Astrochemistry: the First Step in Understanding our Origins

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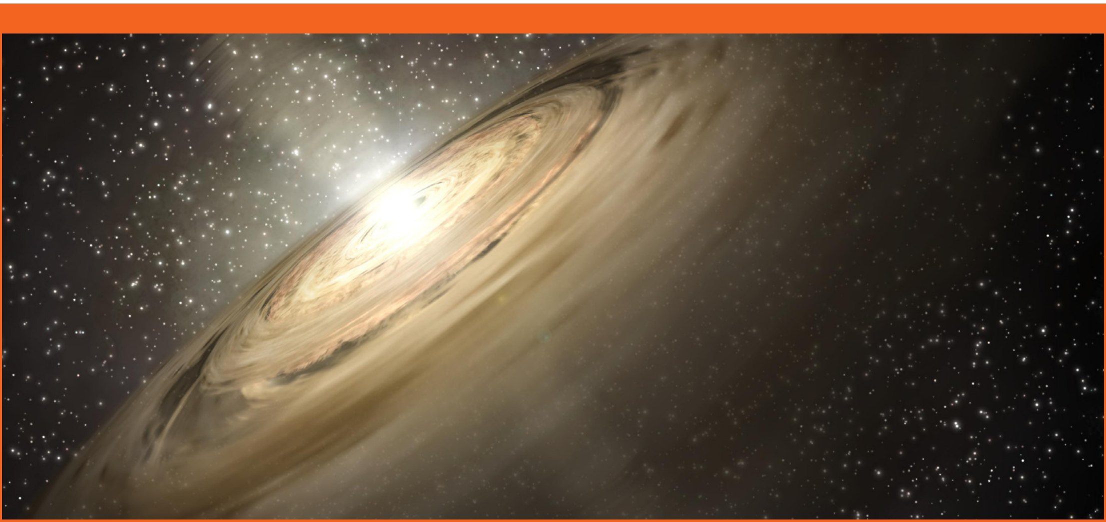
In any given molecular cloud – quiet, collapsing, or turbulent – chemistry practices its endless, slow dance: forming new molecules and dissociating others for eons throughout the history of the universe. These cold, dense clouds are the starting point of star formation and can be as massive as thousands of suns.



Stars form surrounded by disks of gas and dust where different molecules can be formed.
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Depending on a number of factors, including gas temperature and density, we find that chemistry has produced gas with considerably different compositions within these clouds. The interdisciplinary sciences of astrochemistry and astrobiology have experienced a surge of interest in recent years due, in part, to the detection of a multitude of extrasolar planets which could harbor life, and to the discovery of living things on every corner of Earth – from the deep oceans to extremely acidic or alkaline environments. Understanding the chemical processes involved in producing organic molecules in space, especially in star and planet forming regions where these raw materials can be delivered to young planets, will lead to a better understanding of how life itself begins.

Astrochemistry Triad

Astrochemistry is the study of reactions and interactions between atoms and molecules in space.
In the field of astrochemistry, observers, theorists, and experimentalists are tightly bound to one another (Figure 1) and communication between the three groups is difficult but necessary. Experimentalists test the effects of different astronomical phenomena (like high energy radiation) on chemical reactions in

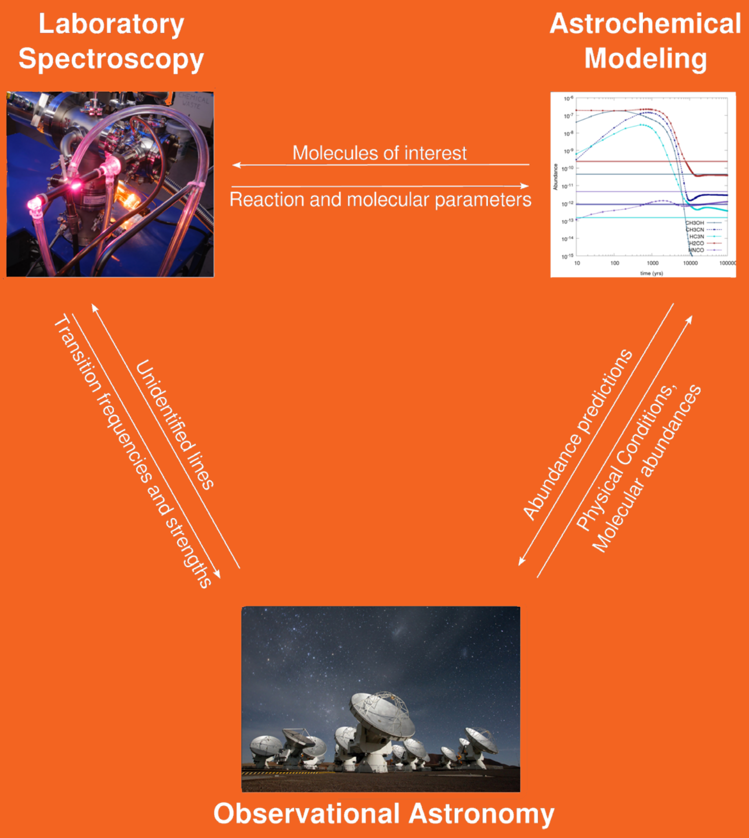

FIGURE 1: The three groups working in astrochemistry are deeply dependent on each other.

a vacuum (or as close to a vacuum as we can achieve on Earth). These results are used by theorists to create chemical models that can show how the abundances of different molecular species change with varying parameters (like gas temperature and density) and over time. Observers study data from different astronomical phenomena and rely on laboratory tested or theoretically calculated frequencies to determine which spectral lines arise from which species and determine the chemical composition of their object. Theorists and observers work together using models to understand how the observed sources got their chemical composition, which at the same time confirms that the models can reproduce reality.

Oftentimes, spectral lines for which there is no clear identity are observed, then it may be the case that the database is incomplete for some species and the experimentalists seek to discover which species may be associated with a particular transition using spectroscopy. Observational astrochemistry has experienced a boom in recent years with the advent of the Atacama Large (sub)Millimeter Array (ALMA), an incredibly sensitive array of telescopes that have the ability to detect very weak signals from rare molecular species. This gives observers the ability to characterise astronomical environments better than before with more accuracy and potentially greater chemical complexity.

Hot Molecular Cores

In the process of star formation, there is a chemically rich phase during which molecular species are released from the icy mantles covering dust grains that have been warmed by the protostar (a star which is still gathering mass from the surrounding molecular cloud and has not begun fusion). Alternatively, molecular species could form in the warm gas surrounding the protostar. In high-mass stars, this is called a hot molecular core and in low-mass stars a hot corino. It is during this stage that we observe complex organic molecules (COMs), molecules with at least 6 atoms containing both carbon and hydrogen [1]. The detection of these species marks an important age milestone for high-mass protostars as they are quickly (within a few thousands of years) destroyed by the

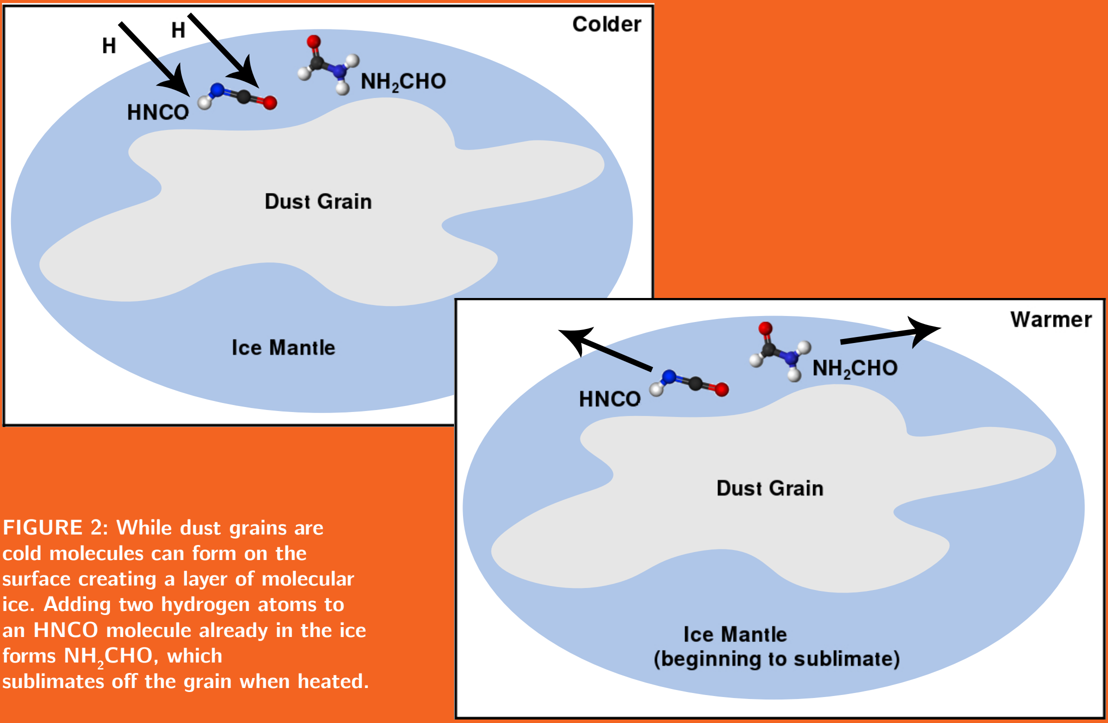

FIGURE 2: While dust grains are cold molecules can form on the surface creating a layer of molecular ice. Adding two hydrogen atoms to an HNCO molecule already in the ice forms NH_2CHO, which sublimates off the grain when heated.

radiation from the star. It is expected that some of these COMs will remain in ice in the outer reaches of a star-forming region or freeze out within the mid-plane of a protoplanetary disk at a later stage of stellar evolution and end up in comets or other star system bodies. This ice is important in an astrobiological sense, given that the delivery of organic compounds to a primitive Earth is likely to have been important in the origin of life. Prebiotic oxygen-bearing COMs like dimethyl ether (CH_3OCH_3); glycolaldehyde (CH_2OHCHO), the simplest sugar; and ethylene glycol [$(CH_2OH)_2$], more commonly known as antifreeze have been well studied [2][3], while their nitrogen-bearing counterparts have not.

> *“Observational evidence for the dominant formation route of formamide is contradictory. ”*

Formamide as a path to life

Formamide (NH_2CHO) is an important molecule to study in the fields of astrochemistry and astrobiology because its structure and content make it a likely precursor for glycine (NH_2CH_2COOH), the simplest amino acid, and an important building block in the synthesis of biotic compounds. Saladino et al. [4] even argue that formamide may have played a key role in creating and sustaining life on the young Earth, since it can lead to a variety of biologically relevant chemistry such as amino acids, nucleic acids, and sugars. Unfortunately, it is unclear how formamide is formed. One possible formation route is on grain mantles from isocyanic acid (HNCO) hydrogenation (adding hydrogen atoms), to be observed in the gas surrounding hot cores and hot corinos during the warm-up phase of star formation when complex species sublimate [5] (See Figure 2). The alternate formation pathway for formamide is from formaldehyde (H_2CO) in the gas phase following the reaction:

$H_2CO + NH_2 \rightarrow NH_2CHO + H$ (Figure 3).

Observational evidence for the dominant formation route of formamide is contradictory. A nearly linear correlation was observed between the abundances of HNCO and formamide which spans several orders of magnitude in molecular abundance and stellar mass [6][7]. This suggests that the two molecules are chemically related. Observations by Coutens et al. [8] of IRAS 16293-2422 showed that the deuterium fraction in HNCO and NH_2CHO in this solar-mass star-forming region are very similar, indicating a chemical link. On the other hand, Codella et al. [9] observed shocked gas (where high velocity gas collides with the surrounding low velocity gas) near L1157-B1, a solar-like protostar, and found that formamide could be made efficiently in this gas from H_2CO.

> *“We found that the morphology and velocity structure of HNCO and NH_2CHO were almost identical.”*

Laboratory studies show that the dominant formation route, either from HNCO in the ice or from H_2CO in the gas, is not completely clear. Recent lab work by Kaňuchová et al. [10] showed that formamide can be formed in ices by cosmic ray irradiated HNCO, but the amount of HNCO formed is not high enough to match observations. Another laboratory study by Noble et al. [11] found that hydrogenating HNCO did not lead to formamide in large quantities and Barone et al. [12] found that gas phase reactions (from H_2CO) can make significant amounts of formamide.

In my previous work, I studied emission extent, peaks, and velocity structure between HNCO and formamide in the high-mass star-forming region G35.20-0.74N [13]. In G35.20-0.74N B, a high-mass protostellar system potentially surrounded by a Keplerian disk, we found that the morphology and velocity structure of HNCO and NH_2CHO were almost identical, and the velocity structure differed by less than 0.5 km/s. While this is convincing evidence for HNCO as the dominant precursor in this source, we could not rule out H_2CO as a precursor because these observations did not cover any H_2CO lines for comparison.

I have recently performed a pilot study [14] using ALMA observations of very high mass Otype (proto) stars, searching for observational evidence that either HNCO or H_2CO is the dominant predecessor to formamide. In this study, I analysed the spatial extent, kinematics, and molecular abundances of formamide and compared them to HNCO and H_2CO in the gas in three high-mass star-forming regions. The result of my analyses was inconclusive, with the spatial extent of formamide being more similar to HNCO, but the velocity structure more similar to H_2CO. Additionally, there were abundance correlations between all three pairs of species, indicating that this may not be a good test of their chemical relationship.

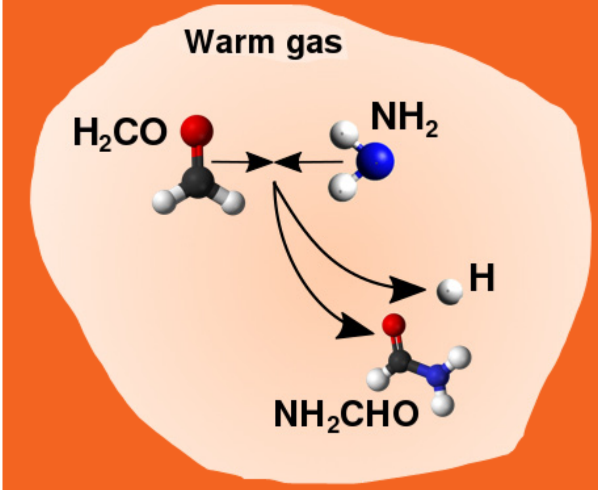

FIGURE 3: In warm gas, H_2CO and NH_2 molecules react to form NH_2CHO and a hydrogen atom.

Future work

The James Webb Space Telescope (JWST) will be launched early this year and early science observations of ices in star-forming regions are planned. This is a space-based infrared telescope that would be able to detect molecular species in ice that were previously undetectable. Observing HNCO, H_2CO and formamide in ices would provide new evidence in the problem of determining the formation route of formamide. The laboratory work of Urso et al. [15] has proposed that formamide can be detected in mid-infrared spectra of ice mantles. HNCO has not yet been detected in ice, but its presence was associated with the "XCN" ice feature at 4.62 µm in infrared observations of interstellar ice [16] [17]. This comes from the assumption that the XCN feature is OCN^-, which becomes HNCO when it is released into the gas phase and the ion recombines to form a neutral species. Additionally, the ice feature at 6.85 µm has been proposed to be NH_4^+ and, when taken together with the potential OCN^- feature, leads to the conclusion that these two ions were formed by an acid-base reaction between NH_3 and HNCO.

> *"JWST ice observations will give insight into the ice formation routes for formamide."*

More work is needed from all three groups of astrochemists. Dedicated ALMA observations of HNCO, H_2CO and formamide near high- and low-mass protostars will improve upon my pilot study greatly. JWST ice observations will give insight into the ice formation routes for formamide. In the laboratory, more experiments are needed to understand the effects of different astronomical phenomena on the formation of formamide. Theorists need to test grids of models simulating different types of sources and the formation of formamide through different stages of star and planet formation. With the three groups working together on this problem we will soon have a clear understanding of the formation of this key species•

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