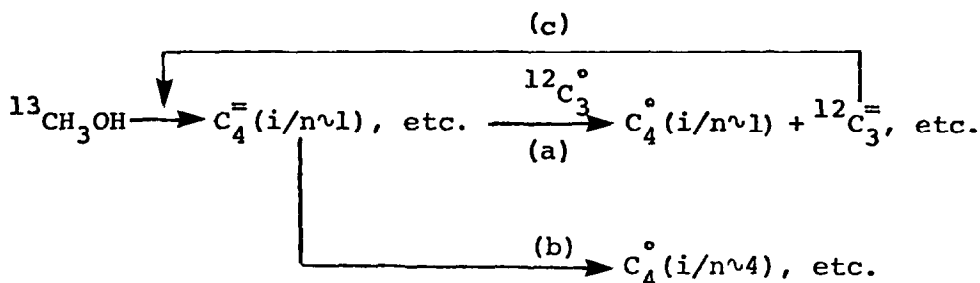# Carbene Intermediates in Methanol Conversion to Hydrocarbons. Reply to van Hooff

The interpretation of van Hooff (1) appears, on the surface, to be an attractive alternative to our hypothesis. Reflection shows, however, that his argument contains a number of flaws, which we will address.

It is necessary to inquire first into the possible origins of the butyl cations themselves, a question which van Hooff has neglected. Prior to our isotope labeling experiments, out initial inclination was also to suspect a connection between the observed low i/n-butane ratios and the precursor butyl cations. Since in this reaction the distribution of the parent butenes is generally close to thermodynamic equilibrium ($iC_4^= \Sigma nC_4^= = 1.1$ at 370°C) it was logical to assume that the added propane could interfere with the normal reaction sequence by interception of alkyl cations through hydride transfer, resulting in i/n-butane ratios identical to the equilibrium ratio of butenes. One would expect also to see a corresponding increase in ethane (and possibly methane) since hydride abstraction by ethyl (and methyl?) cation should be even more favorable (lower ΔH) than by butyl cations. This was not observed (2).

The main weakness in the model of van Hooff, however, is that it is not in accord with the observed isotope distributions. The reason for this can be made clear with the aid of the following diagram containing the essential features of his proposal.

$$
\begin{array}{c}
\text{(c)} \\
^{13}CH_3OH \longrightarrow C_4^= (i/n\sim 1), \text{ etc.} \xrightarrow[\text{(a)}]{^{12}C_3^\circ} C_4^\circ (i/n\sim 1) + {}^{12}C_3^=, \text{ etc.} \\
\xrightarrow{\text{(b)}} C_4^\circ (i/n\sim 4), \text{ etc.}
\end{array}
$$

As shown, two competitive routes must be considered for the fate of the butenes. Path (a) is the postulated hydride transfer. This competes with Path (b), the normal aromatization route for butenes, which yields also butanes in addition to aromatics and other paraffins. The ^{12}C-propene formed via hydride abstraction will re-enter the cycle, Path (c), and be incorporated, resulting in a randomization of the isotope distribution. The theoretical distribution calculated for the butanes based on $0.38\,^{12}C + 0.62\,^{13}C$ is shown in Fig. 1 (dashed line). The observed distribution is superimposed. The lack of agreement between calculated and experimental is obvious. Even more telling is the i/n ratio of the various labeled butanes. Referring again to the above reaction diagram, if van Hooff's model were correct, then the product butanes should have $1 < i/n < 4$, which is the case; however, this ratio will be *constant and independent of the degree of isotope substitution* since isotope scrambling had occurred before hydride abstrac-
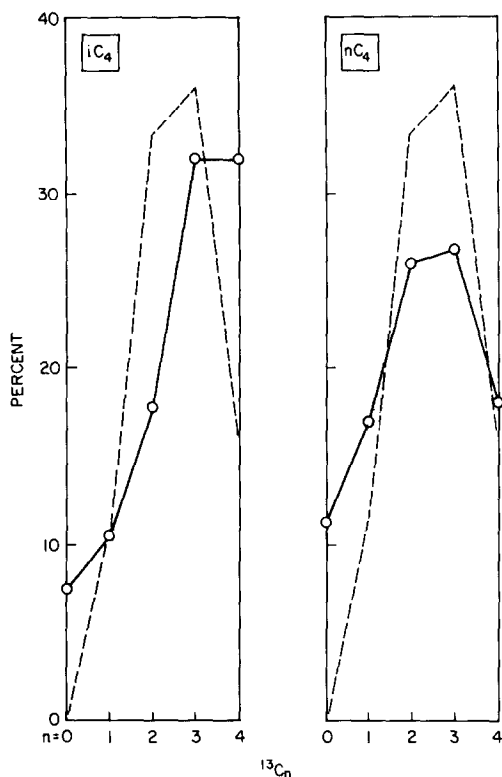
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FIG. 1. ^{13}C distribution in butanes. Dashed line represents random distribution for 38% ^{12}C + 62% ^{13}C. Circles are experimental points.

tion. This also is clearly not in agreement with the experimental data, which show an *increase* in i/n with substitution (2).

Lastly, a calculated ^{13}C content of 62% would also be expected for our mechanism, so that the good agreement with experimental does not constitute support for one mechanism over the other.

It is necessary to emphasize that we are not implying here that hydride abstraction does not occur in methanol transformation. On the contrary, we believe that hydride abstraction reactions play an important role and are most likely here to be implicated in the formation of the doubly and triply labeled butanes in our experiment. We conclude, nonetheless, that the proposal of van Hooff is disputable as a replacement for our hypothesis. The mystery, it seems, remains unsolved.

REFERENCES

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