

## COMPLEX ORGANIC MOLECULES AND STAR FORMATION

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**Abstract.** Star forming regions are characterised by the presence of a wealth of chemical species. For the past two to three decades, ever more complex organic species have been detected in the hot cores of protostars. The evolution of these molecules in the course of the star forming process is still uncertain, but it is likely that they are partially incorporated into protoplanetary disks and then into planetesimals and the small bodies of planetary systems. The complex organic molecules seen in star forming regions are particularly interesting since they probably make up building blocks for prebiotic chemistry. Recently we showed that these species were also present in the cold gas in prestellar cores, which represent the very first stages of star formation. These detections question the models which were until now accepted to account for the presence of complex organic molecules in star forming regions. In this article, we shortly review our current understanding of complex organic molecule formation in the early stages of star formation, in hot and cold cores alike and present new results on the formation of their likely precursor radicals.

Keywords: Stars: formation; Astrochemistry; ISM: molecules; ISM: abundances

### 1 Introduction

An important challenge in present day astrophysics is to understand the emergence of molecular complexity, from simple atoms and molecules to the richness of chemical species observed in the Solar System. During the low-mass star forming process, the interstellar gas evolves towards higher degrees of concentration and build up cores of denser matter. Some of these gravitationally bound cores, called prestellar cores, collapse under their own gravity and form one or several protostar(s). Protostars are still deeply embedded within their parent envelope and are in the process of accreting most of their mass. It is believed that even at a very young stage, they are surrounded by a disk, which becomes the birth place of planetesimals, (exo)planets, asteroids and cometary bodies in the later phases of the process, when the surrounding envelope has been either accreted or dispersed. During the star formation process, molecules present in the interstellar gas can therefore be formed, destroyed, or incorporated at the various stages, and it is therefore possible that part of the chemical species and molecular complexity that are seen nowadays on planets like the Earth are inherited from earlier phases and the interstellar medium.

Like in chemical science, organic molecules are defined in astrochemistry as molecules containing the atoms C, H, O or N. The definition of a complex molecule however is a lot more humble applied to the interstellar medium than to chemistry on Earth. Herbst & van Dishoeck (2009) suggested that molecules with 6 atoms can be considered as complex. In the interstellar medium, highly unsaturated molecules (carbon chains, cyanopolynes) have long been observed, but more saturated, terrestrial like complex organic molecules are also found. These latter species typically include formamide  $\text{NH}_2\text{CHO}$ , acetaldehyde  $\text{CH}_3\text{CHO}$ , ethanol  $\text{CH}_3\text{CH}_2\text{OH}$ , dimethyl ether  $\text{CH}_3\text{OCH}_3$ , methyl formate  $\text{CH}_3\text{OCHO}$  or methanol  $\text{CH}_3\text{OH}$ . They currently draw much attention, as they are believed to be the building blocks for prebiotic chemistry. It is therefore of high interest to investigate where they are found in space and under which conditions, how they are formed, and how they evolve. In what follows, we will only concentrate on these terrestrial saturated molecules.

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## 2 Complex organic molecules in the early phases of star formation

### 2.1 Observations of complex organic molecules

Complex organic molecules (hereafter COMs) have long been detected in the interstellar medium. The first detections date back to the 1970s, where molecules like acetaldehyde (Gottlieb 1973) or methyl formate (Brown et al. 1975) were seen towards the hot molecule-rich regions of Sgr B2 and Orion, where massive stars are forming. A decade later, spectral surveys in the millimeter range revealed that hot cores of massive star forming regions were characterized by the presence of a large variety of COMs (e.g. Sutton et al. 1985; Blake et al. 1987; Cummins et al. 1986). Continuous progress in the sensitivity of millimeter wave telescopes have led to an increase in the number of species detected in the interstellar medium. Whereas about 50 species had been detected in 1980, the inventory reaches over 180 species 35 years later, and molecules with up to 13 atoms have been detected (not including PAHs and fullerenes).

Spectral surveys in low-mass star forming regions have revealed a similar complex organics composition as in high-mass hot cores (van Dishoeck et al. 1995; Cazaux et al. 2003). Interferometric observations of low-mass protostars show that the COM emission originates from a compact region around the central source, corresponding to the area of warm dust and gas heated by the protostar, where ice mantles coating the grains have been evaporated ( $T \sim 100$  K). The resemblance with high-mass hot cores as far as contents and configuration are concerned led to the idea that COMs were characteristic of warm chemistry in young stellar objects.

### 2.2 Physical structure during the first stages of star formation and chemistry

In order to understand how molecules can form in low-mass star forming regions, it is necessary to determine the physical properties (density, temperature, UV radiation field, etc.) of the medium they are found in. The stage immediately before the protostar forms, the prestellar phase, is characterized by low temperatures (around 10 K), since there is no inner heating source, and moderate densities ( $10^4 - 10^6 \text{ cm}^{-3}$ ). The high extinction prevents interstellar UV radiation from penetrating inside the prestellar cores. As gravitational collapse proceeds, the density increases towards the centre of the object until it is high enough for a hydrostatic object to form. The newly-formed source heats up its surroundings, so that a temperature gradient is established between the outer envelope, where  $T$  is still around 10 K, towards the centre of the protostar. The hot core of the protostar is defined as the region where the temperature is above  $\sim 100$  K.

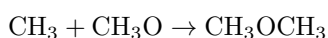
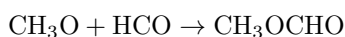
The chemistry during these stages is largely influenced by the physical conditions. In cold pre-stellar cores, atoms and molecules present in the gas phase can stick to the dust grains upon collision with them. This opens up the possibility of grain surface chemistry, as the accreted atoms or simple molecules can react together to form more complex species. During the protostellar stage, two kinds of chemistry can take place: in the outer envelope, the conditions of density and temperatures are similar as in prestellar cores and the chemistry is also similar. As one approaches the protostar the density and temperature increase, and when the temperature reaches about 100 K in the hot core, ice mantles are evaporated in the gas-phase. The only chemistry which can take place is gas-phase chemistry, and since the central protostar emits UV, some photochemistry can be expected, as long as the opacities are not too large.

### 2.3 Complex organic molecule formation in hot cores

Two types of scenario have been invoked in order to account for the presence of COMs in protostellar hot cores. In the first scenario (e.g. Charnley et al. 1992), simple molecules and atoms are accreted during the prestellar phase (i.e. at 10 K) on the grains where they can be hydrogenated. After the protostar forms, the ices are evaporated above a temperature of 100 K, and the contents of the ice mantles are released into the gas-phase, where they can trigger new gas-phase reactions. For example, the methanol molecules formed in the ice mantle during the prestellar phase can be protonated by  $\text{H}_3^+$  after they are desorbed, following:  $\text{CH}_3\text{OH} + \text{H}_3^+ \rightarrow \text{CH}_3\text{OH}_2^+$ . Protonated methanol  $\text{CH}_3\text{OH}_2^+$  can then react with  $\text{H}_2\text{CO}$  and  $\text{CH}_3\text{OH}$  to form  $\text{HCOOCH}_4^+$  (protonated methyl formate) and  $\text{CH}_3\text{OCH}_4^+$  (protonated dimethyl ether), respectively. Upon dissociative recombination (i.e. the reaction of these positive ions with an electron), the protonated species can lose a proton to form  $\text{HCOOCH}_3$  (methyl formate) and  $\text{CH}_3\text{OCH}_3$  (dimethyl ether). Concerns that dissociative recombinations of large ions are inefficient to form COMs have emerged (e.g. Horn et al. 2004), as such energetic reactions most probably completely disrupt the parent ion into small fragments, and that the molecule obtained after the loss of a single proton is only a minor product (Geppert et al. 2006). Gas-phase scenarios are for this

reason not currently favoured, but the issue is still debated, as all gas-phase chemical routes leading to COMs may not have been explored (Cole et al. 2012).

In the currently preferred second chemical scenario, COMs form entirely on grain surfaces (Garrod & Herbst 2006). During the prestellar phase, the chemistry does actually not differ from the previous scenario: simple atoms and molecules stick to the grains where they can be hydrogenated, even at temperatures as low as 10 K. The species present on the grains can be photodissociated by e.g. cosmic rays, thus giving rise to reactive radicals like HCO or CH<sub>3</sub>O. Alternatively, these radicals, often intermediate products in the grain-surface hydrogenation of species like C or CO, can be trapped in the grain mantles and become unavailable for further hydrogenation (Taquet et al. 2012). When the protostar is formed and starts heating its surroundings, the gas and dust temperatures increase and heavy species become mobile on the grains (above  $\sim 30$  K). In particular, reactive radicals can diffuse on the surface and form more complex molecules (Garrod & Herbst 2006), following grain-surface routes like:



Finally, those molecules as well as the whole contents of the ice mantle are evaporated into the gas-phase as the temperature keeps on rising (the temperatures at which it happens depends on the considered species, but above 100 K, all of the grain mantle should have desorbed).

### 3 Complex organic molecules in prestellar cores

As prestellar cores are the direct precursors of protostars studying their chemistry can bring valuable information on the initial conditions of protostellar chemistry. These sources are relatively simple in their structure: the density and temperature gradients are much shallower than in protostars, and they harbour no jet or outflow. Besides, they contain no inner energy source and their inner parts are well shielded from the interstellar radiation field ( $A_V > 10$ ), so that their inner temperatures are around (and often below) 10 K. Their chemistry is therefore dominated by barrierless ion-molecule reactions in the gas phase and accretion of species on the dust grains. Without thermal energy, only cosmic rays or secondary UVs induced by energetic electron collisions on H<sub>2</sub> molecules can help return some of the molecules into the gas phase.

In the view which prevailed until recently and which we highlighted in the previous section, complex organic molecules were not expected to be formed in prestellar cores, due to the very low temperatures precluding radical mobility on the grains. The exception to this is methanol, which is easily observed even in the very cold gas (Friberg et al. 1988; Tafalla et al. 2006). Methanol formation is thought to be inefficient in the gas-phase (as it results from the dissociative recombination of CH<sub>3</sub>OH<sub>2</sub><sup>+</sup>, in which the product branching ratio for CH<sub>3</sub>OH is only 3% – Geppert et al. 2006), but it can form on grain surfaces by successive hydrogenations of CO on the grains. This mechanism has been shown in the laboratory to be efficient even at 10 K (Watanabe & Kouchi 2002). Unlike heavier species like e.g. HCO, H atoms are very mobile on grains at low temperatures and can scan the whole surface of the grains many times before they evaporate back to the gas phase (Tielens & Hagen 1982).

A search for terrestrial complex organic molecules in the prestellar core L1689B has shown the presence of several saturated O-bearing COMs: CH<sub>3</sub>CHO, CH<sub>3</sub>OCH<sub>3</sub>, CH<sub>3</sub>OCHO and CH<sub>2</sub>CO (Bacmann et al. 2012). A spectral survey in the cold source B1-b carried out by Cernicharo et al. (2012) has revealed a similar richness in terrestrial organic molecules. The temperature in L1689B is close to 10 K (Redman et al. 2004), much lower than the temperature above which heavy radicals can diffuse on grain surfaces. The temperature in B1-b is also reported to be around 15 K by Cernicharo et al. (2012). These detections therefore cast doubts on the mechanisms previously proposed to explain the formation of COMs on grain surfaces. In any case, those mechanisms cannot apply to cold gas and prestellar cores.

## 4 How can COMs form at 10 K?

### 4.1 Grain surfaces

In prestellar cores, thermal energy is not sufficiently available to provide heavy radicals with enough mobility to diffuse on the grains, nor is it sufficient to desorb molecules from the grains back into the gas phase. However,

molecules like  $\text{CH}_3\text{OH}$  which are believed to form solely on grain surfaces, are seen in the gas phase, so that other, non-thermal mechanisms which play a role in molecular desorption might also bring the needed energy to provide the mobility to the radicals. Cosmic ray impacts are likely candidates, as well as secondary UVs - which are by-products of cosmic ray impacts on  $\text{H}_2$  molecules that get ionized and generate energetic electrons that excite  $\text{H}_2$ . Laboratory experiments (Gerakines et al. 1996) have shown that complex organic molecules can be formed at low temperatures by UV irradiation of methanol ices.

Quantitatively however, it is still uncertain whether these processes can reproduce the abundances of COMs observed in cold clouds. The parameters involved (cosmic ray spectrum in cores, energy deposited in the grains, energy available for diffusion and evaporation), remain very poorly constrained.

#### 4.2 Gas phase

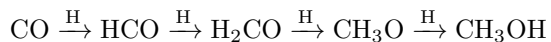
The detection of COMs in the cold gas has revived the interest for gas-phase formation mechanisms, and new chemical routes have been proposed by Vasyunin & Herbst (2013). Exothermic reactions between species on the grains can desorb species into the gas phase, including radicals. The desorbed species can then react together in the gas phase to form COMs or their protonated counterparts following various mechanisms: neutral-neutral reactions, protonation reactions, ion-molecule reactions. Vasyunin & Herbst (2013) suggest that radiative associations such as  $\text{CH}_3\text{O} + \text{CH}_3 \rightarrow \text{CH}_3\text{OCH}_3 + h\nu$  as new possibilities to form COMs. The rate coefficients for these reactions have for the most part not been measured at 10 K and the efficiency of the concerned reactions is therefore uncertain. Another uncertainty factor comes from the reactive desorption efficiency, i.e. the yield of molecular desorption triggered by chemical reactions on the grains, which is unknown.

#### 4.3 Comparison with observations

The gas-phase model of Vasyunin & Herbst (2013) gives the evolution with time of the abundances of several COMs detected in L1689B. The abundances of  $\text{CH}_3\text{OCH}_3$  and  $\text{CH}_3\text{CHO}$ , which are around  $10^{-10}$  in the source can be simultaneously reproduced by the model for an age of around  $5 \cdot 10^5$  years, which is consistent with typical lifetimes of prestellar cores ( $\sim 10^6$  years). In order to account for the abundance of these two species, an efficiency of 10% for the reactive desorption has to be assumed. With this rate however, the model overproduces the abundance of  $\text{CH}_3\text{OH}$  by nearly 2 orders of magnitude. For  $\text{CH}_3\text{OCHO}$ , the model cannot reproduce the observed abundance at any time by at least an order of magnitude. Although this model represents an improvement over previous attempts to account for gas-phase formation of COMs, many parameters/rate coefficients still need to be measured at 10 K in order to confirm whether the proposed new reactions are indeed efficient enough.

#### 4.4 COM precursors

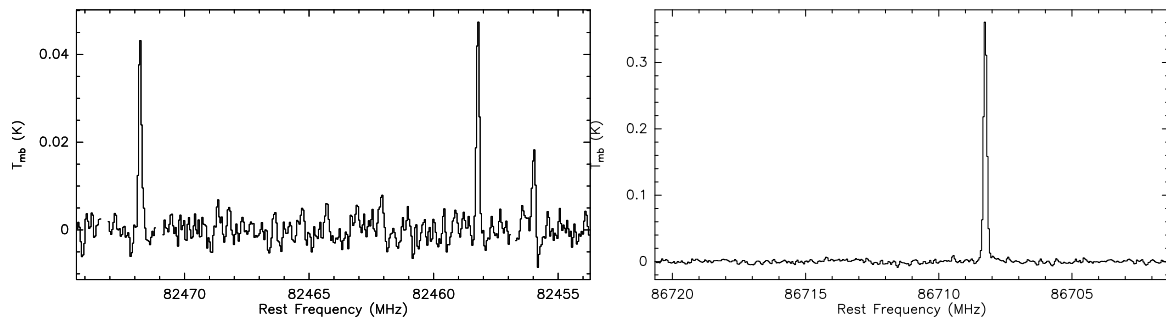
Radicals like  $\text{HCO}$  and  $\text{CH}_3\text{O}$  are believed to play an important role in the synthesis of complex organics. On grain-surfaces, they are intermediate products in the hydrogenation of  $\text{CO}$  leading to  $\text{CH}_3\text{OH}$ :



In COM formation schemes like those of Garrod & Herbst (2006),  $\text{HCO}$  and  $\text{CH}_3\text{O}$  are direct precursors of species like  $\text{CH}_3\text{OCHO}$  or  $\text{CH}_3\text{OCH}_3$ . They might also be direct precursors of some COMs in the gas phase, as suggested by Vasyunin & Herbst (2013).

We have observed these two radicals in a sample of 8 prestellar cores from different star-forming regions (Bacmann & Faure 2015). Both species are widely present in the gas-phase of prestellar cores:  $\text{HCO}$  is detected in all the sources and  $\text{CH}_3\text{O}$  in half of them, as its lines are very weak. Spectra of  $\text{HCO}$  and  $\text{CH}_3\text{O}$  in the prestellar core L1689B are shown in Fig. 1. Absolute abundances vary by about one order of magnitude between the various sources, but the abundance ratios between the species are remarkably similar. We find that the abundance ratios  $\text{HCO} : \text{H}_2\text{CO} : \text{CH}_3\text{O} : \text{CH}_3\text{OH}$  are close to  $10 : 100 : 1 : 100$ . Such ratios cannot be accounted for by the model of Vasyunin & Herbst (2013): in the model, the abundances of  $\text{H}_2\text{CO}$  and  $\text{CH}_3\text{OH}$  are similar only at steady-state, but at steady-state the  $\text{CH}_3\text{OH}$ ,  $\text{H}_2\text{CO}$  and  $\text{CH}_3\text{O}$  abundances are one to two orders of magnitude higher than observed.

New laboratory experiments have recently shown that the neutral-neutral reaction  $\text{CH}_3\text{OH} + \text{OH} \rightarrow \text{CH}_3\text{O} + \text{H}_2\text{O}$  accelerates when the temperature decreases from 200 K to about 50 K, and is fast despite having a barrier (Shan-



**Fig. 1. Left:** CH<sub>3</sub>O spectrum in the core L1689B. **Right:** HCO spectrum in L1689B

non et al. 2014; Gómez-Martín et al. 2014). As OH is abundant in the interstellar medium (about  $\sim 10^{-8}$  with respect to H<sub>2</sub> – Crutcher 1979), this reaction may provide an efficient way to form CH<sub>3</sub>O in the gas-phase. Assuming that CH<sub>3</sub>O is formed in the gas phase by the above reaction and destroyed by reactions with proton donors such as H<sub>3</sub><sup>+</sup>, we find that the abundance ratio [CH<sub>3</sub>O]/[CH<sub>3</sub>OH] is 10<sup>-3</sup> at steady-state, one order of magnitude below the observed abundance ratio. In order to derive this, we assumed that the reaction rate for the formation of CH<sub>3</sub>O at 10 K is the value given by Gómez-Martín et al. (2014) ( $k_{\text{form}} = 5 \cdot 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ ) and that the reaction rate for its destruction is around  $k_{\text{destr}} = 5 \cdot 10^{-8} \text{ cm}^3 \text{ s}^{-1}$ . We have also assumed that the OH abundance is 10<sup>-8</sup> with respect to H<sub>2</sub> (Crutcher 1979; Troland & Crutcher 2008), as is the proton donor abundance (Flower et al. 2005, 2006). Neutral-neutral reactions are therefore not fast enough to account for the CH<sub>3</sub>O abundance in prestellar cores.

Faster formation routes for CH<sub>3</sub>O can be provided by ion-molecule reactions with CH<sub>3</sub>OH as a precursor. A likely formation pathway would be CH<sub>3</sub>OH + H<sub>3</sub><sup>+</sup> → CH<sub>3</sub>OH<sub>2</sub><sup>+</sup> + H<sub>2</sub> followed by the dissociative recombination CH<sub>3</sub>OH<sub>2</sub><sup>+</sup> + e<sup>-</sup> → CH<sub>3</sub>O + H<sub>2</sub>. The protonation of methanol can give several products and it is estimated that the branching ratio for protonated methanol CH<sub>3</sub>OH<sub>2</sub><sup>+</sup> is about 25% (KIDA database). The dissociative recombination of protonated methanol also yields several products, and the branching ratio for CH<sub>3</sub>O has been measured to be 6% (Geppert et al. 2006). Given these numbers and the measured reaction rate for the dissociative recombination, the abundance ratio estimated at steady-state is: [CH<sub>3</sub>O]/[CH<sub>3</sub>OH]  $\sim 0.01$ . This is consistent with the observed abundance ratio. Similar reactions between H<sub>3</sub><sup>+</sup> and H<sub>2</sub>CO can account for the [HCO]/[H<sub>2</sub>CO] abundance ratio. Gas phase ion molecule processes seem able to account for the presence and abundances of the HCO and CH<sub>3</sub>O in the gas phase. We stress however that our model relies on microphysics quantities, which for some of them have not been measured in the laboratory.

## 5 Conclusions

Star forming regions are rich in complex organic molecules from their earliest evolutionary stages. Terrestrial complex organic molecules, which were long believed to be characteristic of the warm/hot gas surrounding both low- and high-mass young stellar objects, are now being detected in the gas-phase of cold prestellar cores (T  $\sim 10$  K). These new detections pose a new challenge in regions where little thermal energy is available for chemical reactions on grain surfaces, and where external UV field do not penetrate because of the high visual extinctions. Grain-surfaces might still play a role in COM synthesis provided the energy necessary for radical formation/diffusion (and molecule desorption) either comes from photoprocesses (cosmic rays, secondary UV radiation) or has a chemical origin. Grain surface chemistry introduces many unconstrained parameters and reliable quantitative predictions are not yet available. Gas-phase chemical models have started including new reactions which leads to better agreements with the observations, although the suggested new processes have not been measured in the laboratory at the relevant temperatures. Finally, our new observations have shown that the abundances of HCO and CH<sub>3</sub>O radicals, which are thought to be precursors of COMs, can be accounted for by pure gas-phase processes.

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