JOURNAL OF CATALYSIS **79,** 242–243 (1983)

# LETTERS TO THE EDITORS

## Comments on Proposed Carbene Intermediacy in Hydrocarbon Formation from Methanol over Zeolite Catalysts

In a recent note (*1*) Chang and Chu presented interesting results on the formation of hydrocarbons from methanol. Their first observation was that addition of propane to the methanol feed causes a significant lowering of the iso-to-normal ratio of the product butanes. Repetition of the experiment using $^{13}C$-enriched methanol resulted in about the same decrease of the $i/n$-$C_4^0$ ratio, but now also the $^{13}C$ distributions for the butanes could be measured. After some recalculations their results can be presented as shown in Table 1.

According to the authors two conclusions can be deduced from these results: (i) the varying *i*/*n* ratios with changing $^{13}C$ substitutions eliminates skeletal isomerization as the principal cause for the observed changes; (ii) the marked deviation from random distribution in each isomer proves that a reaction of propane has taken place.

It is easy to agree with these conclusions. It is, however, difficult to take these results as evidence of direct methylation of propane by methanol. The authors base this conclusion on the observed low *i*/*n* ratio of the singly labeled butanes, which according to them can be explained by carbene insertion into the C–H bonds of propane. However, as they point out themselves, it is not possible to explain the formation of the other butane members in the same way. The origin of the doubly labeled butanes which are present in even larger amounts than the singly labeled compounds remained a mystery for them.

The aim of this letter is to make a contribution to the solution of this mystery. As mentioned above, the reported experiments indicate undoubtedly that propane takes part in the reaction. However, the fact that not only singly labeled but also doubly (and zero and fourfold) labeled butanes are formed indicates that not only complete propane molecules are incorporated in the products but also fragments; thus *C–C scission of propane molecules has to occur!*

In view of the observed stability of pure propane under the experimental conditions (*1*) this means that propane is transferred to a reactive species in the presence of reacting methanol. As the main observed effect is a dramatic change in the iso-to-normal ratio of the product butanes the reaction of propane most probably will be directly related to this butane formation. As generally accepted, the butane formation proceeds via the corresponding carbenium ions. So *n*-butane will be formed by hydride transfer to the secondary butyl cation and *i*-butane by hydride transfer to the tertiary butyl cation. The required hydride ions can be abstracted from alkanes which in turn are transformed to carbenium ions.

When propane is present in large excess the hydride ions will also be abstracted from this alkane to form the propyl cation, according to the reactions:

$$sec\text{-}C_4H_9^+ + C_3H_8 \rightarrow n\text{-butane} + C_3H_7^+ \qquad \Delta H = +16 \text{ kJ/mol}$$

$$tert\text{-}C_4H_9^+ + C_3H_8 \rightarrow i\text{-butane} + C_3H_7^+ \qquad \Delta H = +82 \text{ kJ/mol}$$

The indicated reaction enthalpies have been calculated from the relative stabilities of the distinct carbenium ions (*2*). As a result of the much lower reaction enthalpy the *n*-butane formation will be favored above the *i*-butane formation which might explain the observed change in the *i*/*n* ratio of the butanes. Furthermore, in this way

0021-9517/83/010242-02$03.00/0

TABLE 1

$^{13}C$ Distribution in Butanes

| $^{13}C_n$ | Theoretical[a] (%) | Experimental (%) | $i-C_4^0$ (%) | $n-C_4^0$ (%) | $i/n-C_4^0$ |
|---|---|---|---|---|---|
| $n = 0$ | 0.01 | 9 | 4.7 | 4.3 | 1.1 |
| $n = 1$ | 0.4 | 13 | 6.5 | 6.5 | 1.0 |
| $n = 2$ | 4.9 | 21 | 11 | 10 | 1.1 |
| $n = 3$ | 29.2 | 30 | 19.7 | 10.3 | 1.9 |
| $n = 4$ | 65.6 | 27 | 19.7 | 7.3 | 2.7 |

[a] Expected random distribution from the methanol feed (90% $^{13}C$ + 10% $^{12}C$). Calculated average $^{13}C$ content is 2.53 $^{13}C$ atoms per molecule (63%).

the activation of propane can be understood. Once the propyl cation is formed, it will be inserted in the reaction network and be incorporated in the reaction products.

One of the reaction products of the propyl cation will be propene, and indeed a considerable increase of the propene formation is observed (from 3.63 to 4.53%) when propane is added to the methanol feed. A second support for this model is the observed $^{13}C$ content of the reaction products. In the $^{13}C$ isotope-labeling experiment 1 mol $^{13}CH_3OH$ (90% $^{13}C$) was diluted with 3 mol $^{12}C_3H_8$. Based on 100% conversion of methanol and 5% conversion of propane (*1*) the reaction products will contain $1.00 \times 0.90 = 0.90$ mol $^{13}C$ (62%) and $1.00 \times 0.10 + 0.05 \times 3 \times 3 = 0.55$ mol $^{12}C$ (38%).

If we assume that the $^{13}C$ distribution of the butanes is representative for all products (about 45 wt% of the products are butanes) we can see an excellent agreement between this calculated $^{13}C$ content and the observed average $^{13}C$ content of the butanes (Table 1).

Summarizing it can be said that the claimed evidence for the existence of carbenoid $C_1$ species is disputable and that the reported results can be explained even better by a model in which the added propane molecules undergo hydride transfer to form propyl cations.

## REFERENCES

*1.* Chang, C. D., and Chu, C. T. W., *J. Catal.* **74,** 203 (1982).

2. Franklin, J. L., *in* "Carbonium Ions" (G. A. Olah and P. von R. Schleyer, Eds.), Vol. 1, p. 85. Interscience, New York, 1968.

J. H. C. van Hooff

*Laboratory for Inorganic Chemistry*
*Eindhoven University of Technology*
*P.O. Box 513*
*5600 MB Eindhoven, The Netherlands*

*Received June 17, 1982*