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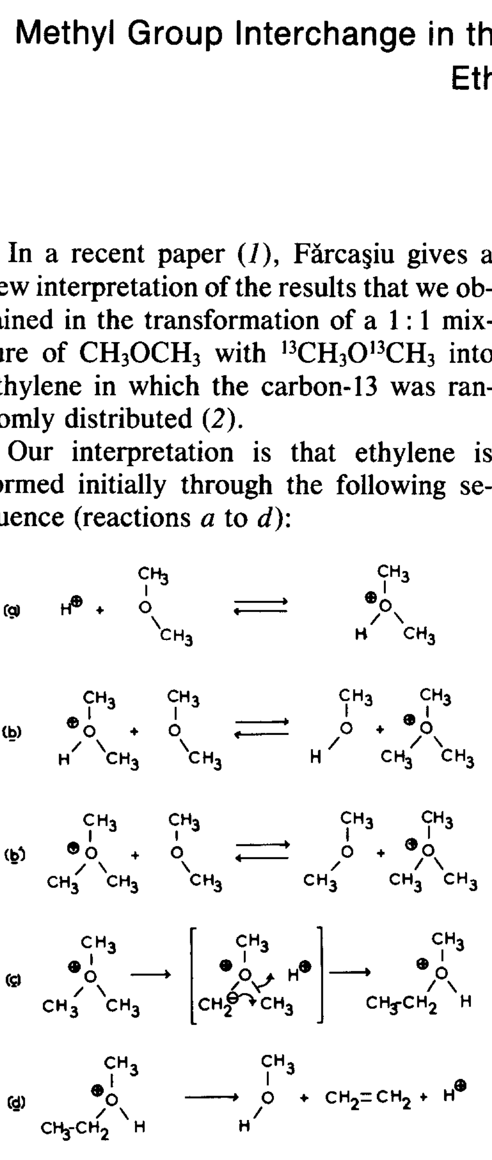
Methyl Group Interchange in the Conversion of Dimethyl Ether to Ethylene

In a recent paper (*1*), Fărcaşiu gives a new interpretation of the results that we obtained in the transformation of a 1 : 1 mixture of CH_3OCH_3 with $^{13}CH_3O^{13}CH_3$ into ethylene in which the carbon-13 was randomly distributed (*2*).

Our interpretation is that ethylene is formed initially through the following sequence (reactions *a* to *d*):



This sequence includes as carbon–carbon bond formation step a Stevens-type rearrangement of trimethyloxonium ions (*3*) (reaction *c*) for which some experimental support has now been obtained (*4, 5*). This step is assumed to be the rate-limiting step, which accounts for the fact that the carbon-13 is rapidly redistributed through two reactions, namely reaction *b* and *b'*. The carbon-13 distribution in the intermediate trimethyloxonium ion is the following: 12.5% $^{13}C_0$, 37.5% $^{13}C_1$, 37.5% $^{13}C_2$, and 12.5% $^{13}C_3$. The Stevens rearrangement of this trimethyloxonium ion followed by the statistical loss of a methanol molecule leads to ethylene with a random distribution of carbon-13: 25% $^{13}C_0$, 50% $^{13}C_1$, and 25% $^{13}C_2$.

On the contrary, in his interpretation of our results, Fărcaşiu (*1*) assumes that reaction *b* is the rate-limiting step. On this hypothesis the intermediate oxonium ion and ethylene should, respectively, have nonrandom carbon-13 distributions of 25% $^{13}C_0$, 25% $^{13}C_1$, 25% $^{13}C_2$, 25% $^{13}C_3$, and 33% $^{13}C_0$, 33% $^{13}C_1$, 33% $^{13}C_2$, which is not verified.

Actually reaction *b* and reaction *b'*, which are of the same type as the formation of dimethyl ether from methanol (*6*), are probably also very fast. If the formation of methanol from pure dimethyl ether is relatively slow, it is due to the fact that (i) methanol formation through reaction *b* requires initially the consumption of a stoichiometric amount of protonic sites, and (ii) methanol formation by hydrolysis of dimethyl ether can only occur with water coming from the formation of hydrocarbons. However, if the transformation of dimethyl ether is carried out in the presence of a stoichiometric amount of water, then the formation of methanol is much faster than the formation of hydrocarbons (*7*).

As for the conclusions to be drawn, we actually pointed out that it was not possible to tell from these results alone whether dimethyl ether was necessary or not as an

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intermediate and, of course, the CH_3 scrambling per se is in accordance with any mechanism involving the partition of dimethyl ether.

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