JOURNAL OF CATALYSIS **82**, 252–253 (1983)

Methyl Group Interchange in the Conversion of Dimethylether to Ethylene

The mechanism of the catalytic conversion of methanol to hydrocarbons (*1*) is still an object of controversy (*2*). One problem is lack of agreement between data from different laboratories. Thus, it was reported that ethylene is the only hydrocarbon product at low methanol conversions (*3*); since at longer reaction times heavier hydrocarbons were formed at the expense of ethylene, it was concluded that the latter is a reaction intermediate (*1, 3, 4*). Other authors, however, reported that ethylene is unreactive, and therefore cannot be an intermediate (*5*).

On the other hand, dimethyl ether is formed from methanol on the acid catalysts used for its conversion to hydrocarbons (*4*). It is rather generally accepted that dimethyl ether is an intermediate in the latter reaction (*2*).

Whether it occurs from methanol or from dimethyl ether, the formation of the first carbon–carbon bond is the crucial step of the synthesis from mechanistic viewpoint. The chain growth can be viewed as a repetition of this first step. No satisfactory mechanism has been proposed so far; this is illustrated by the current coexistence of at least five different pathways advanced by various authors (*2*).

One of the proposed pathways (*6*) involves alkylation of dimethyl ether (**1**) to the trimethyloxonium cation (**2**).

$$\underset{\mathbf{1}}{CH_3OCCH_3} + CH_3X^+ \cdot Z^- \rightarrow \underset{\mathbf{2}}{(CH_3)_2O^+\text{–}CH_3 \cdot Z^-} + X$$

The counter ion Z^-, or another basic but nonnucleophilic site on the catalyst, converts **2** to the corresponding ylide, which undergoes a Stevens-type rearrangement to methyl ethyl ether (**3**), in which a carbon–carbon bond has been established (*6*).

$$\mathbf{2} \xrightarrow[-ZH]{+Z^-} Me_2O^+\text{–}CH_2\!:^- \rightarrow \underset{\mathbf{3}}{MeOCH_2CH_3}$$

An experimental verification of this mechanism has been pursued in a study of conversion of a 1 : 1 mixture of dimethyl ether (**1**) with dimethyl ether doubly labeled with carbon-13 (**1**-$^{13}C_2$) (*7*). The ethylene (**4**) obtained at 60% dimethyl ether conversion was a mixture of unlabeled (**4**-$^{13}C_0$), monolabeled (**4**-$^{13}C_1$), and dilabeled material (**4**-$^{13}C_2$), in a statistical (25 : 50 : 25) distribution (*7*). This result indicated that **4** was not formed by a one-step intramolecular transformation of **1**, which would give 50% **4**-$^{13}C_0$ and 50% **4**-$^{13}C_2$.[1]

On the other hand, at low conversion **1** gave equal amounts of methanol and hydrocarbons, while methanol was converted 20–30 times faster to **1** than to hydrocarbons. Therefore, it was concluded that dimethyl ether (**1**) is most probably converted directly to **4** via the oxonium ion **2.** The carbon scrambling was rationalized by the fact that **1** is alkylated by another molecule of dimethyl ether, protonated by the catalyst (**1-H**$^+$), or by a molecule of protonated methanol, formed in small quantities on the catalyst.

I want to point out that the pattern of scrambling reported by the previous authors (*7*), is not compatible with the direct

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[1] The actual compositions reported in Ref. *7* were 39.2% **1**-$^{13}C_0$, 9.6% **1**-$^{13}C_1$, and 51.2% **1**-$^{13}C_2$ for the starting material, and 19.8% **4**-$^{13}C_0$, 47.7% **4**-$^{13}C_1$, and 32.5% **4**-$^{13}C_2$ for the product. (Calculated statistical distribution: 19.4% **4**-$^{13}C_0$, 49.2% **4**-$^{13}C_1$, 31.4% **4**-$^{13}C_2$.)

0021-9517/83 $3.00

formation of **4** from **1**. On the contrary, statistical distribution of the label in **4** requires that **1** be completely broken apart into methanol or other species containing only one methyl group per molecule (or per site if tied to the catalyst).

If we represent the formation of the oxonium ion **2** as in Ref. (*7*), then we have to describe the reaction of a 50 : 50 mixture of **1** and **1**-$^{13}C_2$, with a 50 : 50 mixture of **1**-H^+ and (**1**-$^{13}C_2$)-H^+, or a 50 : 50 mixture of methanol and methanol-^{13}C. In either case, the trimethyloxonium cation (**2**) formed should consist of 25% **2**-$^{13}C_0$, 25% **2**-$^{13}C_1$, 25% **2**-$^{13}C_2$, and 25% **2**-$^{13}C_3$.[2] This mixture rearranged intramolecularly to form methyl ethyl ether (*6*, *7*):

$$25\%\ CH_3OC_2H_5 + \left|\begin{array}{l} 8.33\%\ CH_3O\text{-}^{13}CH_2CH_3 \\ 8.33\%\ CH_3OCH_2\text{-}^{13}CH_3 \\ 8.33\%\ ^{13}CH_3OCH_2CH_3 \end{array}\right|$$

$$+ \left|\begin{array}{l} 8.33\%\ CH_3O\text{-}^{13}CH_2\text{-}^{13}CH_3 \\ 8.33\%\ ^{13}CH_3O\text{-}^{13}CH_2CH_3 \\ 8.33\%\ ^{13}CH_3O\text{-}CH_2\text{-}^{13}CH_3 \end{array}\right| + 25\%\ ^{13}CH_3O\text{-}^{13}C_2H_5$$

Elimination from the latter leads to ethylene (33% **4**-$^{13}C_0$, 33% **4**-$^{13}C_1$, 33% **4**-$^{13}C_2$) of an isotopic composition different from the statistical label distribution quoted above.

For the actual isotope distribution in the starting material of the previous authors (*7*), one can likewise calculate for the reaction involving alkylation of **1** that the ethylene product should consist of 26% **4**-$^{13}C_0$, 36% **4**-$^{13}C_1$, and 38% **4**-$^{13}C_2$, in total disagreement with the experimental results (*7*). The latter require that the exchange of methyl groups within dimethyl ether (**1**) be very fast, relative to the conversion to hydrocarbons:

$$CH_3OCH_3 + X\text{-}Y \rightleftarrows CH_3X + YOCH_3.$$

Alternatively, the oxonium cation, or even dimethyl ether (**1**) need not be intermediates. Any of the three species present at equilibrium can be the precursor of the hydrocarbon products. The results of the labeling experiments (*7*) are thus compatible with surface alcoxides or carbenes as intermediates (*2*), as well as with the oxonium ion mechanism (*6*, *7*). The symbol XY represents some active site on the catalyst. The intervention of methanol per se (XY = H_2O) appears less probable (*7*), but we must note that in the usual reaction conditions methanol is the starting material, and dimethyl ether is formed together with an equivalent amount of water. The hydrolysis–reetherification equilibrium might be established more easily than in the experiments in which pure dimethyl ether was the starting material (*7*).

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Received December 9, 1982

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[2] The small carbon isotope effect can be neglected.