INTERSTELLAR FORMATION OF "SIMPLE" ORGANIC MOLECULES

Reported by Jacob D. McAlpin March 8, 2016

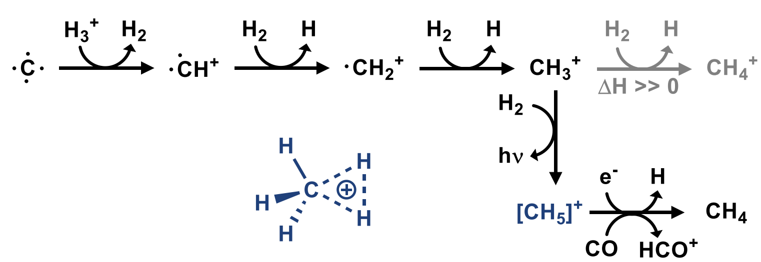
BACKGROUND

The formation of life on Earth required a supply of organic molecules from extraterrestrial sources.[1] The low pressure (10^{-14} atm) and temperature (~10–20 K) of interstellar clouds affects reactions in ways that the average chemist will not experience in typical laboratory work. In interstellar clouds, reactions need to be exothermic ($\Delta H < 0$) and have little if any activation energy ($\Delta H^{\neq} < 1$ kcal/mol) in order to proceed.[2] A less obvious consequence is that it is difficult to dissipate energy radiatively, a task handled by solvent in typical terrestrial reactions. The inability to dissipate this energy causes high-energy intermediates to fall apart into starting materials as opposed to forming products. As a consequence of these restrictions, most chemical reactions in the interstellar medium are between ions and neutral species as electromagnetic forces facilitate attraction between reactants and provide collision energy.

Astrochemists detect astromolecules by collecting absorption or emission spectra through telescopes or satellite dishes.[2] Earth based equipment needs to avoid areas of the spectrum opaque to the atmosphere, but this is not a concern with space-based devices. The spectra are compared with samples collected on Earth in order to assign correct structures.

METHANE

By the standards of most organic chemists, methane is the simplest organic molecule; however, it is complex by the standards of astrochemistry. **Scheme 1** shows a potential reaction pathway for formation of methane in interstellar clouds. In this scheme, carbon reacts repeatedly with H_2 until becoming CH_4, notably through the intermediacy of the protonated methane (CH_5^+).[2] In order to provide experimental evidence for this and other pathways, the spectroscopic analysis of CH_5^+ has been actively pursued by multiple groups.



Scheme 1: Potential formation pathway for CH_4 with "structure" of CH_5^+.

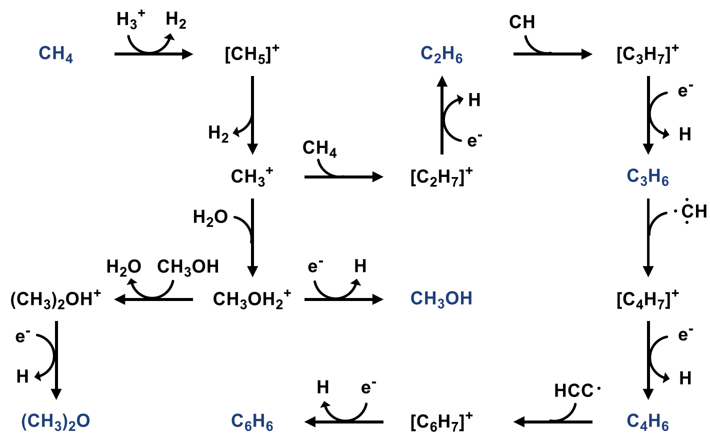
However, CH_5^+ has become known as the "*enfant terrible*" of molecular spectroscopy.[3] For context, the IR spectrum of methane at 10 K has 10 lines while protonated methane has almost 3000! Though CH_5^+ was first detected by mass spectrometry in the 1950s, the first report of the IR spectrum of CH_5^+ was in 1999 presented "as observed without assignment (or even qualitative understanding)".[4] Recently, Asvany et al. has increased the sensitivity of this measurement by using Laser Induced Reaction

(LIR) spectroscopy allowing for a tentative quantum number assignment.[3]

BUILDING COMPLEXITY

More complex hydrocarbons can be formed from methane invoking ideas established in Olah's hypercarbon chemistry.[5] Olah observed that reacting methane with "magic acid" ($F_5Sb\text{-}SFO_3H$) at -60 °C produced higher alkyl cations including trimethyl carbonium ($(CH_3)_3CH_2^+$) and insoluble polymers. The proposed pathway includes the protonation of methane, dissociation of H_2 to produce a methyl cation, and insertion into the C-H σ–bond to form protonated ethane. This chemistry continues on to form larger products. It is reasonable to draw inferences between this work and the interstellar medium with H_3^+ taking the place of "magic acid" as shown in **Scheme 2** (top left corner).

It should be noted that although **Scheme 2** highlights some of the interconnected pathways to form larger molecules, it is not comprehensive of all possible reactions. Starting from the methyl cation, produced previously or by protonation of methane, a reaction with water can produce methanol. From methanol, many reactions can be proposed such as the formation of dimethyl ether and ethylene. A pathway for the formation of benzene starting with ethane illustrates the importance of radical pathways through reactions with methylidyne and the ethynyl radical as well as further supports the presence of nonclassical carbocation intermediates.[6]



Scheme 2: Plausible pathways for formation of some "simple" molecules.

FUTURE DIRECTIONS

The presented reaction pathways have some theoretical and experimental evidence, but more experimental data from the interstellar medium would be valuable to help provide confirmation. Currently, there is no confirmation of interstellar CH_5^+, a species which often appears in these pathways. Further work in understanding the spectroscopy of CH_5^+ will be instrumental in its interstellar detection.

CITATIONS

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(3) Asvany, et al. *Science* **2015**, 309, 1219.
(4) White, E. T.; Tang, J.; Oka, T. *Science* **1999**, 284, 135.
(5) Olah et al., *Hypercarbon Chemistry*, 2nd edition, Wiley, Hoboken, New Jersey, 2011.
(6) Jones et al. *Proc. Nat. Acad. Sci.* **2011**, *108*, 452-457.