JOURNAL OF CATALYSIS 47, 249-259 (1977)

The Conversion of Methanol and Other O-Compounds to Hydrocarbons over Zeolite Catalysts

CLARENCE D. CHANG AND ANTHONY J. SILVESTRI

Central Research Division, Mobil Research and Development Corporation, Princeton, New Jersey 08540

Received October 18, 1976; revised January 24, 1977

The conversion of methanol and other O-compounds to C_2–C_{10} hydrocarbons using a new class of shape-selective zeolites is reported. Methanol, dimethyl ether, or an equilibrium mixture thereof appears to be converted in a first reaction sequence to olefins predominantly in the C_2–C_5 range. In the final steps of the reaction path, the C_2–C_5 olefins are converted to paraffins, aromatics, cycloparaffins and C_6^+ olefins. The final hydrocarbons are largely in the gasoline (C_4–C_{10}) boiling range. The thermochemistry of the methanol to hydrocarbon reaction is described and possible reaction mechanisms are discussed.

I. INTRODUCTION

A new and simple catalytic process for the conversion of methanol to hydrocarbons and water was recently announced by Mobil (*1*). The hydrocarbons produced in this process are aliphatic and aromatic, and are predominantly in the gasoline boiling range (C_4 to C_{10}). Since technology exists for going from coal and natural gas to methanol, the methanol conversion process provides a new link for transformation of fossil fuels other than petroleum to gasoline. The gasoline thus produced is chemically conventional, with unleaded research octane numbers of 90 to 95. This gasoline is substantially superior in both yield and quality to that produced by Fischer-Tropsch chemistry.

The methanol to gasoline conversion process is based on a new class of shape-selective zeolites (*1*) which are distinctly different from and intermediate in pore dimension to the familiar wide-pore faujasites and the very narrow-pore zeolites such as Zeolite A and erionite.

Hydrocarbon formation over the new zeolites is not limited to methanol. A wide variety of hetero-organic compounds can be efficiently transformed to hydrocarbons.

In this paper we describe the conversion of compounds containing various functional groups over the new zeolites. The conversion of methanol in particular is considered in some detail in view of its potential commercial importance. The reaction path for going from a one carbon atom moiety, methanol, to aromatic and paraffin hydrocarbons in the gasoline boiling range is postulated. The thermochemistry of this reaction is discussed and speculation on possible mechanisms is presented.

II. EXPERIMENTAL METHODS

Materials

Methanol, dimethyl ether, *t*-butanol, 1-heptanol, acetone, methyl mercaptan, methylal, acetic acid and *t*-butyl formate were high purity reagents (99 + %). Propanal (bp 47–49°C) and *n*-propyl

ISSN 0021-9517

TABLE 1

Zeolite-Catalyzed Hydrocarbon Formation

Reactant:	Methanol	*t*-Butanol	1-Heptanol	Methanethiol	Propanal	Methylal
Reaction conditions						
T (°C)	371	371	371	482	371	371
LHSV (hr^{-1})	1.0	1.0	0.7	1.0	1.0	1.0
Conversion (%)	100.0	100.0	99.9	99.9[a]	99.9	100.0[b]
Hydrocarbon distribution (wt%)						
Methane	1.0	0.1	0.0	6.6	0.8	1.5
Ethane	0.6	0.7	0.3	8.3	0.4	0.7
Ethylene	0.5	0.5	<0.1	6.7	0.4	0.3
Propane	16.2	18.8	16.4	15.3	7.3	16.4
Propylene	1.0	1.1	0.2	1.3	0.6	0.9
i-Butane	18.7	18.4	19.3	9.0	4.6	15.1
n-Butane	5.6	8.6	11.0	3.1	3.0	5.8
Butenes	1.3	0.7	<0.1	0.2	0.3	0.9
i-Pentane	7.8	6.2	8.7	1.2	1.8	5.8
n-Pentane	1.3	1.4	1.5	<0.1	0.6	1.0
Pentenes	0.5	0.2	0.1	<0.1	0.2	0.2
C_6^+ aliphatics	4.3	7.6	3.0	0.1	1.3	3.2
Benzene	1.7	3.3	3.4	0.2	4.1	1.1
Toluene	10.5	11.6	14.3	1.3	23.7	7.9
Ethylbenzene	0.8	1.3	1.2	<0.1	2.6	0.7
Xylenes	17.2	12.4	11.6	8.9	26.4	20.5
C_9 Aromatics	7.5	6.1	5.3	27.0	18.6	12.4
C_{10} Aromatics	3.3	0.4	2.9	9.5	3.7	5.4
C_{11}^+ Aromatics	0.2	0.6	0.6	1.3	0.6	0.2

[a] 27.2% C converted to $(CH_3)_2S$.

[b] 11.0% C converted to $CO + CO_2$.

acetate (bp 98–102°C) were used without further purification.

Catalysts

The chemical conversions discussed in this paper are reported in a number of patents [for example see Ref. (*23*)] which describe potential catalysts.

Apparatus and Procedure

Fixed-bed continuous flow microreactors were used, and were made from 4.6 and 7.8 mm i.d. 304 stainless steel tubing. The reactors, which contained up to 6 cm^3 catalyst, were equipped with electrical resistance heaters and proportional integral temperature controllers. All feedstocks were charged as liquids by a positive displacement pump. A back-pressure regulator between the pump discharge and reactor preheat zone maintained normally gaseous feeds such as dimethyl ether in liquid phase in the pump cylinder. Liquid products were collected in CO_2–acetone and liquid N_2 traps, and gaseous products in a gas burette. Analyses were carried out using gas chromatography, mass spectrometry and infrared.

III. RESULTS AND DISCUSSION

A. General Scope

The reactions of O-compounds over the new zeolites can be most generally characterized as dehydration or decarboxylation with shape-selective transformation leading to hydrocarbons having a narrow distribution of molecular weights.

The data presented in Tables 1–3 are a representative survey of the conversion of various compounds and provide an indication of the scope of the reaction.

Alcohols

Typical hydrocarbon distributions from alcohol conversion are shown in Table 1 (Examples 1–3) for three representative alcohols: methanol, *t*-butanol, and 1-heptanol. The data were obtained at 371°C, 1 LHSV and atmospheric pressure. Under these conditions, water elimination is essentially complete. The three hydrocarbon product distributions are strikingly similar, suggesting a common reaction pathway. As noted previously, the distribution is shape-selective. Essentially no hydrocarbons above C_{11} are produced. Isoparaffins predominate, as do isoolefins, though the latter have not been detailed in Table 1. Aromatics are mostly methyl-substituted. Detailed aromatics distribution are presented below. Included for comparison in Table 1 are data from a sulfur analogue, methanethiol (Example 4). The reaction temperature for methanethiol, converted with greater difficulty, was 482°C. At this temperature and 1 LHSV, desulfurization was partial, with 27.2% of the feed carbon converted to dimethyl sulfide. The overall hydrocarbon distribution is quite similar to the previous, with

TABLE 2

Effect of Temperature on Acetone Conversion to Hydrocarbons

Reaction conditions				
T (°C)	250	288	329	399
LHSV (hr^{-})	8.0	8.0	8.0	8.0
Conversion (%)	3.9	6.0	24.5	95.3
Carbon selectivity, (%)[a]				
Diacetone	3.5	2.9	0.1	—
Mesityl oxide	27.3	19.7	1.2	—
Isophorone	—	<0.1	5.3	—
Other O-compounds[b]	6.0	15.0	<0.1	—
$CO + CO_2$	—	0.7	10.0	6.1
Hydrocarbons	63.2	61.6	83.4	93.9
Hydrocarbon distribution (wt%)				
Methane	—	—	0.2	0.1
Ethane	—	—	0.4	0.2
Ethylene	<0.1	<0.1	1.2	2.4
Propane	—	0.3	1.9	4.2
Propylene	2.5	3.8	4.2	5.2
i-Butane	—	—	0.1	3.9
n-Butane	—	—	—	1.7
i-Butene	19.1	31.3	83.3	3.6
n-Butenes	—	—	<0.1	2.3
i-Pentane	—	—	—	1.5
n-Pentane	—	—	—	0.6
Pentenes	—	—	—	2.5
C_6^+ Aliphatics	19.1	3.8	1.6	8.2
Benzene	—	—	—	2.6
Toluene	—	—	0.1	13.0
Ethylbenzene	—	—	—	2.7
Xylenes	—	1.3	2.1	22.3
1,2,3-Trimethylbenzene	—	<0.1	<0.1	1.1
1,2,4-Trimethylbenzene	—	7.0	2.0	8.8
1,3,5-Trimethylbenzene	59.3	52.5	2.6	0.6
Other C_9 Aromatics	—	—	0.3	9.7
C_{10} Aromatics	—	—	—	2.8
C_{11}^+ Aromatics	—	—	—	—

[a] (C in product/ΣC converted) × 100.

[b] Mainly C_4 alcohols.

TABLE 3

Hydrocarbons from Carbonyl Compounds

Reactant:	Acetic acid	*n*-Propyl acetate	*n*-Butyl formate
Reaction conditions			
T (°C)	371	371	371
LHSV (hr^{-1})	1.0	1.0	1.0
Conversion (%)	29.9[a]	97.9[b]	100.0[c]
Hydrocarbon distribution (wt%)			
Methane	0.4	0.1	0.1
Ethane	0.1	0.1	0.4
Ethylene	0.4	2.7	0.2
Propane	0.9	2.1	19.4
Propylene	3.3	32.1	0.9
i-Butane	1.0	1.0	19.3
n-Butane	0.6	0.6	9.2
Butenes	71.5[d]	6.9	0.6
i-Pentane	0.1	0.3	7.9
n-Pentane	—	0.5	1.9
Pentenes	0.4	2.0	0.1
C_6^+ Aliphatics	—	3.3	4.8
Benzene	<0.1	0.8	2.1
Toluene	2.0	6.1	10.9
Ethylbenzene	0.5	1.4	1.1
Xylenes	5.1	16.7	11.6
C_9 Aromatics	11.4	15.2	6.2
C_{10} Aromatics	11.4	6.3	3.0
C_{11}^+ Aromatics	2.2	1.8	0.3

[a] Carbon selectivity (%): acetone (0.1); CO (1.0); CO_2 (41.2); hydrocarbons (57.6).

[b] 3% C converted to CO_2.

[c] 18.4% C converted to CO.

[d] 93% *i*-Butene.

TABLE 4

Effect of Space Velocity on Methanol Conversion and Hydrocarbon Distribution

LHSV [vol of liquid methanol/(vol of catalyst/hr)]	1080	108	1
Product distribution (wt%)			
Water	8.9	33.0	56.0
Methanol	67.4	21.4	0.0
Dimethyl ether	23.5	31.0	0.0
Hydrocarbons	0.2	14.6	44.0
Conversion (MeOH + MeOMe) (wt%)	9.1	47.5	100.0
Hydrocarbon distribution (wt%)			
Methane	1.5	1.1	1.1
Ethane	—	0.1	0.6
Ethylene	18.1	12.4	0.5
Propane	2.0	2.5	16.2
Propylene	48.2	26.7	1.0
i-Butane	13.8	6.5	18.7
n-Butane	—	1.3	5.6
Butenes	11.9	15.8	1.3
C_5^+ Aliphatics	4.4	27.0	14.0
Aromatics	—	6.6	41.1

the main difference being that more light gas was produced, a result of the higher severity. Furthermore, the aromatics appear to peak at C_9, rather than C_8, as observed with alcohol feeds.

Aldehydes

The conversion of propanal and methylal, a formaldehyde derivative, is shown also in Table 1 (Examples 5 and 6). Propanal is efficiently converted to hydrocarbons, with higher selectivity to aromatics than the alcohols. Methylal gives a product similar to that obtained from the alcohols. However, some dissociation to CO and CO_2, is evident.

Ketones

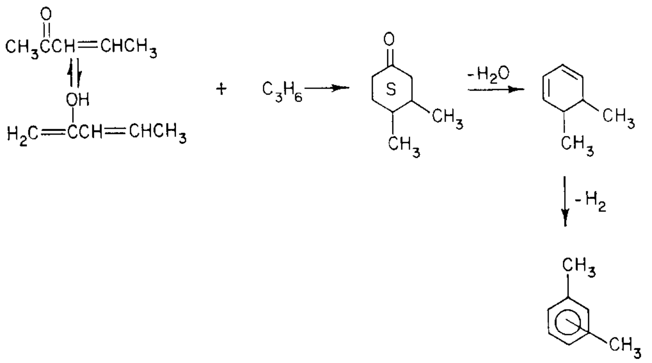
Acetone is an interesting example since it conventionally undergoes the classic acid-catalyzed condensation to mesitylene (*2*). Mesitylene, however, has relatively low diffusivity in the new zeolite (*1*). The behavior of acetone with increasing temperature is shown in Table 2. At 250 and 288°C (8.0 LHSV), conversions are low. The normal aldol products, diacetone and mesityl oxide are present. Mesitylene is the sole aromatic species and is presumably formed via catalysis by the zeolite external surface. A significant amount of isobutene is formed from cracking reactions of diacetone and other mesitylene precursors (*3*, *4*). The C_6^+ hydrocarbons are mostly oligomers of propylene, isobutene, etc. Upon raising the temperature above 288°C, profound changes in hydrocarbon distribution occur. Mesitylene declines abruptly, and the distribution approaches that derived from alcohols and aldehydes.

Carboxylic Acids and Esters

Results from acetic acid, *n*-propyl acetate and *n*-butyl formate are listed in Table 3. Deoxygenation of acetic acid occurs via decarboxylation and dehydration. Under the conditions of the experiment (371°C, 1 LHSV) the major hydrocarbon produced is isobutene. Isobutene is probably formed by the zeolite catalyzed ketonization of acetic acid to acetone (*5*), followed by aldolization and cracking reactions mentioned previously. Detectable amounts of acetone are found in the reaction products. In contrast to acetic acid, deoxygenation of the *n*-propyl ester proceeds mainly via water elimination. Propylene is a major hydrocarbon product of this reaction. The exact reasons for this difference in behavior are not known at this time. However, one may conjecture that upon acid-catalyzed dehydration, an olefin and a surface acylium species are formed from the ester:

$$CH_3COOC_3H_7 \xrightarrow{H^{\oplus}} CH_3COOH_2^{\oplus} + C_3H_6$$
$$\Big\downarrow -H_2O \qquad (1)$$
$$CH_3C^{\oplus}{=}O \quad (ads).$$

The acylium ion can suffer nucleophilic attack by acetate ions, which are likely also to be present, and thus eliminate CO_2 *(6)* to form acetone. On the other hand, the olefin produced may compete successfully with acetate for the acylium ion, forming a β,γ-unsaturated ketone *(7)* which then reacts, with further loss of water, to form aromatics. The following sequence is plausible [for a discussion of 1,3-cyclohexadienes formation by acid-catalyzed dehydration of substituted cyclohexanones see Ref. *(8)*]:



(2)

n-Butyl formate yields a mixture of hydrocarbons similar to the product derived from alkanols, however, CO is also formed as a consequence of formate decomposition.

B. Hydrocarbons from Methanol

The stoichiometric yields of hydrocarbon and water from methanol are 44 and 56% by weight, respectively. Such yields are observed in methanol conversion with the class of zeolites used and referred to above. In contrast, the normal end products of methanol dehydration are dimethyl ether and water, since unlike higher alkanols, methanol cannot form an alkene via simple β-elimination. Under certain conditions, however, small amounts of hydrocarbon products have been observed during catalytic dehydration. Light hydrocarbons have been detected in the product of methanol dehydration over conc H_2SO_4 *(9)*, activated alumina *(10)*, cation exchanged faujasites *(11, 12)*, and H-mordenite *(13)*. Hydrocarbons, including highly substituted aromatics, have been reported when methanol is decomposed in the presence of P_2O_5 or polyphosphoric acid *(14)* at elevated temperature.

Reaction Path

Table 4 shows the effect of contact times over three orders of magnitude on the product distribution in methanol conversion. The results at the lowest contact time (LHSV, 1080) show that the product contains substantial amounts of dimethyl ether (DME) formed by the reversible dehydration of methanol. Solely on the basis of these data, the ether-forming reaction might be regarded as either sequential in or only parallel to the major reaction steps leading to hydrocarbons. However, DME is found (without the addition of water required to form meth-

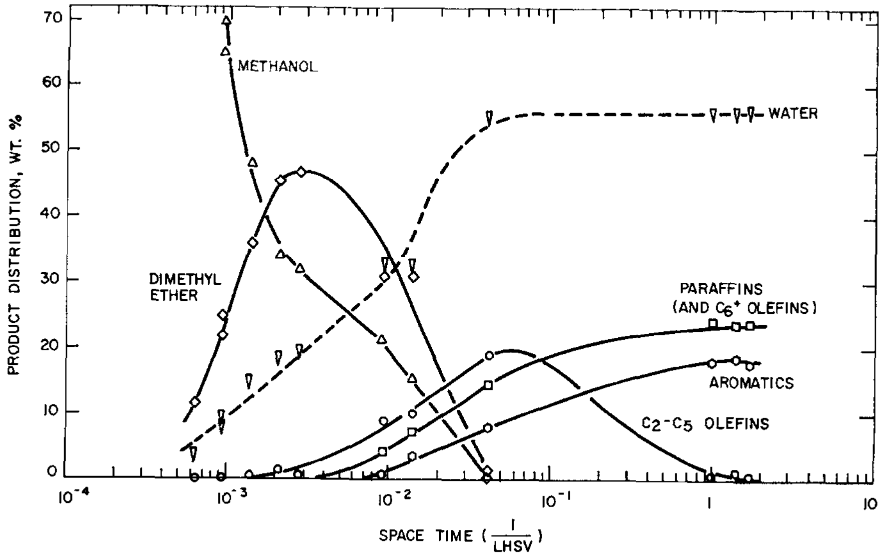


FIG. 1. Reaction path for methanol conversion to hydrocarbons (371°C).

anol) to give essentially the same product distribution as methanol. Thus the conversion of methanol to DME may desirably be a first step in the overall sequence of the conversion of methanol to hydrocarbons.

The hydrocarbon distribution for the run at the lowest conversion (9.1% at LHSV = 1080) shows that 78% of the primary hydrocarbon product is C_2 to C_4 olefins. The interesting question of the mechanism of olefin formation from methanol is discussed at the end of this paper. The olefins formed then undergo condensations and rearrangements leading

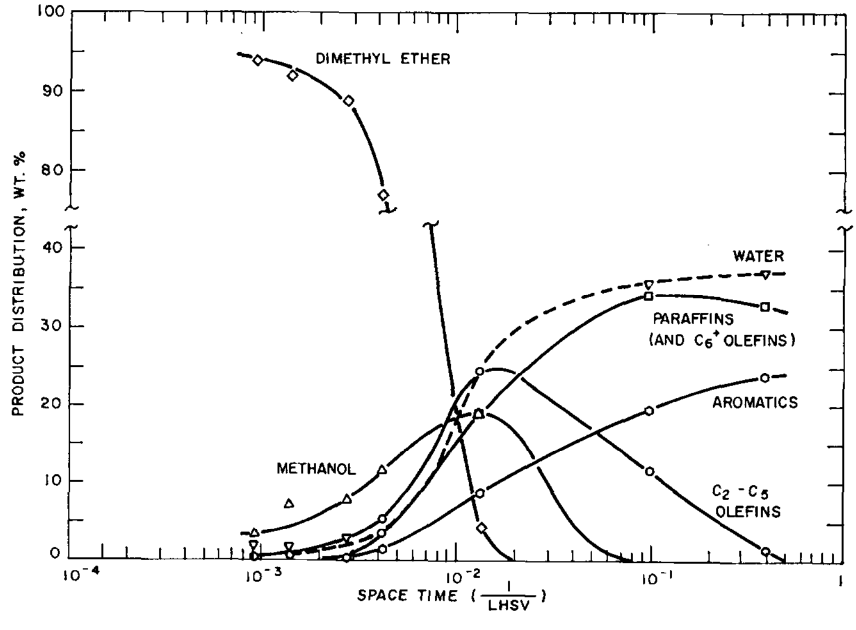


FIG. 2. Reaction path for dimethyl ether conversion to hydrocarbons (371°C).

finally to the aromatic product slate shown in the last column (LHSV = 1) of Table 4.

Figures 1 and 2 show more complete collections of data on the effect of contact time on product distribution in methanol and DME conversions. In summary, the reaction path in going from methanol to hydrocarbons appears to be reasonably well represented by scheme (3).

$$2CH_3OH \underset{+H_2O}{\overset{-H_2O}{\rightleftharpoons}} CH_3OCH_3 \xrightarrow{-H_2O} \begin{matrix} C_2\text{–}C_5 \\ \text{olefins} \end{matrix} \longrightarrow \begin{matrix} \text{paraffins} \\ \text{aromatics} \\ \text{cycloparaffins} \\ C_6^+ \text{ olefins.} \end{matrix} \quad (3)$$

Product Distribution

As noted previously, the hydrocarbons produced exhibit a relatively narrow range of molecular weights, terminating abruptly at about C_{10}, which corresponds to the end point of conventional gasoline. This limited

TABLE 5

Aromatics Distribution from Methanol Conversion[a]

	Normalized distribution (wt%)	Normalized isomer distributions	Equilibrium distributions (371°C)
Benzene	4.1		
Toluene	25.6		
Ethylbenzene	1.9		
Xylenes			
o	9.0	21.5	23.8
m	22.8	54.6	52.7
p	10.0	23.9	23.5
Trimethylbenzenes			
1,2,3	0.9	6.4	7.8
1,2,4	11.1	78.7	66.0
1,3,5	2.1	14.9	26.2
Ethyltoluenes			
o	0.7		
m + *p*	4.1		
Isopropylbenzene	0.2		
Tetramethylbenzenes			
1,2,3,4	0.4	23.3	16.0
1,2,3,5	1.9	44.2	50.6
1,2,4,5	2.0	46.5	33.4
Other A_{10}[b]	2.7		
A_{11}^+	0.4		

[a] See Table 1, Example 1.

[b] Diethylbenzenes + dimethylethylbenzenes.

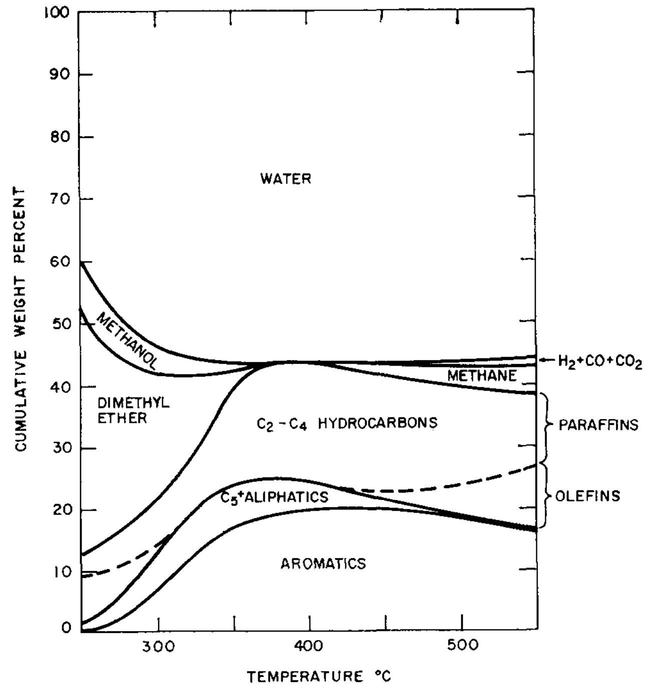


FIG. 3. Zeolite-catalyzed methanol conversion; yield structure vs temperature (0.6–0.7 LHSV, 101.3 kPa).

TABLE 6

Heats of Reaction for Major Reaction Steps in Methanol Conversion to Hydrocarbons

Reaction	ΔH (kcal)[a]	% of total heat of reaction
$CH_3OH \rightarrow \frac{1}{2}CH_3OCH_3 + \frac{1}{2}H_2O$	2.410	22.5
$\frac{1}{2}CH_3OCH_3 \rightarrow (CH_2)_{olefins} + \frac{1}{2}H_2O$ (for typical C_2–C_5 olefin distribution	4.466	41.8
$(CH_2)_{olefins} \rightarrow (CH_2)_{hydrocarbons}$ (for typical final hydrocarbon distribution)	3.814	35.7
$CH_3OH \rightarrow (CH_2)_{hydrocarbons} + H_2O$	10.69	100

[a] 1 kcal = 4.184 J.

distribution results from the unique molecular shape selectivity of the zeolites used (*1*). Aside from limiting product end point, this zeolite shape selectivity also manifests itself in the hydrocarbon isomer distribution. This is illustrated in Table 5 which presents the detailed isomer distribution of the aromatic fraction from Example 1, Table 1. The preponderance of methyl-substituted benzenes may first be noted. The xylenes are seen to be essentially in thermodynamic equilibrium with each other. However, as we progress through the tri- and tetramethylbenzenes it is evident that certain isomers, viz, 1,3,5-trimethylbenzene, 1,2,3,4- and 1,2,3,5-tetramethylbenzenes, fall significantly short of their equilibrium values. These are the isomers with lower diffusivities, due to steric constraints (*1*).

Effect of Temperature

The effect of temperature on product distribution is summarized in Fig. 3. These data were obtained at moderately low space velocity (LHSV = 0.6–0.7), and span a range of 260–538°C. At 260°C, the main reaction is the dehydration of methanol to DME. The hydrocarbons formed are predominantly C_2–C_5 olefins. The conversion of methanol/DME approaches completion between 340 and 375°C, with the formation of substantial amounts of aromatics. With further increase in temperature, only second-order changes in product distribution are evident. Light olefins and methane begin to rise as a result of secondary cracking reactions. Above about 500°C, the decomposition of methanol to H_2 and CO becomes measurable. The sequence of events is formally identical to the reaction path previously defined through variation of contact time at a constant temperature.

Thermochemistry

The heat of reaction for methanol conversion will vary according to the specific product distribution obtained. Because of the sequential nature of the reaction, product slates varying from highly olefinic to aromatic may result depending on location along the reaction path. Using typical product distributions, the heats of reaction, based on 1g-mole of methanol, for the three major steps in scheme (3) are detailed in Table 6 for a temperature of 371°C. As shown, the methanol conversion reaction is exothermic with the heat release proportioned in the approximate ratio 1:2:2 for the major reaction steps.

In Fig. 4 the variation of enthalpy with advance along the reaction path is shown. This plot is a companion to Fig. 1, from which the data in Fig. 4 were calculated.

Reaction Mechanism

The central question to be resolved is the nature of the process whereby methanol and DME, both lacking β-hydrogens, undergo water elimination to form olefins. A number of hypothetical mechanisms have been proposed. A carbene mechanism was first suggested by Venuto and Landis (*15*) who assumed an initial α-elimination step followed by polymerization of the

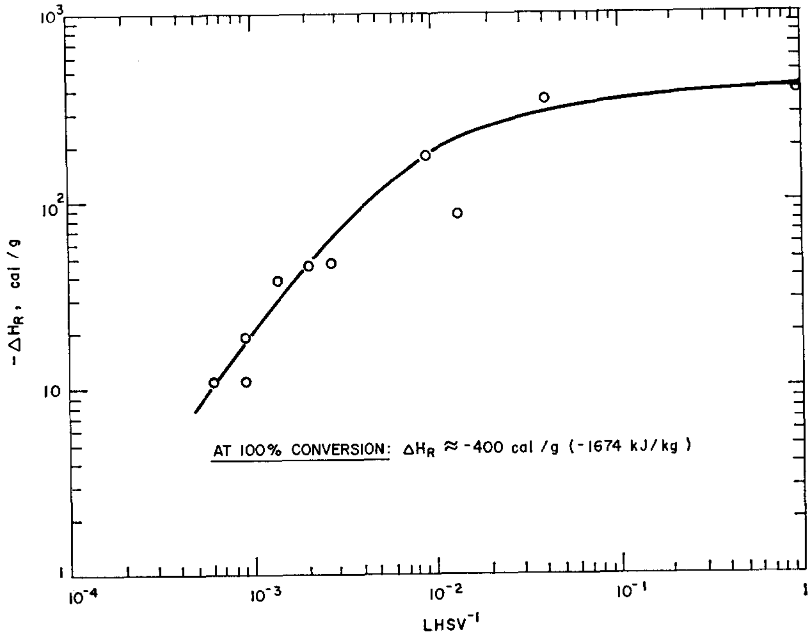


FIG. 4. Methanol conversion to hydrocarbons; heat of reaction vs space–time at 371°C.

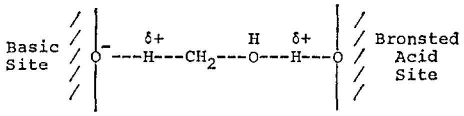
divalent carbenoid species to form olefins.

$$H-CH_2-OH \longrightarrow H_2O + [:CH_2] \qquad (4)$$

$$n[:CH_2] \longrightarrow (CH_2)_n \qquad (5)$$

In pertinent related studies, Venuto and Landis (*15*) described the formation of *trans*-stilbene from reaction of benzyl mercaptan over Na13X and Linde 4A zeolites. This reaction may be explained either by a sulfonium ylid mechanism or an α-elimination mechanism. The carbene route was judged to be most reasonable in light of the experimental data. In this regard, methyl mercaptan has already been shown to convert similarly to methanol over the zeolites of the present study (Table 1, Example 4).

Swabb and Gates (*13*) elaborated on the Venuto–Landis scheme in an effort to explain the role of H-mordenite in catalyzing olefin formation from methanol. These workers proposed a concerted α-elimination mechanism involving both Bronsted acidic and basic lattice site.



(6)

Pearson (*14*) has reported the formation of hydrocarbons from methanol and trimethyl phosphate when these compounds are heated in the presence of P_2O_5 or polyphosphoric acid. Two possible mechanistic pathways were suggested: the first, involving penta-coordinate carbon intermediates, as described by Olah *et al.* (*16*) and the second, the α-elimination of methyl phosphate at elevated temperature.

The uniformly low methane yields observed in the present work over a wide range of conditions would tend to militate against a methyl carbonium ion *primary* mechanism for methanol transformation over the zeolites in question. Significant methane formation via hydride abstraction would otherwise be anticipated.

Zeolite cages and channels are generally viewed as spaces where large electrostatic fields and gradients prevail. Such environments have also been described as ionic "pseudosolvents," capable of promoting high energy ionizations. A striking example may be cited in the ionization of sodium atoms in NaY zeolites (*17*). The electrons released were shown by esr to be trapped, or "solvated." in α-cages surrounded by four sodium ions. Thus it is easy to visualize the formation of carbonium or carbene species in this special environment, as events of high probability. The ions thus formed would be "solvated" by coordination with lattice point charges in configurations which tend to increase the Madelung energy of the crystal (*17*).

Data of the present work obtained at low conversion tend to support a pathway involving formation of carbenoid species as a primary step. The paraffins formed in the early stages of the reaction were probably the consequence of initial coke laydown, since neither hydrogen nor aromatics were in evidence in the reaction effluent.

Methylene diradical once formed can dimerize:

$$2[:CH_2] \rightarrow C_2H_4, \qquad (7)$$

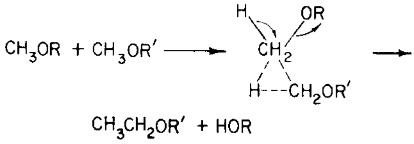
or interact with methanol and dimethyl ether via sp^3 C–H insertion:

$$[:CH_2] + CH_3\text{–}OR \rightarrow CH_3CH_2\text{–}OR, \qquad (8)$$

$$CH_3CH_2\text{–}OR \rightarrow C_2H_4 + HOR. \qquad (9)$$

Results of studies on ketene photolysis (*18*) suggest that the above dimerization reaction (7) has low probability. Photolysis studies on mixtures of diazomethane and methyl ethers (*19*, *20*) reveal that methylene insertion readily occurs with the formation of higher ethers.

On the basis of the foregoing discussion, one may speculate that the primary mechanism in methanol/DME conversion to olefins is a concerted bimolecular reaction between methylene donor (labilized by the zeolite crystal field) and acceptor (methanol or methyl ether). Subsequent protolysis yields olefins.



$$CH_3OR + CH_3OR' \longrightarrow \left[\begin{array}{c} H \quad OR \\ CH_2 \\ H\text{---}CH_2OR' \end{array}\right] \longrightarrow CH_3CH_2OR' + HOR \qquad (10)$$

$$CH_3CH_2OR' \xrightarrow{H^{\oplus}} C_2H_4 + HOR' \qquad (11)$$

R,R′ = H or alkyl. Carbene addition to the double bond of the initially formed olefins may also occur. Some support for this mechanistic picture is found in the work of Chen and Reagan (*21*) who have observed evidence of autocatalytic behavior in a kinetic study of methanol conversion over zeolites. In a process study of gasoline manufacture from methanol, Voltz and Wise (*22*) have suggested that autocatalysis could be the cause of a sigmoid temperature progression in their fixed-bed reactor. Small amounts of methyl ethyl ether have occasionally been detected in the products of this reaction; however, it is not possible at this time to detail its origin.

ACKNOWLEDGMENT

The Authors express their gratitude to Messrs. William H. Lang and Robert L. Smith for their experimental contributions, and to Dr. Heinz Heinemann for his continued encouragement and insight.

REFERENCES

1. Meisel, S. L., McCullough, J. P., Lechthaler, C. H., and Weisz, P. B., *Chemtech* **6**, 86 (1976).
2. Gutsche, C. D., "The Chemistry of Carbonyl Compounds." Prentice-Hall, Englewood Cliffs N. J., 1967.
3. Demorest, M., Mooberry, D., and Danforth, J. D., *Ind. Eng. Chem.* **43**, 2569 (1951).
4. Kurganova, S. Y., Rudenko, A. P., and Balandin, A. A., *Zh. Org. Khim.* **2**, 804 (1966).
5. Sosnina, I. E., and Lysenko, S. V., *Vestn. Mosk. Univ. Khim.* **1973**, 14, 354.
6. Swaminathan, R., and Kuriacose, J. C., *J. Catal.* **16**, 357 (1970).

7. Smit, V. A., Semenovskii, A. V., Lyubrinskaya, O. V., and Kucherov, V. F., *Dokl. Nauk SSSR* **203**, 604 (1972).
8. Spangler, C. W., Maier, P. K., and Bennet, K. E., *J. Org. Chem.* **37**, 3347 (1972).
9. Dolgov, B. N., "Die Katalyse in der Organischen Chemie," p. 439, DVW, Berlin, 1963,
10. Heiba, E. I., and Landis, P. S., *J. Catal.* **3**, 471 (1964).
11. Venuto, P. B., and Landis, P. S., *in* "Advances in Catalysis" (D. D. Eley, H. Pines and P. B. Weisz, Eds.), Vol. 18, p. 308. Academic Press, New York, 1968.
12. Topchieva, K. V., Kubasov, A. A., Dao, T. V., *Vestn. Mosk. Univ., Khim.* **37**, 620 (1972).
13. Swabb, E. A., and Gates, B. C., *Ind. Eng. Chem. Fundam.* **11**, 540 (1972).
14. Pearson, D. E., *J. Chem. Soc. Chem. Commun.* **1974**, 397.
15. Venuto, P. B., and Landis, P. S., *J. Catal.* **21**, 330 (1971).
16. Olah, G. A., Klopman, G., Schlosberg, R. H., *J. Amer. Chem. Soc.* **91**, 3261 (1969).
17. Rabo, J. A., and Kasai, P. H., "Progress in Solid State Chemistry" (J. O. McCaldin and G. Somorjai, Eds.), Vol. 9. Pergammon, Oxford, 1975.
18. Kistiakowsky, G. B., and Saner, K., *J. Amer. Chem. Soc.* **78**, 5699 (1956); **80**, 1066 (1958).
19. Frey, H. M., and Voisey, M. A., *Trans. Faraday Soc.* **64**, 954 (1968).
20. Voisey, M. A., *Trans. Faraday Soc.* **64**, 3058 (1968).
21. Chen. N. Y., and Reagan, W. J., private communication.
22. Voltz, S. E., and Wise, J. J., Quarterly Report, March 1976, Contract No. E(49-18)-1773, prepared for the U.S. Energy Research and Development Administration.
23. Chang, C. D., Lang, W. H., and Silvestri, A. J., *U. S. Pat.* 3,894,106; Butter, S. A., Kaeding, W. W., and Jurewicz, A. T., *U. S. Pat.* 3,894,107; Chang, C. D., Silvestri, A. J., and Smith, R. L., *U. S. Pat.* 3,928,483.