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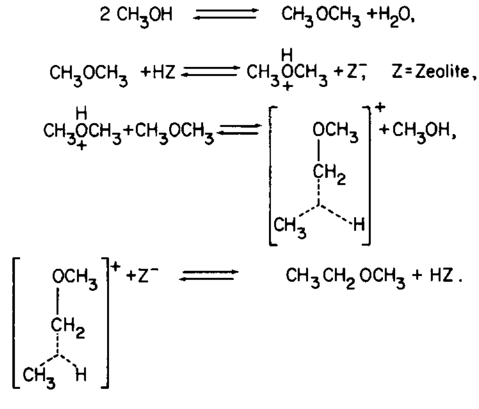
LETTERS TO THE EDITORS

In Re: Mechanism of Conversion of Methanol over ZSM-5 Catalyst

In a recent communication, Anderson *et al.* (*1*) discuss conversion of methanol to gasoline-type hydrocarbons over HZSM-5 catalyst. They conclude that the previously suggested carbene-type species are not involved due to the initial nonlability of C–H bonds in methanol. They propose that the key to the propagation reaction is the production of a reactive olefin containing greater than two carbons. However, they have not detailed how these reactive olefins may be produced. We wish to propose a mechanism for this reaction which is consistent with the available evidence. In view of the accepted Brönsted acidic nature of HZSM-5 (*1, 3*) it appears reasonable that the reaction path is carbonium ion in nature. The work of Olah and his group (*4*) on the behavior of alkanes and other species in superacids in solution indicated the importance of two-electron, three-center bonded carbonium ion transition states. Using Olah's work as the basis, a rationalization of the methanol conversion would be

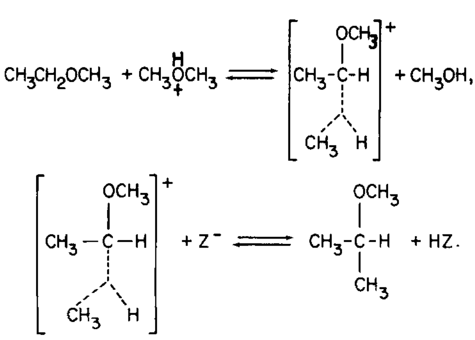


$$2\,CH_3OH \rightleftharpoons CH_3OCH_3 + H_2O,$$

$$CH_3OCH_3 + HZ \rightleftharpoons CH_3\overset{H}{\underset{+}{O}}CH_3 + Z^-; \quad Z = \text{Zeolite},$$

The methyl ethyl ether could eliminate methanol to form ethylene. However,

$CH_3CH_2OCH_3 \rightleftharpoons CH_2 = CH_2 + CH_3OH$; in view of the work of Anderson *et al.* (*1, 5*) ethylene is unlikely to be an important intermediate in methanol conversion. Rather the methyl ethyl ether could suffer further addition of methyl carbonium ion supplied from protonated dimethyl ether. Resultant methyl isopropyl ether



could eliminate methanol to give propylene or suffer addition of methyl carbonium ion. The path is then open to paraffins and aromatics. The considerable reactivity of methanol on HZSM-5 may be explained by the stability of the positively charged two-electron, three-center bonded carbonium ion transition states.

The argument proposed by Chang and Silvestri (*2*) for the involvement of a carbenoid species and that a methyl carbonium ion primary mechanism cannot be involved is not well founded. In the present mechanism a free methyl carbonium ion is not postulated but is envisaged to be transferred from protonated dimethyl ether to another dimethyl ether molecule. Methanol could also suffer insertion by the methyl carbonium ion from protonated dimethyl ether. However, in the HZSM-5 case, dehydration of methanol, to dimethyl ether is rapid and therefore the reaction is likely to proceed through dimethyl ether. The above

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proposed mechanism does not rely on the formation of ethylene which has been shown as unlikely to be a key intermediate in methanol conversion (*1*, *5*). It also explains the presence of methyl ethyl ether and the high ratio of iso to normal paraffins (*3*) in the reaction products.

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