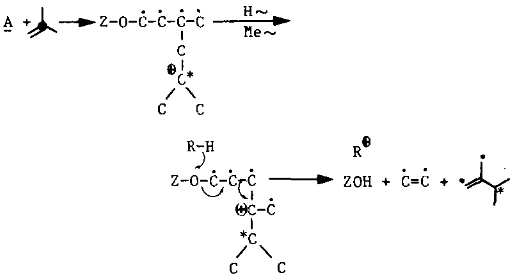
m/e	Isopentane (22.2% ^{13}C)			Isobutane (21.3% ^{13}C)		
	Observed	Calculated (statistical)	Δ	Observed	Calculated (statistical)	Δ
77	0.03	0.05				
76	0.8	0.9				
75	6.5	6.3	0.16			
74	23.1	23.2				
73	40.6	40.7				
72	28.7	28.5				
62	—	—		0.2	0.2	
61	0.15	0.14		3	3.1	
60	2.2	2.4		16.8	17	
59	13.1	13	3	42.1	41.6	0.3
58	31.5	32.9		38	38.2	
57	37	36.5		—	—	
56	12.9	12.5		—	—	
55	3.2	2.4		—	—	
46	0.4	0.4		0.5	0.5	
45	4.4	4.4		6.2	6.2	
44	18.3	17.9	1.26	24.9	24.1	4.6
43	33.5	33.2		35.5	37.4	
42	28.5	28.4		19.9	19.8	
41	14.7	15.7		12.8	12.2	

TABLE 8

Reaction at 400°C: ^{13}C Distribution of the Aromatic Products

Hydrocarbons	^{13}C	Observed	Statistical	Δ	Percentage ^{13}C
Benzene	6	—	0.03		
	5	0.5	0.3		
	4	2.6	2.7		
	3	11.1	11.7	0.6	23.4
	2	28.3	28.5		
	1	37.3	36.9		
	0	20	19.9		
Toluene	7	—	0.003		
	6	—	0.06		
	5	0.7	0.8		
	4	4.5	4.6		
	3	15.5	15.1	0.3	23.1
	2	30.3	30.1		
	1	33.2	33.4		
	0	15.7	15.9		

activated, yielding an allylic cation. The C_4 unit, after scrambling is attached to the zeolite, and species *A* or *B* thus obtained may add another olefin, forming species *C* or *D*. However, the cationic polymerization thus initiated stops there: β-fission liberated partially scrambled olefins and the zeolite is ready for a new reaction. No saturated hydrocarbons are formed in this process and C_8 hydrocarbons predominate in the product distribution.

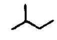
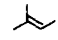


SCHEME A₁: Mechanism D

At 120°C on a *nonstabilized* zeolite, during aging, both hydrocarbon residues and saturated hydrocarbons are formed, and

TABLE 9

Reactions of Propylene and Ethylene at 170°C; Distribution of the Gaseous Products

Reactant	Isobutene	Propylene			Ethylene		
Total hydrocarbon residues (mg/g)	38	62			24		
Gaseous products (%)	12	16	54	100	70	90	100
hydrocarbon residues(%)	8.2	45	85	100	40	88	100
C_3H_8	1	-	-	-	1.4	1.5	1.9
	85.1	83.1	24.9	14.2	82.9	74	61.5
	2.6	-	6.9	9.3	-	-	-
	1.4	2.3	6.9	2.3	0.7	1.5	1.9
	-	-	6.1	13.8	-	-	-
	9.1	12.8	19.2	15	12.4	16	22.3
	0.3	0.7	11.4	9.2	-	0.1	0.1
	-	-	0.9	8.2	-	0.3	0.2
C_6H_{14}	0.5	1.1	10.4	9.3	1.4	2.8	1.6
C_6H_{12}	-	-	12.9	16.7	-	0.5	0.6
Total conversion(%)	97	85	11.5	0.6	2.1	2.7	1.3

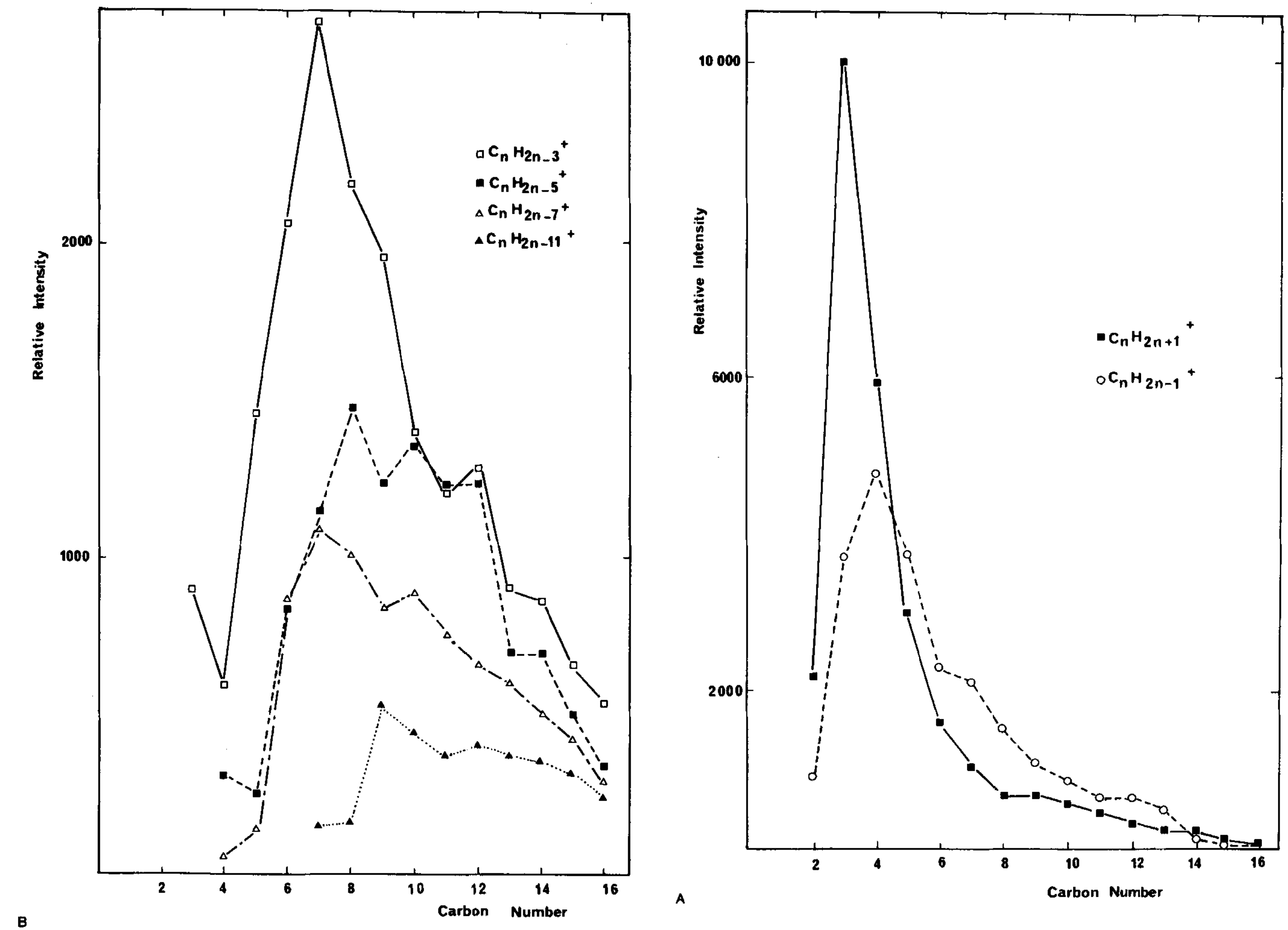


FIG. 1. Ion abundances of aliphatic $C_nH_{2n}^{\oplus}$, olefinic $C_nH_{2n-1}^{\oplus}$, dienic $C_nH_{2n-3}^{\oplus}$, trienic $C_nH_{2n-5}^{\oplus}$, mononuclear aromatic $C_nH_{2n-7}^{\oplus}$, and binuclear aromatic $C_nH_{2n-11}^{\oplus}$, species extracted from a mordenite sample aged at 120°C.

TABLE 10

Relationship between the Amounts of Hydrocarbon Residues and the Product Distributions

Reaction temperature (°C):	50	120		170		400
Aging conditions:	[a]	After	During	After	During	After[b]
Total hydrocarbon residues (mg/g)	0	15		38		2
C_5–C_7 hydrocarbons (%)	2.1	20	71.3[c]	51	93[c]	3.8
Dimethylhexenes (%)[d]	0	18	26[c]	45	65[c]	—
Saturated hydrocarbons (%)[e]	0	7	28[f]	8	42[g] 96[g]	84

[a] No hydrocarbon residues left on the surface (no aging).

[b] The aging period was too short to allow an analysis to be made.

[c] Analysis made after deposition of 50% of the hydrocarbon residues.

[d] Percentage in the octenes.

[e] Percentage in the isopentane + isopentene mixture.

[f] Analysis of the total gaseous products collected during aging at 120°C.

[g] Collected at 170°C during the deposition of the second half (42) or the first half (96) of the hydrocarbon residues.

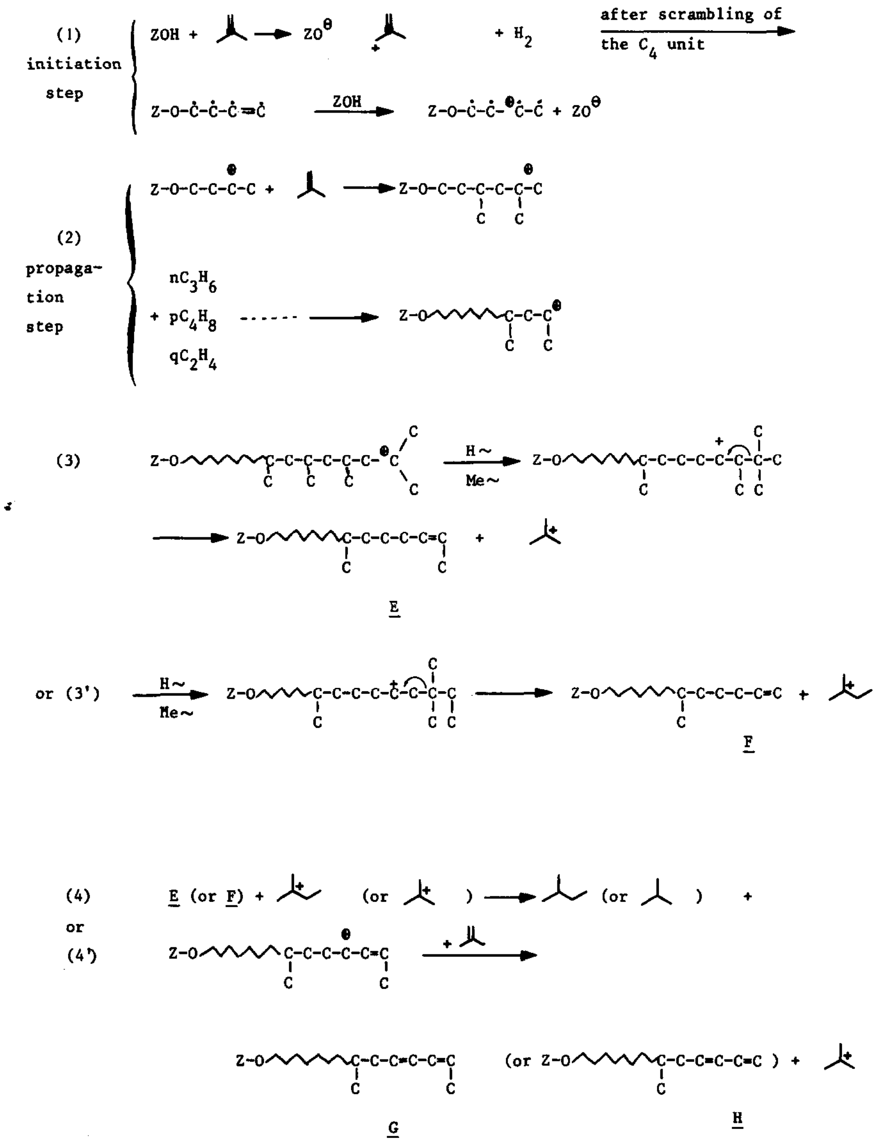
the major gaseous reaction products, deeply rearranged, have the skeleton of isobutane or isopentane. Analysis of the residues left on the zeolite shows the presence of hydrocarbon chains, up to 16 carbon atoms long, consisting of monoenes, dienes, and trienes in decreasing amounts. The formation of these chains could be considered to be the result of a cationic copolymerization involving besides the reactant, isobutene, some of the primary reaction products, propylene, and ethylene, which do not appear in the gas phase. Indeed, propylene and ethylene are also irreversibly adsorbed on the zeolites and yield comparable amounts of hydrocarbon residues.

This copolymerization, however, ceases very early: after the initiation step, namely, the attachment of a C_4 scrambled unit, and the addition of a limited number of olefins to the living oligomer, deactivation takes place, obviously related to the formation of saturated hydrocarbons.

To account for the interrelationship between saturated products and hydrocarbon residues, which both increase with increasing temperature, we suggest the following sequence of reactions [see Reactions (1)–(4) below]. The polymeric cations which are attached to the zeolitic framework are first deactivated by β-fission (Reaction (3)) producing a carbenium ion and an adsorbed olefin radical (*E* or *F*). Species *E* or *F* then may act as a hydride and proton donor (Reaction (4)), yielding saturated hydrocarbons and adsorbed alkadiene radicals (*G* or *H*). These species *E*, *F*, *G*, and *H* represent the strongly adsorbed residues left on the zeolite at 120°C.

During the formation of these residues, the predominance of isobutane and isopentane in the reaction products shows that β-fission (Reaction (3)) yields the most stable t-butyl and t-amyl cations, which can be obtained only after a number of methyl and hydride shifts in the adsorbed cations.

At 400°C, very little hydrocarbon residues are left on the surface, aromatics are formed, and saturated hydrocarbons represent 50–60% of the reaction products. We suggest that at this temperature adsorbed alkadiene radicals would also react, yielding paraffins by hydride transfer and trienes, precursors of the aromatics (*6*), by β-



Reactions (1)–(4)

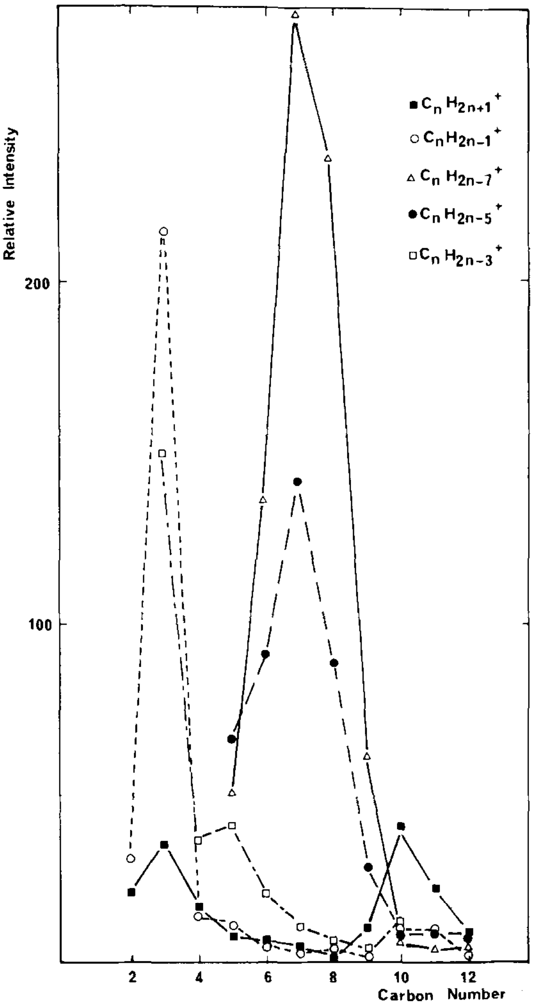
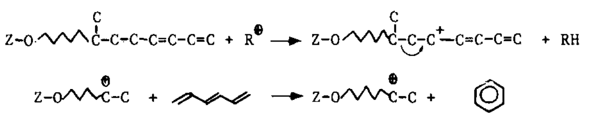


FIG. 2. Ion abundances of aliphatic $C_nH_{2n+1}^{\oplus}$, olefinic $C_nH_{2n-1}^{\oplus}$, dienic $C_nH_{2n-3}^{\oplus}$, trienic $C_nH_{2n-5}^{\oplus}$, and aromatic $C_nH_{2n-7}^{\oplus}$, species desorbed at 280°C from a mordenite sample aged at 120°C.

fission. Active sites available for further reactions would then be liberated and the reaction could, in principle, develop continuously:

(5)



In this way, the puzzling disproportionation reaction

olefins → paraffins + aromatics,

characteristic of zeolite catalysis could be explained.

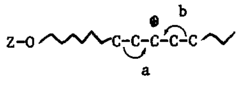
As another possible explanation for the formation of hydrocarbon residues at 120–170°C and of aromatics at 400°C, one could assume that trienes are already formed at low temperatures by the sequence of Reactions (3)–(5) but remain in the channels of the mordenite. The only accessible sites in an aged mordenite at 120–170°C would then be the sites close to the external surface. At 400°C, trienes would be desorbed, cyclizing to aromatics and liberating the inner sites of the zeolite.

The four activity regimes previously described, viz., at 50°C, at 120°C during and after aging, and at 400°C, represent only limiting cases. All intermediate situations may be envisaged, especially at reaction temperatures between 120 and 400°C. At 170°C, before stabilization of the zeolite, the mechanism of polymer formation does not differ qualitatively from that at 120°C. After aging, however, at 170°C but not at 120°C, saturated hydrocarbons are formed and all reaction products are substantially scrambled. We suggest that the polymeric chains, although not completely destroyed as they are at 400°C are continuously being broken and remade, thus contributing appreciably to the formation of C_5–C_7 products, in addition to short chains *A* and *B*.

Mechanism of Scrambling

This continuous breakage and reformation of polymeric chains allows one to understand the mechanism of label scrambling. This scrambling, which is important during aging and at 170°C, does not occur at 120°C. The difference between the two sets of experiments is due, we believe, to a difference in nature and reactivity between the short-chain species, C_4–C_8, predominant at 120°C, and the long-chain species which are formed during aging and at higher temperature.

In short-chain species (*C* or *D*), β-fission yields an olefin and regenerates a site (ZOH) (Scheme A_1). In long-chain species, both olefins and carbenium ions are obtained by Type *a* and Type *b* ruptures and the new sites thus created are adsorbed cations or adsorbed olefins (Scheme A_2)



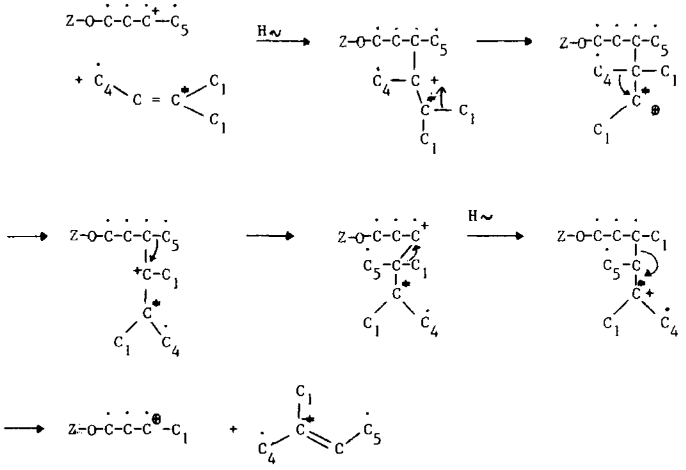
SCHEME A_2

These are able to add olefins or carbonium ions, respectively, and after a number of methyl and hydride shifts to restore by β-fission olefins or cations which have more (or less) label content and are more scrambled than the original ones. Two examples of such an "adsorption–desorption" process are shown in Scheme B below, designated B_1 and B_2, respectively. As shown in Table 11, the original labeling of a primary olefin (obtained on a short chain according to Scheme A_1) is deeply altered by consecutive adsorption–desorption steps. Actually four of these steps are enough to reproduce fairly well the statistical distribution. Under Results, the observed ^{13}C distributions were formally considered to be linear combinations of a

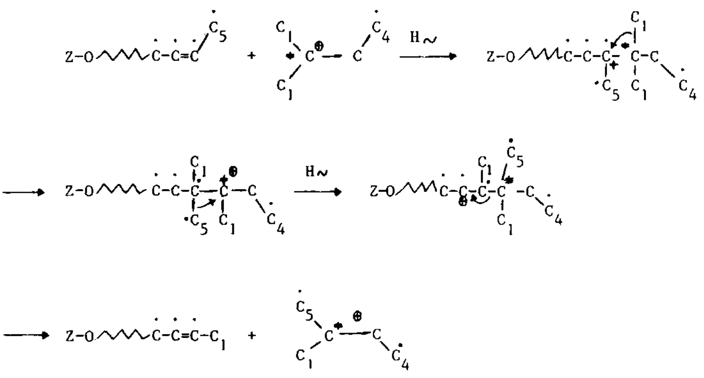
TABLE 11

Scrambling of the Label by "Adsorption–Desorption" Steps in a C_5 Hydrocarbon

^{13}C	Initial distribution Mech. D—22.7% ^{13}C	Step 1	Step 2	Step 3	Step 4	Statistical
$^{13}C_4$	—	—	0.3	0.6	0.7	1
$^{13}C_3$	—	3.8	5.2	6	6.2	7
$^{13}C_2$	27.9	26.2	25.6	25	23.8	23.8
$^{13}C_1$	57.8	51	46.3	43.7	42.3	40.6
$^{13}C_0$	14.2	19.9	22.6	24.6	25.7	27.6
Statistical %	0	40	60	80	90	100



B_1. Olefin readsorption.



B_2. Carbonium ion readsorption.

SCHEME B. Mechanism of label scrambling by an "adsorption–desorption" process.

distribution D according to Scheme A_1 and of a true statistical distribution. If the proposed mechanism of scrambling is correct, they should rather be associated with a variable number of readsorption steps. For instance, contributions of the statistical distribution amounting to 40, 60, and 80% would correspond to 1, 2, and 3 readsorption steps, respectively. The carbon-13 contents of the C_5–C_7 products in the experiments made at 170°C and during aging at 120°C are always slightly higher than in the experiments made at 120°C. This increase of the carbon-13 content can also be accounted for by consecutive readsorption, since during this process originally unlabeled carbon (such as methyl groups in isopentenes) may be replaced by carbon-13.

The existence of two types of chains, namely, short ones responsible for the production of C_5–C_7 hydrocarbons and long ones associated with the formation of hydrocarbon residues, strongly suggests the existence of two types of sites. On the first type (E), where C_4–C_8 hydrocarbon chains are continuously destroyed and remade, the rate of β-fission is greater than the rate of chain growth. The reverse is true on the second type of site (I). We believe that the difference in the behaviours of E-type and I-type sites, which could easily be explained by a difference of local reactant pressure, higher at Type I than at Type E, is due to their location in the zeolite. It has been suggested that the local pressure in the channel and cavities of zeolites is much higher than on the external surface (*7*). One could imagine then that the reactant pressure around I-type sites, in the channels of the mordenite, would be high, thus favouring cationic polymerization over β-fission, while around E-type sites, nearer the surface of the zeolite, the reactant pressure would be low and β-fission would therefore be faster than chain growth. However, this simple topographical explanation is not sufficient to account for all the differences between E and I sites. During aging, at 170°C, isobutene, propylene, and ethylene yield comparable amounts of hydrocarbon residues and the distribution of the gaseous products obtained from these molecules is initially the same. However, on an aged mordenite, the sites which can convert isobutene to C_5–C_7 olefins and dimethylhexenes, i.e., the ones associated with short-chain species (E sites) cannot activate propylene and ethylene. Moreover, the formation of isobutane and isopentane during the formation of long-chain polymers from ethylene (on I sites) suggests a much deeper rearrangement than the methyl or hydride shifts involved in the production of C_5–C_7 hydrocarbons from isobutene (on E sites). Such differences between I and E sites are explicable only if one assumes that the acidity strength differ, the inner (I) sites of the zeolite being more acidic than the external (E) sites.

CONCLUSION

We have proposed in this paper and in Part I the existence of at least two types of sites on H-mordenite, differing in their acidity strengths. They are: (1) weak Brønsted acid sites, which are responsible for simple protonation and cationic dimerization of olefins, and (2) strong acid sites which allow hydride abstraction and the formation of allylic cations. Depending on their location in the zeolite (and their acidity), the latter sites could either (a) promote the formation of long chains and yield hydrocarbon residues (I sites) or (b) permit the continuous breakage and formation of short hydrocarbon chains with production of C_5–C_7 hydrocarbons (E sites).

If these assumptions are correct, the contribution of each type of site should depend strongly upon the pretreatment and the ion content of the zeolite. The dependence of the product distribution upon the zeolite pretreatment will be reported in Part III (*8*).

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