

Trapping of the Methyl Cation by Carbon Monoxide; Formation of Acetic Acid from Methane¹

By H. HOGVEEN,* J. LUKAS, and C. F. ROOBEEK

[Koninklijke/Shell-Laboratorium, Amsterdam (Shell Research N.V.), Netherlands]

Summary The formation of acetic acid from methane, carbon monoxide, antimony pentafluoride, and water is reported, confirming the occurrence of the methyl cation (CH_3^+) in the oligocondensation of methane and indicating that protonated methane (CH_5^+) is not involved in this reaction.

Both CH_5^+ and CH_3^+ ions were stated to be crucial intermediates in this process.³

We report some of our results which have a bearing on the occurrence of CH_5^+ and CH_3^+ ions in reaction (b). In view of the high reactivity even of tertiary carbonium ions towards carbon monoxide ($k = 3 \times 10^4 \text{ l. mole}^{-1} \text{ s.}^{-1}$ in 1:1 $\text{FHSO}_3\text{-SbF}_5$ at 20° for $\text{R} = \text{t-C}_4\text{H}_9^+$ ⁵), it was expected that any CH_3^+ ions formed in reaction (b) would be trapped by it:

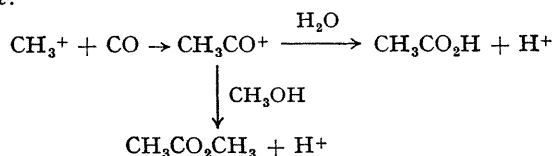
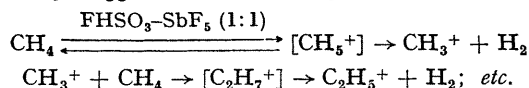
RECENTLY, two reactions of methane in strongly acidic solution were reported:

Reaction (a): Hydrogen-deuterium exchange^{2,3} (classified^{2,4} as electrophilic substitution at alkane-carbon by protons)



In this reaction—which proceeds in $\text{FHSO}_3\text{-SbF}_5$ (1:1) and HF-SbF_5 (11:1) solutions— CH_4D^+ was supposed to be a transition state (or intermediate) with a C_s -type symmetry.^{2,4}

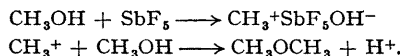
Reaction (b): Oligocondensation, for which Olah and Schlosberg³ suggested the following mechanism:



In some experiments carried out at 60° with 0.5 mole of SbF_5 , † 0.1 mole of CH_4 (25 atm.) and 0.1 mole of CO (25 atm.) the pressure dropped from 50 atm. to about 20 atm. in the course of 3 days. The n.m.r. spectrum of the solution showed an absorption at 3.93 p.p.m., due to the CH_3CO^+ ion.⁷ Quenching of the solution in water afforded acetic acid; quenching in methanol‡ gave a 20–30% yield of methyl acetate (based on methane). This result constitutes strong evidence of the occurrence of the CH_3^+

† In the formation of carbonium ions from alkanes SbF_5 proved to be superior to the usual $\text{FHSO}_3\text{-SbF}_5$ mixture (1:1 molar ratio).⁶

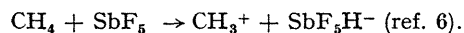
‡ On quenching the SbF_5 solution in CH_3OH at -60° , CH_3OCH_3 was formed also. This reaction may involve the CH_3^+ cation in the following manner



cation in the oligocondensation reaction (b). The absence of methyl t-butyl ether after quenching in methanol proves that no t-butyl ions had been formed in the reaction. When the experiment was carried out at 1 atm. instead of 25 atm. of CO the major product after quenching in methanol was found to be methyl t-butyl ether.

Olah and Schlosberg³ assumed that in reaction (b) the CH_5^+ ion is the precursor of the CH_3^+ species. We do not share their opinion because we found² that in the HF-SbF_5 system (11:1 molar ratio) only the hydrogen-deuterium exchange reaction (a) occurred—which involves CH_5^+ —and no hydrogen and homologues of CH_3^+ were formed.

This strongly suggests that in the $\text{FHSO}_3\text{-SbF}_5$ system³ reactions (a) and (b) proceed *via* different intermediates. Reaction (b) probably involves a direct oxidation of methane to CH_3^+ without prior formation of CH_5^+ :



The fact that the oligocondensation of methane proceeds in pure SbF_5 (without FHSO_3 as Brønsted acid) is in itself a very strong argument against the initial formation of CH_5^+ .

(Received, June 23rd, 1969; Com. 904.)

¹ Previous paper in this series: H. Hogeveen and C. J. Gaasbeek, to be published.

² H. Hogeveen and C. J. Gaasbeek, *Rec. Trav. chim.*, 1968, **87**, 319.

³ G. A. Olah and R. H. Schlosberg, *J. Amer. Chem. Soc.*, 1968, **90**, 2726.

⁴ H. Hogeveen and A. F. Bickel, *Rec. Trav. chim.*, 1969, **88**, 371.

⁵ H. Hogeveen, F. Baardman and C. F. Roobeek, *Rec. Trav. Chim.*, to be published.

⁶ J. Lukas, to be published.

⁷ H. Hogeveen, *Rec. Trav. chim.*, 1967, **86**, 809.