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Gas-phase chemistry and molecular complexity in space: how far do they go?

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Abstract. In the sequence of steps which are alleged to have led from elementary particles to the emergence of life, an important one is the formation of relatively complex organic molecules from the simple parent species abundant in space. The combination of H, O, C, N and other atoms into molecules and their following chemical evolution have been continuously taking place in the Universe, as proved by the detection of *ca.* two hundred gaseous molecules in the interstellar medium, including also species with a prebiotic potential. The processes leading to interstellar complex organic molecules under the extreme conditions of interstellar objects are not fully understood. Most current astrochemical models privilege grain-surface chemistry because gas-phase chemistry is not believed to have the capability of leading to complex species. Nevertheless, as recently pointed out by experimental and theoretical work on several gas-phase reactions, many gas-phase routes have actually been overlooked, while their inclusion in the astrochemical models with the parameters determined in laboratory experiments or via accurate theoretical calculations could be decisive in reproducing the observed abundances of complex organic molecules. In this contribution, the status of our knowledge of interstellar gas-phase chemistry will be addressed.

Key words. ISM: molecules – ISM: abundances – ISM: molecular processes

1. Introduction

Our galaxy features a surprisingly large variety of molecules in the interstellar medium and, in particular, in the interstellar clouds (ISCs), *i.e.*, the regions among stars (and their planetary systems) where the interstellar baryonic matter is mainly confined. ISCs are characterized by temperatures as low as 10 K and number densities between $10^4 - 10^6$ cm^{-3}. The surprise comes from the fact that those physical conditions are far from being favorable to chemical evolution, which is promoted by the energy available to the system and frequent molecular encounters. Yet, more than 200 molecules have been identified so far (McGuire 2018) among which *ca*. 70 contain more than five atoms and can be considered relatively complex given the boundary conditions. All of them are organic molecules and most of them contain, in addition to carbon and hydrogen, either O or N atoms or both. Conventionally, these molecules are indicated as *interstellar complex organic molecules*, from now on indicated with iCOMs (see Ceccarelli et al. 2017; Herbst & van Dishoeck 2009). Interestingly, even though they are much simpler than life-molecules, they contain the same elements and chemical functional groups. For this reason, a fascinating hypothesis is that iCOMs are the seeds that might inseminate planets with organic chemistry via falling comets/asteroids/meteorites after solar system formation. Those small bodies, formed at the periphery of protosolar nebulae, can preserve the inventory of iCOMs during the solar system formation and, subsequently, fecundate the newly formed planets (Caselli & Ceccarelli 2012).

Understanding the chemistry occurring in ISCs is, therefore, both a great challenge to the community of chemists – because the capability of the molecules to react is pushed to its extremes – and a fascinating subject – because of the potential implication in prebiotic chemistry. This is an important part of the research field of *astrochemistry* and it requires a multidisciplinary approach. In the early attempts to interpret interstellar chemical complexity, ion-molecule reactions were first considered to be entirely responsible for molecule formation because of their typically large rate coefficients (Herbst & Klemperer 1973; Dalgarno & Black 1976; Watson 1974). Reactions involving ions (in particular, positive ions) are typically very fast and, therefore, efficient also under the extreme conditions of ISCs. However, the ionization degree of ISCs is small and most atoms or molecules are in neutral form. For this reason, in the astrochemical models the final step in the complex ion-molecule reaction chains is the conversion of the ionic species into their neutral counterparts. This step was believed to consist in electron-ion recombination reactions with the release of one H atom and the preservation of the ion molecular skeleton. Later on, however, there was experimental evidence (Geppert & Larsson 2008) that electron-ion recombination reactions are often strongly dissociative and rather produce small neutral moieties because of the large amount of energy liberated by the process (the ionization potential).

In the early 90s, instead, the role of neutral-neutral reactions was acknowledged after being disregarded for many years. The common belief that they are too slow to give a significant contribution drastically changed thanks to an experimental method specifically devised to investigate the kinetics of bimolecular reactions at very low temperatures, the CRESU (Cinétique de Réaction en Ecoulement Supersonique Uniforme, standing for Reaction Kinetics in a Uniform Supersonic Expansion) technique, which proved, for the first time in laboratory experiments, that the rate coefficients of barrier-less neutral-neutral reactions can reach the gas-kinetics limit at very low T (see, for instance, Smith & Rowe 2000; Smith 2002, 2003). After that, neutral-neutral reactions have been included in astrochemical models, significantly enriching the palette of interstellar chemistry (Wakelam et al. 2012; Millar et al. 1997). Nonetheless, the variety, distribution and abundance of iCOMs remain difficult to be accounted for in astrochemical models.

Given that about 1% of ISCs is composed by submicron sized silicates and amorphous graphite particles, it has been suggested that interstellar grains covered by icy mantles play an important role in synthesizing iCOMs by acting as heterogeneous catalysts (e.g. Garrod & Herbst 2006; Garrod et al. 2008; Linnatz et al. 2015). In this scenario several radicals, which are formed by the far-ultraviolet photodissociation of the ice-trapped molecules or by incomplete hydrogenation of simple species, remain trapped in the iced mantles until they can acquire some mobility (above 30 K) and have the chance to meet each other and recombine into iCOMs. However, the recent observation of several iCOMs also in very cold ISCs (below 30 K only H atoms are able to move around dust particles) has challenged this explanation (see Balucani et al. 2015; Vasyunin et al. 2013, and references therein). In addition, the characterization of several ice-assisted radical recombination reactions at the atomic and molecular level does not seem to support that mechanism unless the radicals are oriented in a way for the recombination reaction to occur, while, in most cases, the interaction with the water-ice molecules might interfere and favour other two-product reactions (Enrique-Romero et al. 2016; Rimola et al.

2018; Enrique-Romero et al. 2019). The inclusion of grain-induced chemistry in recent astrochemical models has improved the capability of reproducing the observed iCOMs abundances (e.g. Garrod et al. 2008; Balucani et al. 2015; Ruaud et al. 2016; Skouteris et al. 2017, 2018; Vasyunin et al. 2017), but critical cases remain. In particular, the abundance of deuterated iCOMs in star forming regions, as determined by accurate ALMA interferometric observations, is difficult to reproduce with the available models and network of chemical reactions (Jorgensen et al. 2018).

A close inspection of the chemical networks (including several thousand elementary reactions, see the most common databases UMIST2012 by McElroy et al. (2013) and KIDA2014 by Wakelam et al. (2015) used in astrochemical models reveals one important drawback of all models: many of the considered processes have never been investigated in laboratory experiments while many others have been investigated under experimental conditions that do not reproduce those of ISCs (either regarding the temperature or the pressure or UV illumination). For the former case, rate coefficients and their temperature dependence are mainly estimated with some chemical intuition or by drawing analogies with similar known processes. In the second case, the values obtained in a temperature or pressure range that does not encompass those of relevance in ISM are used. Both approaches can be seriously wrong, because: *i*) small details in the molecular structure can induce a huge change in the chemical behaviour and reasoning by analogy can cause severe mistakes; *ii*) the extrapolation of the T dependence of rate coefficients outside the investigated range can be very risky as a change in the reaction mechanism can alter the temperature dependence in non-Arrhenius reactions, while a too high pressure can lead to the stabilization of reaction intermediates or affect the reaction outcome via secondary or 3−body collisions.

The only way to improve the predictiveness of astrochemical models relies on a better characterization of the molecular processes at play. Concerning elementary gas-phase reactions, three complementary approaches are to be used, possibly for all the processes which are of any relevance, namely *a*) the CRESU technique to derive low T global rate coefficients, *b*) the crossed molecular beam technique to derive the nature of the primary reaction products and their branching ratios, *c*) quantum theory for chemical reactions to assist the interpretation of the Shannon et al. (2013) experimental data. This combined effort is necessary because *a*) the CRESU technique is able to characterize gas-phase reactions under the appropriate temperature conditions, but cannot reproduce the low number density environment; *b*) crossed molecular beam experiments are able to reproduce the low number density environment, but not the low temperature conditions; *c*) quantum theory for chemical reactions provides support for the interpretation of the experimental results obtained with the CRESU and crossed molecular beam techniques. This allows an extrapolation of the experimental results to the case of ISCs conditions with more confidence. In addition, in all cases where no experimental data are available, a theoretical characterization of a gas-phase reaction can provide a realistic estimate of the reaction rate coefficients and product branching ratios.

In this contribution, several recent examples will be illustrated to highlight the capabilities of the methods *a*) − *c*). Astrophysical implications will also be noted.

2. Recent CRESU experiments on reactions characterized by the presence of a pre-reactive complex

Experimental methods based on cryogenic cooling, where the entire reaction vessel is cooled down at the desired temperature, are not suitable to investigate the reaction kinetics of bimolecular reactions at the temperatures of relevance in cold ISCs because most reactants would condense on the walls rather than reacting. On the contrary, by using supersonic expansion of the reactant gases, it is possible to convert the thermal energy of the gas into kinetic energy and cool down the temperature of the gas at very low values. This is the approach of the CRESU technique which makes

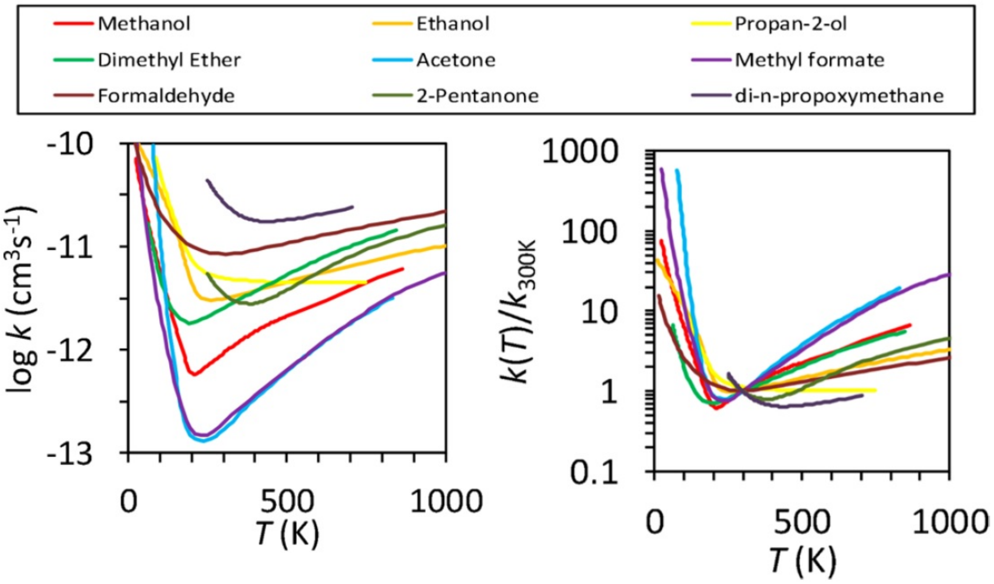

Fig. 1. Reprinted with permission from D.E. Heard (2018). Copyright (2018) American Chemical Society.

use of a collimating axisymmetric, converging-diverging Laval nozzle which leads to the production of a cold and uniform supersonic flow of gas. The basic principles of the CRESU technique have been reported in several review papers (Smith & Rowe 2000; Smith 2002, 2003; Potapov et al. 2017; Heard 2018). Here, we simply remind that, after expansion through a Laval nozzle, a relatively dense medium (between 10^{16} and 10^{17} cm^{-3}) is formed in which the temperature and number density are constant along the axis of the flow. The supersonic flow regime is maintained as such also when a small percentage (1-2%) of additional gases are added, while by using different nozzles and carrier gases it is possible to routinely produce a specific flow temperature at values as low as 10 K. The transient species (atomic or radical species) are typically produced after the supersonic expansion by UV induced photodissociation of a molecular precursor. The decay rate of the reacting transient species is typically followed by laser-induced fluorescence (LIF) or other spectroscopic techniques. In the last generation of CRESU apparatuses, product detection is also possible, which allows recording the product appearance rate (Soorkia et al. 2011; Oldham et al. 2014; Cooke & Sims 2019). Historically, the application of the CRESU technique has been limited to the case of reactions with room temperature rate coefficients of at least 10^{-12} cm^{3}s^{-1}. The reason for this limitation is due to the fact that the supersonic flow is maintained uniform over a certain distance which implies a time scale of 100 – 500 μs within which the decrease of the atom/radical reactant concentration has to be recorded. In recent years, however, the CRESU technique has been applied to a class of reactions involving the OH radical and oxygenated organic compounds for which the room temperature rate coefficients are just at the limit of 10^{-12} cm^{3}s^{-1} or even slightly below (Heard 2018). These reactions are known to have an experimental activation energy and are characterized by a calculated entrance barrier in the range of 10 kJ mol^{-1}. In spite of that, below 200 K the rate coefficients for these reactions change their slope with the temperature and start increasing with decreasing temperature (see Figure 1). In other words, all these reactions are characterized by a strongly non-Arrhenius behavior and the k values below 100 K can be larger by a factor of 10^3 with respect to the room temperature value. The explanation for such a strong effect has been rationalized by invoking the role of pre-reactive complexes (Shannon et al. 2013; Roncero et al. 2018) which is formed by the strong H-bond interaction between the OH radical and the polar functional groups of those molecules (-OH for the alcohols, the ether group for ethers, the carbonyl group for aldehydes, etc.). At very low T, the pre-reactive complex, characterized by a relatively deep potential well, can live for a time long enough to have a significant probability to tunnel through the barrier rather than re-dissociate back to the reactants (Shannon et al. 2013; Heard 2018; Naumkin et al. 2019).

This explanation has been partially confuted by accurate quantum and kinetics calculations (see below) according to which only a part of the increase of the rate coefficient with decreasing T is caused by the invoked mechanism, while a much more significant contribution comes from a partial collisional stabilization of the pre-reactive complex (Gao et al. 2018). Indeed, in some CRESU experimental studies a pressure dependence of the value of $k(T)$ was observed and an extrapolation to the zero pressure limit was necessary (see, for instance, Caravan et al. 2015).

In any case, these studies have had a profound influence in the comprehension of neutral ISCs chemistry because most of the species investigated are oxygenated iCOMs. The effect is double: on the one hand, the reaction of oxygenated iCOMS with OH must be considered as an efficient destruction route of those species because of the abundance of the OH radical; on the other hand, the radicals formed by the H-abstraction process can react further and be involved in the formation of other iCOMs (see, for instance, Balucani et al. 2015; Skouteris et al. 2018).

3. Collision-free experiments, the nature of reaction products and their branching ratios

It is impossible to reproduce in terrestrial laboratory experiments the low number density typical of most ISCs. Nevertheless, it is possible to investigate elementary reactions under collision−free conditions, which means that no secondary or wall collisions that might affect the outcome of a reactive collision are allowed.

The most convenient way to run collision−free experiments is via the crossed molecular beam (CMB) technique (see, for instance, Leonori et al. 2007; Casavecchia et al. 2009, 2015). The main benefit of CMB experiments is that the reactants are confined into distinct supersonic beams which cross each other at a specific angle. The atomic/molecular species in each beam are characterized by a well defined velocity and are made to collide only with the molecules of the other beam.

This allows one to observe the consequences of many identical molecular collisions. The products are formed at the collision center and then fly undisturbed towards the detector because of the large mean free path achieved by operating at 10^{-5} Pa (see Figure 2). Product detection can be achieved by means of spectroscopic techniques or mass-spectrometry. Notable examples of CMB experiments coupled to spectroscopic detection for reactions of relevance in astrochemistry are available in the literature (see, for instance, Costes & Naulin 2010). However, the use of mass spectrometric detection is much more versatile and applicable to the study of (at least in principle) any reaction. An important advantage with respect to common flow reactors with mass spectrometric detection is the possibility to measure product angular and velocity distributions, which allows one to directly derive the enthalpy of reaction. This is crucial when more isomers with the same gross formula can be produced. The advantages of the CMB technique strongly motivate its extension to the study of reactions of interest in astrochemistry. For this reason, it has been extensively used to investigate the reactions of atomic species (e.g., B, C, O, Si, etc.; see, for instance, Mebel & Kaiser 2015; Casavecchia et al. 2009, 2015; Kaiser 2002; Balucani et al. 2010; Kaiser & Osamura 2005), diatomic radicals (CN, CH, SiH, BO, etc.; see for instance, Balucani et al. 2000; Maksyutenko et al. 2011; Parker et al. 2014) and polyatomic radicals (He et al. 2019; Balucani et al. 2011; Leonori et al. 2007).

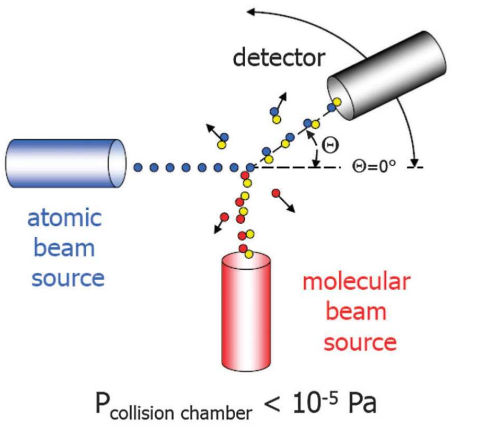

Fig. 2. Block diagram of a crossed molecular beam experiment for a reaction involving an atomic species and a diatomic molecule. Adapted from Balucani (2012).

4. Beyond laboratory experiments: the contribution of theoretical calculations

Broadly speaking, the experimental techniques which can be used to investigate the gas-phase reactions of interest in astrochemistry can either reproduce the low T conditions or the low number density of ISCs, with the nice exception of the Bordeaux apparatus developed by M. Costes and C. Naulin. Therefore, theoretical calculations are essential not only to support the interpretation of the experimental data, but also to assist the extrapolation of the experimental results. In addition to that, many reactions included in astrochemical models involved two transient species. Those reactions are particularly difficult to investigate because the two unstable reactants must be produced under controlled conditions and in a sufficient amount to allow recording experimental data. Even though some important systems have been investigated in this way (e.g., Carty et al. 2006; Balucani et al. 2011; Leonori et al. 2007; Pei et al. 2015), the examples reported in the literature are sparse. In these cases, a theoretical investigation can furnish at least an educated guess of the reaction rate coefficients and product branching ratios.

4.1. A support for the interpretation of laboratory experiments

In a very few successful cases, it has been possible to compare accurate dynamical and kinetics calculations on a complete potential energy surface with the results of both crossed molecular beam and CRESU experiments. A notable example is, for instance, the case of the reaction F+H_2 where the full potential energy surface, widely tested against detailed crossed molecular beam experiments over decades, has been employed to reproduce the rate coefficients measured in a CRESU experiment at very low T (Tizniti et al. 2014). More commonly, for larger systems the theoretical calculations that are used to assist the interpretation of the experimental data are limited to the identification of the stationary points along the potential energy surface. Those calculations can still be used to derive rate coefficients and product branching ratios (see, for instance, Sleiman et al. 2018; Ocaña et al. 2019). When a good agreement between experimental results and theoretical calculations is found, we can assume that the accuracy of the potential energy surface is good enough to allow predicting other properties of the reactive system. On the contrary, if the experimental findings are at odds with theoretical predictions, there might be a mistake in the experimental results or the calculations might not be accurate enough. A notable recent example is the case of the reaction, already mentioned above, between OH and CH_3OH. Three independent sets of CRESU results point to a large increase of the rate coefficients at temperatures below 200 K (Shannon et al. 2013; Ocaña et al. 2019). However, theoretical calculations performed with several methods in several research groups (Gao et al. 2018; Nguyen et al. 2019; Ocaña et al. 2019) are not able to reproduce the trend from a quantitative point of view. Therefore, we do not have a value of $k(T)$ in the range 10−200 K that can be used with any confidence in astrochemical models as the discrepancy between experimental and theoretical values is too large. Possibly, astronomical abundances will allow us to infer which of the two sets of values is more reliable (C. Ceccarelli, private communication).

4.2. When experiments cannot be performed

As mentioned above, elementary reactions involving two transient species are very difficult to investigate in laboratory experiments. Many reactions of this kind populate the chemical networks in the main databases for astrochemical models. In these cases, a theoretical treatment can provide an estimate of the rate coefficients. Even in the absence of experimental results against which one can test the accuracy of the theoretical treatment, the calculated rate coefficients are certainly more realistic than those estimated by analogy or by relying on chemical intuition. Important examples of neutral-neutral gas-phase reactions for which those estimates have recently become available are: $NH + C_2H_5$ (see Balucani et al. 2018), $CN + CH_2NH$ (see Vazart et al. 2015), $NH_2 + H_2CO$ (see Barone et al. 2015; Vazart et al. 2016; Skouteris et al. 2017), $O + C_2H_5O$ (see Skouteris et al. 2018). Also reactions involving ions can be investigated with the same approach (see, for instance, Ascenzi et al. 2019; Skouteris et al. 2015, 2019; Yuen et al. 2019; Ayouz et al. 2019).

5. Astrophysical implications of some recent studies on gas–phase bimolecular reactions

In this section, some successful cases will be illustrated to exemplify how the correct inclusion of the parameters obtained in laboratory experiments or quantum calculations can help astrochemical modelling.

5.1. The use of experimental branching ratios derived by collision–free experiments: the case of the reactions between atomic oxygen and unsaturated hydrocarbons

Recent crossed molecular beam experiments have derived the product branching ratios of several reactions involving atomic oxygen and simple unsaturated hydrocarbons (see Balucani et al. 2012; Casavecchia et al. 2015). Occhiogrosso et al. (2013) presented an upgraded chemical modelling based on the UMIST database where the new branching ratios were included. An important conclusion of this study is that towards hot cores/corinos atomic oxygen easily degrades unsaturated hydrocarbons directly to CO or to one of its precursor species (such as HCCO or HCO) and destroys the double or triple bond of alkenes and alkynes. Therefore, environments rich in atomic oxygen at a relatively high temperature are not expected to be rich in large unsaturated hydrocarbons or polycyclic aromatic hydrocarbons. In contrast, in O-poor and C-rich objects, hydrocarbon growth can occur to a large extent. A second important conclusion is that new radical species, namely ketyl and vinoxy radicals, can be formed in significant amounts and influence the abundances of hydrocarbons towards hot cores. To be noted that, later on, the vinoxy radical was searched for and detected towards the starless core Lupus-1A and the molecular cloud L483 (Agundez et al. 2015).

5.2. Reactions involving two radical species: the case of the $NH + C_2H_5$ reaction

The reaction between the amidogen (NH) radical and the ethyl (C_2H_5) radical has been suggested as a possible formation route of ethanimine, CH_3CHNH, by Quan et al. (2016). Since no data were available at the time, Quan et al. (2016) estimated a value of $k(T)$ by drawing an analogy with a similar system (namely, $N + C_2H_5$) for which only the room temperature coefficient is available. The $NH + C_2H_5$ reaction has been recently characterized by Balucani et al. (2018) via electronic structure calculations of the underlying doublet potential energy surface. In addition, since the reaction was found to be a barrier-less process, rate coefficients and product branching ratios have been estimated by combining capture and RRKM calculations at the temperatures of relevance for ISCs. The global reaction was found to be much faster than what previuously assumed by Quan et al. (2016). However, the main product channel is not the one leading to ethanimine because, with a yield of almost 90% in the range of temperatures investigated, the channel leading to methanimine and methyl radical is by far the dominant one. Balucani et al. (2018) were also able to quantify the branching ratios of the channels leading to the two $E-$, $Z-$ stereoisomers of ethanimine. The resulting ratio [$E-CH_3CHNH$]/[$Z-CH_3CHNH$] is 1.2, which is not far from the value determined in the Green Bank Telescope PRIMOS radio astronomy survey spectra of Sagittarius B2 North (Loomis et al. 2013) which is around 3. Considering that ice chemistry would produce essentially only the most stable isomer, a possible conclusion is that the observed [$E-CH_3CHNH$]/[$Z-CH_3CHNH$] ratio is compatible with a combination of gas-phase and grain chemistry. More observational and laboratory data are needed to definitely address this issue.

5.3. The deuteration of iCOMs from gas–phase reactions: the case of partially deuterated formamide

Formamide, NH_2CHO, is an interesting interstellar molecule with a strong prebiotic potential, since it holds an amide bond. Although detected in the interstellar medium for decades, its formation route is still debated. A very recent review paper by Lopez-Sepulcre et al. (2019) nicely summarized all the relevant aspects concerning the astronomical importance and the possible formation routes of this remarkable molecule. Notably, a gas-phase formation route based on the reaction NH_2 + H_2CO was proposed by Barone et al. (2015) and tested with success in astrochemical models. Other processes catalyzed by interstellar grains and their mantles, have also been considered (see, for instance, Rimola et al. 2018; Enrique-Romero et al. 2019).

Molecular deuteration can be an efficient way to pinpoint the formation routes of iCOMs. For formamide, recent observations towards the IRAS16293-2422 B hot corino show that its three deuterated forms (*trans*-NHDCHO, *cis*-NHCDO and NH_2CDO) have all the same deuteration ratio. This ratio can be nicely reproduced by considering the gas-phase reactions NH_2 + H_2CO starting from monodeuterated NH_2 or H_2CO. It is interesting to note that, at the 100 K temperature of the hot corino, the rate coefficients of the reactions leading to the three deuterated forms are the same, while the reaction involving non-deuterated species proceeds three times faster. In other words there is a significant kinetic isotope effect for this reactive system. These results confirm that a gas-phase route for the formation of formamide is perfectly in agreement with the available observations, as already indicated by the modelling of shocked regions (Codella et al. 2017).

6. Conclusions

Many reactions among neutral species in the gas-phase remain to be explored, either via the experimental techniques that allow simulating the temperature and the number density of ISCs or via quantum and kinetics calculations. The possibility to derive the spatial distributions of iCOMs via interferometric detection campaigns and the improved sensivity of ALMA and NOEMA will provide stringent tests for astrochemical modelling and proposed formation routes of iCOMs. More than 8000 reactions are included in the databases for astrochemical modelling and only a small percentage of them has been characterized in laboratory experiments or via theoretical calculations. A lot of work remains to be done before we can claim we have understood the gas-phase chemistry of ISCs and its complexity.

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