Remarks on the Mechanism of Ethylene Formation from Methyl Alcohol¹

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Comments on two recent communications are made, while the oxonium ylide mechanism of ethylene formation from methyl alcohol is re-emphasized.

The ZSM-5 zeolite catalysed conversion of methyl alcohol into higher hydrocarbons² is frequently referred to as shape selective catalysis. Although this correctly depicts the effect of the zeolite catalyst in limiting the size distribution of products, it hardly describes its role in the crucial initial $C_1 \rightarrow C_2$ conversion step. In our preceding studies³ we reported on the bifunctional acid-base catalysed conversion of heterosubstituted methanes, including methyl alcohol, methyl chloride, etc., over heterogeneous catalysts lacking any ordered structure, to ethylene (and lower alkenes). In other studies⁴ we provided additional experimental evidence to establish the oxonium ylide mechanism of these conversions. Van den Berg et al.5 independently suggested a related mechanism for the initial step of the ZSM-5 catalysed methyl alcohol conversion although they at the time provided no experimental evidence for possible ylide formation from the trimethyloxonium ion nor concerned themselves with the nature of the $C_1 \rightarrow C_2$ forming step from the ylide. Such evidence was, however, provided in our studies,⁴ as well as by Sommer et al.,⁶ by treating trimethyloxonium salts with strong bases. It was also established in our labelling experiments that the dimethyloxonium methylide undergoes intermolecular methylation to ethyl dimethyloxonium ion instead of intramolecular Stevens rearrangement to methyl ethyl ether (Scheme 1).

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Chang *et al.* of the Mobil group in their publications suggested that in the conversion of methyl alcohol into ethylene (including methyl ethyl ether formation) first α -elimination of methyl alcohol or dimethyl ether to methylene occurs followed by the formation of an initial surface-bound carbenoid. Further, they suggested zeolite-mediated interconversion of carbenoid and methyl cation according to Scheme 2.⁷

Lee and Wu⁸ in a recent communication reiterated this mechanistic scheme and reported that the conversion of diazomethane over ZSM-5 catalyst giving ethylene (as well as propene and butenes) supports the mechanism. They suggested that diazomethane over the acidic sites of the zeolite forms a methyloxonium species, which further reacts with excess of methylene *via* C-H insertion to an ethyloxonium species which then undergoes β -elimination to ethylene (Scheme 3).

There is, however, no analogy known for the insertion of singlet methylene into methyloxonium ions. To ascertain whether the reaction is feasible we have carried out the model reaction of trimethyloxonium tetrafluoroborate with singlet methylene generated by the photolysis of diazomethane and found (by ¹³C n.m.r.) no insertion to give dimethyloxonium ion. Therefore, the suggested reaction path is improbable although obviously the behaviour on catalytic surfaces cannot be closely duplicated in experiments of model compounds.











Scheme 3

$$\begin{array}{cccc} \mathrm{CH}_{2}\mathrm{N}_{2} & \xrightarrow{\mathrm{H}^{+}} & \mathrm{CH}_{3}\mathrm{N}_{2}^{+} & \xrightarrow{\mathrm{CH}_{2}\mathrm{N}_{2}} & \mathrm{CH}_{3}\mathrm{CH}_{2}\mathrm{N}_{2}^{+} + \mathrm{N}_{2} \\ & & & & & \\ & & & & \\ & & & \\ & & & & \\ & & & & \\ & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & \\ & & & & \\ & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & \\ & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & \\ & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & \\ & & & & & \\ & & & & & \\ & & & & \\ & & & & & \\ & & & & & \\ & & & & \\ & & & & & \\ & & & & \\ & & & & \\ & & & & & \\ & & & &$$

Scheme 4

Alkyl cations (or their equivalent alkylating agents), however, are readily capable of alkylating diazomethane. Thus, methylation of diazomethane by an incipient methyl cation formed on the acidic site of the zeolite can account for the acid catalysed formation of ethylene from diazomethane (Scheme 4).

On the other hand, singlet methylene itself can also dimerize to give ethylene (and subsequently propene, *etc.*).⁹ Regardless, the reactions of diazomethane (or singlet methylene) cannot directly relate to the methyl alcohol-to-ethylene condensation as α -elimination of water from methyl alcohol to methylene is thermodynamically endothermic by some 349.3 kcal/mol.^{10†} Further, the well known bimolecular dehydration of methyl alcohol to dimethyl ether is exothermic by *ca.* -24.5 kcal/mol. Even if the singlet methylene is stabilized on the heterogeneous catalytic surface, the monomolecular elimination of methyl alcohol to methylene is improbable.

CH₃OH →: CH₂ + H₂O -200.7 +390.4 -241.8 ΔH = +349.3 kcal/mol 2CH₃OH → CH₃OCH₃ + H₂O 2×(-200.7) -184.1 -241.8 ΔH = -24.5 kcal/mol

The initial reaction of methyl alcohol in all probability is the bimolecular dehydration forming dimethyl ether. It then, through the involvement of acidic sites of the catalyst which promote transalkylation, forms the trimethyloxonium ion, *i.e.*, Me₃O^{+ 4a} or related Me₂O⁺-zeolite complex. The methyloxonium ions subsequently undergo base catalysed deprotonation to give the corresponding very reactive oxonium methylides, which then in turn are readily methylated by excess of methyl alcohol/dimethyl ether (Scheme 1).

As indicated, evidence for the suggested oxonium ylide mechanism was based in part on study of model compounds, such as the trimethyloxonium salts which were found to be deprotonated with strong bases to give intermediate reactive dimethyloxonium methylide which subsequently, *via* its methylation and cleavages, gives ethylene and derived products.^{4,6}

Engelen *et al.*¹¹ in a simultaneously published communication claimed to have obtained further proof for the oxonium ylide mechanism by having found that trimethyloxonium tetrafluoroborate reacts in the presence of weak bases to give products with C–C bond formation (*i.e.* ethylene, propene, butenes as well as methyl ethyl ether). The experiments were carried out by heating (MeO)₃O+BF₄⁻ either neat or in nitromethane solution. It was suggested that the weak base BF₄⁻ and polar nitromethane solvent have sufficient strong basic properties to cause proton abstraction, *i.e.* oxonium ylide formation.

The experiments were carried out with commercial (Fluka) trimethyloxonium tetrafluoroborate. As we have already pointed out earlier,^{4a} but Engelen *et al.*¹¹ seem to be unaware, commercial samples of trimethyloxonium salts, generally prepared by Meerwein's procedure¹² from triethyloxonium ion, always contain ethyldimethyloxonium ion $[(CH_3)_2OC_2H_5]^+$ as impurity. This ion on heating undergoes

facile β -elimination to provide ethylene. We have consequently analysed the Fluka brand of trimethyloxonium tetrafluoroborate used by Engelen *et al.* and found it by ¹³C n.m.r. spectroscopy to contain 6.6% ethyldimethyloxonium ion impurity.‡ When pure trimethyloxonium tetrafluoroborate (prepared from dimethyl ether, methyl iodide, and AgBF₄ in SO₂ solution) is thermally decomposed no ethylene or derived products are observed. Dimethyl ether and methyl fluoride (as well as BF₃) are the only products. Deprotonation of *bona fide* trimethyloxonium salts with strong bases, however, as reported^{3b,4a,6} generates the dimethyloxonium methylide, which subsequently forms ethylene. The experiments reported by Engelen *et al.*, thus, regretfully cannot be used as further evidence for oxonium ylide mechanism, which is, however, well established.

Whereas our own studies did not involve ZSM-5 zeolite, but only non-shape selective acidic-basic bifunctional catalysts such as WO₃/Al₂O₃, we believe that the crucial $C_1 \rightarrow C_2$ transformation step is also similar in ZSM-5 catalysis, which posseses both acidic and basic sites. The role of the shape selective nature of zeolites is only to control subsequent product formation from ethylene by avoiding higher molecular weight products which cannot fit it into the cavities and channels of the zeolite.

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[‡] The relative percentages were obtained by the integration of ¹³C signals in the nuclear Overhauser enhancement suppressed protondecoupled ¹³C n.m.r. spectrum obtained on a Varian XL-200 spectrometer. A 20% SO₂ solution of Fluka trimethyloxonium tetrafluoroborate was used at -50 °C. The authenticity of ethyldimethyloxonium tetrafluoroborate impurity was confirmed by matching the spectra of the independently prepared salt from dimethyl ether, ethyl iodide, and AgBF₄ in SO₂ solution.