JOURNAL OF CATALYSIS **114**, 190–195 (1988)

Conversion of [^{14}C]Methanol and Propane Mixtures with H–ZSM-5

INTRODUCTION

One of the major discoveries in zeolite catalysis was the conversion of mathanol to gasoline using H–ZSM-5 catalysts (*1*, *2*). While there have been many mechanistic studies, the reaction pathway and the C_1 species involved in the reaction remain uncertain. The proposed mechanisms may be classified into three groups based upon the required intermediate: (a) mechanisms utilizing carbene ($:CH_2$), (b) mechanisms utilizing cations (e.g., CH_3^+), and (c) mechanisms utilizing trimethyloxonium ions ($(CH_3)_3O^+$) or similar oxygen-containing species. Our preliminary ^{14}C tracer studies provided evidence that was consistent with the oxonium ion intermediate (*3*). Refinements in our ^{14}C analytical procedures showed that the ^{14}C added in propanol had completely scrambled with the methanol carbon and the data could therefore not define the intermediate species (*4*).

A significant mechanistic study produced evidence to support a carbene mechanism. Chang and Chu (*5*) added propane to a methanol feed and observed a significant lowering of the iso/normal butane ratio (*i*/*n* = 3.8 for methanol alone, but 1.1 for a propane–methanol mixture; the ratio is 0.75 for thermodynamic equilibrium). Furthermore, when $^{13}CH_3OH$ was utilized, 30–45 times more singly labeled butane was observed than could be expected from a random distribution of ^{13}C in the products. These authors argued that insertion of carbene, derived from methanol, into propane C–H bonds was the most likely mechanism and that mechanisms involving cationic species, which should produce isobutane, were unlikely. Howevcer, doubly labeled butanes were formed in even larger amounts than singly-labeled butanes; van Hooff (*6*) attempted to explain the mystery of multiply labeled, and unlabeled, butanes by hydride ion abstraction and the relative stability of the alkane products. However, Chang and Chu discounted this explanation (*7*). Subsequently, Odell reported results to support the view that propane cracking was responsible for the lower *i*/*n* ratio (*8*). Considering the importance of the experiments with the methanol–propane mixture to an understanding of the methanol to gasoline conversion, we have carried out studies using $^{14}CH_3OH$ and unlabeled propane.

EXPERIMENTAL

The ZSM-5 catalyst was supplied by Mobil Research & Development Corp. in the ammonium form as their "X-ray diffraction standard sample." Prior to use, 1 g of a calcined (550°C) ZSM-5 material was diluted with 1 g of α-alumina; this mixture was placed in a plug–flow reactor. Methanol was fed by a syringe pump and the propane gas flow was controlled by a needle-valve regulator. The propane was Matheson research purity (99.97%). Products were collected, first, in a trap maintained at ca. 5°C and then in a trap at dry ice–isopropanol temperature. The gaseous effluent was led directly to one of two chromatographs (a Hach gas analyzer or an HP 5790 GC equipped with a Porapack R column). The effluent from the thermal conductivity cell of the GC was led through a heat-traced line to a proportional counter.

After each run, the catalyst was regenerated by air passing over the catalyst, first at reaction temperature and then at 550°C overnight.

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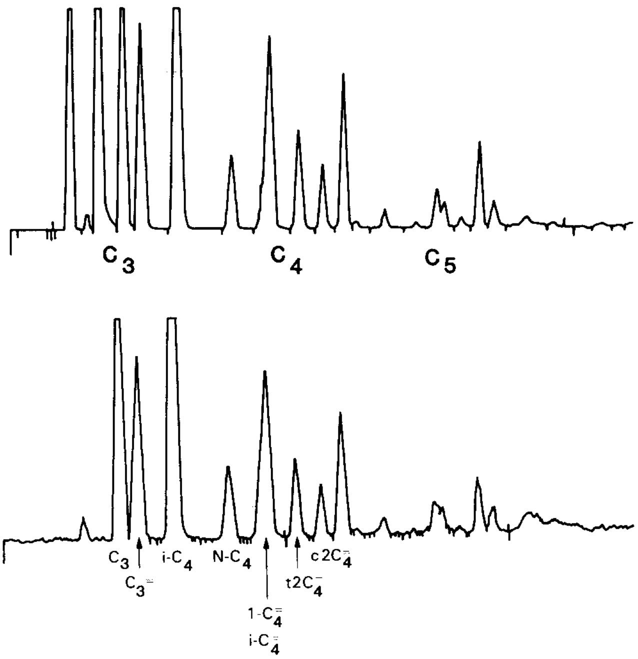

FIG. 1. Gas chromatograph trace (top) and proportional counter trace (bottom) for a dry ice trap sample from the conversion of a mixture of unlabeled methanol and ^{14}C-labeled propanol.

The component(s) of each chromatograph peak effluent was burned to CO_2 and mixed with a methane quench gas prior to passing through the proportional counter. Typical GC (top trace, Fig. 1) and proportional counter (bottom trace, Fig. 1) recorder outputs are illustrated for a gaseous effluent that contains ^{14}C in all of the gaseous products that resulted from the conversion of unlabeled methanol and ^{14}C-labeled propanol with a ZSM-5 catalyst. Except for overlap of isobutene and 1-butene, all C_3 and C_4 products have nearly baseline separation for both the GC and the proportional counter outputs.

RESULTS AND DISCUSSION

In our numerous runs using methanol or methanol mixed with ethanol, propanol, or pentanol, the ratio of *i*-butane to *n*-butane was found to be in the range 3.5 to 4.5. This ratio was obtained at 300°C for 1 atm conditions without a diluent, and with a flow rate of 10–40 GHSV. Under these reaction conditions alcohol and the corresponding ethers were not observed in significant quantities in the products; in other words, the conversion was sufficiently high so that the products consisted of essentially hydrocarbon components. In some pure methanol runs, dimethyl ether was observed at our highest flow rates.

The data in Fig. 2 show that the *i*-/*n*-butane ratio depends upon gas flow at both 300 and 370°C. At lower flow rates, corresponding to smaller quantities of added propane, the *i*-/*n*-butane ratio approaches the value of 4 to 5 normally obtained with an alcohol only feed. At increasingly higher flow rates, the *i*/*n* ratio shows an increasing change to favor the *i*-butane isomer. It also appears that the *i*-/*n*-butane ratios obtained at 300 and 370°C for varying flow rates define a common curve. Therefore, to the extent that higher flow rates correspond to an increasing fraction of initial products, it appears that *i*-butane, not *n*-butane, is the initial C_4 product during the conversion of propane and methanol.

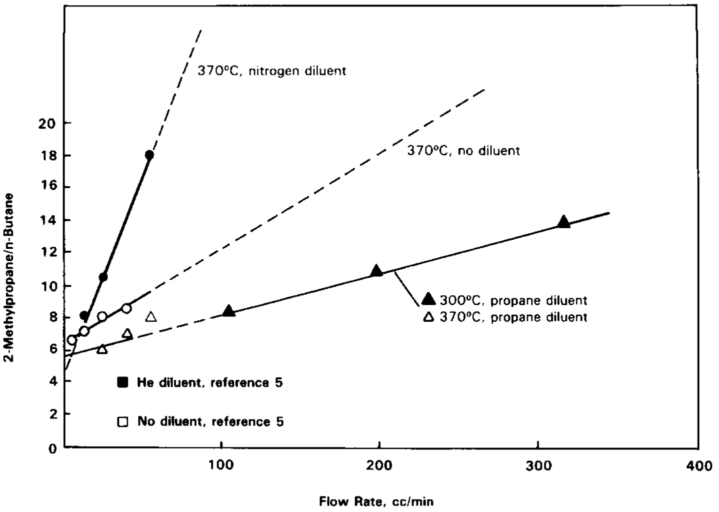

FIG. 2. Variation of the *i*-butane/*n*-butane with total gas flow at 1 atm for undiluted methanol at 370°C (○), methanol diluted with nitrogen at 370°C (●), and methanol diluted with propane at 300°C (▲) or 370°C (△). Methanol gas flow, when a diluent was used, was 6 cc/min for the 370°C conversions and 30 cc/min for the 300°C conversion.

The *i*-/*n*-butane ratio increases, with increasing flow rate, much more rapidly when nitrogen, rather than propane, is the diluent. It also appears that the variation with flow rate for *i*-/*n*-butane for undiluted methanol falls between those obtained for nitrogen or propane diluent.[1] The difference between the *i*-/*n*-butane ratios at higher flow rates for the nitrogen and propane diluents suggests that some propane is converted to C_4 products that have a low *i*-/*n*-butane ratio. It should be realized that propane always contains propene as an impurity and it cannot be ruled out that this propene, rather than propane, is responsible for the formation of the C_4 products. It also appears that within experimental error, the three lines for the 370°C data extrapolate to a common *i*-/*n*-butane ratio that falls in the range 4 to 7.

For the conversions at 370°C the *i*-/*n*-butane remained constant during the 8 h when methanol was passed over the catalyst at 6 cc/min g. When methanol was added alone at 1 atm, the *i*-/*n*-butane ratio was 6.6 during an 8-h run; when 6 cc/min g each of nitrogen and methanol was passed over the catalyst the ratio was constant at 8.0 during the 8 h. At 300°C, the ratio did not remain constant. During the first 4 h of operation with a 6 cc/min g flow of only methanol the *i*-/*n*-butane ratio decreased from ca. 7.0 to ca. 2.8 to 3.0 and appeared to remain essentially constant at this ratio during the next 4 h. When 6 cc/min g each of nitrogen and methanol was passed over the regenerated catalyst the decline during the first 4 h, and the constant ratio during the next 4 h, paralleled that of methanol except that the ratio was ca. 1.0 greater when nitrogen was present than when it was absent.

A C_4 alkane formed only from ^{14}C-labeled methanol would have four times as much ^{14}C activity as the C_4 alkane formed from the addition of methanol, or one other carbon species derived from methanol, to unlabeled propane. A comparison of the rela-

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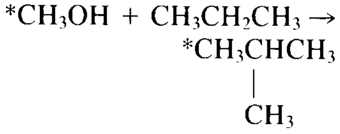
[1] The data in Fig. 2 were obtained with one sample of ZSM-5. When a batch of ZSM-5 from a different synthesis was used a similar pattern of *i*-/*n*-butane versus flow rate was obtained but the value of the *i*-/*n*-butane, for a given flow rate, was lower than that shown in Fig. 2.

tive ^{14}C activity in *n*-butane and *i*-butane makes it possible to calculate the ratio of C_4 alkane products that were formed from methanol only and from methanol plus propane. Consider the following reactions of ^{14}C-labeled methanol and unlabeled propane (where * represents position with ^{14}C label):

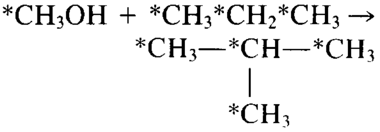
Fraction

$$\mathrm{{}^*CH_3OH + CH_3CH_2CH_3 \rightarrow CH_3CH_2CH_2{}^*CH_3} \qquad X_n \qquad (1)$$

$$\mathrm{{}^*CH_3OH + {}^*CH_3{}^*CH_2{}^*CH_3 \rightarrow {}^*CH_3{}^*CH_2{}^*CH_2{}^*CH_3} \qquad Y_n \qquad (2)$$



$$\mathrm{{}^*CH_3OH + CH_3CH_2CH_3 \rightarrow {}^*CH_3\underset{\substack{|\\ CH_3}}{CH}CH_3} \qquad X_i \qquad (3)$$



$$\mathrm{{}^*CH_3OH + {}^*CH_3{}^*CH_2{}^*CH_3 \rightarrow {}^*CH_3{-}\underset{\substack{|\\ {}^*CH_3}}{{}^*CH}{-}{}^*CH_3} \qquad Y_i \qquad (4)$$

Thus, the fraction *n*-butane derived from methanol and unlabeled propane, X_n, has only one-fourth as much radioactivity as the *n*-butane, Y_n, formed from methanol and labeled propane that was derived from methanol. For isobutane, a similar argument applies so that the activity X_i is only one-fourth of that of Y_i. This permits one to write the following equations to express the amount of radioactivity in the *n*- and *i*-butane products:

$$[X_n/(X_n + Y_n)] + 4.0[Y_n/(X_n + Y_n)] = A \qquad (5)$$

$$[X_i/(X_i + Y_i)] + 4.0[(Y_i/(X_i + Y_i)] = B. \qquad (6)$$

A and *B* are the relative molar radioactivities of *n*-butane and *i*-butane, respectively; the values of *A* and *B* are attainable from experimental data. The ratio of the total amount of *i*-butane and *n*-butane may be written (*C* is also attainable from experimental data) as

$$(X_i + Y_i)/(X_n + Y_n) = C. \qquad (7)$$

The ratio of *i*-butane and *n*-butane derived from methanol only is

$$Y_i/Y_n = D. \qquad (8)$$

An experimental value for the ratio, *D*, can be obtained for varying flow rates by converting methanol diluted with nitrogen. The data in Fig. 3 clearly show, based upon calculations outlined above, that the fraction of C_4 derived from propane plus methanol increases with increasing flow rates. If propane is viewed as a scavenger that traps a fraction of the surface C_1 species derived from methanol, then increasing the propane fraction in the feed should increase the fraction of methanol-derived C_1 species that are scavenged. For example, an Eley-Rideal mechanism, where the adsorbed C_1 species are derived from methanol and the gas-phase reactant is propane, leads to a linear dependence upon propane partial pressure, and the formation of products from propane plus methanol. Considering the data in Figs. 2 and 3 and accepting a role of scavenger for propane, one is led to the conclusion that the C_1 species adds to propane to form only, or a very high fraction of, *i*-butane as the primary product.

The molar ^{14}C ratio of *i*-butane and *n*-butane may be calculated since the relative activity per mole in each isomer (Fig. 3) and the chemical composition of the C_4 alkanes (Fig. 2) are measured. Thus, from mass balances of the ^{14}C and *i*- and *n*-butane, the ratio of *i*-/*n*-butane for the C_4 alkanes derived from the combination of four methanol species and for the C_4 alkanes derived from propane plus one methanol-derived species is calculated. The data for the *i*-/*n*-butane derived from methanol only are approximately 6 for three flow rates (Fig. 4); it appears that this ratio may be gradually decreasing with flow rate but, if this is the case, it decreases slowly. In either case (a constant *i*/*n* ratio of 6 or an apparent decrease to approach 4), the ratio for those alkanes that are derived from methanol when propane is a diluent is the same as that when methanol is converted alone. The

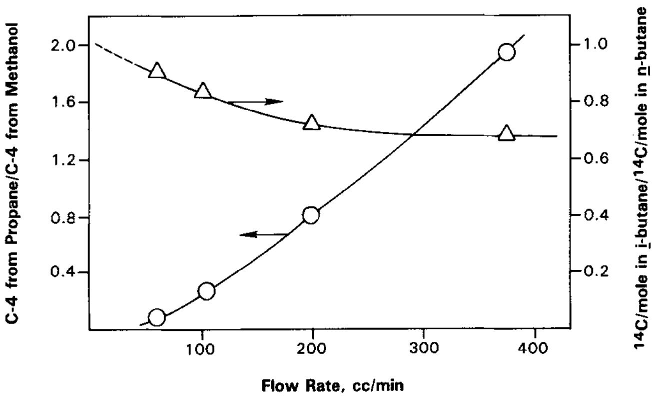


FIG. 3. The variation with flow rate of the ^{14}C/mole for *i*-butane/*n*-butane and the calculated ratio for C_4 produced from methanol plus propane and from methanol alone (300°C reaction temperature and methanol gas flow of 30 cc/min).

i-/*n*-butane ratios of the alkanes derived from propane and one methanol-derived C_1 species stand in marked contrast to those corresponding to the methanol-derived C_4 alkanes. The *i*-/*n*-butane ratio for propane-derived C_4 alkanes is approximately 30 to 40. While the great difference in the ^{14}C content in the isobutane and *n*-butane leads to appreciable error in these calculated ratios, the differences between the two ratios, ca. 6 and ca. 30 to 40, is much greater than the experimental error.

Odell (*8*) found that propane cracking produced an *i*-/*n*-butane ratio of 0.4. He suggested that the observation that adding propane changed the *i*-/*n*-butane ratio from 4 to 1 could be simply due to diluting the products from methanol conversion with products from propane conversion. When we convert ^{14}C-labeled methanol, or [^{14}C]methanol with unlabeled propanol, the ratio (^{14}C/mole *i*-butane)/(^{14}C/mole *n*-butane) is 1. Unless the propane cracking produces unlabeled butane with an *i*/*n* ratio that is the same as, or larger than, the *i*-/*n*-butane ratio produced from ^{14}C-labeled methanol, the ratio of (^{14}C/mole *i*-butane)/(^{14}C/mole *n*-butane) must be greater than 1. Hence, dilution of the C_4 fraction with cracked products with an *i*-/*n*-butane ratio of less than ca. 7.0 will cause our ^{14}C/mole activity ratio to be greater than 1; this is in contrast to the values observed. Thus, the proposed dilution with unlabeled butanes derived from propane cracking to explain the lower *i*-/*n*-butane ratio is not compatible with our data.

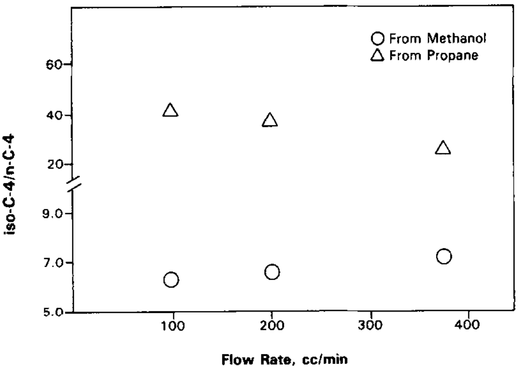


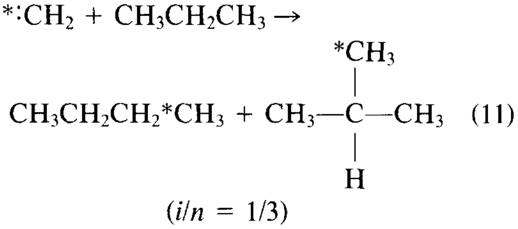
FIG. 4. *i*-Butane/*n*-butane ratios for the C_4 alkanes derived from methanol only (○) and from the propane plus methanol reaction (△).

The different ^{14}C/mole in *i*- and *n*- butane provides strong evidence for (i) the contribution of two reaction pathways to C_4 alkane formation in these runs and (ii) the conversion of propane to C_4 alkane while retaining the integrity of the C_3 species, a marked contrast to a scrambling of the propane and methanol carbons to provide carbon equivalency (*9*). In summary, the evidence strongly supports the operation of two reaction pathways to produce C_4 alkanes (where * represents ^{14}C):

$$4\ {}^*CH_3OH \rightarrow i\text{-butane} + n\text{-butane} \quad (9)$$
$$(i/n = \text{ca. } 6)$$

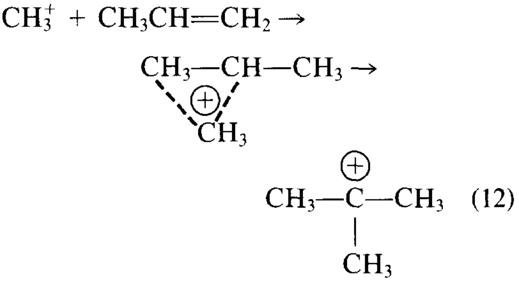
$$^*CH_3OH + C_3H_8 \rightarrow i\text{-butane} + n\text{-butane}$$
$$(i/n = \text{ca. } 30) \quad (10)$$

The *i*-/*n*-butane ratio obtained from the propane plus methanol reaction (ca. 30) is in marked contrast to that reported in Ref. (*5*) (ca. 1.1). The ^{14}C results from our study are inconsistent with a random insertion mechanism where $:CH_2$ substitution into C–H bonds should be statistical, the view expressed in Ref. (*5*):

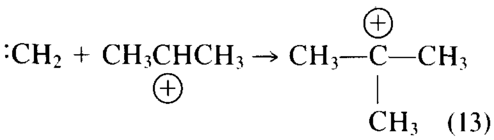


$$^*{:}CH_2 + CH_3CH_2CH_3 \rightarrow CH_3CH_2CH_2{}^*CH_3 + CH_3\text{—}\overset{\overset{^*CH_3}{|}}{\underset{\underset{H}{|}}{C}}\text{—}CH_3 \quad (11)$$
$$(i/n = 1/3)$$

The selective formation of *i*-butane from propane may occur by either of the pathways considered, and discarded, by Chang and Chu's pathway as outlined in



$$CH_3^+ + CH_3CH{=}CH_2 \rightarrow CH_3\text{—}CH\text{—}CH_3 \text{ (bridged } \oplus \text{ } CH_3) \rightarrow CH_3\text{—}\overset{\oplus}{\underset{\underset{CH_3}{|}}{C}}\text{—}CH_3 \quad (12)$$



$$:CH_2 + CH_3\underset{\oplus}{C}HCH_3 \rightarrow CH_3\text{—}\overset{\oplus}{\underset{\underset{CH_3}{|}}{C}}\text{—}CH_3 \quad (13)$$

Either of these reactions produces a high *i*/*n* ratio and is, therefore, not in agreement with the data of Chang and Chu but is compatible with our data.

It is of interest to learn the reaction pathway that selectively produces *i*-butane from propane. However, the current study indicates that, since much different *i*-/*n*- butane ratios are obtained from the methanol only and from propane/methanol reactions, it would not be applicable to the methanol to gasoline synthesis. While we realize that Chang and Chu (*5*) utilized lower flow rates and a somewhat higher reaction temperature, it would be necessary for the propane reaction pathway observed in the present study to approach zero with lower flow rates and for a second propane to butane pathway to dominate if the results from the two studies are compatible. The results of this study suggest that alkanes, or at least propane, can form a species that adds on methanol-derived C_1 species that uniquely differs from the C_3 species that is responsible for producing C_4 and higher hydrocarbons in the normal methanol to gasoline reaction pathway.

ACKNOWLEDGMENTS

This work was performed at the Kentucky Energy Cabinet Laboratory (KECL) with funding from the Commonwealth of Kentucky, Kentucky Energy Cabinet. The KECL is administered under contract by the University of Louisville.

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Received May 6, 1987; revised April 26, 1988