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Homologation of Olefins by Methanol over ZSM-5 Zeolite

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^{13}C-Labeled methanol has been coreacted with excess C_6 olefins (2-methylpentene-1 or hexene-1) over the proton form of ZSM-5 zeolite under such conditions (ca. 550 K and a 2-s contact time) that the C_6 olefins undergo extensive reaction while the methanol undergoes partial conversion to hydrocarbons. The resulting mixture of olefins was then hydrogenated to facilitate isotopic analysis. The ^{13}C label was most abundant in the C_7 products, consistent with the hypothesis that the methanol is converted mainly by the homologation of an olefin to form an olefin with one more methylene group.

INTRODUCTION

ZSM-5 zeolite is an excellent acid catalyst for the conversion of methanol to hydrocarbons and water (*1*). It is generally agreed that lower olefins are first formed from methanol/dimethyl ether (reaction (1)) and that other hydrocarbons are then formed from the lower olefins (*1*). Considerable interest attaches to the mechanism of reaction (1):

$$n\ CH_3OH\ (\text{or } n/2\ CH_3OCH_3) \rightarrow C_nH_{2n} + n\ H_2O \quad (n = 2,3,4, \text{etc.}) \qquad (1)$$

Our view (*2–4*), which appears to be widely shared, (*1, 5–8*), is that acid-catalyzed homologation (reaction (2)) of an olefin by methanol (or dimethyl ether) is an important feature of reaction (1). Hitherto, conclusive evidence in support of the view has been lacking, because oligomerization and cracking of olefins are so facile over the proton form of ZSM-5 zeolite that olefin equilibrium (3) is normally established at or below the temperature required for methanol conversion.

$$C_nH_{2n} + CH_3OH \xrightarrow{H^+} [C_{n+1}H_{2n+3}]^+ \rightarrow C_{n+1}H_{2n+2} + H_2O \qquad (2)$$

$$1/3\ C_3H_6 \rightleftharpoons 1/4\ C_4H_8 \rightleftharpoons 1/5\ C_5H_{10}, \text{etc.} \qquad (3)$$

Consequently, one cannot expect reaction of a C_n olefin with methanol to give a C_{n+1} olefin specifically.

Nevertheless, Wu and Kaeding (*7*) have obtained results, from the reaction of ethylene and of propylene with excess methanol and excess water over H-ZSM-5 of very high silica content, indicative of conversion of methanol by reaction (2).

A better test of reaction (2) would be provided by the reaction of a C_n olefin with labeled methanol to give a labeled C_{n+1} olefin. We now describe work in which 2-methylpentene-1, or hexene-1, is reacted with ^{13}C-labeled methanol under such mild conditions that the olefin equilibrium is not completely established and methanol conversion is only partial. The results obtained provide unequivocal support for the homologation hypothesis, supplementing the earlier ^{13}C work reported from this laboratory (*2*) and by Dessau and La Pierre (*6*).

EXPERIMENTAL

ZSM-5 zeolite. The zeolite, of 0.71 wt% aluminum content, was that described in a previous paper (*2*). Morphologically it consists of 1- to 5-μm aggregates of small laths. The proton form of the zeolite was pelleted, broken, and sieved to particles of 80–100 mesh size. It was then activated in the reactor in oxygen at 773 K before use.

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Materials. 2-Methylpentene-1 (Koch-Light) of >99.5% purity, was coreacted with [^{13}C]methanol of 99% isotopic purity (CEA). Hexene-1 (Aldrich) was >96% pure; almost all the impurity comprised isomeric hexenes. This hexene-1 was coreacted with [^{13}C]methanol of 90% isotopic purity (Stohler).

Apparatus. The tubular microreactor and its use have been described previously (*2*, *9*). Products were analyzed by an on-line gas chromatograph (Varian 3700) with flame ionization detectors, using a 4-m × $\frac{1}{8}$-in o.d. OV101-packed column.

Mass spectra (70 eV, electron emission) were measured off-line using a Hewlett–Packard 5995A gas chromatograph/mass spectrometer fitted with a 50-m SE30 capillary column. Gaseous reactor effluent and product condensed (at 273 K) from the gaseous effluent were examined. Particular attention was paid to condensed product which had been hydrogenated (2 bar H_2) over palladium (5%)-on-charcoal at ca. 300 K. The ^{13}C isotopic content of each GC/MS component was estimated by comparison of the observed mass spectrum with that of the corresponding GC/MS peak of product from a control experiment (using unlabeled methanol and the corresponding olefin reactant).

Conversion of 2-methylpentene-1/[^{13}C] methanol. Mixed 2-methylpentene-1/[^{13}C] methanol (99% isotopic purity) liquid (in 6/1 w/w ratio) was continuously fed by syringe (0.96 ml/h) to the reactor tube in a stream of nitrogen vector gas (8 ml/min). The reactor tube contained an activated bed of ZSM-5 zeolite (0.20 g). Space velocity = 3 wt feed/wt catalyst/h; nominal contact time = 2 s. For the first 2 h the catalyst bed was maintained at 548 K. There was a significant fall in catalyst activity during this time, and the catalyst turned light grey.

The temperature of the (unregenerated) catalyst was then raised to 563 K, and the experiment was continued for a further 2 h, during which time there was again significant loss of activity.

TABLE 1

Approximate Composition (C%) of Products from Conversion of [^{13}C]Methanol (9C%)/2-Methylpentene-1 (91C%)[a]

Products	At 548 K	At 563 K
Methane + ethylene	<0.1 (0.1)	<0.1 (<0.1)
C_3[b]	0.1 (0.5)	0.1 (0.1)
C_4[b]	0.2 (1.3)	0.1 (0.1)
C_5[b]	0.1 (1.5)	<0.1 (0.1)
C_6[b]	56 (41)	71 (57)
C_7[b]	0.9 (6)	1.2 (3.4)
C_{8+}[c]	43 (50)	27 (37)

[a] From on-line gas chromatographic analysis. At each temperature, conversion fell during the 2 h of the run. Compositions given refer to the end of the hour run (figures in parentheses refer to the beginning). Dimethyl ether and unchanged methanol are not included in the analysis.

[b] The C_3–C_7 hydrocarbons are almost entirely olefins.

[c] The C_{8+} hydrocarbons are mainly a complex mixture of branched-chain hexene dimers. Minor products are discussed in the text.

At each of the two temperatures, the final approximate overall composition of the product was determined by on-line gas chromatography and is shown in Table 1; initial composition is shown in parentheses, to indicate the extent of activity loss. The values in Table 1 are only a rough guide to product composition,[1] and take no account of unchanged methanol and dimethyl ether, which could not be analyzed adequately under the conditions of the experiment. We estimate that conversion of methanol to hydrocarbons is only of the order of 10% at each temperature (see Discussion).

At each temperature, condensate was collected from the reactor effluent in a mini-catchpot at 273 K; 0.65 g was collected during 1.5 h (66% recovery of feed as condensate). GC/MS analysis of the product and product from a control experiment using

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[1] The simple on-line GC analysis is not well suited to an effluent containing such less-volatile products as hexene-dimers.

TABLE 2

^{13}C Content of the Major C_5–C_8 Hydrogenated Products Derived from Conversion of [^{13}C]Methanol/2-Methylpentene-1 over ZSM-5 Catalyst at 548 and 563 K

Product (C_nH_{2n+2})	At 548 K			At 563 K		
	Composition[a]	%Single ^{13}C label in C_nH_{2n+2}[b]	%Single ^{13}C label in C_4 fragment[c]	Composition[a]	%Single ^{13}C label in C_nH_{2n+2}[b]	%Single ^{13}C label in C_4 fragment[c]
C_5						
2-Methylbutane	0.2	21	13	<0.1	nd[e]	12
n-Pentane	0.2	13	10	<0.1	nd	nd
C_6						
2-Methylpentane	50	Nil[d]	Nil	53	Nil	Nil
3-Methylpentane	41	Nil	Nil	40	Nil	Nil
n-Hexane	9	Nil	Nil	7	Nil	Nil
C_7						
2,4-Dimethylpentane	0.3	55	37	0.3	92	46
2-Methylhexane	1.7	57	32	1.0	65	44
2,3-Dimethylpentane	<0.1	nd	nd	0.4	nd	33
3-Methylhexane	1.6	53	35	1.3	69	41
n-Heptane	0.4	38	26	0.3	47	33
C_8						
2,5-Dimethylhexane	0.1	nd	8	<0.1	nd	nd
2,4-Dimethylhexane	0.2	nd	3	0.15	nd	10
2-Methylheptane	0.5	nd	6	0.3	2	4
4-Methylheptane	<0.1	nd	nd	0.2	5	nd
3-Methylheptane	0.5	nd	6	0.4	9	5
n-Octane	0.1	nd	12	0.1	7	nd

[a] The composition is expressed on a carbon content basis (i.e., fid response) normalized to total C_6 alkanes = 100.

[b] From the intensity of the singly ^{13}C-labeled parent ion relative to the unlabeled parent ion; the contribution of naturally abundant ^{13}C (1.1%) has been subtracted.

[c] Derived from the intensities of all the peaks in m/e 55–58 range. The contribution of natural abundance of ^{13}C has been subtracted.

[d] "Nil" indicates no significant ^{13}C label in excess of natural abundance.

[e] "nd" indicates that the extent of ^{13}C label could not be reliably estimated because of low peak intensities or inadequate chromatographic separation.

unlabeled methanol showed that the condensate consisted very largely of a complex mixture of olefins.

Each of the condensates was separated into a rejected aqueous methanol layer (density ca. 0.8 g/cm^3) and a hydrocarbon layer. The latter was hydrogenated over palladium(5%)-on-charcoal under hydrogen (2 bar) at ca. 300 K for 18 h. The resulting mixture (mainly alkanes) was then subjected to GC and GC/MS analysis for determination of its composition. The major C_5–C_8 alkanes and their ^{13}C contents are listed in Table 2, and Table 3 gives the mass spectra of the most important group of alkane products, namely the heptanes.

Conversion of hexene-1/[^{13}C]methanol. A mixture of hexene-1/[^{13}C]methanol (90% isotopic purity) was reacted over freshly regenerated ZSM-5 zeolite in exactly the manner described above. For the first 2 h the catalyst bed was maintained at 558 K.

TABLE 3

Mass Spectra of C_7-Alkanes from Reaction of 2-Methylpentene-1 with [^{13}C]Methanol at 563 K

m/e	2,4-Dimethylpentane	2-Methylhexane	2,3-Dimethylpentane	3-Methylhexane	*n*-Heptane
101	4.0	5.8	4.7	6.3	11.6
100	v. low	2.3	4.7	1.9	9.5
87	—	1.4	—	—	—
86	17.0	23.7	9.4	2.2	0.3
85	7.5	20.6	7.9	3.0	2.0
84	—	3.3	3.7	0.7	—
73	—	—	4.3	1.3	—
72	—	1.4	25.1	27.4	18.0
71	1.1	1.9	24.1	51.0	36.4
70	—	1.3	6.8	26.6	16.0
59	2.5	0.8	3.7	1.0	—
58	42.8	14.8	34.0	23.6	15.6
57	77.3	30.3	100.0	50.5	39.1
56	37.1	20.6	93.2	35.1	26.9
55	3.7	5.3	13.6	13.0	10.2
54	3.1	2.3	4.7	3.5	2.7
53	2.0	2.7	3.1	4.2	4.8
45	2.8	1.5	1.0	1.3	3.1
44	66.6	38.9	57.1	42.4	30.6
43	100.0	100.0	94.2	100	100.0
42	55.5	51.1	64.4	41.4	39.5
41	55.2	43.5	88.0	57.6	59.5
40	15.6	11.0	18.3	13.1	10.2
39	22.7	17.5	27.7	27.2	20.7
38	1.1	1.2	1.6	0.8	3.7

There was significant fall in catalyst activity during this time, and the catalyst turned brown. The temperature of the (unregenerated) catalyst was then raised to 577 K, and the experiment was continued, again with loss of activity, for a further 2-h period.

Table 4 gives the approximate overall composition of the product at the end of the run at each temperature; the corresponding initial composition is shown in parentheses. Table 4 takes inadequate account of unchanged methanol and dimethyl ether, which could not be adequately analyzed. The condensate was collected at each temperature (ca. 66% recovery of feed as condensate), and subjected to hydrogenation and analysis in the same way as the product from 2-methylpentene-1. Table 5 lists the major C_5–C_8 alkanes and their ^{13}C contents. The noncondensed gases (prehydrogenation) were also subjected to GC and GC/MS analysis (see below).

TABLE 4

Approximate Composition (C%) of Products from Conversion of ^{13}C-Methanol (9C%)/Hexene-1 (91C%)[a]

	At 558 K	At 577 K
Methane	Trace (trace)	Trace (trace)
Ethylene	0.1 (0.2)	0.2 (0.2)
C_3 hydrocarbons[b]	0.2 (1.2)	1 (1)
C_4 hydrocarbons[c]	1 (4)	3 (2)
C_5 hydrocarbons[d]	1 (5)	4 (3)
C_6 hydrocarbons[d]	88 (52)	68 (60)
C_7 hydrocarbons[d]	1 (7)	6 (6)
Higher hydrocarbons[e]	5 (14)	3 (15)

[a] From on-line gas chromatographic analysis. At each temperature, conversion fell markedly during the run; final composition is given, with the initial composition in parentheses. Methanol and dimethyl ether are not included in the analysis.

[b] Mainly propene.

[c] Mainly butenes.

[d] Mainly alkenes.

[e] Mainly branched-chain hexene-dimers (but see text).

TABLE 5

^{13}C Content of the Major C_5–C_8 Hydrogenated Products Derived from Conversion of [^{13}C]Methanol/Hexene-1 over ZSM-5 Catalyst at 558 and 577 K

Product (C_nH_{2n+2})	At 558 K			At 577 K		
	Composition[a]	% Single ^{13}C label in C_nH_{2n+2}[b]	% Single ^{13}C label in C_4 fragments[c]	Composition[a]	% Single ^{13}C label in C_nH_{2n+2}[b]	% Single ^{13}C label in C_4 fragments[c]
C_5						
2-Methylbutane	0.5	8	4	1.5	6	4
n-Pentane	0.8	4	7	0.9	5	7
C_6						
2-Methylpentane	28	2	Nil	29	Nil	Nil
3-Methylpentane	25	Nil[d]	Nil	34	Nil	Nil
n-Hexane	47	Nil	Nil	37	Nil	Nil
C_7						
2,4-Dimethylpentane	0.3	32	23	0.9	32	19
2-Methylhexane	2.1	21	15	4.3	26	16
3-Methylhexane	2.3	25	14	4.1	28	20
n-Heptane	0.9	17	10	1.2	21	16
C_8						
2,5-Dimethylhexane	0.2	nd[e]	5	0.4	nd	5
2,4-Dimethylhexane	0.3	nd	1	0.7	nd	3
2,3-Methylhexane	0.1	nd	nd	0.4	nd	nd
2-Methylheptane	0.8	6	3	0.9	4	3
4-Methylheptane	0.5	nd	nd	0.6	nd	nd
3-Methylheptane	1.4	3	2	1.6	6	4
n-Octane	0.5	9	6	0.4	nd	nd

[a] Composition is expressed on a carbon content basis (i.e., fid response) normalized to total C_6 alkanes = 100.

[b] From the intensity of the singly ^{13}C-labeled parent ion relative to the unlabeled parent ion. The contribution of naturally abundant ^{13}C (1.1%) has been subtracted.

[c] Derived from the intensities of all the peaks in *m/e* 55–58 range. The contribution of naturally abundant ^{13}C has been subtracted.

[d] "Nil" indicates no significant ^{13}C label in excess of natural abundance.

[e] "nd" indicates that the extent of ^{13}C label could not be reliably estimated because of low peak intensities or inadequate chromatographic separation.

RESULTS AND DISCUSSION

Abbot *et al.* (*10*) have studied the behavior of hexene-1 over ZSM-5 zeolite, and found that the hexene undergoes extensive reaction at temperatures below the ca. 570 K of the present experiments. A complex mixture of hexenes of both straight and branched chains results, along with a complex mixture of hexene dimers and other C_3–C_9 olefins formed by cracking of the dimers. We should expect branched-chain hexenes, such as 2-methylpentene-1, to behave similarly.

In its present work, each of two hexenes, namely 2-methylpentene-1 or hexene-1, undergoes conversion in the presence of ^{13}C-labeled methanol (0.44 mol per mole of the hexene). The conditions are so chosen that the hexene undergoes extensive conversion (particularly isomerization) while the methanol undergoes only partial conversion. Methanol is much less reactive than simple olefins over ZSM-5 zeolite. We are of the view that both methanol and any water formed from it lower the activity of the zeolite by solvating the Brønsted acid sites.

The activity of the catalyst toward the hexene/methanol mixture falls with time. Table 1 summarizes the approximate overall composition of the product from 2-methylpentene-1 and methanol at the end of a 2-h run at 548 K, and at the end of a following 2 h run at 563 K. The corresponding compositions at the beginning of each run are given in parentheses. Similarly Table 4 shows the corresponding results for the products from hexene-1 and methanol at the end of 2-h runs at 558 and 577 K; again the corresponding initial product compositions are given in parentheses.

Restriction of the channels of the zeolite and consequent loss of activity may occur in two ways. First, olefin oligomers may accumulate. Second, since the zeolite turns grey or brown during the run, more conventional coking may be occurring. It should be noted that ZSM-5 zeolite behaves in a less time-dependent manner when used for conversion of olefins at much higher temperatures and when used for conversion of methanol alone.

In each of the hexene/methanol experiments, the products consist very largely of a mixture of olefins. In order to simplify the analysis of the products, and particularly the C_5–C_8 products in which we are most interested, each of the liquid products was condensed and hydrogenated over palladium-on-charcoal to give a much simpler mixture of mainly alkanes.

Table 2 lists the major C_5–C_8 constituents of the hydrogenated condensates from 2-methylpentene-1. Table 5 likewise lists the major C_5–C_8 constituents of the hydrogenated condensates from hexene-1. The percentage of singly ^{13}C-labeled material in each constituent (percentage $[^{13}C]^{12}C_{n-1}H_{2n+2}$ in C_nH_{2n+2}) was estimated from the intensity of the unlabeled parent (P) ion and the intensity of the (P + 1) ion.

Multiple ^{13}C-labeling is not found to a significant extent, indicating that no significant amount of any of the products is derived largely from the methanol (except for traces of aromatic hydrocarbons, see below). Thus, most of the product molecules are derived entirely from 2-methylpentene (or hexene as the case may be) or from 2-methylpentene and relatively small amounts of methanol. Accordingly the isotopic results can be discussed entirely in terms of the extent of labeling of molecules by a single ^{13}C atom.

Almost all the mass spectra showed the usual intense mass spectral peaks in the *m/e* 55 to 58 region due to C_4 fragments. The percentage of ^{13}C label in the C_4 fragments (percentage $^{13}C\ ^{12}C_3$ fragments in total C_4 fragments) was estimated for the C_4 fragments of each component by comparison of the mass spectrum in the *m/e* 55–58 region with that of the mass spectrum of the same unlabeled component (from a blank experiment using unlabeled methanol). The C_4 data provide a check on the extent of ^{13}C-labeling estimated from the parent ion data, and give some idea of ^{13}C content for the C_8 products for which reliable parent ion data were not obtained.

Major Products from 2-Methylpentene-1

More definitive and detailed results were obtained from 2-methylpentene-1 than hexene-1, and so we discuss them first. Table 2 summarizes the ^{13}C contents of the C_5–C_8 hydrocarbons obtained by reaction of 2-methylpentene-1 with labeled methanol and subsequent hydrogenation. The recovered hexanes are mainly a mixture of 2-methylpentane, 3-methylpentane, and *n*-hexane, all having no ^{13}C label in excess of natural abundance, consistent with extensive skeletal isomerization of the 2-methylpentene-1. The C_5 alkanes/(*n*-pentane and 2-methylbutane) contain low levels of ^{13}C label, as do the C_8 alkanes (ca. four- and twofold natural abundance, respectively).

By contrast, the C_7 alkanes, which are formed in much larger amounts than the C_5 and C_8 alkanes, contain far more ^{13}C label. The 563 K experiment shows particularly clearly that most of the C_7 hydrocarbons are derived from an unlabeled hexene and a ^{13}C-labeled methanol molecule. Thus 92% of the 2,4-dimethylpentane is singly ^{13}C-labeled, as is 65 and 69% of the 2- and 3-methylhexane, respectively, and 47% of the *n*-heptane. The mass spectra of the 563 K heptanes are shown in Table 3.

The mass spectra in the 55 to 59 *m/e* region show not only strong 58 ($[^{13}C]^{12}C_3H_9^+$) and 57 ($^{12}C_4H_9^+$) peaks, but also a weak 59 ($[^{13}C_2]^{12}C_2H_9^+$) peak due to C_4 fragments with naturally abundant ^{13}C in addition to the high level of ^{13}C label from the methanol.

The degree of ^{13}C incorporation into the 563 K heptanes increases with chain branching from 47% for *n*-heptane to 65–69% for 2- and 3-methylhexanes to 92% for 2,4-dimethylpentane. (The same tendency is seen, but less markedly, for the other heptane data of Tables 2 and 5.) Thus, the less highly branched alkanes are more likely to be formed by reactions not involving the labeled methanol.

Some, but not all, of the mass spectral data of Table 3 can be interpreted as indicating that most of the ^{13}C label is in the methyl groups. For example, 2,4-dimethylpentane, 92% singly ^{13}C-labeled and having four equivalent methyl groups, loses a methyl group to give a C_6 ion which is ca. 63% labeled; clearly the label is mainly in the methyl groups. By contrast, *n*-heptane shows a parent ion 47% labeled, with the C_5, C_4, and C_3 fragments 36, 33, and 22% labeled, respectively, suggesting that the label is fairly evenly spread along the carbon chain.

The essential conclusion to be drawn from the 2-methylpentene-1 experiment is that the ^{13}C label of the converted methanol is found mainly as a single ^{13}C label in the C_7 hydrocarbons, and that most of the C_7 alkenes (which give C_7 alkanes on hydrogenation) are formed by

$$[^{13}C]CH_3OH + C_6H_{12} \xrightarrow{H^+} \text{mono-}[^{13}C]C_7H_{14} \quad (4)$$

The isomerization, oligomerization, and cracking reactions[2] which occur greatly complicate the overall result. Thus, the C_7 alkanes (obtained after hydrogenation) are not completely ^{13}C-labeled, and some ^{13}C label is found in C_5 and C_8 alkanes. Furthermore, even though reaction (4) is thought to be an electrophilic methylation of a hexene to a heptene (reaction (5)), the ^{13}C label is not found exclusively in the methyl groups of the C_7 hydrocarbons (presumably because of the kind of skeletal isomerization apparent in the recovered C_6 hydrocarbons).

$$[^{13}C]CH_3OH + C_6H_{12} \xrightarrow{H^+} ([^{13}C]CH_3)\text{—}C_6H_{11} \quad (5)$$

Other Products from 2-Methylpentene-1

The minor components of the hydrogenated product from the 563 K 2-methylpentene-1 experiment were also examined. Some 1C% (w.r.t. total hexanes) of C_9 alkanes were identified, comprising (in order of decreasing amount) 2-methyloctane (with single ^{13}C label 14% in excess of natural abundance; 5% label in the C_4 fragments), 3-methyloctane (10% labeled; 5% in C_4 fragments) and *n*-nonane (10% labeled; 7% in C_4 fragments). The C_9 alkanes appear to be derived mainly from the 2-methylpentene-1 (rather than from olefin and labeled methanol).

Two kinds of nonalkane components were also found. One kind comprises very small amounts of a small number of benzenoid hydrocarbons; the total yield is ⩽1C% as compared with the hexanes. A xylene (probably *o*-xylene) and a trimethylbenzene (probably the 1,2,4- or 1,2,3-isomer) were identified; their mass spectra indicated a wide range of multiple ^{13}C-labeling (0–8 ^{13}C atoms in the xylene and 0–9 ^{13}C atoms in the trimethylbenzene). An unidentified C_{10} benzenoid aromatic hydrocarbon was likewise multiply labeled. These small amounts of aromatic hydrocarbons are derived largely from the labeled methanol

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[2] For discussion of such reactions see Poutsma (*11*).

(rather than 2-methylpentene-1). We do not offer a detailed presentation or interpretation of these results but draw attention to the extensive, related observations of Dessau and La Pierre (*6*) (and to our earlier observations of aromatic cocatalysis of methanol conversion (*12*) which may be relevant).

The other kind of nonalkane component, namely compounds of formula C_nH_{2n}, are probably all cycloalkanes (rather than alkenes which have survived hydrogenation). All the structures which we could assign by GC/MS proved to be cycloalkanes, namely methylcyclopentane (a trace), 1,3-dimethylcyclopentanes plus methylcyclohexane (<0.3C% w.r.t. hexanes), methylethylcyclopentanes plus ethylcyclohexane (<1C% w.r.t. hexanes), and a methyl-*n*-propylcyclopentane plus diethylcyclopentanes (<1C% w.r.t. hexanes). The extent of ^{13}C-labeling in the cycloalkanes (and their fragment ions, particularly C_4) was estimated by GC/MS. The 1,3-dimethylcyclopentanes were labeled with one ^{13}C atom and ca. 21% labeled in the C_4 fragments; almost half the label was lost in the C_6 fragment, suggesting that most of the label was in the methyl groups. Methylcyclohexane had single ^{13}C label ca. 48% in excess of natural abundance. Thus, the C_7 cycloalkanes are about as extensively labeled as the C_7 alkanes.

By contrast, the C_8 and C_9 cycloalkanes are more extensively labeled than the corresponding C_8 and C_9 alkanes. The C_8 cycloalkanes are 18–31% singly ^{13}C-labeled (13–16% in the C_4 fragments) as compared with 10–20% in the C_8 alkanes. The C_9 cycloalkanes are 27–43% singly ^{13}C-labeled (13–16% in the C_4 fragments) as compared with 10–14% in the C_9 alkanes.

C_{10} and C_{11} cycloalkanes, formed in only small amounts have about 40% single ^{13}C label, while the C_{10} and C_{11} alkanes, also formed in only small amounts, have little ^{13}C label. The C_{12} hydrocarbons which are more abundant, are mainly unidentified alkanes ($C_{12}H_{26}$) without excess ^{13}C label, but included some cycloalkanes ($C_{12}H_{24}$) containing a little ^{13}C (approximately twice the natural abundance). All the C_{13} hydrocarbons also were of cycloalkane formula ($C_{13}H_{26}$) and were fully labelled with a single ^{13}C atom.

The origin of the cycloalkanes is of interest. They may be present as such in the condensate. Alternatively they may be obtained from cycloalkanes by hydrogenation. In any case the cycloalkyl skeleton probably comes from cyclization of an unsaturated carbenium ion (*11*). If this ion were formed by hydride abstraction from an olefin, one might expect cycloalkanes ^{13}C-labeled to much the same extent as the alkanes of the corresponding carbon number. In fact, the cycloalkanes are mostly more extensively labeled, possibly indicating that the unsaturated carbenium ions result from protonated dienes, such as might be formed by oxymethylation of olefins, as suggested by Langner (*13*) (cf. Ref. (*2*)).

Products from Hexene-1

Table 4 summarizes the products obtained from hexene-1 and methanol, and Table 5 summarizes the main C_5–C_8 products (obtained after hydrogenation) and their ^{13}C contents. Again it is clear that the ^{13}C label is far more abundant in the C_7 alkanes than in the C_5 and C_8 alkanes. The C_6 alkanes, which comprise most of the product contain little or no ^{13}C in excess of natural abundance; they are obviously the products of extensive isomerization of the hexene-1 (and subsequent hydrogenation). Even so, only about one-third of the C_7 molecules incorporate a ^{13}C atom of methanol. The remaining two-thirds must arise from the oligomerization and cracking of the mixture of hexenes, e.g.,

$$2\ C_6H_{12} \rightarrow C_{12}H_{24} \rightarrow C_5H_{10} + C_7H_{14} \quad (6)$$

The ^{13}C-labeled heptanes represent only about 2% of the hexene-1 feed and about 4% of the methanol feed. However, they represent over one-half of the ^{13}C label incorporated into C_5–C_8 products. We have not been able to measure directly the extent of the conversion of methanol to hydrocarbons, but the overall ^{13}C results indicate that it is low (as was intended)—of the order of 10%.

The level of ^{13}C incorporation was generally lower for hexene-1 reagent than for 2-methylpentene-1, possibly because the straight chain olefins are less reactive toward methanol than branched-chain ones. For this reason the ^{13}C distribution in the minor products was not examined in detail.

However, the extent of formation of C_3 and C_4 products was greater for hexene-1, and so attention was paid to the noncondensed effluent from the reactor. This was examined by GC/MS (without prior hydrogenation) and was found to contain mainly C_3–C_6 olefins and dimethyl ether. The mass spectrum of the dimethyl ether component (in the *m/e* 45–48 region) was entirely consistent with the expectation that methanol of 90% ^{13}C content gives 81% doubly ^{13}C-labeled (and 18% singly labeled) dimethyl ether; the parent ion is of *m/e* 48, and the base peak 47.

The propene is mainly unlabeled. Less than 17% is singly labeled and less than 3% doubly labeled (any propane impurity would make these estimates high). Likewise, less than 6% of the butenes is singly labeled. Thus, the C_3 and C_4 olefins, like the C_5 olefins, are mainly derived from unlabeled hexenes. We could not determine the extent of ^{13}C-labeling of the small amount of ethylene produced in the present work. We think it likely, on the basis of our own earlier work (*2*) and that of Dessau and La Pierre (*6*), that ethylene is much more extensively ^{13}C-labeled than the C_3–C_5 hydrocarbons.

CONCLUSIONS

[^{13}C]Methanol has been reacted with excess of 2-methylpentene-1 or hexene-1 over the proton form of ZSM-5 zeolite under conditions where conversion of the methanol to hydrocarbons is low, where the C_6 olefin undergoes extensive isomerization, oligomerization, and cracking, and where the products are a complex mixture of olefins. Much of the ^{13}C label of the converted methanol is found in singly labeled C_7 hydrocarbons. This is consistent with electrophilic methylation of a C_6 olefin (reaction (7)) to give a C_7 olefin. The finding substantiates the hypothesis that homologation of a C_n olefin to a C_{n+1} olefin is the most common C–C bond-forming reaction in the more general conversion of methanol to hydrocarbons.

$$\underset{\text{a hexene}}{C_6H_{12}} \xrightarrow{CH_3OH/H^+} [C_6H_{12}\text{—}CH_3]^+ \rightarrow \underset{\text{a heptene}}{C_7H_{14}} \qquad (7)$$

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