JOURNAL OF CATALYSIS 74, 203–206 (1982)

On the Mechanism of Hydrocarbon Formation from Methanol over Zeolite Catalysts: Evidence for Carbene Intermediacy

Evidence has been obtained from ^{13}C isotope-labeling experiments showing the existence of carbenoid C_1 species during methanol reactions over HZSM-5 zeolites.

I. INTRODUCTION

The zeolite-catalyzed formation of hydrocarbons from methanol is the critical step of the Mobil process for the synthesis of gasoline from coal or natural gas (*1, 2*) via CO and H_2. The general reaction path is summarized by the following scheme (2):

$$2CH_3OH \overset{-H_2O}{\rightleftharpoons} CH_3OCH_3 \xrightarrow{-H_2O} C_2\text{–}C_5 \text{ alkenes} \rightarrow \left\{ \begin{array}{c} \text{isoalkanes} \\ + \\ \text{aromatics} \end{array} \right.$$

While reactions of olefins over acidic zeolites leading to isoalkanes and aromatics are well understood and explainable by classical carbenium ion mechanisms (*3, 4, 25*), the mechanism of initial C–C bond formation from methanol is unknown and has been subject to much speculation. The gamut of mechanistic schemes, invoking surface alkoxyls (*5–8*), carbenes (*2, 3, 7, 9–11*), carbenium ions (*12*), oxonium ions (*13, 14*), free radicals (*15*), and pentacoordinate carbon (*10, 16*), has been postulated. Compelling experimental evidence in support of any of these possibilities has thus far been lacking, although an interesting recent study (*19*) of the reaction over SiO_2–Al_2O_3 catalyst concluded, on the basis of kinetic evidence, that initial C–C formation from methanol occurs via two successive CH_2 insertions into chemisorbed dimethyl ether, leading to MeOPr, which yields C_3H_6 on protolysis.

We present here evidence, based on a ^{13}C isotope-labeling study, for the existence of carbenoid C_1 species during methanol conversion to hydrocarbons over ZSM-5 zeolites.

II. EXPERIMENTAL METHODS

Materials. Methanol was 90% enriched in ^{13}C (Prochem). Propane was research grade (99.99%, Matheson). The catalyst used was HZSM-5 (*17, 18*).

Apparatus. The reactor was a Pyrex tube equipped with a thermowell containing 1.4 ml catalyst in a bed 4 cm in length. The reactor was heated electrically. Methanol was charged to the reactor by a Sage syringe pump. Propane was metered through a rotameter. Products were analyzed by gas chromatography (GC) and gas chromatography/mass spectrometry (GC/MS). GC/MS were performed on both Hewlett–Packard 7985 and 5992 instruments with electron energy of 10–15 eV. ^{13}C distributions were obtained based on molecular ions calculation.

III. RESULTS AND DISCUSSION

This study was prompted by an observation that when methanol is reacted over ZSM-5 in the presence of added propane, the characteristic high iso-to-normal ratio of the product butanes (*2*) is significantly lowered. This was noteworthy particularly since propane itself, under the experimental conditions, proved to be virtually inert (ca. 0.3% conversion). Data illustrating this effect are shown in Table 1. Reaction conditions were 370°C, 101.3 kPa, and 0.4 hr^{-1} methanol liquid hourly space velocity (LHSV). The first column contains data from the control run, where methanol was diluted with helium ($He/CH_3OH = 3$, molar ratio). The ratio of isobutane to normal butane (i/n) is seen to be 3.8, within expectation. In the second experiment, helium

0021-9517/82/030203-04$02.00/0

TABLE 1

Effect of Propane on Methanol Conversion over HZSM-5[a,b]

Hydrocarbon product (wt%)[c]	CH_3OH/He	CH_3OH/C_3H_8
CH_4	0.86	0.90
C_2°	0.93	0.90
C_2^{2-}	2.35	2.36
(C_3°)	(—)[d]	(—)[e]
C_3^{2-}	3.63	4.53
iC_4°	35.17	23.13
nC_4°	9.20	20.24
C_4^{2-}	1.88	2.34
C_5^+ aliphatic	21.32	20.98
Aromatics	24.66	24.62
Total	100.00	100.00
i/n C_4°	3.8	1.1

[a] 370°C, 101.3 kPa, 0.4 hr^{-1} LHSV (CH_3OH).

[b] 3 mol CH_3OH/1 mol diluent.

[c] Normalized on a propane-free basis.

[d] Actual C_3° = 25.36% of hydrocarbon.

[e] Net conversion of C_3° ~5%.

was replaced by propane. The resulting i/n butane ratio was 1.1. Since the thermodynamic equilibrium ratio is 0.75, an obvious rationale was that propane, by some as yet undefined mechanism, facilitated the isomerization of i-butane to n-butane. It will be shown later that this cannot be the case.

To elucidate the nature of the methanol/propane interaction, whether chemical or physical, the experiments were repeated using ^{13}C-enriched methanol. The resultant C_4° i/n was 1.6. Isotope distributions in the products were monitored by mass spectrometry. ^{13}C distributions for the butanes are plotted in Fig. 1. Superimposed (broken line) is the expected random distribution from the methanol feed (90% ^{13}C + 10% ^{12}C) in the absence of specific interaction with $^{12}C_3H_8$. The plots show clearly a marked deviation from random distribution in each isomer, confirming that a reaction between methanol and propane (ca. 5% based on C_3°) had indeed taken place.

Addressing, then, the question of the anomalous butane selectivities, we focus on the individual i/n ratios of the labeled butanes. These data are plotted in Fig. 2. It can be seen that the ratios are not constant but increase with increasing ^{13}C substitution. This eliminates skeletal isomerization as the principal cause of the low i/n ratios (*23*), as the individual ratios would then be virtually identical. Nor can a ^{13}C kinetic isotope effect on isomerization account for the observed differences, since the magnitude of such an effect would be <5% (*20*).

In view of the observed stability of propane to C–C scission under the experimental conditions, and the nonstatistical ^{13}C distribution, the presence of singly labeled butanes is taken as evidence of direct methylation of propane by methanol.

The nature of the C_1 attacking species can be inferred from the low i/n ratio of the singly labeled butanes. We submit that this species must be carbene-like, and the mode of attack is insertion into an *sp*^{3} C–H bond. Such carbene insertions are indiscriminate

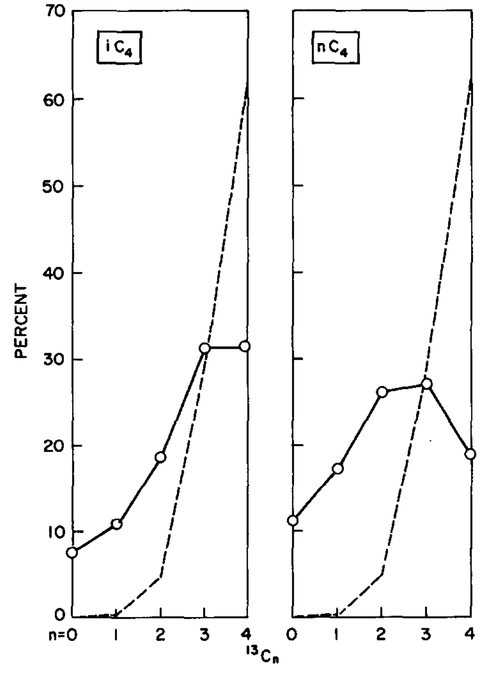


FIG. 1. ^{13}C distribution in butanes. Comparison against the random distribution (broken line) for a 90% ^{13}C + 10% ^{12}C mixture.

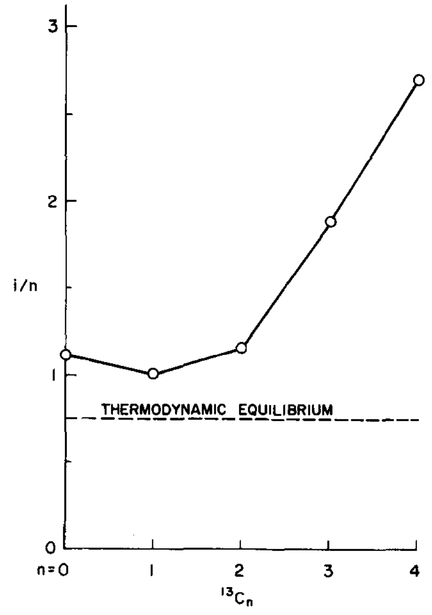
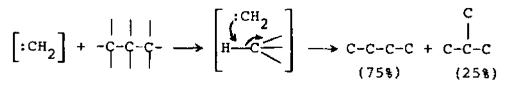
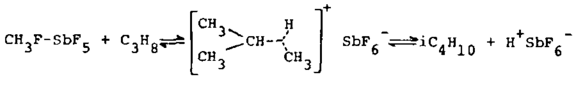


FIG. 2. Iso/normal ratio of ^{13}C-labeled butanes.

in liquid phase, all C–H bonds of the substrate being subject to attack with equal probability (21),

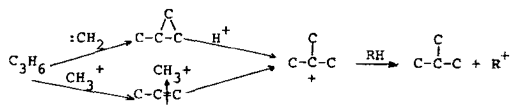


although for homogeneous gas phase reaction there is some evidence of discrimination in favor of secondary over primary C–H bonds (*22*). In the CH_3OH/C_3H_8 reaction, carbene insertion will lead statistically to higher concentrations of n-butane relative to i-butane. Attack by a cationic species such as CH_3^+ or methyloxonium ion according to an Olah-type mechanism (*16*), on the other hand, will yield high i/n butane ratios due to stability of tertiary carbenium ions in the transition state. In the methylation of propane with CH_3F–SbF_5 complex in SO_2ClF (*24*), CH_4 is formed via H transfer, and i-butane is the major alkylation product. The following pathway was proposed to account for i-butane:



The alternative possibility to C–H insertion, namely, C_1 addition to the double bond of propene generated from propane via dehydrogenation, also received consideration. Although propane itself is largely unreactive, it was believed possible that the unfavorable dehydrogenation equilibrium could be displaced by a "drain-off" reaction involving addition of a highly reactive species across the double bond of propene. Carbene addition would yield, classically, methylcyclopropane (*21*). However, subsequent protonation and rearrangement gives preferentially the tertiary butyl cation, which will either yield 2-methylpropene via loss of a proton, or i-butane via H transfer. If the attacking species were cationic, branched products would similarly result.

$$C_3H_8 \rightleftharpoons C_3H_6 + H_2$$



Another pathway involving propylium ion as electrophile can also be written

$$C_3H_6 \overset{H^+}{\rightleftharpoons} C_3H_7^+ \xrightarrow{:CH_2} iC_4H_9^+$$

but leads to the same conclusion. Thus this alternative can be rejected as an explanation of the present results. However, in the case of reaction of methanol alone, the high i-butane selectivity can be attributed to one of the above mechanisms, with propene as precursor.

The discussion thus far has centered on

the singly labeled butanes. Much less can be said about the other C_4° members. The fully labeled butanes arise from $^{13}CH_3OH$ only and exhibit the expected high i/n ratio, albeit lower than the control. The low i/n ratio of the unlabeled butanes reflects primarily the methylation of $^{12}C_3H_8$ with $^{12}CH_3OH$. The contribution from the self-interaction of $^{12}CH_3OH$ will be minor in view of the low probability (see Fig. 1). This methylation yields, as expected, a C_4° i/n ratio identical to that of the singly labeled butanes. The origin of doubly labeled butanes is unknown at the present time, and is probably the result of secondary reactions. The triply labeled butanes agree with the predicted random distribution (Fig. 1). Their relatively high i/n ratio indicates that they are mostly formed from the methanol feed alone.

IV. CONCLUDING REMARKS

This study has produced evidence for the existence of carbene-like C_1 intermediates when methanol is reacted over HZSM-5. It thus lends support to the view (*2*) that these species are involved in the initial C–C bond forming process in methanol conversion to hydrocarbons. The precise details of this involvement, however, remain a mystery at this writing.

ACKNOWLEDGMENTS

We express our gratitude to P. Montgomery for his expert technical assistance, and to R. B. LaPierre, P. D. Perkins, and T. Roy for their invaluable advice on the mass spectrometry.

REFERENCES

1. Meisel, S. L., McCullough, J. P., Lechthaler, C. H., and Weisz, P. B., *Chemtech* **6,** 86 (1976).
2. Chang, C. D., and Silvestri, A. J., *J. Catal.* **47,** 249 (1977).
3. Venuto, P. B., and Landis, P. S., *Advan. Catal.* **18,** 259 (1968).
4. Poutsma, M. L., *in* "Zeolite Chemistry and Catalysis" (J. A. Rabo, Ed.), p. 437. ACS Monograph 171, Amer. Chem. Soc., Washington, D.C., 1976.
5. Topchieva, K. V., and Ballod, A. P., *Dokl. Akad Nauk SSSR* **75,** 247 (1950).
6. Heiba, E. I., and Landis, P. S., *J. Catal.* **3,** 471 (1964).
7. Salvador, P., and Kladnig, W., *J. Chem. Soc. Faraday I* **1977,** 1153 (1977).
8. Ono, Y., Imai, E., and Mori, T., *Z. Phys. Chem. Neue Folge* **115,** 99 (1979).
9. Swabb, E. A., and Gates, B. C., *Ind. Eng. Chem. Fund.* **11,** 540 (1972).
10. Pearson, D. E., *J. Chem. Soc. Chem. Commun.* **1974,** 397 (1974).
11. Kim, L., Wald, M. M., and Brandenberger, S. G., *J. Org. Chem.* **43,** 3433 (1978).
12. Nagy, J. B., Gilson, J. P., and Derouane, E. G., *J. Molec. Catal.* **5,** 393 (1979).
13. Kaeding, W. W., and Butter, S. A., *J. Catal.* **61,** 155 (1980).
14. van den Berg, J. P., Wolthuizen, J. P., and van Hooff, J. H. C., *in* "Proceedings, Vth Conference on Zeolites (Naples, Italy), p. 649 (1980).
15. Zatorski, W., and Krzyzanowski, S., *Acta Phys. Chem.* **29,** 347 (1978).
16. See also Olah, G. A., Sommer, J., and Namanworth, E., *J. Amer. Chem. Soc.* **89,** 3576 (1967); Olah, G. A., and Schlosberg, R. H., *J. Amer. Chem. Soc.* **90,** 2726 (1968); Olah, G. A., Mo, Y. K., and Olah, J. A., *J. Amer. Chem. Soc.* **95,** 4939 (1973).
17. Argauer, R. J., and Landolt, G. R., U.S. Patent 3,702,886.
18. Kokotailo, G. T., Lawton, S. L., Olson, D. H., and Meier, W. M., *Nature* (*London*) **272,** 432 (1978).
19. Cormerais, F. X., Perot, G., Chevalier, F., and Guisnet, M., *J. Chem. Res.* **1980,** 362 (1980).
20. Melander, L., "Isotope Effects on Reaction Rates." Ronald Press, New York, 1960.
21. Kirmse, W., "Carbene Chemistry," 2nd ed. Academic Press, New York, 1971.
22. Frey, H. M., and Kistiakowsky, G. B., *J. Amer. Chem. Soc.* **79,** 6373 (1957).
23. In a separate experiment pure isobutane, under the same conditions, gave a resultant i/n >20.
24. Olah, G. A., DeMember, J. R., and Shen, J., *J. Amer. Chem. Soc.* **95,** 4952 (1973).
25. Defaifve, P., Vedrine, J. C., Bolis, V., van Hooff, J. H. C., and Derouane, E. G., *Prepr. Div. Petrol. Chem., Amer. Chem. Soc.* **24,** 286 (1979).

CLARENCE D. CHANG
CYNTHIA T-W. CHU

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

Received September 15, 1981; revised November 13, 1981