JOURNAL OF CATALYSIS 84, 435–445 (1983)

Conversion of Methanol to Hydrocarbons over ZSM-5 Zeolite: An Examination of the Role of Aromatic Hydrocarbons Using ^{13}Carbon- and Deuterium-Labeled Feeds[1]

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Received March 28, 1983

A mechanism is suggested for the acceleration by aromatic hydrocarbons of zeolite-catalyzed methanol conversion. According to this mechanism, the aromatic hydrocarbon undergoes successive ring methylation, prototropic conversion to an *exo*-methylene-cyclohexadiene, side-chain methylation, and ring de-ethylation. The overall result is that two methanol molecules give an ethylene molecule. The mechanism is supported by various reactions observed over ZSM-5 catalyst at methanol conversion temperatures: (i) deuteration of *p*-xylene by D_2O in the ring and methyl positions; (ii) de-alkylation of *p*-ethyltoluene and *n*-propylbenzene; and (iii) incorporation of the aromatic carbon of benzenes and alkylbenzenes into ethylene product, as revealed by ^{13}C-labeling studies.

INTRODUCTION

The preceding paper (*1*) showed that when aqueous methanol is converted to hydrocarbons in the presence of propylene or isobutylene (supplied as *n*-propanol or *t*-butanol, respectively), some of the carbon of the olefin is incorporated into the ethylene product. Detailed analysis of the results led to the conclusion that part of the ethylene is formed directly from two methanol molecules (or one of dimethyl ether) and part indirectly via species incorporating both carbon of the methanol and carbon of the olefin, as earlier revealed by Dessau and La Pierre (*2*).

The ethylene formed directly from methanol is thought to be formed by an oxonium–ylide mechanism (*1, 3–4*). The mechanism by which ethylene is formed from methanol indirectly is not known (*1*). Homologation of olefins by methanol, followed by "cracking," is an attractive explanation for formation of olefins of three or more carbon atoms, but not for ethylene, because ethylene is not formed in substantial amounts in typical reactions over ZSM-5 zeolite at 300–400°C.[3]

Another possibility is that methanol is incorporated into olefins that cyclize to ethyl–aromatics, which in turn undergo de-ethylation to ethylene over the Brønsted acid ZSM-5 catalyst.

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[3] Typical products formed over ZSM-5 are like those of acid-catalyzed cracking reactions, which do not usually give ethylene in large amounts (*5, 6a*).

0021-9517/83 $3.00
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Simple aromatic hydrocarbons (benzene, toluene, *p*-xylene, etc.) have been observed to accelerate the conversion of methanol to hydrocarbons over ZSM-5 catalyst (*7*). We now describe experiments with ^{13}C-labeled feedstocks which show that aromatic carbon is incorporated into the ethylene (and other light hydrocarbons) produced by methanol conversion. We also describe the de-alkylation of alkylbenzenes and the deuteration of *p*-xylene and toluene by D_2O over ZSM-5 zeolite. On the basis of the experiments, we propose a mechanism for conversion of methanol to ethylene.

EXPERIMENTAL

General. The ZSM-5 catalysts, apparatus and experimental methods were as described in the preceding paper (*1*), with the exception that aromatic hydrocarbons were generally introduced into the feed by diverting the vector gas through a small (ca. 2 cm^3) bubbler before the reactor. The amount introduced could be varied by varying the bubbler temperature and flow of vector gas.

Conversion of aqueous methanol in the presence of benzene-$^{13}C_6$. ZSM-5/1 catalyst (0.20 g), which had been used and regenerated repeatedly, was fed with aqueous methanol (H_2O/CH_3OH, 2.75/1 w/w; 0.17 g/hr) at 310°C in argon vector gas (240 ml/hr). Conversion was complete. The argon vector gas was then diverted through a bubbler containing benzene-$^{13}C_6$ (90% universal label) at 5°C. Yields at various reactor temperatures were measured by gas chromatography on an OV101 column, and the isotopic composition of the ethylene was estimated from the on-line mass spectrum (UTI) of the ethylene eluted from a Porapak Q column. In the isotopic analysis the relative intensities of the *m/e* 30, 29, 27, and 26 peaks (stray nitrogen made the *m/e* 28 intensity unreliable) were compared with the measured spectrum of unlabeled ethylene. The propylene and propane products were not adequately separated in high enough concentrations for proper isotopic analysis, but the ratio of the intensities of the *m/e* 29 and 30 peaks allowed an estimate of the ratio of the $^{12}C_2H_5/^{12}C^{13}CH_5$ fragments of the propane component.

A second experiment was carried out under the same conditions but with the aqueous methanol feed rate raised to 0.46 g/hr. This allowed the isotopic compositions of the ethylene, propylene, C_2H_5 fragments of propane (incompletely separated from propylene), and isobutane to be estimated, so as to establish the presence of ^{13}C label. Details of both experiments are given in Table 1 of the Results section.

Conversion of aqueous methanol in the presence of toluene-α-^{13}C. Regenerated ZSM-5/1 catalyst (0.20 g), as in the previous experiment, was fed with aqueous methanol (H_2O/CH_3OH 2.75/1 w/w; 0.46 g/hr) at 279°C in argon vector gas (180 ml/hr) which had been bubbled through toluene-α-^{13}C (90% label) at 10°C. Product yields and the isotopic composition of ethylene were estimated as above. The presence of ^{13}C in the propane product was determined from the relative intensities of the *m/e* 30 and 29 (C_2H_5) fragments of the propane eluted from a Porapak Q column. Details are given in Table 1 of the Results section.

Conversion of aqueous methanol-^{13}C in the presence of unlabeled aromatic hydrocarbons. Regenerated ZSM-5/1 catalyst (0.20 g), as in the previous experiment, was fed with a mixture (0.29 g/hr) of water (1.36 g)/[^{13}C]-methanol (0.48 g; 90% label) in nitrogen vector gas (240 ml/hr) which was bubbled through various aromatic hydrocarbons (benzene, toluene, and ethylbenzene). Product yields and the isotopic composition of the ethylene were measured in each case. Details are given in Table 2 of the Results section.

Dealkylation of alkylbenzenes. Regenerated ZSM-5/1 catalyst (0.20 g), as in the previous experiment, was fed with water (0.36 ml/hr), together with nitrogen vector gas (360 ml/hr) which was bubbled through *p*-ethyltoluene or *n*-propylbenzene at 19°C (saturated vapor press. ~2 mm Hg). Prod-

uct yields were measured at various reactor temperatures.

Deuteration of p-xylene. Regenerated ZSM-5/1 catalyst (0.20 g) was fed with deuterated water (0.96 ml/hr) in a stream of nitrogen vector gas (300 ml/hr). Pulses of *p*-xylene (5 μl) were fed, each over 4 min, at various temperatures. The aqueous product from each pulse was collected in a trap at ca. 5°C, and a pentane extract of the mixed xylenes so trapped was analyzed using a Hewlett–Packard 5995A gas chromatograph/mass spectrometer.

Deuteration of toluene. An experiment similar to that described above was carried out, but with 5-μl pulses of toluene instead of *p*-xylene.

RESULTS

^{13}*Carbon-Labeling Experiments*

One of the two series of carbon-labeling experiments used unlabeled methanol and ^{13}C-labeled hydrocarbons; the results are summarized in Table 1. The other series used ^{13}C-labeled methanol and unlabeled hydrocarbons, and the results are summarized in Table 2.

The experiments listed in Table 1 were all carried out at or above the minimum temperature of complete conversion. This temperature is lower, by about 20°C, in the presence of the aromatic hydrocarbon than in its absence (*7*). A temperature of ca. 320°C is required for complete conversion in the absence of the aromatic (*1*).

The products obtained are listed in Table 1. The aliphatic hydrocarbons—ethylene, propylene plus propane, isobutane and other C_4 hydrocarbons, and smaller amounts of C_{5-7} hydrocarbons—are those expected from conversion of aqueous methanol (*1, 3*). The aromatic products from benzene are toluene, C_8 aromatics (mainly an unresolved mixture of *m*- and *p*-xylene), *n*-propylbenzene, an unresolved mixture of *m*- and *p*-ethyltoluene, and 1,2,4-trimethylbenzene. The aromatic products from toluene are similar but exclude benzene. These aromatic hydrocarbons represent mainly the aromatic hydrocarbon introduced and its methylation products, but include small amounts of products having alkyl groups of two or three carbon atoms.

The ethylene is mainly unlabeled, as would be expected if it were derived from unlabeled methanol. However, the ^{13}C label of the benzene is incorporated into the ethylene to a significant extent; 10–30% of the ethylene is mono-^{13}C labeled, and the degree of incorporation increases with temperature and with benzene/methanol ratio.

It is easier to separate ethylene (and isotopically analyze it) than individual aliphatic hydrocarbons of three or more carbon atoms. However, two analyses of propane product indicated the presence of 20–40% mono-^{13}C-labeled material, and in one case propylene and isobutane were also examined and each was found to contain ca. 25% mono-^{13}C-labeled material (see the footnotes of Table 1).

It is noteworthy that the mass spectrum of the recovered benzene is identical with that of the starting material. Thus the loss of the ^{13}C label is confined to benzene which has undergone chemical change.

The last column of Table 1 refers to toluene labeled in the methyl group, and shows that some of this label is incorporated into the ethylene product.

Table 2 summarizes the results obtained when ^{13}C-labeled methanol was fed to ZSM-5 catalyst along with various unlabeled aromatic hydrocarbons. If the carbon of the unlabeled aromatic is not incorporated into the ethylene, one expects 90% ^{13}C-labeled methanol to give ethylene which is 1% unlabeled, 18% mono-^{13}C labeled, and 81% di-^{13}C labeled. In every case the ethylene is less extensively labeled than expected; ca. 35% is mono-^{13}C labeled. Thus, some of the unlabeled carbon of the aromatic hydrocarbon is incorporated into the ethylene.

The isotopic composition of the ethylene is similar in every case except for that from

TABLE 1

Conversion of Aqueous Methanol in the Presence of ^{13}C-Labeled Benzene or Toluene over ZSM-5/1 Catalyst[a]

Liquid feed rate (g/hr)	0.17			0.46	0.46
Methanol feed rate (mmole/hr)	1.4			3.7	3.7
Aromatic feed	Benzene[b] at 5°C			Benzene[b] at 5°C	Toluene[c] at 10°C
Feed rate (mmole/hr)	0.45			0.45	0.12
Temperature (°C)	289	310	350	310	279
Yields[d]	[e]	[e]	[e]	[f]	
C_2H_4	5	3	6		10
$C_3H_6 + C_3H_8$	3		4	12	10
C_4 hydrocarbons	4	4	13		13
C_{5-7} hydrocarbons[g]	2	1	4		15
Benzene	47	41	9		—
Toluene	15	15	13		15
C_8 Aromatics	11	18	31		15
n-Propylbenzene	3	1	0		—
m/p-Ethyltoluene	4	7	5		9
1,2,4-Trimethylbenzene	3	3	5		4
% of mono-^{13}C label in C_2H_4[h]	20	23	30	14	6
% of mono-^{13}C label in propane (and other products—see footnotes)			40[i] 45[j]	25[i,k]	

[a] Water/methanol, 2.75/1 w/w was fed to ZSM-5/1 catalyst (0.20 g) in 240 ml/hr argon vector gas which was bubbled through the ^{13}C-labeled aromatic hydrocarbon before reaching the reactor.

[b] 90% ^{13}C labeled at all carbon atoms; svp ~35 mm Hg.

[c] 90% ^{13}C labeled in the methyl group; svp ~13 mm Hg.

[d] Yields are expressed as C% of total feed, including aromatic.

[e] ca. 35 C% of the feed is methanol, ca. 65% benzene.

[f] ca. 80 C% of the feed is methanol, ca. 20% toluene.

[g] Excluding aromatic hydrocarbons.

[h] ± ca. 4%. There is less than ca. 4% of di-^{13}C label in the ethylene in every case.

[i] Estimated from the relative intensities of the *m/e* 45 and 44 peaks of the propane.

[j] Estimated from (3/2×) the relative intensities of the *m/e* 30 and 29 ethyl fragments of the propane.

[k] Mono-^{13}C label (20–25%) in the propylene product was estimated from the relative intensities of the *m/e* 43 and 42 peaks. ca. 25% of mono-^{13}C label in the *iso*butane product was estimated from (4/3×) the relative intensities of the *m/e* 44 and 43 peaks in its propyl fragments. The mass spectrum of recovered benzene did not differ significantly from that of the starting material.

the ethylbenzene experiment, which gave a higher ethylene yield and a higher proportion of unlabeled ethylene than the other experiments, consistent with part (ca. 10%) of the ethylene coming from de-ethylation of ethylbenzene (see below).

Dealkylation Experiments

Dealkylation of alkylbenzenes over ZSM-5/2 catalyst under conditions of methanol conversion was established for *p*-ethyltoluene and *n*-propylbenzene. When nitrogen was passed through a *p*-ethyltoluene bubbler at 19°C (saturated vapor pressure ~2 mm Hg) and fed together with water to the catalyst (in an experiment designed to simulate methanol conversion conditions), 36C% of the ethyltoluene underwent conversion at 330°C.[4] The products are toluene

[4] Thermodynamic data predict a 70% equilibrium conversion of ethylbenzene to benzene and ethylene, at this temperature and partial pressure.

TABLE 2

Conversion of Aqueous ^{13}C-Labeled Methanol in the Presence of Various Unlabeled Aromatic Hydrocarbons over ZSM-5/1 Catalyst[a]

Aromatic hydrocarbon	Benzene (7°C)[b]	Toluene (10°C)[c]	Toluene (17.5°C)[d]	Ethylbenzene (19°C)[e]
Feed ratio				
C of aromatic/C of methanol	1.5	0.5	0.9	0.3
Temperature (°C)	306	304	294	293
Yields[f]				
C_2H_4	5	13	10	22
$C_3H_6 + C_3H_8$[g]	5	10	7	15
C_4 hydrocarbons[g]	6	11	8	13
C_{5-7} hydrocarbons[h]	3	8	6	9
Benzene	35	—	—	—
Toluene	14	22	38	4
C_8 aromatics[g]	15	23	16	21
n-Propylbenzene	2	—	—	—
m/*p*-Ethyltoluene	6	6	4	6
1,2,4-Trimethylbenzene	3	5	3	4
$^{12}C_2H_4$[i]	6	6	6	14
$^{12}C^{13}CH_4$[i]	35	35	39	29
$^{13}C_2H_4$[i]	59	59	55	57

[a] A mixture (0.29 g/hr) of water (1.36 g) and 90% ^{13}C-labeled methanol (0.48 g) was fed to ZSM-5/1 catalyst (0.20 g); methanol feed rate = 2.3 mmole/hr. Nitrogen vector gas (240 ml/hr) was bubbled through the aromatic hydrocarbon.

[b] svp ~38 mm Hg.

[c] svp ~13 mm Hg.

[d] svp ~22 mm Hg.

[e] svp ~7 mm Hg.

[f] C% of total feed (methanol plus aromatic hydrocarbon).

[g] Detailed composition not investigated.

[h] Excluding aromatic hydrocarbons.

[i] ± ca. 4%.

(23C%) and ethylene (4.5C%), benzene (1C%), and C_8 aromatics (8C%).

Similarly when nitrogen was bubbled through *n*-propylbenzene at 19°C (saturated vapor pressure ~2 mm Hg) and fed, with water, to ZSM-5/2 catalyst, 66% of the *n*-propylbenzene was converted at 301°C.[5] The main products are benzene and C_3 hydrocarbons, as expected. At 340°C, conversion was >90%.

Deuteration Experiments

These experiments were designed to investigate whether D^+ from D_2O can be incorporated into the methyl groups of toluene and *p*-xylene. Each experiment consisted of injecting a pulse of toluene or *p*-xylene into the heated nitrogen vector gas to a bed of ZSM-5 catalyst continuously fed by D_2O, then measuring the mass spectrum of the recovered hydrocarbon so as to estimate the extent of deuteration.

Analysis of the results obtained with *p*-xylene was complicated by the occurrence of extensive xylene isomerization and by the fact that the capillary gas chromatography column differentiated between the variously deuterated levels of each isomer to such an extent as to make adequate separation of *m*-xylene from *p*-xylene impossible. The gas chromatograph temperature was

[5] Thermodynamic date predict >90% equilibrium conversion to propylene and benzene, at this temperature and partial pressure.

TABLE 3

Mass Spectra of Xylenes and Toluene

m/e	Intensity							
	Xylenes[a,b,c]					Toluene[c]		
	No label	D_2O/ 290°	D_2O/ 330°	D_2O/ 390°	D_2O/ 460°	No label	D_2O/ 325°	D_2O/ 460°
116		0	2	7	36(d_{10})			
115		0	3	10	35			
114		0	4	16	49			
113		2	10	25(d_7)	54			
112		7	22(d_6)	38	51			
111		29(d_5)	44	51	43			
110		74	62	51	30(d_4)			
109		34(d_3)	28(d_3)	26(d_3)	14			
108		13	11	11	7			
107		7	7	7	6			
106	47	5	5	4	3			
105	22	3	2	2	2			
99			1	2	6			7
98		1	5	20	88(d_7)		14	43(d_6)
97		3	15	38(d_6)	98		100(d_5)	100
96		23	45(d_5)	76	100		99	97(d_4)
95		100(d_4)	100	100	76		70	55
94		64(d_3)	51(d_3)	54(d_3)	28(d_3)		9	7
93		23	21	18	10		5	
92	9	6	4	4	3	60		
91	100	1	1	1	1	100		

[a] All three isomers of undeuterated xylene show essentially the same spectrum.

[b] The spectra recorded are for an unresolved mixture of *meta*- and *para*-xylene. Xylene isomerization occurs. The percentage of *ortho*-isomer is 14% at 290°C, 20% at 330°C, 22% at 390°C, and 25% at 460°C. The mass spectrum of the deuterated *ortho* isomer is slightly different from that of the *meta/para* mixture, indicating a slightly different level of deuteration.

[c] No correction has been made for the presence of naturally abundant ^{13}carbon.

therefore ramped quickly and mass spectra of completely merged mixtures of *m* and *p* isomers were recorded. Table 3 shows the observed mass spectra for the *m/p*-xylene mixtures.

Analysis of the results obtained with toluene is largely free from complications, and results obtained at 325 and 460°C are also shown in Table 3. Toluene, at 325°C, is mainly d_5 deuterated, consistent with fast exchange of the five aryl hydrogens. The intensity of the *m/e* 98 peak, after allowing for natural ^{13}C abundance, indicates that the abundance of d_6-toluene is 7% that of d_5-toluene. At 460°C, d_6-toluene has an abundance about half that of d_5-toluene. It is clear that, in the range 325–460°C, toluene is rapidly deuterated in the five ring positions but only slowly deuterated in the methyl group. Deuteration in the methyl group is barely significant at 325°C.

The *m/p*-xylene is much more extensively deuterated. At 460°C, the mass spectrum corresponds to a broad d_4–d_{10} distribution. Thus xylene is extensively deuterated at both ring and methyl positions at 460°C.

At 290°C d_4 deuteration is dominant, with d_3 deuteration being ca. 20% of d_4, d_5 ca. 40% of d_4, and d_6 ca. 10% of d_4. Thus at

290°C ring deuteration is fast, and methyl group deuteration is slow but significant in extent. At 330°C the concentration of d_5-xylene is about the same as that of d_4-xylene, i.e., ring deuteration is complete and, on average, one methyl proton of every other xylene molecule has been replaced by deuterium.

DISCUSSION

The present paper is concerned with the question of how aromatic hydrocarbons accelerate the conversion of aqueous methanol of hydrocarbons (*7*). We develop a mechanism whereby two molecules of methanol can be converted indirectly to one molecule of ethylene by the intervention of a molecule of aromatic hydrocarbon.

Aromatic Dealkylation

An essential element in the mechanism is recognition that deethylation (1) of ethyl–aromatic compounds represents a selective route to ethylene. The present results have shown that ethylene may be formed from *p*-ethyltoluene under conditions of methanol conversion.

$$\text{aryl-}C_2H_5 \xrightarrow{H^+} \text{aryl-H} + C_2H_4. \quad (1)$$

Similarly it is has been shown that propylene may be formed from propylbenzene. In general,

$$\text{aryl-}C_nH_{2n+1} \xrightarrow{H^+} \text{aryl-H} + C_nH_{2n} \quad (2)$$

(aryl = C_6H_5, etc.; $n \geq 2$).

It is worth noting that the conversion of methanol under mild conditions yields some ethyltoluenes, but that reactions over ZSM-5 at temperatures of 400°C or more typically give methylaromatics; other alkylaromatics are found in only small amounts, presumably because reaction (2) strips alkyl groups of two or more carbon atoms.

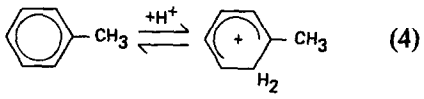
The occurrence of dealkylation reactions is obviously important in determining the aromatic products of reactions over ZSM-5 zeolite quite generally. The typical aromatic products—toluene, xylenes, and 1,2,4-trimethylbenzene—formed from an aliphatic feed at 300–400°C should be regarded as formed by a sequence of cyclization, aromatization, and dealkylation reactions. Thus, for example, xylene should not be regarded as exclusively the product of a C_8 cyclization.

Deuteration in the Methyl Group

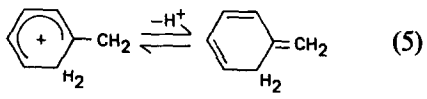
Our main concern, however, is with the possible formation of olefin as a consequence of reaction of methanol or dimethyl ether with aromatic molecules. In particular we are concerned with the possibility of a reaction such as (3):

$$\text{aryl-}CH_3 \xrightarrow{CH_3OH} \text{aryl-}CH_2\text{-}CH_3 \quad (\rightarrow \text{aryl-H} + C_2H_4). \quad (3)$$

Such reactions are normally base-catalyzed (*6b*). They are also known to occur over alkali-exchanged zeolites (*8, 9*), but are not well defined mechanistically (*10, 11*); it has been suggested (*10*) that acid protonates the ring and that base deprotonates the methyl substituent which is to be methylated. Thus a prototropic shift might occur as depicted in reactions (4)–(5):



(4)



(5)

The product of reaction (5) is 5-methylene-1,3-cyclohexadiene. If protonation (4) occurred at the *para* position in toluene, the corresponding product of reaction (5) would be 1-methylene-2,5-cyclohexadiene. These are known compounds (*12–15*) but their formation from toluene is strongly endothermic (*16*), and they tend to isomerize to toluene.[6]

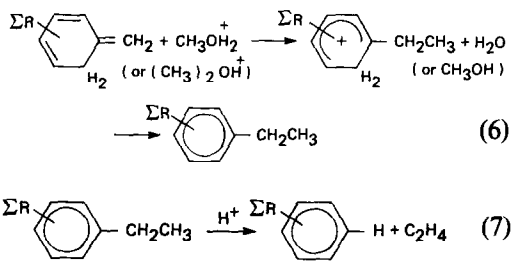
[6] 4-Methylene-1,1,2,3,5,6-hexamethylcyclohexa-2,5-diene from deprotonation of heptamethylbenzenium cation is better known (*17*).

Data consistent with the occurrence of reactions of types (4) and (5) was obtained by treating toluene and xylene with D_2O over ZSM-5 zeolite. Occurrence of only reaction (4) should allow the aromatic hydrocarbon to be deuterated in the ring. Occurrence of (5) should allow deuteration in the methyl group as well.

Both toluene and *p*-xylene undergo facile aromatic deuteration at temperatures around the ca. 300°C required for methanol conversion. Toluene undergoes marked deuteration in the methyl group at 460°C but very little at 325°C (consistent with an earlier report (*18*) on exchange between toluene and perdeuterobenzene).

p-Xylene undergoes deuteration in the methyl group much more readily than toluene. Significant deuteration is observed at 290°C, and at 330°C is as extensive as for toluene at 460°C. The increase in rate of methyl group deuteration from toluene to xylene is to be expected: first, because increasing substitution will lower the rate of diffusion and so increase the possibility of reaction within the zeolite; second, because the rate of protonation must increase with increased substitution by methyl groups; and third, because of the increased number of methyl protons available for abstraction. More highly substituted hydrocarbons, for example 1,2,4-trimethylbenzene and durene, might well undergo still more facile deuteration in the methyl groups.

The *exo*-methylene group formed by reaction (5) must be subject to other electrophilic attack (besides protonation). In particular methylation (6) should give an ethyl–aromatic compound, and subsequent deethylation (7) should give ethylene.



(ΣR = one or more methyl substituents).

Thus a sequence of reactions in which an aromatic hydrocarbon undergoes successive aromatic methylation, prototropic shift, methylation at the *exo*-methylene group, and deethylation has the overall effect of converting two molecules of methanol to one of ethylene.[7]

^{13}C *Isotopic Evidence*

The above discussion shows the mechanistic feasibility of conversion of methanol to ethylene by successive methylations of aromatic hydrocarbon. The mechanism implies that the carbon of the methyl group of a methyl–aromatic compound should be incorporated into the ethylene product, and this was indeed shown.

The simplest evidence is that obtained from conversion of methanol in the presence of toluene ^{13}C labeled in the methyl group. Of the ethylene, 6% is mono-^{13}C labeled. Of the feed, 2.5C% is provided by the toluene methyl group of which one-eighth (0.3C%) is found in the ethylene.

However, not only methyl carbon but also aromatic carbon can be incorporated into the ethylene. This is shown most clearly by the series of experiments (of Table 1) in which methanol is converted in the presence of ^{13}C-labeled benzene. In these experiments 14–30% of the ethylene is mono-^{13}C labeled, with the percentage increasing with benzene/methanol ratio and with temperature.

The 350°C experiment of Table 1 can be considered as follows. Of the feed 35C% is methanol and 65C% is benzene. The product comprises 6C% ethylene of which 1C% is derived from the benzene, 12C% C_3 hydrocarbons of which 1C% is derived from the benzene, and 13C% C_4 hydrocarbons of which we suppose (using the information of footnote *k* of the Table) that 1C% is derived from benzene. Thus, in total, some 3C% of the 65C% labeled benzene is incorporated into light (C_{2-4}) hydrocarbons. There is lit-

[7] See, however, the discussion of ^{13}C-isotopic evidence, below.

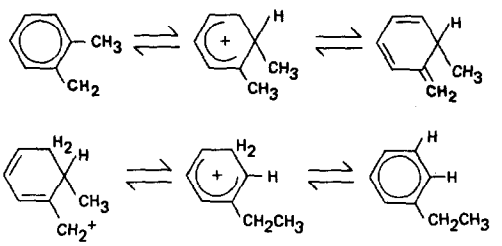
tle, if any, loss of ^{13}C label from the recovered benzene, so the loss of label must occur in the benzene which has undergone reaction. Direct formation of ethylene from aromatic carbon is mechanistically improbable, so some scrambling of aromatic carbon between ring and side chain must occur.

The data of Table 2 largely confirm that of Table 1, but using labeled methanol and unlabeled aromatic hydrocarbons. The isotopic composition of the ethylene varies little from one experiment to another, except in that ethylbenzene gave more unlabeled ethylene (presumably by deethylation). The benzene and toluene experiments all gave 6% $^{12}C_2H_4$ and 35–39% $^{12}C^{13}CH_4$. This is consistent with 70% of the ethylene being derived entirely from methanol, and the other 30% deriving one carbon from methanol and the other from the unlabeled benzene or toluene. Alternatively all of the ethylene could derive one carbon from the methanol and the other from carbon of 60% ^{13}C label, which could arise out of scrambling of carbon between ring and side chain.

It is particularly difficult to define the nature of the reaction which scrambles carbon between ring and side-chain in that the reacting species have not been defined. It has generally been assumed that protonation of the benzene ring over an acid catalyst can lead to a cationic 6 → 5 ring contraction (*6a*) and this mechanism appears to be established for the scrambling of ^{14}C label in naphthalene (*19*).

Generally, however, this mechanism is assumed rather than proven. Thus a 6 → 5 contraction is thought (*6a*) to be involved in the conversion of xylenes to ethylbenzene at 515°C over silica/alumina (*20*), even though an *exo*-methylene–cyclohexadiene intermediate is an alternative explanation (reaction (8)).

Again, a 6 → 5 ring contraction is postulated but not proven for the conversion of hexamethylbenzenes to less methylated benzenes and alkanes at 344°C over silica alumina (*21*).



(8)

A 6 → 5 ring contraction would account for the ^{13}C-isotopic results now reported, and might account for the methyl-deuteration of toluene and xylenes.[8]

However, Brønsted acid-catalyzed reaction of *exo*-methylenecyclohexadiene species might also account for the ^{13}C-isotopic results. Furthermore, it should be noted that there is an extensive literature (*22, 23*) on isotopic scrambling of hydrogen and carbon in $C_7H_7^+$ and $C_7H_8^+$ species under mass spectroscopic conditions.

The Mechanism of Methanol Conversion

It is now possible to formulate a view of the conversion of methanol to hydrocarbons in which all carbon–carbon bond formation from methanol results from proton-transfer reactions and electrophilic methylations. This view is consistent with ZSM-5 zeolite's Brønsted acid character and with the well-known autocatalytic character (*7*) of the reaction.

The first step in conversion is Brønsted acid-mediated establishment of the equilibrium between methanol and dimethyl ether. The second step is the initial formation of carbon–carbon bonded materials from methanol. We have now recognized two routes to ethylene. The first route is the oxonium–ylide mechanism, where dimethyl ether undergoes O-protonation (or O-alkylation) and C-deprotonation to an oxonium–

[8] We are grateful to a referee for pointing out the possible significance of 6 → 5 ring contraction in interpretation of our results. Our interpretation should be regarded as working hypothesis rather than rigorously established mechanism.

ylide, which undergoes intramolecular electrophilic methylation to ethylene. The various features of this mechanism have been discussed previously (*3*).

The second route from methanol to ethylene is the aromatic-assisted process discussed above. The essential steps are aromatic protonation, methyl deprotonation, and electrophilic methylation.

Both processes occur around 300°C, and they cause ethylene to be formed with a selectivity of up to 30C%. Normally, however, the selectivity for ethylene is much lower than 30C%. The fall in ethylene selectivity may result in part from the consumption of ethylene under more severe reaction conditions, but probably results mainly from the existence of "propagation" conversion which is faster than the "initiation" discussed above. The propagation reactions are thought to involve repeated electrophilic methylation of olefins (*15*). Methylation converts one olefin to the next homolog. Repeated methylation, followed by Brønsted acid-mediated cracking, leads to formation of a second molecule of olefin. This reaction (9) is chain branching (*18*):

$$C_mH_{2m} + nCH_3OH \rightarrow C_{m+n}H_{2m+2n} \rightarrow C_mH_{2m} + C_nH_{2n}. \quad (9)$$

What is most important is that the propagation reactions have very low selectivity for ethylene formation.

The olefins involved in propagation are very reactive towards Brønsted acid, and so undergo isomerization, oligomerization, and cracking reactions besides the reactions required for the propagation.

Chain termination involves hydride transfer reactions[9] which result in the formation of isoalkanes and aromatic hydrocarbons. Since the aromatic hydrocarbons effectively assist one of the initiating reactions, the effectiveness of chain termination is correspondingly limited.

[9] Our view is that hydride transfer is not involved in homologation. However, homologation by oxymethyl cations (the Prins reaction) (*24*) is feasible, and was discussed in the previous paper (*1*).

ACKNOWLEDGMENTS

This work was carried out with the support of the Australian National Energy Research Development and Demonstration Council. The authors are indebted to Dr. J. R. Anderson for advice, encouragement, and help with this manuscript, and to Keith Wilshier and Paul Smart for invaluable help with the experimental work.

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