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Investigation of Hydrogen Transfer from Carbon-14 Ring Labeled Methylcyclohexane during the Methanol-to-Gasoline Reaction

INTRODUCTION

The selective conversion of methanol to hydrocarbons using a ZSM-5 catalyst was a significant discovery (*1*). The products follow an Anderson–Schulz–Flory distribution (*2, 3*) but with at least one important exception, the products above C_{10} make an insignificant contribution to total product yield. The mechanism for the polymerization reaction is complex and three of the more widely accepted reaction pathways involve different reaction intermediates: (i) carbocations, e.g., CH_3^+ (ii) carbene ($:CH_2$), and (iii) oxonium ion (e.g., $(CH_3)_3O^+$).

Common to the above three reaction pathways is the final step(s), dehydrogenation to produce aromatics. There is strong evidence to support the view that the formation of one aromatic molecule is accompanied by the formation of three alkane molecules (*4*). Thus, the reaction stoichiometry is consistent with, for example, reaction (1).

(1)

To obtain information about the contribution of the above reaction to the methanol-to-gasoline synthesis, a mixture of methanol and ^{14}C-labeled methylcyclohexane has been converted using an HZSM-5 catalyst. Determining the distribution of ^{14}C in the products would permit at least a semiquantitative measure of the importance of cyclohexane dehydrogenation as well as cycloalkane isomerization and cracking in the overall reaction work.

EXPERIMENTAL

A "standard for X-ray calibration" ZSM-5 sample was obtained from Mobil Research and Development Corp. This sample was calcined at 550°C, placed in a plug flow reactor, and then recalcined *in situ* at 500°C. The HZSM-5 catalyst was diluted with α-alumina (less than 1 m^2/g after calcination at 1200°C); glass beads placed above the catalyst bed served as a preheater. Reaction temperature was monitored by a thermocouple that was located at the midpoint of the catalyst bed. The feed, 20 vol of methanol per volume of methylcyclohexane (ca. 70 moles of methanol per mole of methylcyclohexane) was pumped over the catalyst at ca. 19 LHSV. The labeled methylcyclohexane was prepared by hydrogenating toluene labeled at the ring 1 position (the ring carbon attached to the methyl group) provided by a commercial supplier. Reaction temperature was 310°C; pressure was atmospheric without added diluents. Samples were collected in three traps in series that were maintained at 5°C, −78°C, and liquid nitrogen temperature, respectively. Samples from each trap were analyzed by gas radiochromatography. The higher boiling sample was separated into components using a OV-101 $\frac{1}{8}$-in. packed column and the effluent from the thermal conductivity detector was passed through a heated connector to a proportional counter. Prior to counting, each peak was oxidized (CuO) to CO_2 which was mixed with the prescribed amount of methane quench gas. Thus two chromatographs are produced for each sample, one corresponding to the mass based upon the thermal conductivity

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TABLE 1

^{14}C Activity Distribution in Hydrocarbon Fractions[a]

	Radioactivity (%)
C_7 and lower hydrocarbons[b] (to C_4)	4.4
Methyl[1-^{14}C]cyclohexane	90.7
Toluene	1.3
Xylene and higher aromatic compounds	3.6

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[a] The average for five activity determinations.

[b] There is some overlap between *n*-heptane and methylcyclohexane.

cell and one for the relative radioactivity. Gas samples were analyzed using a Carle gas analyzer in series with a Packard proportional counter system. For the major components, appropriate calibration factors were applied to the thermal conductivity detector response.

The ^{14}C content of some fractions was so low that it could not be distinguished from the background of the proportional counter. The data in Table 1 were therefore obtained by trapping the effluent from the thermal conductivity cell in traps maintained at dry ice temperature. Multiple sample injection and trapping cycles were carried out to obtain sufficient sample for counting. Thus, several effluent fractions were trapped and diluted with unlabeled toluene; these fractions included all of the peaks eluting before methylcyclohexane, methylcyclohexane, toluene, and xylene peaks. Liquid scintillation counting, which is much more sensitive than the proportional counter, was utilized to obtain the activity for each of the trapped samples.

RESULTS AND DISCUSSION

With the exception of the large peak due to added methylcyclohexane, the gas chromatogram of the run with added methylcyclohexane is essentially the same as that obtained without added methylcyclohexane, as shown in Fig. 1 (note that the time scale is not exactly the same as that in the two chromatograms). In addition the product distribution is, within experimental error, the same in the two runs, as shown by the data in Table 2. Consequently, the addition of methylcyclohexane did not appre-

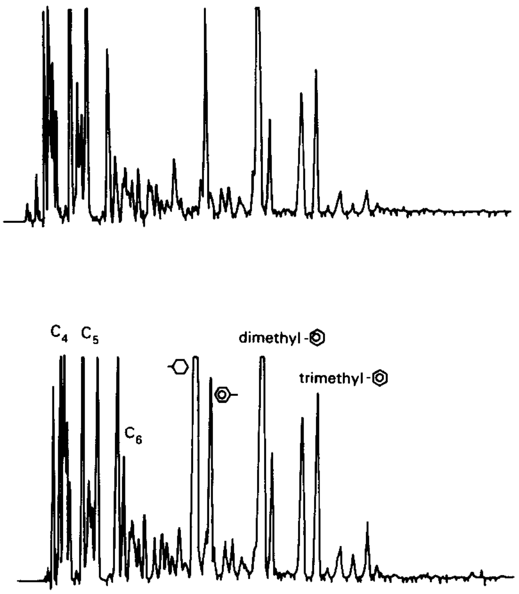
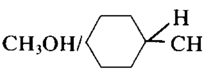


FIG. 1. Comparison of gas chromatogram for the products from methanol only conversion (top) and methanol plus methylcyclohexane conversion (bottom).

TABLE 2

Hydrocarbon Distribution[a] for Methanol Only and for Methanol/Methylcyclohexane Reaction over HZSM-5 Catalyst

Compounds	CH_3OH	CH_3OH/ H CH_3[b]
C_5	15.2	14.9
C_6	14.9	15.3
Benzene	1.8	1.7
C_7	12.8	12.0
Toluene	7.8	7.3
C_8	4.0	4.2
Xylene	26.0	25.4
Trimethyl benzene and isomers	17.5	19.2

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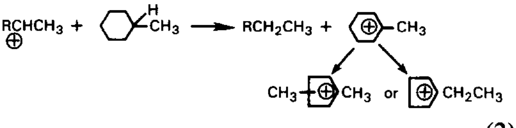
[a] Based upon Fig. 1.

[b] The amount of methylcyclohexane is not included but the amount of methylcyclohexane is 3.75 times more than that of toluene.

ciably alter the distribution of the products from pure methanol. Comparing the two chromatograms also makes it apparent that little, or no, methylcyclohexane is produced in the run with methanol alone.

The distribution of the ^{14}C in the products starting with methanol and labeled methylcyclohexane is shown in Table 1. *n*-Heptane coelutes with methylcyclohexane for the column used to generate the chromatograms shown in Fig. 1; however, the very low activity of the methylhexane isomers indicates that the activity of *n*-heptane should be low so that this should not impact the data on our conclusions. The ^{14}C distribution in Table 1 clearly shows that only a minor amount of the ^{14}C present in methylcyclohexane was incorporated into products eluting earlier (alkanes and alkenes) or later (benzene and higher boiling aromatic compounds).

The amount of aromatics was sufficiently large that a significant fraction of the ^{14}C should have appeared in the aromatic products if methylcyclohexane dehydrogenation occurred during aromatic formation. For example, the weight ratio of (methylcyclohexane/toluene, xylenes, and trimethylbenzene) in our products was 0.5 and the ratio of (methylcyclohexane/toluene) was only 3.8. If a significant amount of toluene had resulted from dehydrogenation of labeled methylcyclohexane it should have been detected. The alkylation of benzene and toluene is as rapid as the formation of aromatics from methanol (*6*), and many agree that this alkylation reaction is many times faster than the formation of aromatics from methanol. Consequently, the data indicate that dehydrogenation of a cyclohexane, once formed, is an insignificant reaction in the MTG synthesis. Furthermore, substituted cyclopentanes, ethycyclopentane and dimethylcyclopentanes, would be rapidly formed with this acidic catalyst if either methylcyclohexane or its carbocation had been formed. The absence of significant amounts of ^{14}C-labeled alkylcyclopentanes is additional support for the absence of methylcyclohexane dehydrogenation even to the extent that the carbocation is formed. The abstraction of a hydride ion from methylcyclohexane by an alkyl carbocation would produce the methylcyclohexyl cation; this should undergo subsequent isomerization.



(2)

Likewise, the cyclization pathway should not produce substituted alkylcyclopentane cations since they should interconvert by the pathway outlined in Eq. (2) to interconvert with methylcyclohexane.

The data from this study indicate that the dehydrogenation that produces three alkanes for every aromatic does not involve a cyclohexane or, by inference, cyclopentane compound. Furthermore, the data require that any methylcyclohexane, and presumably any cycloalkane, that is present is not incorporated into the dynamic methanol to a higher hydrocarbon synthesis scheme. It is difficult to understand why a methyl cation, if present in the zeolite as a consequence of methanol dehydration, should not abstract hydrogen from methylcyclohexane to form methane and a methylcyclohexyl cation that would undergo subsequent reactions. Likewise, if carbene is present as the dominate MTG C_1 species, methylcyclohexane should react with this carbene to form a significant amount of dimethylcyclohexane even if dehydrogenation to aromatics does not occur. Therefore, it appears that the results from this study provide indirect support for an oxonium ion mechanism for the MTG reaction (*7*). The data demonstrate the inertness of cyclohexanes under the 310°C MTG synthesis conditions and eliminates them as intermediates in the formation of aromatics.

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REFERENCES

1. Chang, C. D., and Silvestri, A. J., *J. Catal.* **47,** 249 (1977).
2. Wu, M. M., and Kaeding, W. W., *J. Catal.* **88,** 428 (1984).
3. Tau, L.-M., Fort, A. W., and Davis, B. H., *in* "Proc. 7th Int. Zeolite Conf." (Y. Murakami, A. Iijima, and J. W. Ward, Eds.), p. 899. Kodansha/Elsevier, Amsterdam, 1986.
4. Haag, W. O., "International Symposium on Zeolite Catalysis," Siofok, Hungary, May 13–16, 1985.
5. Vedrine, J. C., Dejaifve, P., Garbowski, E. D., and Derouane, E. G., "Catalysis by Zeolites" (B. Imelik, *et al.*, Eds.), p. 29. Elsevier, Amsterdam, 1980.
6. Fort, A. W., and Davis, B. H., *J. Catal.* **96,** 357 (1985).
7. Chang, C. D., *Catal. Rev. Sci. Eng.* **25,** (1983).

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