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The Thermal Decomposition of Trimethyloxonium Salts and its Relation to the Conversion of Methanol into Hydrocarbons

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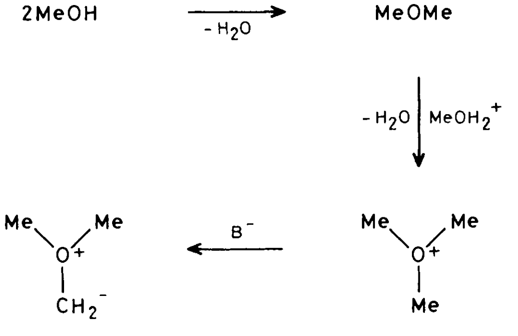
The thermal decomposition of trimethyloxonium hexachloroantimonate and tetrafluoroborate has been studied in the 50—350 °C temperature range; C–C bond formation was only observed at high temperatures in the chlorine-containing system under radical-type reaction conditions.

In the past two years a number of papers have appeared describing model reactions in support of various hypotheses for the formation of the first C–C bond in the zeolite-catalysed conversion of methanol into hydrocarbons.[1—6] The most debated pathway which has been suggested is *via* an oxonium ylide intermediate[7] (Scheme 1).[7] In a recent paper even the carbene-type mechanism supporters envisage a 'surface' onium ylide[3b] (Scheme 2). Whereas acid-catalysed trimethyloxonium salt formation from dimethyl ether is not controversial, the subsequent necessary deprotonation step towards onium ylide formation has not received general agreement. This point is also relevant in the hypothesis of surface methoxy groups,[3b] as it is not plausible that 'CH_3^+' insertion into a CH bond[8] would occur in preference to *O*-alkylation of dimethyl ether. From the onium ylide the C–C bond is formed *via* intermolecular methylation as proposed by Olah on the basis of labelling experiments.

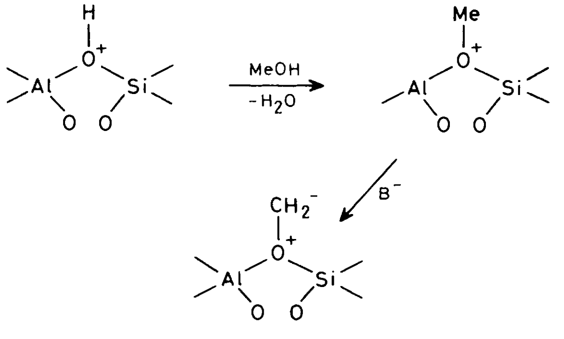
We showed earlier that the deprotonation of trimethyloxonium hexachloroantimonate has to be induced by a strong hindered base (in our case lithium 2,2,6,6-tetramethylpiperidide). In contrast with these results and those published by Olah,[1a] Van Hoof claimed recently[9] to have obtained high yields of ethylene and dimethyl ether by simple heating of trimethyloxonium tetrafluoroborate either neat or in nitromethane solvent. The deprotonation was ascribed to the basicity of the BF_4^- anion.

This prompted us to investigate the thermal decomposition of both the tetrafluoroborate and hexachloroantimonate salts over a larger temperature range, *i.e.* from room temperature up to 350 °C, the working temperature of zeolite catalysts. The experiments at $\leqslant 100$ °C were carried out by heating under nitrogen 1.5 mmol of the salt in a 50 ml vessel closed by a serum cap, and analysing the head space gases after 20 min. In the experiments at 350 °C the salts were heated in a microreactor under a helium stream, the products being condensed in a liquid nitrogen trap and analysed by g.c.–mass spectrometry after 30 min of reaction. Trimethyloxonium hexachloroantimonate was prepared following Meerwein's procedure.[10] The tetrafluoroborate salt was commercially available (EGA chemie). Both salts were purified by recrystallisation from liquid SO_2 and checked by ^1H n.m.r. spectroscopy for purity (1 singlet at δ 4.44).

The results (Table 1) show clearly that C–C bond formation does not occur by thermal decomposition *via* an eventual oxonium ylide. Besides the traces of ethylene and ethyl methyl ether found in the commercial tetrafluoroborate salt no higher hydrocarbons could be detected even at 350 °C. However



Scheme 1



Scheme 2

Table 1. Products from the thermal decomposition of trimethyloxonium salts.

	$Me_3O^+BF_4^-$			$MeO^+SbCl_6^-$		
Temp./°C	60	100	350	60	100	350
MeOH	0.7	—	1.4	—	—	—
MeOMe	94.2	82.0	53.2	25.8	16.2	29.1
MeF	—	10.9	42.4			
MeCl				74.2	83.7	64.0
C_2H_4	—	0.8	0.9	—	—	—
EtOMe	0.8	0.7	0.8	—	—	2.0
EtF	—	—	—			
EtCl				—	—	0.2
CH_2F_2	—	0.5	0.8			
CH_2Cl_2				—	—	1.5
Me_2SiF_2	3.0	4.1	0.5			
$MeSiF_3$	1.2	0.9	—			
$CHCl_3$						0.5

quite large amounts of fluorinated silyl derivatives could be found in the gas phase. These compounds, produced by attack of the glassware, have retention times close to that of ethylene and for this reason could previously have been mistaken for hydrocarbons. At 350 °C small amounts of ethyl methyl ether were found in the decomposition of the hexachloroantimonate salt. However the simultaneous formation of CH_2Cl_2, $CHCl_3$, $(MeO)_2CH_2$, and traces of CCl_4 indicates a radical mechanism which cannot be related to the occurrence of an onium ylide intermediate, but rather with the radical mechanism shown by the recent results of Clarke *et al.*[11]

Our results confirm the necessity of a strong hindered base to induce the onium ylide rearrangement to ethyl methyl ether at low temperature. We stress that a model reaction can only add credibility to a mechanistic hypothesis concerning the zeolite catalysed reaction but cannot be considered as evidence against another type of mechanism.

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