Synthesis and Decomposition of Trimethyloxonium ZSM-5, a Purported Intermediate in Methanol Conversion into Gasoline

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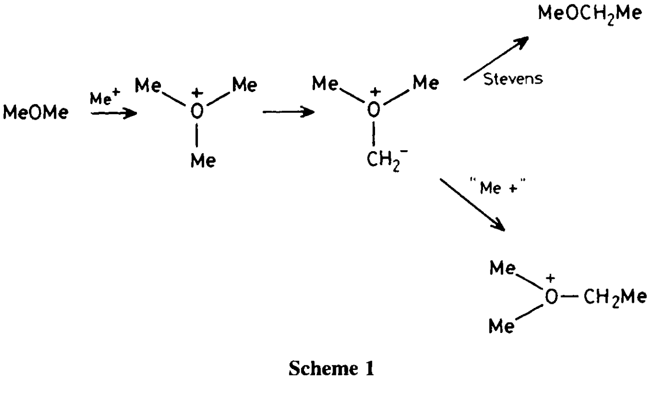
Trimethyloxonium cation (TMO) in zeolite ZSM-5 reacts principally as a surface methylating agent, similar to TMO salt decomposition with other weak conjugate bases (*e.g.* BF_4, arenesulphonates); recent reports of C_2 product formation from dimethyloxonium methylide generated by heating TMO salts with strong, poorly nucleophilic bases such as NaH and Li(2,2,6,6-tetramethylpiperidyl) do not accurately model the actual behaviour of this cation in ZSM-5.

Though mechanistic work has shown that methanol into gasoline conversion[1] is autocatalytic[2] and involves synthesis of alkane and aromatic products *via* alkene intermediates,[3] the nature of the initiating step to form C_2 products remains controversial. Early proposals invoked intermediate trimethyloxonium (TMO) cations which were assumed to deprotonate to oxonium ylides, followed by either an oxa-Stevens type rearrangement[4] or intermolecular methylation (Scheme 1).[5] Deprotonation of TMO salts was inferred from various C_2 products observed when these salts are heated with strong, non-nucleophilic bases.[6] On the other hand, methylation of weakly basic TMO counterions, such arenesulphonate,[7] fluoride,†[6a,8,9] and chloride[6b] during thermal decomposition is well known. In fact, TMO salts are among the most powerful methylating agents known.[10]



Scheme 1

The existence of TMO cations under methanol conversion conditions is not unreasonable since they are detected as a major product from proton-held methanol and dimethyl ether

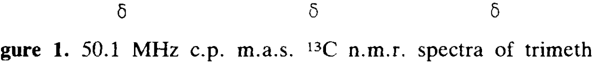


Figure 1. 50.1 MHz c.p. m.a.s. ^{13}C n.m.r. spectra of trimethyloxonium ion in ZSM-5 after (a) 4.3, (b) 9.3, and (c) 11.3 h. Spectra show the slow decomposition of TMO–ZSM-5 (δ 79) and appearance of methyl-ZSM-5 (δ 62).

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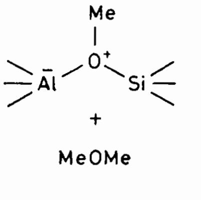
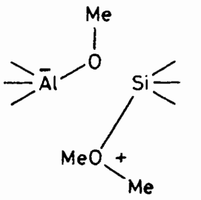
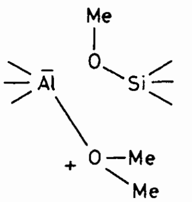
† A recent claim that the weakly basic anion in $TMO^+BF_4^-$ leads to C_2 products through deprotonation[8] has received criticism[9] and may be best explained by impure starting materials.



(1)



(2)



(3)

dimers in high-temperature gas-phase experiments.[11] The question arises, however, whether the conjugate base of ZSM-5 will deprotonate the TMO cation, or simply undergo surface methylation.

A zeolitic conjugate base modelled using lithium aluminium tetraisopropoxide showed only methylation products when heated with TMO salts.[12] This suggested aluminates are insufficiently basic to produce an ylide. We now report that the conjugate base in TMO–ZSM-5 reacts nucleophilically, rather than as a Brønsted base.

Cross-polarisation magic-angle spinning (c.p. m.a.s.)‡[13,14] ^{13}C n.m.r. spectra of TMO-cation exchanged ZSM-5[6] showed a singlet at δ 79.2 as the major signal (Figure 1). This is assigned to the methyl groups of the TMO-cation and is consistent with literature values.[15]

There also appeared a smaller signal at δ 62 in this initial sample (4.3 h). Spectra collected through the next day (20 °C) showed a steady increase in this signal with concurrent loss of the TMO-methyl singlet at δ 79. A simple first-order decay of the TMO cation is plotted in Figure 2, which also indicates little or no *total* signal intensity loss during 24 h. Comparison of spectra after 4.3 and 11.3 h shows the peak near δ 62 to be about 1.5 p.p.m. broader and slightly asymmetric. This, plus constant signal intensity, leads to the conclusion that the product peak is a coincidental superposition from two species.§ Furthermore, we detected no aliphatic methyl signal in the δ 13—18 region which indicates absence of C–C bond formation at this temperature.

We considered three modifications of the aluminosilicate site[16]. The most likely assignment for the decomposition product of TMO–ZSM-5 is a structure with a bridged methoxide and physisorbed dimethyl ether, (**1**). Overlap of these signals is consistent with the previous assignment of the peak at δ 59.2 to dimethyl ether formed on ZSM-5,[17] and HY[18] treated with methanol at high temperature; and with assignment of the δ 60.5 peak to the methoxy carbon in protonated methoxytrimethylsilane.[15] In the latter model compound, we suggest that deshielding due to protonation is similar to that caused by bridging to aluminium.

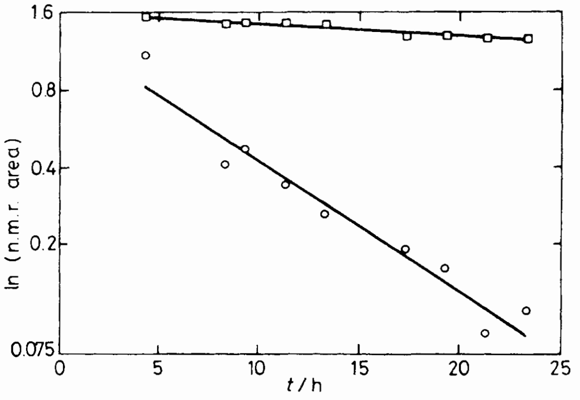
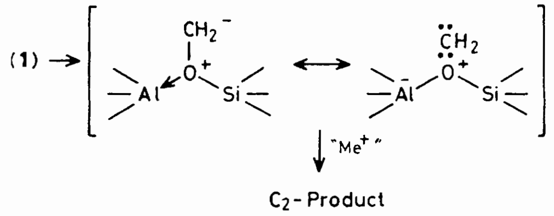


Figure 2. Plot of ln trimethyloxonium intensity ^{13}C n.m.r. signal (δ 79) (○) and ln the sum of the TMO peak and the peak at δ 62 (□) *vs.* time at 20 °C. The decomposition of TMO cation follows simple first-order kinetics while the total ^{13}C signal intensity is virtually unchanged. This demonstrates that the peak at δ 79 changes into the peak at δ 62.



Scheme 2

An alternative structure could involve addition of dimethyl ether to one of the T sites in (**1**).[19] Addition to silicon would give (**2**) in which the oxonium cation would be analogous to a dimethyl(trimethylsilyl)oxonium salt which resonates near to our observed signal [δ(OMe) 60.5].[15] However, a free methoxy group on four-co-ordinate aluminium expected in (**2**) would be analogous to $LiAl(OMe)_4$ and should resonate around δ 50.¶[20,21] Since no signal is observed at δ 50 for the decomposition product of TMO–ZSM-5, (**2**) seems an unlikely assignment.

Dimethyl ether addition to aluminium in (**1**) to give (**3**) would be analogous to a Lewis acid–ether complex and a free methoxysilane. This also seems an unlikely assignment for the TMO–ZSM-5 decomposition product since typical chemical shifts for methoxysilanes are upfield from that observed [*e.g.* Me_3SiOMe, δ(OMe) 49.7].[15]

C_2 products can derive from (**1**) *via* deprotonation to a surface stabilized ylide, which is a resonance form of surface

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‡ Vacuum dried (400 °C, 0.01 Torr, overnight) H-ZSM-5[13] (2.5 g; SiO_2/Al_2O_3 70) was suspended in pre-cooled, dry nitromethane (15 g) and to it was added trimethyloxonium tetrafluoroborate (1.5 g) in the same solvent (5 g; −20 °C). All operations were carried out using anhydrous Schlenkware and a Vacuum Atmospheres glovebox (1 p.p.m. oxygen, ≤0.25 p.p.m. water). After vigorous manual shaking this suspension was set aside (−20 °C; 1 h), filtered, washed with a small portion of pre-cooled nitromethane, then dried *in vacuo* (room temp.; 3 h). 50.18 MHz ^{13}C m.a.s. n.m.r. spectra using a greased rotor[14] were obtained at 20 °C, spinning at 3.2 kHz under N_2 with 10 gauss proton decoupling under both cross polarization (c.p.) and single pulse excitation. For c.p., contact times of both 1 and 10 ms were used at 1 s intervals. For single pulse excitation, 45° pulses were used at 12 s intervals.

§ The experiment was repeated using [$^2H_3$]nitromethane to verify that no peaks were due to retained solvent.

¶ The synthesis of lithium aluminium tetramethoxide from $LiAlH_4$ and methanol was adapted from the procedure reported by Turova.[20] The resulting white solid (98% yield) showed an Al shift of δ 76 p.p.m., quadrupole coupling constant 3.8 MHz (confirmed by its 2D central transition excitation spectrum),[21] and η = 0.25, which is consistent with the assigned structure. Proton decoupling substantially narrowed the Al spectrum, consistent with the proximity of methyl protons to the Al. The proton decoupled ^{13}C m.a.s. spectrum was obtained under both single pulse and c.p. conditions. In both cases a single peak, δ 50.5, was observed. Quantitative measurement of the single pulse spectrum ($C\ T_1$ = 7.5 s *via* saturation comb) *vs.* the methyl carbon of a weighed sample of hexamethylbenzene ($C\ T_1$ = 0.50 s *via* inversion recovery) gave 26.2% C *vs.* an expected 30.5% C for LiAl $(OMe)_4$, which confirms that the observed peak is not from an impurity.

carbenoid (Scheme 2). Subsequent methylation of the reactive surface intermediate could produce ethyl–ZSM-5. The methylating agent could in fact be TMO cations formed at higher temperature. Methylene insertion would give C_2 products directly. The alternative possibility of homolytic C–H or C–O bond cleavage[9b,22] of (**1**) to form C_2 products *via* free radical processes cannot be eliminated based on our current experiments. In fact, evidence for free radicals in methanol conversion product streams using spin trapping reagents was reported recently.[22b]

From these results, the TMO cation is expected initially to methylate the zeolite surface. Systems using strong, non-nucleophilic bases[6] do not accurately model the conjugate base in TMO-exchanged ZSM-5. C_2 product formation from methanol either *via* or accompanying methylated surface intermediates[3,9a,23] are likely even in the presence of TMO cation.

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