

Formation of complex organic molecules in cold objects: the role of gas-phase reactions

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ABSTRACT

While astrochemical models are successful in reproducing many of the observed interstellar species, they have been struggling to explain the observed abundances of complex organic molecules. Current models tend to privilege grain surface over gas-phase chemistry in their formation. One key assumption of those models is that radicals trapped in the grain mantles gain mobility and react on lukewarm ($\gtrsim 30$ K) dust grains. Thus, the recent detections of methyl formate (MF) and dimethyl ether (DME) in cold objects represent a challenge and may clarify the respective role of grain-surface and gas-phase chemistry. We propose here a new model to form DME and MF with gas-phase reactions in cold environments, where DME is the precursor of MF via an efficient reaction overlooked by previous models. Furthermore, methoxy, a precursor of DME, is also synthesized in the gas phase from methanol, which is desorbed by a non-thermal process from the ices. Our new model reproduces fairly well the observations towards L1544. It also explains, in a natural way, the observed correlation between DME and MF. We conclude that gas-phase reactions are major actors in the formation of MF, DME and methoxy in cold gas. This challenges the exclusive role of grain-surface chemistry and favours a combined grain-gas chemistry.

Key words: ISM: abundances – ISM: molecules.

1 INTRODUCTION

Relatively complex (i.e. containing more than six atoms) organic molecules, referred in the literature as COMs, were first discovered in the warm ($\gtrsim 100$ K) and dense ($\gtrsim 10^6$ cm⁻³) regions surrounding high-mass protostars, called hot cores (Blake et al. 1987). Several models were then developed to explain the observed abundances of those COMs (Millar, Herbst & Charnley 1991; Charnley, Tielens & Millar 1992; Caselli, Hasegawa & Herbst 1993). The basic idea of those models was that simple hydrogenated molecules like H₂CO, CH₃OH and NH₃ are formed during the cold pre-collapse phase on the cold ($\lesssim 20$ K) grain surfaces (e.g. Tielens & Hagen 1982). Upon heating from the accreting central protostar, the grain ices sublimate injecting those molecules in the gas phase and starting in this way what was then called a warm gas-phase chemistry. This paradigm has lasted for almost two decades, until new observations (e.g. Cazaux et al. 2003; Requena-Torres et al. 2006; Bottinelli et al. 2007), laboratory experiments (Geppert et al. 2007) and theoretic

cal studies (Horn et al. 2004) challenged it. The warm gas-phase chemistry paradigm left the place to the grain-surface chemistry.

In the new paradigm, grain-surface chemistry is not only responsible for the hydrogenated molecules of the pre-collapse phase, but also for the (almost) whole set of observed COMs. The basic idea of this class of models (Garrod & Herbst 2006) is that radicals trapped in the iced mantles acquire mobility and react forming COMs when the dust temperature reaches ~ 30 K. The origin and quantity of the trapped radicals depend on the adopted model. They might be the pieces of iced species (e.g. methanol) broken by the far-ultraviolet (FUV) photons produced by the interaction of cosmic rays with H₂ (e.g. Garrod & Herbst 2006; Chang & Herbst 2014), or, alternatively, they are the result of the incomplete hydrogenation of the simple mother species (e.g. Taquet, Ceccarelli & Kahane 2012). Recent observations, however, show the presence of some COMs – notably methoxy (CH₃O), methyl formate (HCOOCH₃, MF) and dimethyl ether (CH₃OCH₃, DME) – in regions where the dust temperature is less than 30 K: pre-stellar cores (Bacmann et al. 2012; Vastel et al. 2014) and cold envelopes of low-mass protostars (Öberg et al. 2010; Cernicharo et al. 2012; Jaber et al. 2014). Two recent models have been published trying to explain these new observations, assuming

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that the detected COMs are present inside the cold and dense core (Vasyunin & Herbst 2013, hereinafter VH2013; Chang & Herbst 2014).

More recent observations towards the pre-stellar core L1544 (Bizzocchi et al. 2014; Vastel et al. 2014) added a crucial information: the methanol emission originates from the outer shell of the cold core, where the H_2 density is $\sim 3 \times 10^4 \text{ cm}^{-3}$ and the temperature is $\sim 10 \text{ K}$, and not from the inner and denser region, as previously assumed. Therefore, methanol is ejected from the grain mantles into the gas because of some non-thermal ice desorption, as it was previously claimed for water (Caselli et al. 2012). Finally, Vastel et al. (2014) argued that the COMs emission detected in L1544 also comes from the same outer shell and speculated that this is likely the case also for the other cold sources where COMs have been detected (Öberg et al. 2010; Bacmann et al. 2012; Cernicharo et al. 2012).

Following these last findings and building up on the VH2013 model, we propose here a new model where gas-phase reactions, triggered by the non-thermal desorption of methanol from the ices, play a major role in the formation of methoxy, MF and DME in cold regions. Specifically, we consider a set of gas-phase reactions, which were previously overlooked or whose coefficients we have refined based on recent experimental and theoretical works.

2 MODEL AND ADOPTED CHEMICAL NETWORK

2.1 The model

We used the `GRAINOBLE` code (Taquet et al. 2012; Taquet, Charnley & Sipilä 2014) to compute the mantle species from hydrogenation of CO and O. Briefly, `GRAINOBLE` couples the gas-phase and grain-surface chemistry with the rate equations approach introduced by Hasegawa, Herbst & Leung (1992), and takes into account the multilayer and porous nature of the ice mantles. Species accrete on the grain surfaces and are desorbed by cosmic ray-induced heating of grains (Hasegawa & Herbst 1993) and by a non-thermal process that injects into the gas phase 1 percent of the species formed on the surface, following a process called ‘chemical desorption’ (Garrod, Wakelam & Herbst 2007). We followed the chemical composition evolution of a gas with an H density of $6 \times 10^4 \text{ cm}^{-3}$ and a temperature of 10 K (to simulate the conditions in L1544; Vastel et al. 2014). We started with a gas having the initial abundances quoted by Wakelam & Herbst (2008) for the diffuse clouds (their Table 1, column EA2; note that hydrogen is initially molecular). We follow the chemical evolution for 10^6 yr.

In addition to this ‘standard’ model, we run a few more models to evaluate the impact on the results when some crucial parameters are changed. Specifically, we considered the following cases: (i) a

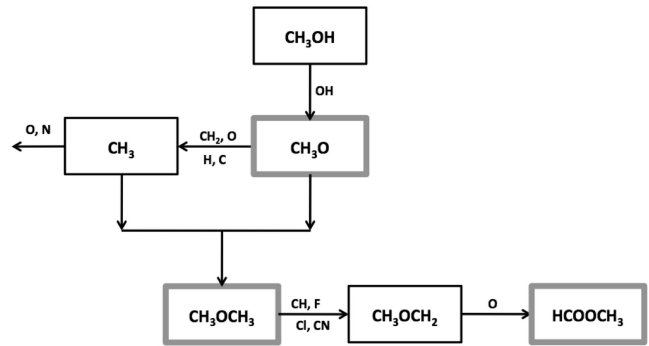


Figure 1. Scheme of the added reactions that form DME, MF and methoxy (boxes with grey large contours).

0 per cent or 10 per cent non-thermal desorption fraction, the latter chosen based on the experiment by Dulieu et al. (2013), although new experiments by Minissale & Dulieu (2014) suggest a dependence of this value on the substrate and other parameters; (ii) a gas with a five times larger density, and with 20 K temperature; (iii) a high and low Cl and F abundances to evaluate their impact on the results, as some important reactions introduced in this work depend on them (see the next section); (iv) the rate coefficient of reaction (2) of Table 1 reduced by a factor of 10 (see below).

2.2 The chemical network

The surface chemical network is based on the one presented by Taquet et al. (2013) but does not include the formation of deuterated species. We used the binding energies listed in Taquet et al. (2014) and the energy barrier for the CO and H_2CO hydrogenation recently computed by Rimola et al. (2014).

For the gas-phase chemistry, we used the OSU2009 network (Harada & Herbst 2008; <http://faculty.virginia.edu/ericherb>) as a basis and added a set of new reactions for the formation of MF, DME and methoxy, and involving atomic chlorine and fluorine for the conversion of DME into its radical CH_3OCH_2 . The scheme of the chemical reactions added in this work is shown in Fig. 1 and their list is reported in Table 1. We comment the novelties of the adopted network, for each species, in the following.

Methoxy is mostly formed by reaction (1). This reaction was also considered by VH2013, with a rate coefficient equal to $4 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$. We instead adopted the value calculated by Shannon et al. (2013) at 20 K, $3 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$, which, according to their suggestion, is likely a lower limit. Note that the reactions involving the methoxy reported by VH2013 in Table 1 are not in line with the cited NIST Chemical Kinetics Database

Table 1. List of the added reactions that form DME, MF and methoxy.

Reaction	Rate coefficient ($\text{cm}^3 \text{ s}^{-1}$ at 10 K)	References and notes
(1) $OH + CH_3OH \rightarrow CH_3O + H_2O$	3.0×10^{-10}	1
(2) $CH_3O + CH_3 \rightarrow CH_3OCH_3 + \text{photon}$	3.0×10^{-10}	see text
(3) $O + CH_3OCH_2 \rightarrow HCOOCH_3 + H$	2.0×10^{-10}	2, 3
(4) $F + CH_3OCH_3 \rightarrow CH_3OCH_2 + HF$	2.0×10^{-10}	2
(5) $Cl + CH_3OCH_3 \rightarrow CH_3OCH_2 + HCl$	2.0×10^{-10}	4

References: 1 – Shannon et al. (2013), 2 – Hoyerermann & Nacke (1996), 3 – Song, Hou & Wang (2005) and 4 – Wallington et al. (1988).

(<http://kinetics.nist.gov/kinetics/Search.jsp>), where the rate coefficients are different from those quoted by [VH2013](#).¹

DME is mainly formed by reaction (2). The rate coefficient for the radiative association of methyl and methoxy is not known. Recent theoretical work by [Vuitton et al. \(2012\)](#) suggests that radiative association can be very efficient when two relatively large radicals interact and form a stable molecule, if two-body exothermic channels are not available to the system. [VH2013](#) quote the presence of a competitive exothermic channel leading to $\text{H}_2\text{CO} + \text{CH}_4$ and, therefore, employed a rate coefficient at 10 K of $2.6 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$. However, a recent study by [Sivaramakrishnan et al. \(2011\)](#) has clearly pointed out that the reaction $\text{CH}_3\text{O} + \text{CH}_3 \rightarrow \text{H}_2\text{CO} + \text{CH}_4$ is a direct abstraction process, not correlating with the bound intermediate CH_3OCH_3 . For this reason, we have increased the rate coefficient for reaction (2) by an order of magnitude, as there are no alternative two-body reaction channels and the hot DME formed after the association of CH_3 and CH_3O can only dissociate back or stabilize by radiative association. Yet, we have run also a model with the reaction (2) rate coefficient a factor of 10 smaller to evaluate the impact on the results.

MF is formed by reaction (3), namely the oxidation of CH_3OCH_2 . This radical is formed by several reactions involving DME (Fig. 1) and common atomic and radical species, such as atomic chlorine and fluorine following reactions (4) and (5). The employed rate coefficients for reactions (3)–(5) have been determined by [Hoyermann & Nacke \(1996\)](#) and [Wallington et al. \(1988\)](#) at 298 K. Reactions (3)–(5), however, do not have an entrance barrier and we can retain their value also at much lower temperatures (as a matter of fact, a moderate increase of the rate coefficient with decreasing temperature is expected in this case). These reactions, well characterized in laboratory experiments, were not included in previous astrochemical models. We emphasize that they provide a direct link between DME and MF, being the former a precursor of the latter.

In addition, the standard loss mechanisms of COMs present in OSU (such as the reactions with H^+ , He^+ , etc.) have all been retained and we have added similar loss pathways (with similar rate coefficients) also for the new species, such as CH_3OCH_2 , which are not present in OSU. In addition, we considered the standard reactions of atomic F ([Neufeld, Wolfire & Schilke 2005](#)) and employed the recent determination of the rate coefficients for $\text{F} + \text{H}_2$ by [Tizniti et al. \(2014\)](#). As for the reactions of atomic Cl, we note that the $\text{Cl} + \text{H}_2$ reaction is endothermic ([Balucani et al. 2004](#) and references therein) and cannot occur in the conditions of the ISM ([Neufeld & Wolfire 2009](#)). Other reactions between chlorine and small saturated molecules are known to be very inefficient. Therefore, Cl is left to react with larger molecules, such as those of interest here. Please note that the Cl role in the COMs chemistry has been overlooked so far, although it can (only) react with large molecules.

3 RESULTS

Fig. 2 shows the evolution with time of the abundances of methoxy, DME and MF, plus CH_3 and methanol. In the standard case, the methoxy, DME and MF gaseous abundances reach a peak

¹The rate coefficients reported by [VH2013](#) for the reactions $\text{CH}_3\text{O} + \text{H}$ and $\text{CH}_3\text{O} + \text{O}$ are erroneous: the NIST values are 3×10^{-11} and $2.5 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$, respectively, rather than 1.6×10^{-10} and 1.0×10^{-10} . In addition, the dominant reaction channel for $\text{CH}_3\text{O} + \text{H}$ is the one leading to $\text{H}_2\text{CO} + \text{H}_2$ and not the one leading to $\text{CH}_3 + \text{OH}$, as claimed by [VH2013](#).

of $\sim 2 \times 10^{-10}$, $\sim 2 \times 10^{-11}$ and $\sim 5 \times 10^{-12}$, respectively, at $\sim 10^5$ yr and then decrease to lower values because they freeze-out on to the grain mantles. The peak occurs at $\sim 10^5$ yr because of the formation of methanol on the grains, which occurs when CO starts to freeze-out on to the grain mantles. A fraction of the methanol is then released in the gas phase and this triggers the reactions of Fig. 1, which form methoxy, DME and MF. In the same panel, we also show the predicted abundances obtained without considering the new reactions of Table 1. As expected, the predicted abundances of DME and MF are respectively about three and one order of magnitude lower.

The panel (b) of Fig. 2 shows the impact on the abundances when the chemical desorption is varied. The increase by a factor of 10 causes a proportional increase of gaseous methanol and methoxy, but a larger increase of DME and MF abundances, because methoxy is the bottleneck to the formation of DME. Caused by the dominance of reactions (4) and (5), the MF abundance increases by the same factor than DME. Conversely, putting the chemical desorption to zero kills the Fig. 1 gas-phase reactions as standard cosmic ray induced desorption is not effective to desorb methanol from the ices (as [GRAINOBLE](#) considers layer and not bulk chemistry in mantles).

The increase of density by a factor of 5, shown in the panel (c) of Fig. 2, causes a shorter time of residence of the molecules in the gas phase but only slightly affects the absolute abundance of the species. On the contrary, the increase of the temperature to 20 K causes a decrease of the methoxy, DME and MF peak abundances. This is due to the higher abundance of gaseous atomic H (whose density is about 1 cm^{-3} at 10 K). At 20 K, the density of atomic H increases by one order of magnitude due to the higher evaporation rate. The decrease by a factor 10 of the rate coefficient of reaction (2) leads to a similar decrease of the DME abundance. It also leads to the MF abundance forming earlier (because of other reactions than reaction 3 of Table 1) than DME and reaching a similar low abundance. Finally, decreasing the Cl and F elemental abundance (to the low values quoted by [Graedel, Langer & Frerking 1982](#)) results in a similar behaviour of the MF abundance, as reactions (4) and (5) of Table 1 do not form enough CH_3OCH_2 . Note that F is quickly ($\sim 10^3$ yr) locked into HF, while Cl remains mostly atomic until the freeze-out kicks on ($\sim 10^5$ yr). Therefore, reaction (5) of Table 1 plays a major role than reaction (4) in the formation of CH_3OCH_2 and, consequently, in the formation of MF from DME.

4 DISCUSSION

Whether the proposed new model reproduces the COMs abundances observed in cold objects depends on the interpretation of where their emission comes from. [Vastel et al. \(2014\)](#) and [Bizzocchi et al. \(2014\)](#) showed that methanol emission originates in a shell at the border of the condensation of the pre-stellar core L1544. These authors claim that methanol is non-thermally desorbed from the grain mantles and that, given the lower gas density, the rate of desorption overruns the rate of freezing-out. Since the same argument in principle applies also to the COMs, [Vastel et al. \(2014\)](#) suggested that COM emission originates from the same outer shell. If this is true, the derived abundance of the COMs detected by [Vastel et al. \(2014\)](#) would be 20 times larger than if they originated in the cold and dense inner part of the L1544. Evidently, a similar factor may affect the COMs abundance derived in the other cold regions ([Bacmann et al. 2012](#); [Cernicharo et al. 2012](#)).

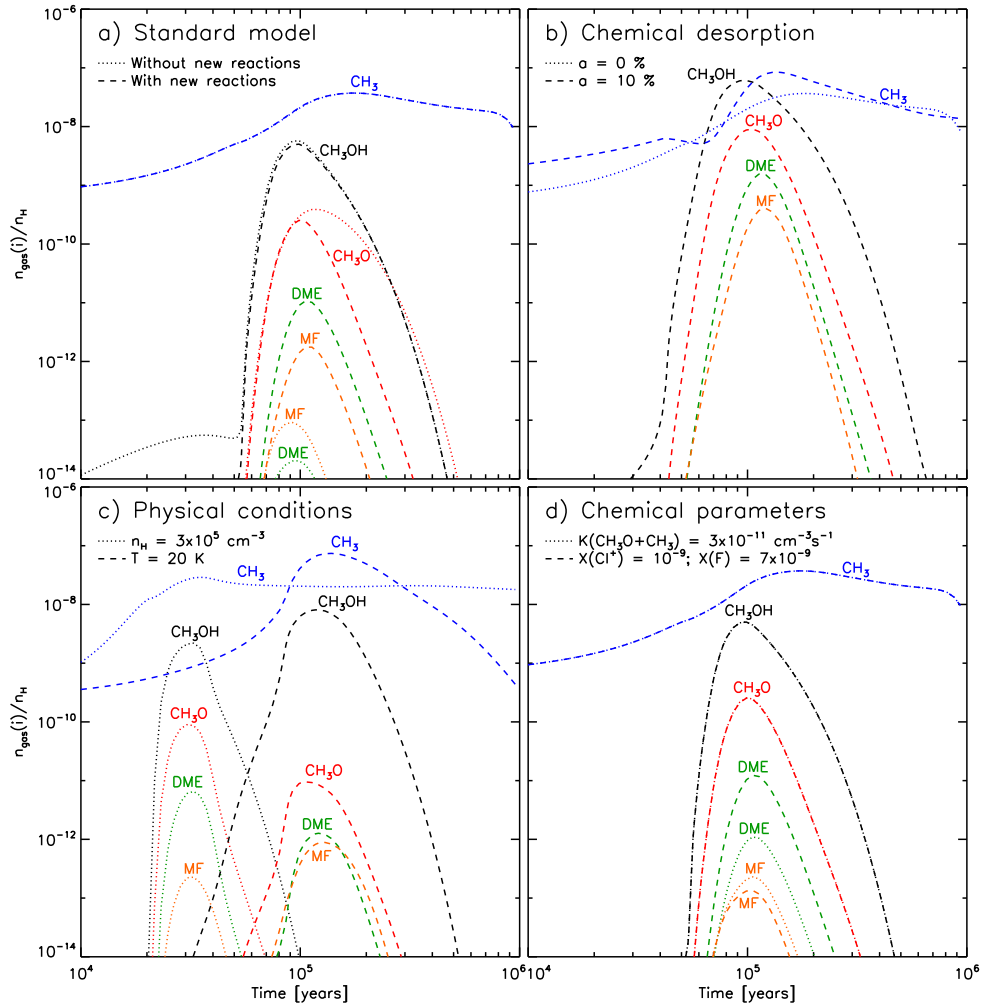


Figure 2. Predicted abundances (with respect to H nuclei) of MF (HCOOCH_3), DME (CH_3OCH_3) and methoxy (CH_3O) as a function of the time, plus some species that intervene in their formation, CH_3 and methanol (CH_3OH). The upper-left panel (a) refers to the standard case (dashed lines) and the case without the new reactions of Table 1 (dotted lines). The upper-right panel (b) is the same than (a) but with a chemical desorption rate equal to 0 (dotted lines) and 10 per cent (dashed lines), respectively. The lower-left panel (c) shows a gas with a H density of $3 \times 10^5 \text{ cm}^{-3}$ (dotted lines) and temperature 20 K (dashed lines). The lower-right panel (d) shows the standard case but with the rate of reaction (2) of Table 1 10 times lower (dotted lines) and with low (see text) Cl and F abundances (dashed lines).

Vastel et al. (2014) estimated a gaseous methanol abundance in the FUV-illuminated shell of $\sim 6 \times 10^{-9}$, and an upper limit to the methoxy, DME and MF abundances of $\sim 2 \times 10^{-10}$, $\sim 2 \times 10^{-10}$ and $\sim 2 \times 10^{-9}$, respectively. These numbers agree very well with the predictions of our standard model. On the contrary, the 10 per cent chemical desorption model predicts too large abundances. Unfortunately, the upper limit on the MF does not allow to put constraint on the role of Cl and F, nor on the value of the reaction (2) rate coefficient. Although we cannot directly compare our predictions with the absolute abundances quoted by Bacmann et al. (2012) and Cernicharo et al. (2012) because the assumed H_2 column densities may be overestimated, the DME over MF abundance ratios are compatible with our predictions. On the contrary, the methoxy abundance measured by Cernicharo et al. (2012) is five times lower than the DME and MF abundances, at odds with our predictions.

Constraints on the reactions (3)–(5) come from measures of the DME and MF abundances in different objects. Specifically, Jaber

et al. (2014) showed that there is a linear correlation between these two quantities over a six orders of magnitude range, confirming a direct link between DME and MF. The reactions (3)–(5) that we propose here explain in a natural way that link. Similarly, we predict the methoxy to be correlated with the methanol abundance, as it is the product of the reaction of CH_3OH with OH. This reaction has been recently studied and found to be much more efficient than previously expected (Shannon et al. 2013). Finally, we predict a possible correlation between methoxy and DME, although the correlation could be broken if CH_3 becomes the bottleneck of reaction (2). This correlation is based on the associative reaction between CH_3 and CH_3O , a likely process at 10 K, which, however, has never been investigated (Section 2). Since the determination of the product yield and rate coefficients for this reaction will be extremely difficult, if not impossible, in laboratory experiments, we urge our colleagues to carry out theoretical calculations of the same kind as those carried out by Vuitton et al. (2012) for other species.

5 CONCLUSIONS

We propose a new model to explain the formation of MF, DME and methoxy, based on recent experimental and theoretical works. The major conclusions of this work are the following:

- (i) the non-thermal desorption of iced methanol starts a series of gas-phase reactions leading to the formation of methoxy, DME and MF;
- (ii) methoxy is formed via the methanol-hydroxyl reaction;
- (iii) DME is mainly formed via the radiative association reaction of methoxy with CH₃;
- (iv) MF is formed from DME via the oxidation of CH₃OCH₂, a reaction overlooked by previously models;
- (v) MF is, therefore, the daughter of DME, which explains the observed correlation (e.g. Jaber et al. 2014).

In conclusion, gain-surface chemistry certainly plays a role, for example in forming hydrogenated species during the pre-stellar phase (Tielens & Hagen 1982; Caselli & Ceccarelli 2012), but not necessarily in the formation of all COMs. Gas-phase and grain-surface chemistry will have to share the reign of the formation of COMs.

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