Trapping of the Methyl Cation by Carbon Monoxide; Formation of Acetic Acid from Methane[1]

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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.

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)

$$CH_3D + H^+ \rightleftarrows [CH_4D^+] \rightleftarrows CH_4 + D^+$$

In this reaction—which proceeds in $FHSO_3$–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 Schlosberg[3] suggested the following mechanism:

$$CH_4 \xrightleftharpoons{FHSO_3\text{–}SbF_5\ (1:1)} [CH_5^+] \rightarrow CH_3^+ + H_2$$
$$CH_3^+ + CH_4 \rightarrow [C_2H_7^+] \rightarrow C_2H_5^+ + H_2;\ \textit{etc.}$$

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 ($k = 3 \times 10^4$ l. mole^{-1} s.$^{-1}$ in 1 : 1 $FHSO_3$–SbF_5 at 20° for $R = t\text{-}C_4H_9^+$ [5]), it was expected that any CH_3^+ ions formed in reaction (*b*) would be trapped by it:

$$\begin{tikzcd}
CH_3^+ + CO \arrow[r] & CH_3CO^+ \arrow[r, "H_2O"] \arrow[d, "CH_3OH"] & CH_3CO_2H + H^+ \\
 & CH_3CO_2CH_3 + H^+ &
\end{tikzcd}$$

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^+

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† In the formation of carbonium ions from alkanes SbF_5 proved to be superior to the usual $FHSO_3$–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

$$CH_3OH + SbF_5 \longrightarrow CH_3^+SbF_5OH^-$$
$$CH_3^+ + CH_3OH \longrightarrow CH_3OCH_3 + H^+.$$

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 Schlosberg[3] 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 found[2] 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 $FHSO_3$–SbF_5 system[3] 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^+:

$$CH_4 + SbF_5 \rightarrow CH_3^+ + SbF_5H^- \text{ (ref. 6).}$$

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^+.

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