Chemical modelling of complex organic molecules with peptide-like bonds in star-forming regions

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ABSTRACT
Peptide bonds (N–C = O) play a key role in metabolic processes since they link amino acids into peptide chains or proteins. Recently, several molecules containing peptide-like bonds have been detected across multiple environments in the interstellar medium, growing the need to fully understand their chemistry and their role in forming larger pre-biotic molecules. We present a comprehensive study of the chemistry of three molecules containing peptide-like bonds: HNCO, NH₂CHO, and CH₃NCO. We also included other CHNO isomers (HCNO, HOCN) and C₂H₃NO isomers (CH₃OCN, CH₃CNO) to the study. We have used the UCLCHEM gas–grain chemical code and included in our chemical network all possible formation/destruction pathways of these peptide-like molecules recently investigated either by theoretical calculations or in laboratory experiments. Our predictions are compared to observations obtained towards the proto-star IRAS 16293−2422 and the L1544 pre-stellar core. Our results show that some key reactions involving the CHNO and C₂H₃NO isomers need to be modified to match the observations. Consistently with recent laboratory findings, hydrogenation is unlikely to produce NH₂CHO on grain surfaces, while a combination of radical–radical surface reactions and gas-phase reactions is a better alternative. In addition, better results are obtained for NH₂CHO when a slightly higher activation energy of 25 K is considered for the gas-phase reaction NH₂ + H₂CO → NH₂CHO + H. Finally, our modelling shows that the observed correlation between NH₂CHO and HNCO in star-forming regions may come from the fact that HNCO and NH₂CHO react to temperature in the same manner rather than from a direct chemical link between the two species.

Key words: astrochemistry – molecular data – methods: numerical – ISM: abundances.

1 INTRODUCTION
Complex organic molecules (COMs) are molecules with more than six atoms in their structure containing at least one carbon atom (Herbst & van Dishoeck 2009). Among them, O-bearing and N-bearing COMs have attracted much interest in recent years because of their role in pre-biotic chemistry (Saladino et al. 2012). Numerous O-bearing and N-bearing COMs have been detected in the interstellar medium (ISM) and towards comets, suggesting a potential link between the two (e.g. Crovisier et al. 2004; Goesmann et al. 2015; Altwegg et al. 2017). N-bearing COMs containing peptide-like bonds (N–C=O bond) are of particular interest because of their role in linking amino acids into protein chains. Some peptide-like molecules are isocyanic acid (HNCO), formamide (NH₂CHO), and methyl isocyanate (CH₃NCO).

Isocyanic acid and formamide were first detected in space in early observations towards Sgr B2 (Rubin et al. 1971; Snyder & Buhl 1972), and since then they have been found in a variety of astrophysical environments (see Turner, Terzieva & Herbst 1999; Quan et al. 2010; López-Sepulcre et al. 2015, and references therein). The stable isomers of HNCO, cyanic acid (HOCN) and fulminic acid (HCNO), have also been reported, respectively, in Sgr B2(OH) (Brünken et al. 2009) and in several cold sources (e.g. B1 and L1544) and the lukewarm environment of L1527 (Marcelino et al. 2009).

Several efforts have been made recently to understand the chemistry of these species in various environments, especially for formamide for which its formation pathways are under strong debate. Indeed, observational and theoretical studies (Charnley 1997; Mendoza et al. 2014; López-Sepulcre et al. 2015; Song
Kästner (2016) initially proposed a scenario in which formamide formed through successive hydrogenation of HNCO on grain surfaces. However, laboratory experiments showed that hydrogenation is ineffective (Fedoseev et al. 2015; Noble et al. 2015) and radical–radical reactions such as the one between NH3 and H2CO (or HCO) are instead favoured (Jones, Bennett & Kaiser 2011; Fedoseev et al. 2016). The equivalent gas-phase formation reaction also seems to be a possible route, as shown by recent theoretical calculations presented by Barone et al. (2015) and Skouteris et al. (2017).

In contrast to HNCO and NH2CHO, methyl isocyanate has been discovered only recently in high-mass star-forming regions (towards Sgr B2 and Orion; Halfen, Ilyushin & Ziurs 2015; Cernicharo et al. 2016). The first detection of this molecule around a solar-type proto-star (IRAS 16293—2422, hereafter IRAS 16293) has just been reported by Martín-Doménech et al. (2017) and Ligterink et al. (2017). CH3NCO was proposed to be tentatively detected in the comet 67P/Churyumov–Gerasimenko by the Cometary Sampling and Composition mass spectrometer on board the Rosetta spacecraft’s Philae lander (Goessmann et al. 2015), but this detection does not seem to be confirmed (Altweg et al. 2017). Several formation routes for this molecule (both in the gas phase and on the grain surface) have been suggested (Charnley 1997; Halfen et al. 2015; Cernicharo et al. 2016; Belloche et al. 2017), but a comprehensive modelling of the chemistry of the C3H5NO isomers is still missing.

In this paper, we investigate the dominant formation pathways of these molecules in various relevant astrophysical environments (the IRAS 16293B hot corino and its cold envelope, and the L1544 pre-stellar core), by comparing the observed abundance of HNCO, NH2CHO, and CH3NCO to the predicted one obtained by chemical modelling. In Section 2, we present the gas–grain chemical code UCLCHEM and we report the chemical network of the CHNO isomers, NH2CHO and the C2H3NO isomers used in our modelling, for which we have collected all recent information available from laboratory experiments and theoretical calculations. In Section 3, we describe the sources to be modelled, and Section 4 reports our modelling results. In Sections 5 and 6, we discuss the formation and origin of formamide in various environments, and Section 7 finally summarizes our conclusions.

2 CHEMICAL CODE AND NETWORK

We have used the gas–grain chemical code UCLCHEM (Holdship et al. 2017) to model the chemistry of the peptide-like species HNCO, NH2CHO, and CH3NCO in star-forming regions. The gas-phase reaction network of UCLCHEM is based on the UMIST data base (McElroy et al. 2013), although additional gas-phase reactions have been included (see below). In the context of our work, UCLCHEM has been updated with a new treatment for grain-surface reactions that now considers the processes of grain-surface diffusion (Hasegawa, Herbst & Leung 1992), chemical reactive desorption (Minissale et al. 2016c), and reaction–diffusion competition (Chang, Cuppen & Herbst 2007; Garrod & Pauly 2011; Ruaud, Wakelam & Hersant 2016). In Appendix A, we describe how these processes have been implemented in the code.

Following this new treatment for grain-surface reactions in UCLCHEM, we have added reactions to hydrogenate C, N, and O atoms into their non-saturated and saturated forms. These hydrogenation processes can also now lead to chemical reactive desorption, releasing newly formed molecules in the gas phase. The full network contains 364 species (243 in the gas phase and 121 on the surface of the grains) and 3446 reactions. Binding energies of molecules have been taken from Wakelam et al. (2017). In the following, we describe the chemical reactions (both gas phase and grain surface) that have been added for HNCO and its isomers, NH2CHO, and CH3NCO and its isomers to the chemical network of UCLCHEM.

2.1 HNCO and isomers

Isocyanic acid (HNCO) is the most stable isomer of the CHNO species. The other isomers are, in order of energy difference with respect to HNCO, cyanic acid (HOCN), fulminic acid (HCNO), and isofulminic acid (HONC). The chemistry of these molecules has been recently studied by Quan et al. (2010) following the observations of HNCO, HCNO, and HOCN towards several molecular dark clouds (e.g. Turner et al. 1999; Marcelino et al. 2009, 2010). A similar study of the chemistry of HNCO has been performed by Tideswell et al. (2010). The gas-phase chemical network of Quan et al. (2010), see their table 1) is already included in the UMIST data base. We note, however, that we had to modify the parameters (reaction rate and/or activation energy barrier) for some of these gas-phase reactions in order to match the observations. We have also implemented in UCLCHEM their grain-surface network, as presented in table 2 of Quan et al. (2010).

For HNCO, we also added the following grain-surface reaction:1

\[ \text{NH} + \text{CO} \rightarrow \text{HNCO}. \]  

Belloche et al. (2017) investigated the energy barrier for this reaction (originally estimated to be 2500 K by Garrod, Widicus Weaver & Herbst (2008)) by varying it in grid models. They found that an efficient reaction (1) with a barrier of 1250 K provided the best fit to their observations; however, they did not use the Quan et al. (2010) network. This reaction has been extensively investigated by Himmel, Junker & Schnöckel (2002) both experimentally and through quantum chemical calculations, and they derive a barrier of 4200 K. This value has also been used by Fedoseev et al. (2015), and this is the one we consider in our work.

The complete chemical network is provided in Tables 1 and 2, and the modifications will be discussed in Section 4.1.

2.2 NH2CHO

In the literature, two major grain-surface formation routes of formamide (NH2CHO) are proposed. The first one is the successive hydrogenation of isocyanic acid, HNCO, on the grain surface:

\[ \text{HNCO} + \text{H} \rightarrow \text{H2NCO} \]  \[ \text{H2NCO} + \text{H} \rightarrow \text{NH2CHO}. \]  

Reaction (3) is barrierless since it is a radical–radical reaction but this is not the case for reaction (2) \((E_a = 1962 \text{ K}, \text{see Table 1})\). These reactions have been first proposed by Charnley (1997) and supported by Raunier et al. (2004) following an experiment of UV irradiation of pure ices of HNCO at 10 K. Mendoza et al. (2014) and López-Sepulcre et al. (2015) showed an observational correlation between the abundance of HNCO and NH2CHO for different star-forming regions spanning from low-mass to high-mass star-forming regions, shock regions, and cold envelopes (see their fig. 2). In their works, they proposed that HNCO and NH2CHO are chemically linked: either both species are formed from the same precursor or one forms from the other. In their view, NH2CHO forms on the grain surface.

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1 In the following, ‘#’ means that the species is located on the grain surface.
## Table 1. Grain-surface reactions related to NH$_2$CHO and C$_2$H$_5$NO isomers.

| Reaction | Parameters | Ref. |
|----------|------------|------|
| Radical diffusion reactions | $E_A^0$ (K) | $E_A^0$ (K) |
| #NH + #CO → #HNCO | 1300 | 650 | 9,10 |
| #H + #HOCN → #H$_2$O + #CN | 325 | 2200 | 1 |
| #H + #HOCN → #H$_2$CO | 325 | 2200 | 1 |
| #H + #HOCN → #CH$_3$ + #NO | 325 | 2200 | 1 |
| #H + #HNCN → #H$_2$NCO | 325 | 2200 | 2,3,5 |
| #NH + #HNCN → #NH$_2$ + #CO | 325 | 2200 | 2,3,4 |
| #H + #H$_2$NCO → #NH$_2$CHO | 325 | 2200 | 2,35 |
| #H + #H$_2$NCO → #HNCN + #H | 325 | 2553 | 2 |
| #NH + #H$_2$NCO → #NH$_3$CHO | 325 | 1200 | 7 |
| #NH$_2$ + #HOCN → #NH$_3$ + #CO | 1600 | 1200 | 7 |
| #NH$_2$ + #H$_2$CO → #NH$_3$CHO | 1600 | 1200 | 7 |
| #NH$_2$ + #H$_2$CO → #NH$_3$ + #HCO | 1600 | 2250 | 7 |
| #NH$_2$ + #H$_2$CO → #NH$_3$CHO + #H | 1600 | 2250 | 7 |
| #NH$_2$CHO + #OH → #NH$_2$NCO + #H$_2$O | 3150 | 2300 | 8 |
| #NH$_2$CHO + #CH$_3$ → #CH$_3$CONH$_2$ | 800 | 1200 | 8,11 |
| #H$_2$NCO + #H$_2$ → #CH$_3$CONH$_2$ | 800 | 1200 | 1 |
| #CH$_3$ + #OCN → #CH$_3$NCO | 800 | 1200 | 1 |
| #CH$_3$ + #OCN → #CH$_3$CONC | 800 | 1200 | 1 |
| #CH$_3$ + #OCN → #CH$_3$CNO | 800 | 1200 | 1 |
| #CH$_3$ + #OCN → #CH$_3$OS | 800 | 1200 | 1 |
| Direct cosmic ray desorption | $E_D$ (K) |
| H$_2$ formation-induced desorption | $E_A$ (K) |
| #HCO → NHCO | 4400 | 1 |
| #HOCN → HCN | 4400 | 1 |
| #HCON → HCN | 4400 | 1 |
| #HNCN → H$_2$NCO$^+$ | 5106 | 1 |
| #H$_2$NCO → H$_2$NCO$^+$ | 5106 | 1 |
| References. (1) Estimation based on analogous reactions; (2) Song & Kästner (2016); (3) Garrod (2013); (4) Nguyen et al. (1996); (5) Tsang (1992); (6) Noble et al. (2015); (7) Fedoseev et al. (2016); (8) Bellocchi et al. (2017); (9) Fedoseev et al. (2015); (10) Himmel et al. (2002); (11) Ligerink et al. (2017). |

from successive hydrogenation of HNCO and is released when the temperature rises enough to sublime the ice. This is consistent with the spatial correlation as well as the similar deuteration found in IRAS 16293 for the two species (Coutens et al. 2016). This theory has been supported by calculations performed by Song & Kästner (2016) on the formation of NH$_2$CHO on amorphous solid water (ASW) surfaces and in the gas phase. In particular, they show that quantum tunnelling of hydrogen atoms greatly increases the rate of reaction (2). However, note that these calculations were performed down to 103 K in the ASW surfaces, which is much larger than the cold conditions found in molecular dark clouds (~10–20 K).

Recent laboratory experiments have however challenged this scenario (see Fedoseev et al. 2015; Noble et al. 2015). Noble et al. (2015) bombarded a pure HNCO ice with H atoms, and they followed both the gas-phase and grain-surface composition. In their experiments, no formamide was produced within the detectable
Fedoseev et al. (2015). and hence reaction (3) does not lead to NH$_2$CHO but to HNCO via limits, which led them to conclude that HNCO does not saturate, and hence reaction (3) does not lead to NH$_2$CHO but to HNCO via

\[ \text{HNCO} + \text{H} \rightarrow \text{HNCO} + \text{H}_2 \]  

This result was confirmed by similar experiments performed by Fedoseev et al. (2015).

The second grain-surface formation route involves the radical-radical reaction between NH$_3$ and HCO or H$_2$CO:

\[ \text{NH}_3 + \text{HCO} \rightarrow \text{NH}_2\text{CHO} \]  
\[ \text{NH}_3 + \text{H}_2\text{CO} \rightarrow \text{NH}_2\text{CHO} + \text{H} \]  

This grain-surface chemistry was proposed by Fedoseev et al. (2016) after carrying out low-temperature (∼13 K) laboratory experiments. In their work, they show that the UV irradiation of hydroxylamine (NH$_2$OH, formed from NO contained in CO-, H$_2$CO-, and CH$_3$OH-rich ices at 13 K) yields a significant amount of NH$_2$ and, subsequently, HNCO, OCN$^-$, and NH$_2$CHO (see their fig. 7). This result may explain the observed correlation between HNCO and
NH$_2$CHO (Mendoza et al. 2014; López-Sepulcre et al. 2015), since both species may originate from the same precursor on the grain surface.

In the gas phase, a similar network was proposed by Kahane et al. (2013) ensuing a study of the low-mass proto-star IRAS 16293:

\[ \text{NH}_2 + \text{H}_2\text{CO} \rightarrow \text{NH}_2\text{CHO} + \text{H}. \]  

The gas-phase pathway has been studied theoretically by Barone et al. (2015) and Skouteris et al. (2017). Barone et al. (2015) found that reaction (9) has a small activation energy of 26.9 K. However, in their computation, they did not consider the formation of a Van der Waals complex in the reaction path. This has been considered in Skouteris et al. (2017), and they re-evaluated both the reaction rate and the activation energy of the reaction, now equal to 4.88 K, i.e. much lower than the one found by Barone et al. (2015). One should note that Song & Kästner (2016), from their calculations, disputed the feasibility of reaction (9) arguing that a significant barrier prevents the reaction from occurring. In Section 4.3, we will discuss the effects of these two different rates on the chemistry of NH$_2$CHO.

Other gas-phase formation reactions involving NH$_2$CHO have been introduced in our network as, for instance, the one proposed by Quan & Herbst (2007):

\[ \text{NH}_2^+ + \text{H}_2\text{CO} \rightarrow \text{NH}_2\text{CHO}^+ + \text{hv}, \]  

followed by dissociative recombination to form formamide. According to the same authors, this pathway is not efficient and does not produce much formamide. Halfen, Ilyushin & Ziurys (2011) also proposed a formation route, based on the previous one:

\[ \text{NH}_2^+ + \text{H}_2\text{CO} \rightarrow \text{NH}_2\text{CHO}^+ + \text{H}_2. \]  

\[ \text{NH}_2\text{CHO}^+ + e^- \rightarrow \text{NH}_2\text{CHO} + \text{H}. \]

Calculations performed by Redondo et al. (2014b) showed that reaction (11) has a high barrier and is unlikely to occur. In a previous work, Redondo, Barrientos & Largo (2014a, see their table 1) also studied the formation of formamide via the interaction of (NH$_2$)$_2$, NH$_2$OH$^+$, and NH$_2$OH$^+$ with (HCO, H$_2$CO, and HCOOH). Some of these reactions are as follows:

\[ \text{NH}_2^+ + \text{HCOOH} \rightarrow \text{NH}_2\text{CHO}^+ + \text{H}_2\text{O}. \]  

\[ \text{NH}_2\text{OH}^+ + \text{H}_2\text{CO} \rightarrow \text{NH}_2\text{CHO}^+ + \text{H}_2\text{O}. \]  

\[ \text{NH}_2\text{OH}^+ + \text{H}_2\text{CO} \rightarrow \text{NH}_2\text{CHO}^+ + \text{H}_2\text{O}. \]  

\[ \text{NH}_2\text{OH} + \text{H}_2\text{CO} \rightarrow \text{NH}_2\text{CHO} + \text{H}_2\text{O}. \]  

Their computational results show that all their proposed reactions are subject to a high barrier and are not feasible under interstellar conditions.

The destruction routes of formamide are poorly constrained. From the KIDA data base$^2$ (Wakelam et al. 2012), we have considered a set of destruction reactions of formamide with ions in the gas phase. On the grain surface, formamide is destroyed following two reaction pathways:

\[ \text{NH}_2\text{CHO} + \text{OH} \rightarrow \text{H}_2\text{NCO} + \text{H}_2\text{O}. \]  

\[ \text{NH}_2\text{CHO} + \text{CH}_3 \rightarrow \text{CH}_3\text{CONH}_2. \]

Reaction (18) has been discussed by Belloche et al. (2017) where they show that H$_2$NCO is more likely to be produced than HNCHO, according to their best results. Thus, we did not include HNCHO in our study.

The complete set of grain-surface and gas-phase reactions included in our study is shown in Tables 1 and 2, respectively.

### 2.3 CH$_3$NCO and isomers

Halfen et al. (2015) proposed a basic reaction network to form methyl isocyanate in space. It was mostly a gas-phase chemistry where CH$_3$NCO is mainly formed from methylation of HNCO:

\[ \text{CH}_3 + \text{HNCO} \rightarrow \text{CH}_3\text{NCO} + \text{H}. \]

This pathway is also favoured by Gomesmann et al. (2015). The grain-surface route proposed by Belloche et al. (2017) has also been introduced in our chemical network:

\[ \text{CH}_3 + \text{OCN} \rightarrow \text{CH}_3\text{NCO}. \]

Similar reactions have also been included for the different isomers. CH$_3$NCO is not the only stable isomer of C$_2$H$_3$NO: methyl cyanate (CH$_3$OCN), acetoniitrile N-oxide (CH$_3$CNO), fulminate (CH$_3$OCN), and CH$_3$CON are all stable isomers, although the stability of CH$_3$CON is still under debate (Dalbouha et al. 2016). The energy difference of these isomers, with respect to methyl isocyanate, is +109.8, +239.9, +347.8, and +618.0 kJ mol$^{-1}$, respectively. A preliminary chemistry study of these species has been performed by Martín-Doménech et al. (2017) for the physical conditions of the low-mass proto-star IRAS 16293 B. A more complete network is reported here where the whole chemical network is built up based on the reactions of CH$_3$NCO. We discuss the parameters of these reactions in Section 4.2. All the reactions added to UCLCHEM involving the C$_2$H$_3$NO isomers are reported in Tables 1 and 2 for the grain surface and the gas phase, respectively.

### 3 CHEMICAL MODELLING AND SOURCE SELECTION

**UCLCHEM** is run in three steps or phases. 

**Ambient cloud phase:** The first phase (referred to as Phase 0) computes the evolution of the chemistry in a diffuse cloud for 10$^6$ yr. The initial gas-phase atomic abundances (with respect to the total proton density $n_H$) are given in Table 3. These values are taken from Wakelam & Herbst (2008, case EA1) and are consistent with recent studies performed towards L1544 (Quénard et al. 2017; Vasyunin et al. 2017) and IRAS 16293 (Hincelin et al. 2011; Bottinelli et al. 2014). Such atomic abundances should be suitable initial conditions in cold dark clouds where heavy elements are depleted on dust grains. The initial density is kept constant to $n_H = 10^5$ cm$^{-3}$, as suggested by a similar chemical study of the pre-stellar core L1544 by Quénard et al. (2017). The temperature is set to $T = 10$ K. The visual extinction is set to $A_V = 2$ mag, corresponding to a size of $\sim 10$ pc. These are typical values for diffuse clouds.
3.1 The pre-stellar core L1544

L1544 is a proto-typical pre-stellar core, which has been extensively studied in the past (e.g. Caselli et al. 2002, 2003; Quenard et al. 2016, 2017). The 1D physical structure of the source has been derived by Kato, Rawlings & Caselli (2014), and it has been used to derive the values shown in Table 4. In our modelling, we consider the position of the core centre, where most species are frozen out on to dust grains, and the position of the methanol peak reported by Bizzocchi et al. (2014) and studied by Jiménez-Serra et al. (2016).

The core centre is characterized by $n(H_2) \sim 5 \times 10^6$ cm$^{-3}$ and large extinction ($A_V \sim 60$ mag).

The methanol peak is detected \~4000 au away from the core centre. This ‘methanol peak’ position reveals an enhancement of several COMs, as shown by Vastel et al. (2014) and Jiménez-Serra et al. (2016). This position has a density of a few $10^5$ cm$^{-3}$ and a moderate visual extinction ($A_V \sim$7–8 mag) within the core and not along the line of sight; see Jiménez-Serra et al. (2016). In our study, we will compare the molecular richness in these two different environments.

3.2 The proto-star IRAS 16293

IRAS 16293 is a class 0 low-mass proto-star located in the $\rho$ Ophiuchus star-forming region, 147.3 ± 3.4 pc away from us (Ortiz-León et al. 2017). IRAS 16293 is at least a binary system (Wootten 1989; Pech et al. 2010), with sources A and B separated by 5 arcsec (or \~740 au at 147.3 pc).

Source B has been the object of numerous observations due to its chemical complexity (e.g. Coudert et al. 2016; Jørgensen et al. 2016). Among the molecules detected in this source, we find methyl isocyanate, which has been recently reported towards this object (Ligterink et al. 2017; Martín-Domènech et al. 2017). Both studies give detection limits for many isomers of $\text{C}_2\text{H}_5\text{NO}$ and CHNO.

We have used the 1D physical structure of IRAS 16293 determined by Crimier et al. (2010) to infer the physical conditions of its hot corino and cold envelope (see Table 4). The parameters selected for the cold envelope are also consistent with previous modelling of this source by Barone et al. (2015). We have used the same chemical network as for L1544 to model the abundances of the same set of molecules for both the IRAS 16293 B hot corino and the cold envelope surrounding it.

4 RESULTS

In this section, we will present the results of the chemical modelling for HNCO and its isomers (Section 4.1), $\text{CH}_3\text{NCO}$ and its isomers (Section 4.2), and $\text{NH}_2\text{CHO}$ (Section 4.3). Each section discusses the results for each of the four environments considered in our study (L1544 core centre and methanol peak and IRAS 16293 hot corino and cold envelope) and the impact of the network related to each species on these results (e.g. key reactions, modifications).

4.1 HNCO and isomers

As explained in Section 2.1, the CHNO gas–grain network is the one proposed by Quan et al. (2010). The modelling using the original network of Quan et al. (2010), however, did not match the observations neither towards IRAS 16293 nor towards L1544 [we stress that this was already noted by Quan et al. (2010) for HOCN and HCNO towards L1544, see their fig. 6]. Indeed, with the original

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**Table 3.** Initial gas-phase elemental abundances assumed relative to the total nuclear hydrogen density $n_H$.

| Species | EA1 |
|---------|-----|
| He      | $1.40 \times 10^{-1}$ |
| N       | $2.14 \times 10^{-5}$ |
| O       | $1.76 \times 10^{-5}$ |
| C$^+$   | $7.30 \times 10^{-5}$ |
| S$^+$   | $8.00 \times 10^{-8}$ |
| Si$^+$  | $8.00 \times 10^{-9}$ |
| Mg$^+$  | $7.00 \times 10^{-9}$ |
| Cl$^+$  | $1.00 \times 10^{-9}$ |
| P$^+$   | $2.00 \times 10^{-10}$ |
| F$^+$   | $6.68 \times 10^{-9}$ |

Notes. EA1 refers to the first elemental abundance model considered by Wakelam & Herbst (2008).

**Table 4.** Temperature, density, and visual extinction of the different sources modelled with UCLCHEM at the end of each phase.

| Source | Temperature (K) | H density (cm$^{-3}$) | $A_V$ (mag) |
|--------|----------------|----------------------|-------------|
| All sources | 10 | $1 \times 10^5$ | 2 |
| Phase 0 | | | |
| L1544 (core centre) | 10 | $5 \times 10^3$ | 100 |
| L1544 (methanol peak) | 10 | $4 \times 10^3$ | 8 |
| IRAS 16293 B (hot corino) | 10 | $5 \times 10^3$ | 1000 |
| IRAS 16293 (cold envelope) | 10 | $2 \times 10^3$ | 30 |
| Phase 1 | | | |
| IRAS 16293 B (hot corino) | 250 | $5 \times 10^3$ | 1000 |
| IRAS 16293 (cold envelope) | 20 | $2 \times 10^3$ | 30 |

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network, HOCN and HCNO are overestimated by a large factor (∼1000 and ∼30, respectively). Therefore, we needed to perform some changes to six key gas-phase reactions involving the formation and destruction of these two species (see reactions with an * in Table 2). Since the study of HOCN and HCNO is not the main focus of this work, we just investigate which reaction rates should be modified – and by how much – to obtain a better result. We however note that we did not modify any reaction involving HNCO, the most important isomer in our study.

In our chemical network, we increased the destruction rates of HOCN/HCNO + O from $3.33 \times 10^{-11}$ to $3.33 \times 10^{-12}$ cm$^3$ s$^{-1}$. We note that these reaction rates and energy barriers were just educated guesses assumed by Quan et al. (2010), and no experimental results do exist yet. In the case of HOCN, we also changed its barrier of 2470 K to be the same as the reaction with HCN (195 K). For the two key gas-phase formation routes

$$\text{H}_2\text{OCN}^+ / \text{HNO}_2^+ \rightarrow \text{HOCN} + \text{H}, \quad (23)$$

decreased the reaction rate from $1.50 \times 10^{-7}$ and $1.00 \times 10^{-12}$ cm$^3$ s$^{-1}$, respectively, to $5.00 \times 10^{-14}$ cm$^3$ s$^{-1}$. These dissociative recombination reactions were first introduced by Marcelino et al. (2010) and their rates are poorly constrained (Quan et al. 2010).

For HCN, we found that the reaction $\text{CH}_3 + \text{NO} \rightarrow \text{HCNO}$ is the main formation route of HCN. It decreased its reaction rate from $3.65 \times 10^{-11}$ to $2.00 \times 10^{-12}$ cm$^3$ s$^{-1}$. The latter reaction has been investigated theoretically and experimentally but the branching ratios for the outcomes are still debated. For some studies, HCN is the dominant product (Glarborg et al. 1998; Fikri et al. 2001; Eshchenko et al. 2002) while for others it is not (Zhang, Du & Feng 2004). Marcelino et al. (2010) showed that this reaction can vary the final abundance of HCN by several orders of magnitude. Although the conclusion obtained by Zhang et al. (2004) is not supported by many other authors, it shows that this reaction is still poorly constrained.

The results of the best-fitting model to the observed abundances of HNCO and its isomers for the four different environments considered here are shown in Fig. 1. The hot corino abundances (top-left panel) of HNCO as well as the upper limits for HCN and HOCN are reproduced within the best-fitting time-scale of [2.3–4] × 10$^5$ yr. The abundance of HCNCO varies by several orders of magnitude in this time-scale, and it even goes slightly above the upper limits (within a factor of ∼4) for a short period of time. Afterwards, its abundance drops quickly to values ≤10$^{-14}$. HOCN is well below the upper limit during this period. The sharp increase of the abundances of these molecules at ∼2 × 10$^6$ yr is due to the increase of the temperature in the hot corino above 100 K, which triggers the release of numerous radicals into the gas phase induced by the desorption of water.

For the cold envelope of IRAS 16293, the HNCO and HOCN abundances are also correctly reproduced, during the same period of time as the hot corino. Again, HNCO goes above the upper limits (within a factor of ∼3.5) but this time for an extended period of time, and it does not go below the observed upper limit during our best-fitting time-scale.

For both regions (hot corino and cold envelope), the HNCO and HOCN observed abundances (taken from Marcelino et al. 2010 and Martín-Doménech et al. 2017) are well reproduced while HCN seems to lay above the measured upper limits. Even though these differences are really small (less than a factor of 4 in both cases), it shows that HCN is still slightly overestimated. Finally, the time-scale of IRAS 16293 predicted by our modelling (of a few 10$^4$ yr) is consistent with the evolutionary stage of this object (Jaber Al-Edhari et al. 2017). In the hot corino, HNCO and its isomers are produced ∼75 per cent in the gas phase and ∼25 per cent on grain surfaces. The fraction formed on grains is then released into the gas phase via thermal desorption when the temperature reaches 100 K. However, in the cold envelope, grain-surface and gas-phase reactions are equally efficient. The fraction of HNCO (and of its isomers) formed on grains is non-thermally desorbed mainly via cosmic ray-induced UV photons. Chemical reactive desorption is not efficient in the release of HNCO in the cold envelope due to the high binding energy of this molecule to the grain surface.

For the two positions of the L1544 pre-stellar core, the best agreement between the observations and the modelled abundances is obtained [1–2] × 10$^7$ yr after reaching the final density during the collapse. At 5.35 × 10$^9$ yr, the final density is reached, allowing species to be efficiently produced on grain surfaces since the high visual extinction prevents UV photons from destroying or desorbing molecules. These newly and rapidly formed species are then injected in the gas phase thanks to non-thermal desorption (such as chemical reactive desorption), explaining the sharp peak of abundances seen at this time. Later on, these species are frozen back on to the grain surface, dramatically decreasing their gas-phase abundances.

Single-dish observations of HNCO and its isomers cannot disentangle whether the emission of these molecules comes from an external layer coincident with the methanol peak or from the core centre. Therefore, we used the same observed abundances for both cases (extracted from Marcelino et al. 2010). For the methanol peak position (lower-right panel), the HNCO and HOCN abundances are well fitted but HCNO is underestimated by a factor of ∼1.5 at least. While the HNCO and HOCN abundances remain rather constant within the best-fitting time-scale, HCNO is efficiently destroyed and its abundance drops by one order of magnitude in the time range of [1–2] × 10$^3$ yr after the end of the collapse. In contrast, for the core centre position, all species present much lower abundances than the observed values. This suggests that these molecules are likely formed in an external layer and not in the core centre, as also suggested for O-bearing COMs (Vastel et al. 2014; Jiménez-Serra et al. 2016). Moreover, recent observations performed by Spezzano et al. (2017) using the IRAM 30 m telescope show emission maps of HNCO towards this source. Even though the main emission region of HNCO is not coming from the same position where methanol peaks, it clearly comes from a region ∼30 arcsec (∼4000 au) away from the core centre, where the physical conditions are similar (see their fig. 1).

We note that the set of reactions modified to obtain a better agreement with the HCNO and HOCN observations were selected since they are the most efficient forming or destroying these two species. However, other reactions, not included yet in our network, might play an important role in the determination of the abundances of HCNO and HOCN. Indeed, Eshchenko et al. (2002) and Glarborg et al. (1998) have shown that the HCCO + NO ⇌ HCNO + CO could be an important pathway to form or destroy HCNO. The recent detection of unexpected high abundances of HCCO towards cold dark clouds (Agúndez et al. 2015) favours this idea. Glarborg et al. (1998) also suggested that HCNO could be efficiently recycled to NO through the reaction with OH. The two latter reactions are not included yet in the present network since further experimental investigations of reactions involving HCNO and HOCN are needed.

Finally, although the chemistry of HONC is included in the network, we do not analyse it here since its predicted abundances are always very low (< 10$^{-15}$) for all the different models. Moreover,
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4.2 CH$_3$NCO and isomers

As presented in Section 2.3, the CH$_3$NCO gas-phase network comes from Halfen et al. (2015). They proposed that reaction (20) could have a reaction rate up to $\sim 10^{-10}$ cm$^3$ s$^{-1}$ (Woodall et al. 2007). Since we also included the isomers of CH$_3$NCO in our study, as first approximation we consider that CH$_3$OCN and CH$_3$CNO follow similar formation and destruction routes to those of CH$_3$NCO (see Table 2). We have varied the reaction rate of these reactions to obtain satisfactory results for the measured upper limits of CH$_3$CNO and CH$_3$OCN towards the hot corino of IRAS 16293 (Ligerink et al. 2017; Martín-Doménech et al. 2017). We have used the same reaction rate for reactions between HNCO/HOCN/HCNO/HONC and CH$_3$ to produce CH$_3$NCO/CH$_3$OCN/CH$_3$CNO/CH$_3$ONC, respectively. The final reaction rate that best fits the observations is $5 \times 10^{-11}$ cm$^3$ s$^{-1}$. We also included the following set of reactions in the gas phase:

$$\text{HNCO} + \text{CH}_3 \rightarrow \text{CH}_3\text{OCN}$$
$$\text{HOCN} + \text{CH}_3 \rightarrow \text{CH}_3\text{NCO}$$
$$\text{HCNO} + \text{CH}_3 \rightarrow \text{CH}_3\text{ONC}$$
$$\text{HONC} + \text{CH}_3 \rightarrow \text{CH}_3\text{CNO}.$$
occurring. New experimental data will be needed to test this finding. In any case, if reaction (25) is set to $5 \times 10^{-11}$ cm$^3$ s$^{-1}$ (same as for HNCO + CH$_3$), the final abundance of CH$_3$NCO is only a factor of $\sim 3$ of the observed abundance, which is still a satisfactory result compared to observations.

The results of the modelling for CH$_3$NCO and its isomers, for the four different environments, are shown in Fig. 2. Since CH$_3$NCO has been detected recently in the ISM, only a few observational constraints exist for the different regions investigated here. CH$_3$NCO is clearly detected around the hot corino of IRAS 16293 (top-left panel), with an upper limit abundance of $[1.0–1.5] \times 10^{-10}$ (Ligterink et al. 2017; Martín-Domènech et al. 2017). In our model, the CH$_3$NCO abundance sharply increases around $2 \times 10^4$ yr. Indeed, once the temperature reaches 100 K, species such as CH$_3$ or HNCO (and its isomers) are thermally desorbed from the grain surface, enhancing the formation of CH$_3$NCO in the gas phase. From our analysis, CH$_3$NCO is produced in large quantities on the grain surface but it is then efficiently destroyed again on the surface through reaction (22). This conclusion is supported by recent experimental results where methylamine is detected while performing experiments on CH$_3$:HNCO mixtures at 20 K (Ligterink, private communication). Another possible destruction pathway on grain surfaces may involve the formation of N-methylformamide from successive hydrogenation of methyl isocyanate (Belloche et al. 2017):

\[
\text{#CH}_3\text{NCO} + \text{#H} \rightarrow \text{#CH}_3\text{NHCO} \quad (28)
\]

\[
\text{#CH}_3\text{NHCO} + \text{#H} \rightarrow \text{#CH}_3\text{NHCHO} \quad (29)
\]

However, N-methylformamide is not detected as a product in the experiments of the CH$_3$:HNCO mixtures at 20 K (Ligterink, private communication), suggesting that the hydrogenation of CH$_3$NCO could be ineffective. We note that models including the destruction reactions of CH$_3$NCO into N-methylformamide provided similar results to those considering the methylamine destruction route. In either case, the main contribution to the final gas-phase abundance of CH$_3$NCO comes from gas-phase reactions. The predicted abundances of CH$_3$OCN and CH$_3$CNO are orders of magnitude lower than that of CH$_3$NCO as a result of the low abundances of HOCN and HCNO in the gas phase. The CH$_3$NCO abundance and the upper limits of CH$_3$OCN and CH$_3$CNO are well
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4.3 NH$_2$CHO

As presented in Section 2.2, the main mechanisms proposed to form formamide are hydrogenation of HNCO (Charnley 1997; Raunier et al. 2004), the radical–radical reactions of NH$_2$ and HCO/H$_2$CO on the surface of dust grains (Fedoseev et al. 2016), and the gas-phase reaction NH$_2$ + H$_2$CO → NH$_2$CHO + H (Barone et al. 2015; Skouteris et al. 2017). When considering these three formation routes in our models, discrepancies (by more than a factor of 10) clearly arise between the predicted and observed abundances of formamide for the cold envelope and the L1544 models. At low temperatures (≤20 K), the formation of this molecule is driven by hydrogenation and/or gas-phase formation.

In order to obtain a better match to the observations, we investigated the possibility that the rate of the gas-phase reaction NH$_2$ + H$_2$CO → NH$_2$CHO + H has an energy barrier slightly higher than 4.88 K as recently estimated by Skouteris et al. (2017). In Fig. 3 (top-left panel), we compare the different reaction rates calculated by Barone et al. (2015) and Skouteris et al. (2017, see the red and blue lines). In this figure (top-right panel and lower panels), we also present the predicted abundances of formamide for the hot corino and cold envelope cases of IRAS 16293, and for the methanol peak of L1544, considering only the production

![Figure 3.](https://example.com/figure3.png)

**Figure 3.** Top left panel: reaction rates of NH$_2$ + H$_2$CO → NH$_2$CHO as a function of temperature for several rates taken from the literature (in blue and red) and our study (in yellow). Other panels: final abundance of NH$_2$CHO as a function of time for three different environments: hot corino IRAS 16293 B (top-right panel), cold envelope of IRAS 16293 (bottom-left panel), and methanol peak of L1544 (bottom-right panel). The two different colours represent the rate used in our study for this reaction (in red) and the rate described in Skouteris et al. (2017, in blue). The time-scale for which we obtain the best agreement between the modelling and observations is shown in vertical grey-scale. Observational constraints are shown in horizontal coloured area or in dashed lines for upper limits.
of this molecule via gas-phase reactions. From Fig. 3, the Barone et al. (2015) rate is at least two orders of magnitude higher than the Skouteris et al. (2017) rates for temperatures $\geq 10$ K, and therefore it largely overproduces formamide in all sources considered in this study (e.g. by a factor of 100 for L1544). The new Skouteris et al. (2017) rate provides a better agreement with observations, although a small overproduction (by a factor of $\sim 2$) exists for the model of the cold envelope of IRAS 16293 (see the light blue line in the lower-left panel of Fig. 3). In any case, when hydrogenation and radical–radical surface reactions are considered, this overproduction is even clearer not only for the model of the IRAS 16293 cold envelope, but also for the L1544 pre-stellar core (by factors of $\geq 10$ for both sources). Therefore, we changed the small barrier of 4.88 K calculated by Skouteris et al. (2017) to a higher value of 25 K closer to the one found by Barone et al. (2015) of 26.9 K. The resulting reaction rate, which is a combination of both the Barone et al. (2015) and Skouteris et al. (2017) rates (see the yellow curve in the top-left panel of Fig. 3), is smaller at 10–20 K, and hence the predicted abundance of formamide in the cold envelope of IRAS 16293 is better reproduced. At higher temperatures ($\geq 70$ K), our proposed reaction rate is very close to the one from Skouteris et al. (2017, see the top-left panel of Fig. 3), so that the inclusion of the 25 K activation barrier does not affect the predicted abundances of formamide at temperature $\geq 70$ K, as shown for the hot corino model (see the top-right panel in Fig. 3). In the models below, we therefore assume an activation barrier of 25 K for the gas-phase formation route of formamide $\text{NH}_2 + \text{H}_2\text{CO} \rightarrow \text{NH}_2\text{CHO} + \text{H}$.

The results of the modelling for $\text{NH}_2\text{CHO}$, for the four different environments considered in this work, are shown in Fig. 4. This figure presents the abundances of $\text{NH}_2\text{CHO}$ alongside those of $\text{NH}_2$ and $\text{H}_2\text{CO}$, two important parent species of formamide. For the hot corino of IRAS 16293, the observed abundance of formamide was taken from Coutens et al. (2016, note that this value should be considered as an upper limit) and from the inferred value of López-Sepulcre et al. (2015). In both cases, our predicted abundance agrees well (within a factor of 1.7) with the observed values. The modelled abundance of $\text{H}_2\text{CO}$ also agrees well while the $\text{NH}_2$ abundance is consistent within a factor of $\sim 2.2$ with respect to observations. The large enhancement of these species at $\sim 2 \times 10^4$ yr is again due to the thermal desorption of the ices once the temperature in
the hot corino reaches 100 K. Indeed, the formamide abundance greatly increases when H$_2$CO – a key parent species of formamide in the gas phase – also increases. Moreover, at this temperature, all the formamide contained on the grain surface and formed at lower temperatures through radical–radical and hydrogenation reactions (with $T \gtrsim 40$ K) is also released into the gas phase.

The abundance of formamide in the cold envelope of IRAS 16293 agrees well (within a factor of 3) with the observed value derived by López-Sepulcre et al. (2015). The abundance of formamide is enhanced around $\sim 10^7$ yr because of the higher temperature (20 K), which favours the hydrogenation of HNCO. For NH$_3$ and H$_2$CO, we use the observed abundances presented in Hily-Blant et al. (2010) and Ceccarelli et al. (2000). While the predicted abundance of H$_2$CO matches the observations, the NH$_3$ abundance is overestimated by factors of 2–8. As we discuss in Section 5, better agreement between the predicted and observed abundances of formamide is achieved for the cold envelope of IRAS 16293 when hydrogenation reactions are switched off in our models.

For the cold core L1544, NH$_3$ abundance has not been observationally constrained, and therefore we use the chemically related species NH$_2$ to test the chemical network of NH$_3$. As for HNCO and its isomers, the H$_2$CO single-dish observations cannot disentangle whether their emission arises from the core centre or from an external layer coincident with the methanol peak position, and hence we use the same observed abundances for the two positions. By comparing the results shown in the bottom-left and bottom-right panels of Fig. 4, we conclude that the emission region of H$_2$CO has to be located in an external layer of the core, since the abundances predicted for the methanol peak position reproduce the observed values. Moreover, the H$_2$CO abundance for the core centre is much lower as a result of the severe freeze-out, showing that this species is not expected to be abundant in the gas phase towards this region. For NH$_3$, the predicted abundance of the methanol peak is only overestimated by a factor of 2 with respect to the value obtained by the interferometric observations of Crapsi et al. (2007). However, for the core centre, the modelled abundance is much lower than the observed value. Recently, Caselli et al. (2017) also found that their chemical model predicts a much lower abundance in the central part of L1544 and they concluded that several factors might play an important role in this discrepancy, such as the underestimation of the production of gas-phase NH$_3$. The observed upper limits of NH$_2$CHO in L1544 ($\lesssim 2.4 \times 10^{-11}$; Jiménez-Serrra et al. 2016) agree well with our predictions for the estimated age of the core. As for HNCO and its isomers, the same effect is seen between $[5.3–5.4] \times 10^6$ yr when the final density in the collapse is reached: the abundances of NH$_3$, H$_2$CO, and NH$_2$CHO reach their peak values to then decrease later on as a consequence of severe freeze-out on to dust grains (see Section 4.1 for a more detailed explanation).

5 THE FORMATION OF FORMAMIDE ACROSS MULTIPLE ENVIRONMENTS

The origin of formamide is a subject of strong debate and, as presented in Section 2.2, three main processes have been proposed for the formation of this molecule based on laboratory experiments, theoretical calculations, and observations: (i) the hydrogenation of HNCO on grain surfaces; (ii) radical–radical formation on grains; (iii) or radical–radical association in the gas phase. In the following, we investigate which of these processes are strictly needed to reproduce the observations of this molecule across multiple environments, and which processes dominate depending on the physical conditions of the source.

In Fig. 5, we show the modelled abundance of NH$_2$CHO using different combinations of these processes for the hot corino (upper panel), cold envelope of IRAS 16293, and for the methanol peak of the L1544 pre-stellar core. From these figures, one notes that if we switch off one or several of these processes, the predicted abundance of formamide can vary up to an order of magnitude. For the hot corino case (Fig. 5, top panel), the gas-phase-only network does not produce enough formamide in the gas phase, indicating that grain-surface reactions may be required to match the observations. In contrast, the network considering only grain-surface reactions gives closer values to the observed abundance, with the radical–radical network alone providing the best match (see the purple line in the top panel of Fig. 5).

For the cold envelope of IRAS 16293, an interesting behaviour is found with three distinct groups of reactions (see the middle panel of Fig. 5). Due to the low temperatures in the envelope ($\lesssim 20$ K), the radical–radical-only network predicts very low abundances of formamide (see the purple arrow) because NH$_3$ and H$_2$CO are not mobile on the grain surface. Therefore, the chemistry of formamide in this region is driven either by hydrogenation or gas-phase reactions. Three options are then considered: hydrogenation only, gas phase only, and the combination of the two. The hydrogenation-only network gives a higher abundance for formamide than the gas-phase one (by a factor of 3), with the gas-phase-only network perfectly matching the observations.

A similar behaviour is found for the methanol peak position of L1544 where a very low formamide abundance is expected (see the lower panel in Fig. 5). Again, radical–radical reactions are ineffective and the chemistry is only driven either by hydrogenation or gas-phase reactions. In this case, however, it is not possible to constrain which of the two processes govern the formation of formamide since both predict abundances below the measured upper limits.

In summary, this experiment thus favours a combination of gas-phase reactions and radical–radical reactions on grain surfaces to explain the observed abundances of formamide across multiple astrophysical environments. This result is in agreement with the laboratory experiments of Noble et al. (2015) and Fedoseev et al. (2015), who showed that the intermediate product #H$_3$NCO formed after the hydrogenation of HNCO on grain surfaces does not yield #NH$_2$CHO but HNCO after another successive hydrogenation.

6 THE ORIGIN OF THE OBSERVED CORRELATION BETWEEN HNCO AND NH$_2$CHO

As discussed in Section 5, hydrogenation reactions on the surface of dust grains are likely not responsible for the formation of formamide in the ISM. This mechanism was proposed to explain the tight correlation observed between HNCO and NH$_2$CHO in star-forming regions and reported by Mendoza et al. (2014) and López-Sepulcre et al. (2015). In this section, we analyse whether this correlation is due to other factors associated with the chemistry of HNCO and NH$_2$CHO.

In Fig. 6, we show the NH$_2$CHO abundance as a function of the HNCO (left-hand panel) and H$_2$CO (right-hand panel) abundances predicted by our model for the four different environments selected in our study. Similar plots have been presented by Mendoza et al. (2014, green rectangular points associated with the dotted line) and López-Sepulcre et al. (2015, brown diamond points associated with the dash–dotted line) but mainly for sources with higher abundances of formamide and isocyanic acid. The black dashed and solid lines
Figure 5. Final abundance of NH$_2$CHO as a function of time for three different environments: hot corino IRAS 16293 B (top panel), cold envelope of IRAS 16293 (middle panel), and methanol peak of L1544 (bottom panel). Each colour represents a different chemical network for the formation of formamide. The time-scale for which we obtain the best agreement between the modelling and observations is shown in vertical grey-scale. Observational constraints are shown in horizontal coloured area or in dashed lines for upper limits.

are, respectively, a power-law fit to the observed and to the modelled abundance values. In our study, we derive different trends than the one derived by Mendoza et al. (2014) and López-Sepulcre et al. (2015) because we are considering the observed abundance values derived in cold sources for which the abundances of NH$_2$CHO, HNCO, and H$_2$CO are lower than in other type of source (e.g. hot corino or shock regions). Indeed, even though the study of López-Sepulcre et al. (2015) also contains cold sources (see the brown diamond points), the authors only considered some of these points to derive their fit (see the filled points in the left-hand panel of Fig. 6). The power-law fits we derive for all the observed points (red, green, and brown points) are given by the equations $[\text{NH}_2\text{CHO}] = 32.14 \times [\text{HNCO}]^{1.29}$ and $[\text{NH}_2\text{CHO}] = 4.65 \times [\text{H}_2\text{CO}]^{1.39}$.

The left-hand panel shows that a tight correlation between HNCO and NH$_2$CHO can be drawn. However, note that hydrogenation reactions for NH$_2$CHO have been removed in this example. This clearly illustrates how the correlation of HNCO and NH$_2$CHO does not come from a direct chemical link between the two, but rather from the same response of the two species to environmental conditions (more precisely to temperature). The changes in gas density do not seem to drive this correlation because the L1544 core centre model has a higher density than the cold envelope of IRAS 16293 but the abundance of both species is much lower in the former than in the latter. However, the temperature progressively increases from L1544 to the cold envelope of IRAS 16293, to the hot corino, triggering different processes on the surface of dust grains such as radical diffusion and thermal evaporation, both important mechanisms in the formation of formamide. Note that non-thermal desorption processes are responsible for the difference between the predicted abundances of NH$_2$CHO and HNCO between the positions of the core centre and the methanol peak.

In the right-hand panel of Fig. 6, we demonstrate that NH$_2$CHO is correlated with H$_2$CO but this time the correlation is due to a chemical link between the two molecules. The latter observational trend was less clear in Mendoza et al. (2014) than for HNCO because H$_2$CO is much more reactive in the gas phase than HNCO. This shows that one should be cautious over interpreting correlations between two molecules because it does not necessary imply that the two species are chemically linked (chemical correlation) but rather that they are formed through similar processes across different environments (physical correlation).

7 CONCLUSIONS

We have updated UCLCHEM with a new treatment of grain-surface reactions by adding several processes such as diffusion of molecules on the grain surface, chemical reactive desorption, and reaction–diffusion competition. With this new treatment, we implemented a new set of reactions to model the abundance of molecules with peptide-like bonds (e.g. HNCO, NH$_2$CHO, CH$_3$NCO) in various star-forming environments ranging from cold dark cores to hot cores found in low-mass proto-stars. We studied the impact of gas-phase and grain-surface chemistry on the formation of formamide, and we found that hydrogenation of HNCO to form NH$_2$CHO tends to overestimate its abundance. The gas-phase reaction needs to be coupled with radical–radical reactions on the grain surface to recover the observed abundance in the hot corino model. Moreover, our results show that the gas-phase reaction to form formamide $\text{NH}_2 + \text{H}_2\text{CO} \rightarrow \text{NH}_2\text{CHO} + \text{H}$ might have a higher activation barrier of 25 K instead of the calculated 4.88 K. HNCO and CH$_3$NCO abundances are well reproduced, and we discussed the impact of important reactions to form and destroy these two species.
Figure 6. Left-hand panel: modelled (in blue) and observed (in red) \( \text{NH}_2\text{CHO} \) abundance as a function of HNCO for the four different environments selected in our study. Green rectangular and brown diamond points represent the values taken from Mendoza et al. (2014) and López-Sepulcre et al. (2015), respectively. The black line shows a fitted power-law profile to the modelled abundances. The dotted and dash–dotted lines are previous fits obtained by Mendoza et al. (2014) and López-Sepulcre et al. (2015), respectively. The black dashed line represents a fitted power-law profile to all the observations (red, green, and brown points). Filled points are the ones used to determine the López-Sepulcre et al. (2015) fit. The small insert on the bottom right shows a better representation of the distribution of the observed points around the fitted profile (dashed line). Right-hand panel: same as the left-hand panel with \( \text{H}_2\text{CO} \) instead of HNCO.

and we give better constraints to the reaction rates of the methylation of CHNO isomers. Finally, the modelled abundances of HNCO and \( \text{NH}_2\text{CHO} \) show a power-law correlation despite the absence of the hydrogenation of HNCO to form \( \text{NH}_2\text{CHO} \), demonstrating that this correlation inherits from an environmental behaviour driven by the temperature instead of a pure chemical link.

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REFERENCES

Agúndez M. et al., 2015, A&A, 579, L10
Altweg K. et al., 2017, MNRAS, 469, S130
Awad Z., Viti S., Collings M. P., Williams D. A., 2010, MNRAS, 407, 2511
Bacmann A., Lefloch B., Ceccarelli C., Steinacker J., Castets A., Loinard L., 2003, ApJ, 585, L55
Barone V., Latouche C., Skouteris D., Vazart F., Balucani N., Ceccarelli C., Lefloch B., 2015, MNRAS, 453, L31
Belloche A. et al., 2017, A&A, 601, A49
Bizzocchi L., Caselli P., Spezzano S., Leonardo E., 2014, A&A, 569, A27
Bottinelli S., Wakelam V., Caux E., Vastel C., Aikawa Y., Ceccarelli C., 2014, MNRAS, 441, 1964
Brünen S., Gottlieb C. A., McCarthy M. C., Thaddeus P., 2009, ApJ, 697, 880
Caselli P., Walmsley C. M., Zucconi A., Tafalla M., Dore L., Myers P. C., 2002, ApJ, 565, 344
Caselli P., van der Tak F. F. S., Ceccarelli C., Bacmann A., 2003, A&A, 403, L37
Caselli P. et al., 2017, A&A, 603, L1
Ceccarelli C., Loinard L., Castets A., Tielens A. G. G. M., Caux E., 2000, A&A, 357, L9
Cernicharo J. et al., 2016, A&A, 587, L4
Chang Q., Herbst E., 2014, ApJ, 787, 135
Chang Q., Herbst E., 2016, ApJ, 819, 145
Chang Q., Cuppen H. M., Herbst E., 2007, A&A, 469, 973
Charnley S. B., 1997, in Cosmovici C. B., Bowyer S., Werthimer D., eds, IAU Colloq. 177: Astronomical and Biochemical Origins and the Search for Life in the Universe. Editrice Compositori, Bologna, p. 89
Charnley S. B., 2001, ApJ, 562, L99
Coutens A. et al., 2016, A&A, 590, L6
Crapsi A., Caselli P., Walmsley M. C., Tafalla M., 2007, A&A, 470, 221
Crimier N., Ceccarelli C., Maret S., Bottinelli S., Caux E., Kahane C., Lis D. C., Olofsson J., 2010, A&A, 519, A65
Crovister J., Bockelée-Morvan D., Colom P., Biver N., Despois D., Lis D. C., Team target-of-opportunity radio observations of comets, 2004, A&A, 418, 1141
Cuppen H. M., van Dishoeck E. F., Herbst E., Tielens A. G. G. M., 2009, A&A, 508, 275
Cuppen H. M., Walsh C., Lamberts T., Semenov D., Garrod R. T., Pentelho E. M., Ioppolo S., 2017, Space Sci. Rev., 212, 1
Dalbouha S., Senent M. L., Domínguez-Gómez R., 2016, J. Chem. Phys., 145, 124309
Eshchenko G., Köcher T., Kerst C., Temps F., 2002, Chem. Phys. Lett., 356, 181
Fedoseev G., Ioppolo S., Zhao D., Lamberts T., Linnartz H., 2015, MNRAS, 446, 439
Fedoseev G., Chuang K.-J., van Dishoeck E. F., Ioppolo S., Linnartz H., 2016, MNRAS, 460, 4297
Fikri M., Meyer S., Roggenbuck J., Temps F., 2001, Faraday Discuss., 119, 223
Garrod R. T., 2013, ApJ, 765, 60
Garrod R. T., Pauly T., 2011, ApJ, 735, 15
Garrod R. T., Widicus Weaver S. L., Herbst E., 2008, ApJ, 682, 283
Gillespie D. T., 1976, J. Comput. Phys., 22, 403

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In this appendix, we detail our updates to the treatment of the grain-surface processes applied to the gas–grain chemical code uclchem.

## A1 Grain-surface diffusion

We have implemented in uclchem the diffusion mechanism described in Hasegawa et al. (1992). This formalism is extensively used in the literature in several chemical codes (e.g., NAUTILUS; Raud et al. 2016). Briefly, the rate at which two species A and B can diffuse and mix on the grain surface is given by

\[ k_{AB} = \kappa_{AB} \left( \frac{k_{\text{hop}}^A + k_{\text{hop}}^B}{n_{\text{site}} n_{\text{dust}}} \right), \tag{A1} \]

where \( n_{\text{site}} \sim 2 \times 10^6 \) is the number of sites on the grain surface and \( n_{\text{dust}} \) is the number density of dust grains:

\[ n_{\text{dust}} = \frac{3 n_{\text{H}} \text{amu}}{4\pi r_{\text{gr}}^2 n_{\text{gtd}} \text{gd}^2}, \tag{A2} \]

where \( r_{\text{gr}} = 0.1 \mu\text{m} \) is the grain radius, \( n_{\text{gtd}} \) is the density of a dust grain assumed to be \( 3 \text{ g cm}^{-3} \), \( \text{gd} = 100 \) is the gas-to-dust mass ratio, \( n_{\text{H}} \) is the total hydrogen number density, and \( \text{amu} = 1.66053892 \times 10^{-24} \) is the atomic mass unit.

\( k_{\text{hop}}^X \) is the thermal hopping rate of the species \( X \) on the grain surface defined as (Hasegawa et al. 1992)

\[ k_{\text{hop}}^X = \frac{1}{h_{\text{hop}}} = v_0 \exp \left( -\frac{E_h}{T_{\text{gr}}} \right), \tag{A3} \]

where \( h_{\text{hop}} \) is the hopping time between two grain-surface sites, \( T_{\text{gr}} \) is the grain temperature, and \( E_h \) is the diffusion energy in K (potential energy well to be overcome between two surface sites). \( E_h \) is estimated using the binding energy of the species on to the grain surface. \( E_h \). Several values have been tested in the literature, and we adopted the most commonly used of \( E_h = 0.5 E_b \) as suggested by recent results from Minissale, Congiu & Dulieu (2016b). This value has also been used recently by Vasyunin et al. (2017). \( v_0 \) is

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**APPENDIX A: CHEMICAL PROCESSES ADDED TO uCLCHEM**

- Taquet V., López-Sepulcre A., Ceccarelli C., Neri R., Kahane C., Coutens A., Vastel C., 2013, ApJ, 768, L29
- Tideswell D. M., Fuller G. A., Millar T. J., Markwick A. J., 2010, A&A, 510, A85
- Tsang W., 1992, J. Phys. Chem. Ref. Data, 21, 753
- Turner B. E., Terziva R., Herbst E., 1999, ApJ, 518, 699
- van Dishoeck E. F., Blake G. A., Jansen D. J., Groesbeck T. D., 1995, ApJ, 447, 760

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**REFERENCES**

- Vasyunin A. I., Semenov D. A., Wibe D. S., Henning T., 2009, ApJ, 691, 1459
- Vasyunin A. I., Caselli P., Dulieu F., Jiménez-Serra I., 2017, ApJ, 842, 33

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**Notes:**

- The equations and references are extracted from the scientific document. The text is formatted to match the original style as closely as possible.
the characteristic vibration frequency of species X and is calculated as (Hasegawa et al. 1992)

\[ \nu_0 = \sqrt{\frac{2k_B n_S E_D}{\pi^2 m}}. \tag{A4} \]

where \( k_B \) is the Boltzmann constant, \( n_S \) is the site density on the grain surface, and \( m \) is the mass of species X. \( n_S \) is linked to \( N_{\text{site}} \) using

\[ n_S = \frac{N_{\text{site}}}{4 \pi r_g^2}. \tag{A5} \]

In UCLCHEM, \( n_S \) is fixed to \( 1.5 \times 10^{15} \text{ cm}^{-2} \) and is used to calculate the value of \( N_{\text{site}} \). The typical range value for \( \nu_0 \) is between \( 10^2 \) and \( 10^3 \text{ s}^{-1} \). The term \( \kappa_{AB} \) in equation (A1) defines the probability for the reaction between species A and B to occur. This probability can be described using a quantum mechanical probability for tunnelling through a rectangular barrier of thickness \( a \):

\[ \kappa_{AB} = \exp \left[ -\frac{2a}{\hbar} \sqrt{\frac{2}{\mu k_B E_A}} \right], \tag{A6} \]

where \( \hbar \) is the reduced Planck constant, \( \mu \) is the reduced mass, and \( E_A \) is the activation energy in K of the reaction. The rectangular barrier thickness is typically assumed to be 1 Å (Hasegawa et al. 1992). However, we use a value of 1.4 Å in our study as it fits better the ice composition. A similar approach has been taken by Vasyunin et al. (2017), who found that a width of 1.2 Å fitted better their results. We note that the rectangular barrier thickness value has been modified in recent studies to range between 1.0–2.0 Å (Garrod & Pauly 2011; Taquet et al. 2013; Vasyunin et al. 2017).

The probability \( \kappa_{AB} \) can also be expressed as

\[ \kappa_{AB} = \exp \left[ -\frac{E_A}{T_{gr}} \right]. \tag{A7} \]

UCLCHEM automatically chooses which probability is the largest between equations (A6) and (A7) and uses it in equation (A1). For exothermic and barrierless reactions, \( E_A \) is null and equations (A6) and (A7) give a probability \( \kappa_{AB} \) equal to one.

### A2 Reaction–diffusion competition

The grain-surface diffusion rate calculated above only considers that the species A and B are moving on the grain surface prior to reacting. However, molecules and radicals may directly form in a given surface site and directly react in situ before moving to an adjacent site. Finally, the species A and B can also evaporate from the grain surface before having the opportunity to react or diffuse. The combination of these effects is called the reaction–diffusion competition, and it has been introduced by Chang et al. (2007) and Garrod & Pauly (2011). To take into account this effect, we define the probabilities for the diffusion, reaction, and evaporation for species A and B (Chang et al. 2007):

\[ p_{\text{diff}} = \kappa_{\text{hop}}^{AB} + \kappa_{\text{hop}}^B, \tag{A8} \]

\[ p_{\text{reac}} = \max(v_0^{A}, v_0^{B}) \times \kappa_{AB}, \tag{A9} \]

\[ p_{\text{evap}} = v_0^A \exp \left( -\frac{E_A}{T_{gr}} \right) + v_0^B \exp \left( -\frac{E_B}{T_{gr}} \right), \tag{A10} \]

where the result of \( \max(v_0^{A}, v_0^{B}) \) represents the largest value of the characteristic frequencies of species A and B (Garrod &

### A3 Chemical reactive desorption

Desorption of species from the grain surface can occur thanks to various thermal and non-thermal processes such as direct and cosmic ray-induced UV photons, direct cosmic rays, and \( \text{H}_2 \) formation, as described in Holdship et al. (2017). We have added to UCLCHEM the chemical reactive desorption formalism defined by Minissale et al. (2016a). This semi-empirical formalism describes the efficiency \( \eta_{CD} \) of an exothermic reaction occurring on the surface of dust grains, to release products in the gas phase. \( \eta_{CD} \) depends on the binding energies of the reactants and the exothermicity of the reaction (Minissale et al. 2016a; Vasyunin et al. 2017):

\[ \eta_{CD} = \exp \left[ \frac{-E_D N_{\text{det}}}{\epsilon_{CD} \Delta H_R} \right], \tag{A12} \]

where \( N_{\text{det}} \) is the degree of freedom and is defined by \( N_{\text{det}} = 3 \times n_{\text{atoms}} \). \( \Delta H_R \) is the enthalpy of the reaction, and it can be derived using the following equation:

\[ \Delta H_R[K] = \left[ \sum_{\text{reac}} \Delta_{1} H - \sum_{\text{prod}} \Delta_{1} H \right] \times \frac{4184}{k_B N_A} + E_A. \tag{A13} \]

The enthalpy of formation \( \Delta H \) of both reactants and products is given in kcal mol\(^{-1}\) and converted in K using the kcal-to-J conversion factor of 4184 J kcal\(^{-1}\). \( N_A \) is the Avogadro number.

To be desorbed from the grain surface to the gas phase, products need to gain velocity in a direction perpendicular to the surface. Therefore, in the Minissale et al. (2016a) formalism, products need to bounce against the surface in an elastic collision. The fraction of kinetic energy \( \epsilon_{CD} \) retained by the product of mass \( m \) colliding with the surface with effective mass \( M \) is then defined by

\[ \epsilon_{CD} = \frac{(m - M)^2}{(m + M)^2}. \tag{A14} \]

The effective mass \( M \) of the grain surface is a poorly constrained parameter. Its value has been estimated to be approximately 130 amu (equivalent to the mass of 11 carbon atoms; Hayes et al. 2012). This mass is larger than that of a single carbon atom because the surface is acting as a group rather than individually in the collision. Minissale et al. (2016a) suggested that a value of 120 amu well reproduces the trend of their experimental chemical reactive desorption measurement for bare grains. Vasyunin et al. (2017) varied the effective mass between 80 and 120 amu, and the resulting abundances can change by an order of magnitude, although their predicted trend does not. In order to be consistent with the studies of Minissale et al. (2016a) and Vasyunin et al. (2017), we have fixed the value of \( M \) to 120 amu.

Finally, the expression (A12) is only valid for bare grains. In the case of ASW surfaces, Minissale et al. (2016a) derived that \( \eta_{CD}^{\text{bare}} = \eta_{CD}^{\text{bare}}/10 \). We have also used this value in UCLCHEM. In addition, we have adopted their constraints to the following chemical reactive desorption coefficients: \( \eta_{CD}^{\text{OH}}(\text{OH} + \text{H}) = 25 \text{ per cent} \), \( \eta_{CD}^{\text{OH}}(\text{O} + \text{H}) = 30 \text{ per cent} \), \( \eta_{CD}^{\text{N}}(\text{N} + \text{N}) = 50 \text{ per cent} \).
A4 Limitations of the rate equation approach

We note that large differences can be found between the rate equation approach and stochastic methods (such as Monte Carlo models; see e.g. Cuppen et al. 2009; Vasyunin et al. 2009; Chang & Herbst 2014, 2016; Lamberts, de Vries & Cuppen 2014). The rate equation approach considers macroscopic effects directly applied to grain surfaces that may lead to large uncertainties, especially when abundances of reactants on the grain surface are low (Gillespie 1976; Charnley 2001; Green et al. 2001). However, we use the rate equation approach in UCLCHEM because of the convenience, stability, and the rather fast numerical performance of the code, even for reaction networks consisting of thousands of reactions involving hundreds of molecules (see review by Cuppen et al. 2017). More complex codes (stochastic or not) can be much slower, depending on the complexity of the chemistry (bulk chemistry, 2D, 3D,...) taking typically days or weeks to run compared to the minutes required for the rate equation approach.

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