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The Self-condensation of Methyl Iodide. The Intermediacy of Methylium Ions in C-C Bond Formation

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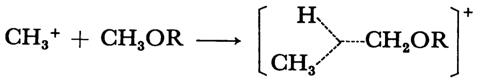
Synopsis. Hydrocarbons are formed by the reaction of methyl iodide vapor with solid-silver dodecatungstophosphate. The self-condensation is plausibly initiated by the attack of the methylium ion on the C-H bond of methyl iodide. It is suggested that the methylium ion is a key intermediate also in the conversion of methanol into hydrocarbons.

Since the conversion of methanol into hydrocarbons over ZSM-5 zeolites was discovered, many discussions have been reported on the mechanism of the reaction, especially with regard to the first C–C bond formation.[1] As for the first C–C bond formation, three major intermediates proposed are carbenoid species,[2] the trimethyloxonium ion,[3] and the methylium ion.[4]

Ono and Mori[4] proposed the intermediacy of the methylium ion, which attacks the C–H bond of methanol or dimethyl ether by forming a three center-two electron bond. The methylium ion would be generated by the reaction of the acidic sites and methanol (or dimethyl ether).

$$H^+ + CH_3OH \longrightarrow CH_3^+ + H_2O$$



$$CH_3^+ + CH_3OR \longrightarrow \left[\begin{matrix} H \\ CH_3 \end{matrix} \!\!> \!\!\cdots CH_2OR \right]^+$$

$$\longrightarrow CH_3CH_2OR + H^+$$

The carbon–carbon bond formation *via* the direct attack of the methylium ion on a C–H bond has been established in superacid chemistry, as examplified by the polymerization of methane.[5] According to the above shceme, the C–C bond formation should occur even without acid centers if the methylium ion is provided in some another way. We have attempted such experiments.

As the source of methylium ions, the reaction of methyl iodide and silver cation was selected, since combinations of methyl iodide and a metal cation are known to be good methylating reagents.

$$CH_3I + Ag^+ \longrightarrow CH_3^+ + AgI \qquad (1)$$

As a silver salt, silver dodecatungstophosphate ($Ag_3PW_{12}O_{40}$, AgTP) was selected. The ease of the reaction between methyl iodide and AgTP is evidently shown by the fact that the immediate precipitation of silver iodide is observed when methyl iodide is added to a methanol solution of AgTP at room temperature.

If methylium ions are generated by Reaction (1), they would attack C–H bonds of methyliodide molecules to form C–C bonds.

We wish to report here the formation of hydrocarbons by the reaction of methyl iodide vapor with solid AgTP.

The reaction was carried out as follows: The powder of AgTP (1 g=8.3×10^{-4} mol of Ag^+) was placed in a reactor which was a part of a closed-recirculation system (dead volume, 234 ml), heated under a vacuum at 573 K, and then kept at the reaction temperature. Methyl iodide vapor (17.7×10^{-4} mol) was then admitted to the system, and the change in the gas phase composition was monitored with the time by withdrawing small portions of the gas at appropriate intervals.

In Fig. 1, the amount of methyl iodide which disappeared from the gas phase and the amount of hydrocarbons which appeared in the gas phase at 373 K are plotted as functions of the reaction time. The distribution of hydrocarbons produced is also shown. Both the yield and the distribution of hydrocarbons are expressed on a carbon-number basis. The amount of methyl iodide consumed and that of hydrocarbons produced increased gradually with the time, until the reaction almost ceased after 5 h, when hydrocarbons amounting to 6.6×10^{-4} mol of carbon atoms appeared in the gas phase. This amount corresponds to about 80% of that Ag^+ ions in the salt, indicating that the reaction is a stoichiometric one.

The amount of methyl iodide disappearing from the gas phase was more than the amount of hydro carbons and even more than the amount of Ag^+ in the salt. The difference may be due to the sorption of unreacted methyl iodide in the bulk of the solid and/or the accumulation of part of the hydrocarbon prod-

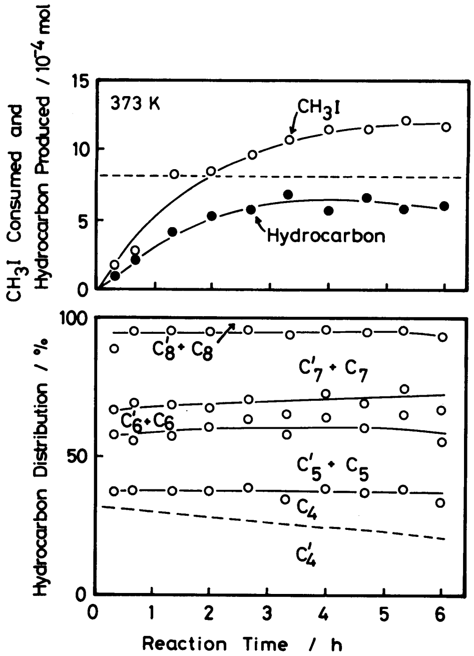


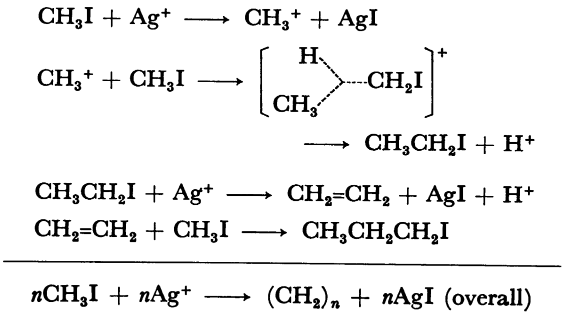
Fig. 1. Change in the amount of CH_3I consumed and hydrocarbons produced with time in the reaction of CH_3I and $Ag_3PW_{12}O_{40}$ at 373 K.

ucts in the solid. The main hydrocarbon products at this temperature are aliphatic hydrocarbons with carbon atoms of 4—7.

At 423 K, the reaction procceded faster. The methyl iodide disappearing from the gas phase amounted to 10.6×10^{-4} mol after 1.5 h. The amount of hydrocarbon produced was 8.3×10^{-4} mol after a reaction of 15 min.

At 573 K, the stoichiometric amount of methyl iodide was consumed within 5 min, as is shown in Fig. 2. The further consumption of methyl iodide continued for another 30 min, even though the amount of hydrocarbons in the gas phase did not increase any longer. At this temperature, the main hydrocarbon products were propane and isobutane. Propylene and butenes found at the early stage disappeared after 1 h, probably because of their further reactions with methyl iodide. This may be account for the consumption of methyl iodide beyond the stoichiometry based on the silver cation.

The fact that hydrocarbons are formed from methyl iodide in the presence of AgTP strongly indicates the importance of the methylium ion in forming C–C bonds from one-carbon molecules. The reaction is essentially a stoichiometric one. The reaction mechanism may be expressed as follows:



$$CH_3I + Ag^+ \longrightarrow CH_3^+ + AgI$$

$$CH_3^+ + CH_3I \longrightarrow \left[\begin{matrix}H\\ CH_3\end{matrix}\!>\!\!-CH_2I\right]^+ \longrightarrow CH_3CH_2I + H^+$$

$$CH_3CH_2I + Ag^+ \longrightarrow CH_2{=}CH_2 + AgI + H^+$$

$$CH_2{=}CH_2 + CH_3I \longrightarrow CH_3CH_2CH_2I$$

$$nCH_3I + nAg^+ \longrightarrow (CH_2)_n + nAgI \text{ (overall)}$$

Besides the reactions described above, various reactions involving carbenium-ion intermediates, like H-transfer, alkylation, and dimerization, may well occur, resulting in the formation of paraffins. It should be noted that a similar mechanism for the C–C bond formation has been proposed for the self-condensation of methyl fluoride in neat antimony fluoride.[9,10]

AgTP is an effective catalyst for converting methanol into hydrocarbons.[11–13] It has been eatablished that the active centers in this system are Brönsted-acid sites, which are produced by the reduction of silver cations by hydrogen molecules (or atoms) provided by the partial decomposiiton of methanol under the present reaction conditions.[12–14]

The distribution of hydrocarbons in the catalytic conversion of methanol over AgTP at 573 K is very similar to that in the stoichiometric reaction of methyl iodide and AgTP at the same temperature, indicating that the mechanism of the propagation of the C–C chain is the same in the two systems. This again argues favorably for the intermediacy of methylium ions in the conversion of methanol into hydrocarbons over acidic catalysts.

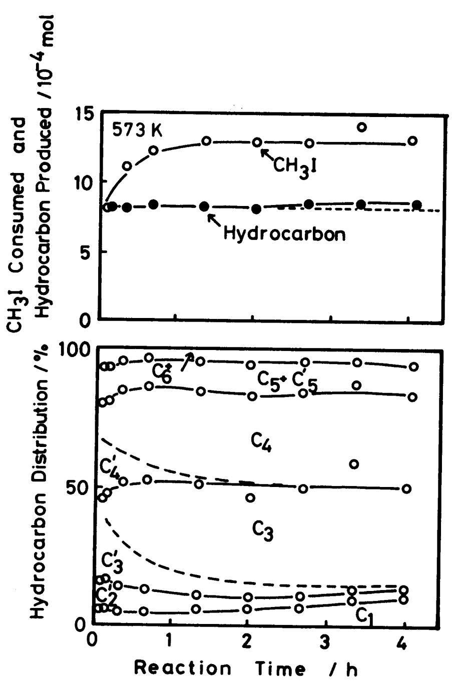


Fig. 2. Change in the amount of CH_3I consumed and hydrocarbons produced with time in the reaction of CH_3I and $Ag_3PW_{12}O_{40}$ at 573 K.

It is important to note that hydrocarbons are formed from methyl iodide at temperature at which the hydrocarbon formation from methanol over zeolites or heteropolyacids is practically unobservable. The easier formation of the C–C bonds in the methyl iodide-Ag^+ system may be attributed to the facile generation of incipient methylium ions.

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