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On the Mechanism of C–C Bond Formation from Methanol over H-ZSM 5. New Evidence for Trimethyloxonium Ion Intermediacy

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In the presence of a weak base, trimethyloxonium ions can react to give products with C–C bonds.

The formation of small alkenes from separated methyl groups in the methanol-to-gasoline process over the zeolite H-ZSM 5 is an intriguing reaction. It is known that methanol is rapidly dehydrated to dimethyl ether on weak acid sites, and so the same will happen initially on the strong acidic sites of H-ZSM 5. The next step in our view is a methyl-shift from protonated Me₂O to physisorbed Me₂O molecules resulting in trimethyloxonium ions (Me₃O⁺) (see Scheme 1). The given reaction enthalpies are based on heats of formation of gas phase molecules calculated with MINDO 3. The highest energy barrier in the route to Me₃O⁺ (+20 kJ mol⁻¹) is small compared with the energy required for the formation of CH₂ or CH₃⁺ (about 320 and 200 kJ mol⁻¹ respectively). Thus, of the main intermediates mentioned in the literature, Me₃O⁺ is the most energetically favourable. Nevertheless it is in doubt whether Me₃O⁺ can generate an ethyl group, i.e. to give methyl ethyl ether (MeOEt).

Previously²⁻⁵ we stated that the formation of a C–C bond proceeds via a methylenedimethyloxonium ylide (see Scheme 2). The main argument against this rearrangement concerns the proton shift from one of the methyl groups of Me₃O⁺ to an adjoining basic zeolite site; it is questionable whether the basic
Scheme 1. The different reaction steps in the route from methanol to the trimethyloxonium ion. Heats of reaction are given in kJ mol\(^{-1}\).

Scheme 2. The rearrangement of the trimethyloxonium ion initiated by a basic zeolite site.

sites of ZSM 5 are strong enough to accomplish this abstraction. However, in accordance with the ylide formation is the observation of Mole and Whiteside\(^6\) that the methyl group of methanol can be deuteriated in the presence of D\(_2\)O over H-ZSM 5.

In order to obtain support for our mechanism we performed model experiments without zeolite. We heated the salt trimethyloxonium tetrafluoroborate Me\(_3\)OBF\(_4\) (Fluka) under dried nitrogen at different temperatures and analysed the gaseous products by gas chromatography. The product distributions are given in Table 1(a).

The presence of MeOEt and ethene in the gases formed shows that Me\(_3\)O\(^+\) can generate species with C–C bonds. The observation of propene and butene indicates that an oligomerization of the initially formed ethene takes place. The observed Me\(_2\)O is probably a product of a side reaction. At higher temperatures the conversion into products with C–C bonds becomes more favourable. Also when Me\(_3\)OBF\(_4\) dissolved in nitromethane was heated at about the same temperatures we found C–C bond containing products.

These experiments show that the trimethyloxonium ion can be activated to produce C–C bonds; they do not however exclude the possibility of a bimolecular formation of these bonds. It appears that the weak base BF\(_4^-\) and the polar molecule nitromethane have sufficiently strong basic properties for this activation, i.e. a proton abstraction.

We believe that these results make the ylide formation by a basic site of the zeolite more credible. The conjugated basic sites of the weakly acidic silanol groups may play an important role in this C–C bond formation.

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References

| Table 1. Composition of the gas formed during 20 minutes thermolysis of: (a) solid Me\(_3\)OBF\(_4\), (b) Me\(_3\)OBF\(_4\) in nitromethane, at the temperatures indicated. |
|---|---|---|---|---|---|
| T/K | C\(_2\)H\(_4\) | C\(_3\)H\(_6\) | C\(_4\)H\(_8\) | MeOEt | Me\(_2\)O |
| (a) 313 | 1 | 1 | 1 | 3 | 94 |
| 333 | 3 | 2.5 | 3 | 2.5 | 88 |
| 353 | 4 | 3 | 5 | 2.5 | 85 |
| 373 | 24 | 3 | 8 | 1 | 61 |
| (b) 323 | 1 | 1 | 0 | 3 | 95 |