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A Reply to Kagi: Mechanism of Conversion of Methanol over ZSM-5 Catalyst

The proposal that hydrocarbon formation from methanol might be explainable in terms of Olah's pentacoordinate carbon (*1*) has already been advanced by Pearson (*2*). Various reaction mechanisms involving oxonium-type intermediates have been postulated by Kaeding and Butter (*3*), and van den Berg *et al.* (*4*). Therefore, the mechanistic scheme of Kagi appears to contribute little if anything new to an already crowded field of speculative methanol-to-hydrocarbon mechanisms presently in the literature.

I would like to make the following comments:

1. The cited work of Anderson *et al.* (*5*), which involves benzene methylation with CD_3OD over ZSM-5, was carried out at 207°C. At this temperature, hydrocarbon formation from methanol itself is minimal if not absent. The observed integrity of the CD_3 group cannot therefore be considered hard evidence for or against any primary mechanism of C–C bond formation from methanol.

2. The Olah mechanism is an intriguing one, devised to explain the unique behavior of methane in superacids. Unfortunately, an analogous reaction of methane has never been observed on zeolites. Moreover, methanol in superacids appears to behave differently from methane (*6*).

3. In considering reaction mechanisms in zeolites, one must not lose sight of the geometrical constraints imposed by the crystal structure. Since the maximum free widths of ZSM-5 channels is <6 Å (*7*), a transition state such as the one proposed by Kagi arising from the interaction of $CH_3CH_2OCH_3$ and $(CH_3)_2OH^{\oplus}$ may be too bulky to exist in the zeolite interior. Such "transition state selectivity" in zeolites has been observed (*8*, *9*).

4. The question, "carbene or carbenium" is probably an oversimplification. Mechanisms involving both species can be written, such as the generation of a carbene from dimethyl ether:

$$CH_3OCH_3 + HZ \rightarrow \underset{\text{(I)}}{(CH_3)_2OH^{\oplus}Z^{\ominus}},$$

$$\text{(I)} \xrightarrow{-CH_3OH} [CH_3{}^{\oplus}Z^{\ominus}] \rightarrow [:CH_2] + HZ,$$
$$HZ = \text{zeolite}.$$

The latter reaction as written is not meant to imply the existence of a free carbene. The final step would be accompanied by a concerted insertion into C–H or addition to a double bond as previously suggested (*10*).

In any case, until the appearance of convincing experimental evidence, which is singularly lacking up to now, the primary mechanism of C–C bond formation from methanol remains an open question.

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