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COMPLEX ORGANIC MOLECULES AND INTERSTELLAR ICES: RECENT PROGRESSES FROM LABORATORY ASTROPHYSICS

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Abstract. We present recent advances on the origin of complex organic molecules (COMs) in space brought by original laboratory experimental approaches. These studies highlight the role of solid-gas interface and bulk processes in the chemistry in the cold and dense regions of the interstellar medium.

Keywords: Laboratory astrophysics, interstellar ices, complex organic molecules

1 Introduction

Interstellar ices are known to play a central role in the formation of various molecules. This includes large molecules, such as the so-called Complex Organic Molecules (COM), referring to organics containing more than 5 atoms. Chemical origins of numerous COMs can be explained by taking into account gas-grain chemistry, in addition to pure gas-phase chemistry. Grain-surface chemistry in cold cores, as adsorbates accrete onto cold surface, is leading to the synthesis of number of saturated species identified as main component of the ices (H_2O, CH_4, NH_3, CH_3OH ...). Ices most probably contain traces of other larger molecules with abundances far below their observational detection limit in the solid state. Standard scenario of ice evolution in protostellar environments have stated that much of the chemistry leading to the synthesis of large organics should occur bewteen photoproducts (or products resulting from the bombardment by energetic particles) within the ice mantle, during a warm-up phase, and in the gas-phase after mantle evaporation. This scenario might not be sufficient to explain all observations. The predictive power of such models remains limited, since some COMs have also been detected in cold cores, that is in the absence of warming phase. In this context, the role of theoretical and experimental laboratory astrophysics are crucial to simulate and explore new chemical routes at low temperatures. In this paper, we review some recent and/or new experimental approaches opening perspectives for the understanding of the chemical pathways in cold environments. Methanol, a major COM playing a pivotal role in the formation of larger molecules, will be used here to illustrate important aspects of the gas-ice interplay and ice (photo)chemistry.

2 Gas-surface interplay

2.1 Desorption induced by surface chemistry

Among the surface reactions which have been investigated at low temparatures (< 30 K), the CO hydrogenation is so far one of the most experimentally studied. CO hydrogenation is of interest because (i) this process on cold surfaces can lead to the formation of formaldehyde and methanol through a sequential H-addition scheme and (ii) the formation of methanol isn't efficient into the gas-phase under interstellar conditions, as recently strengthened by the investigation of the first reaction step CO+H by radiative association (Stoecklin et al. 2018). H-addition reactions are affiliated with H_2-abstraction reactions leading to a dehydrogenation of CO-bearing compounds, that have been shown to play a critical role in the deuteration processes. In this context, new experimental investigations *via* H- exposure of carbon monoxide, formaldehyde and methanol-thin ices ($<$ 2.5

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ML deposited on oxidized graphite) focusing on low flux and fluences conditions, have revealed an unexpected desorption phenomenon which complete our view on the relevant scheme for the CO-H chemistry (Minissale et al. 2016b). The authors used an experimental protocol consisting in monitoring species during the H-exposure. This protocol reveals that the desorption of CO bearing species, induced by surface chemistry, the so-called *chemical desorption*, needs to be taken into account in the reaction budget. This experiment confirms that the methanol formation on surface is possible, but that the chemical network needs to take into account that a significant part of the chemical products/reactants can be released into the gas phase. An updated scheme of the CO hydrogenation, described by a chemical equilibrium between successive H-addition and H_2-abstraction reactions, is shown in Fig. 1.

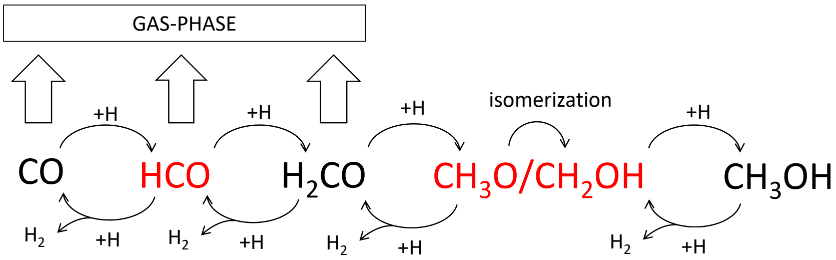

Fig. 1. Scheme of the CO-H chemistry. Radicals in red are not detected in the experiments. Large arrows correspond to desorption into the gas phase. Methanol desorption is not observed.

The experiments discussed in the present paper have shown that methanol is not consumed due to the H-additions or H_2-abstraction mechanisms. To explain this anomaly, the authors have proposed that CH_3O may isomerise to CH_2OH thanks to its lower enthalpy of formation. As shown in Fig. 1, CH_3O/CH_2OH isomerisation is at the center of two separate hydrogenation/abstraction loops, giving an asymmetrical character of the sequences leading to methanol. The net result would be that the return from CH_3OH to H_2CO is not possible, making methanol very stable.

The chemical desorption has been experimentally quantified for many reactive systems involving H, O or N atoms (Minissale et al. 2016a). This systematic approach shows high desorption probabilities for many products at very low coverage. The desorption was found to depend on the nature of the substrate. As an example the reactions O + H producing H_2O into the gas phase is efficient on graphite surface but much less efficient on non-porous amorphous solid water. Therefore, this phenomenon will play a critical role a the very first stages of the ice mantle formation. An empirical formula predicting the efficiency of the chemical desorption derived from this work have been used to investigate the role of the chemical desorption in the three phases chemical model applied to ρ-Oph A physical conditions (Cazaux et al. 2016). Time evolution of gas-phase abundances of species such methanol and H_2O_2 are increasing by a few orders of magnitude before the cloud frost when chemical desorption is taken into account. This study demonstrates that desorption process induced by surface chemistry and gas-ice interplay are strongly impacting the chemical ice composition.

2.2 *Desorption induced by photons*

The desorption induced by photons is known to be a non-thermal desorption process from which molecular material condensed at very low temperatures can be released into the gas phase. This phenomenon, whose efficiencies are *a priori* very difficult to predict theoretically, has accordingly attracted considerable attention by the laboratory astrophysics community these last years. Studies on pure ice mantles have shown that the most weakly bound species photodesorb under vacuum UV (VUV) irradiation with yields ranging typically from 10^{-4} to 10^{-3} molecule/photon. Multiple mechanisms are at the origin of the desorption, as highlighted by recent studies. Desorption Induced by Electronic Transition (DIET) is a direct mechanism which has been clearly identified in the case of CO and N_2 desorption (Fayolle et al. 2011, 2013). Wavelength dependent studies using synchrotron radiation (SOLEIL facility, St Aubin, France) have revealed another indirect DIET process at play, for which the molecule initially excited is left into the solid, but its relaxation is followed by an energy transfer inducing the desorption of surroundings species (Bertin et al. 2013, 2012). All theses processes do not require surface chemistry. Other polyatomic systems such as H_2O or CO_2 can in addition photodissociate, which open competitive indirect desorption pathways driven by secondary chemistry (Fillion et al. 2014) or by photofragments balistic momentum transfer (kick-out mechanisms). In this context the desorption of intact COMs is puzzling because most of the large species are expected to be easily destroyed by VUV irradiation.

Wavelength-dependent photodesorption rates have been determined using synchrotron radiation for condensed pure and CO-mixed methanol ices in the 7-14 eV range (Bertin et al. 2016). The overall photodesorption process is dominated by the desorption of the photofragments CO, CH_3, OH, H_2CO, and CH_3O/CH_2OH. The photodesorption of intact CH_3OH parent molecule is also observed, presumably due to a recombination reaction at the surface of the ice involving CH_3O/CH_2OH radicals. An important finding of this study is that the photoprocessing of a pure or mixed methanol ice induces the desorption of photofragments, with efficiencies at least as high as the photodesorption of the methanol (e.g. 10^{-5} molecule/photon). The rates extracted for $CO{:}CH_3OH$ mixed ices are particularly interesting since both species are expected to be mixed in the colder interstellar ices, as explained in the previous section. Among the desorbing photofragments, the case of the CH_3O/CH_2OH is again of specific interest since these radicals can therefore participate to the formation of other complex molecules into the gas-phase.

In conclusion, the photodesorption of methanol (and more generally polyatomic species) from ices may stand at the origin of the gas phase presence of radicals, which are opening new gas phase chemical routes for the formation of complex molecules in photon-dominated-regions.

3 Bulk Chemistry

As discussed above, the top layers of an ice mantle are sources of new molecular material injected into the gas-phase. However, a complex chemistry is also taking place within the underlying layers of the ice mantle. Cryogenic matrix techniques and VUV photoprocessing of ice analogs provide complementary clues for understanding the bulk chemistry.

3.1 Cryogenic matrix technique: a powerfull tool for radical reactivity in ices

Experiments in cryogenic rare gases (Rg) matrices present many interests for understanding radical-radical chemistry. At first, the initial species can be trapped in a cold and inert environment (typically Ar or Xe matrices). Infrared absorption spectra of the sample can be recorded and analysed with easier characterisation as compared to pure solid films, since species are isolated in cages and are not interacting. Butscher et al. (2015) have applied this technique to study radical-induced chemistry at low temperature. As an illustration, a mixture $H_2CO{:}Ar$ (2:1000) matrix is condensed at 12 K and irradiated using a microwave discharge H_2 plasmas lamp peaking at Lyman-α wavelength (121.6 nm). VUV photolysis produces the formyl radical (HCO) and free H atoms which remain trapped within the Rg matrix together with the remaining H_2CO precusor. An annealing step to 30 K triggers the H-atom diffusion through the matrix. The composition of the sample is monitored by IR spectroscopy after cooling down to 12K. The analysis of the spectrum clearly reveals the formation of the hydroxymethyl radical (CH_2OH). By constrast, the methoxy radical (CH_3O) also expected from the hydrogenation of H_2CO is not observed. Finally, the last hydrogenated product observed after the annealing is methanol coming from the hydrogenation of the CH_2OH. One has to note that most of previous experimental studies do not detect the intermediate species, which prevents them from confidently determining the formation mechanism of COMs in ice. This is obsviously not the case here, where CH_2OH is assigned to the main intermediate radical species in the H_2CO to CH_3OH hydrogenation process. This is consistent with the sheme presented in Fig. 1.

Additional experiments performed by Butscher et al. (2015) consisting of annealing at higher temperature to Rg sublimation (35 K for solid Ar or 85 K for solid Xe) allows the investigation of the radical-radical reactivity. The IR spectral analysis of the solid film and analysis made by mass spectroscopy after complete desorption of the sample both confirm the formation of glycolaldehyde ($HOCH_2CHO$) and ethylene glycol ($HOCH_2CH_2OH$), and possibly glyoxal (HCOCHO). Indeed as soon as the Rg is removed the radicals are no longer isolated and they are free to react as it follows:

$$HCO + CH_2OH \rightarrow HOCH_2CHO$$

$$\mathrm{CH_2OH + CH_2OH \rightarrow HOCH_2CH_2OH}$$

One can think that HCO would also dimerise as easily as CH_2OH forming the glyoxal which is not the case since glyoxal is barely detected in these experiments probably due to its low quantity compared to the main products. Thus, this study provides a scenario for the formation of ethylene glycol and glycolaldehyde at very low temperatures, which can be seen as secondary products linked to methanol formation through CO hydrogenation. This mechanism is entirely consistent with the detection of these two species in star-forming regions and comets. Further VUV photolysis of formaldehyde in water-free and water dominated ices have evidenced the ability of water ices to store free radicals at low temperatures (Butscher et al. 2016) and strengthen the preferential role of CH_2OH as intermediate radical arising from H-atom addition to formadehyde.

In the near future, Electron Paramagnetic Resonance (EPR) spectroscopy to monitor open-shell molecules (radicals) chemistry at low-temperature in interstellar ice analogues is expected to provide additional information on radical-induced chemistry. This technique recently adapted to ice chemistry is a very promising to get the signatures of atoms and radicals involved in many elementary reactions. It is expected to shed light upon the observation of interstellar complex organic molecules in different prestellar environments.

3.2 VUV photolysis of interstellar ice analogues

Other types of experiments aim at simulating the complex chemistry occuring within more realistic solid films, instead of trying to isolate specific reactions. A new experimental approach using the VAHIIA system (standing for Volatile Analysis from the Heating of Interstellar Ice Analogues) has been recently developed for the purpose of interstellar ice chemistry. This experiment is based on gas chromatography (GC) coupled to Mass Spectrometry (MS), which provides unprecedented sensitivity to the chemical composition of the samples (Abou Mrad et al. 2014). The capabilities of this experiment is well-illustratd by the study of a (simple) CH_3OH ice. The samples are condensed at 20 K and subjected to VUV irradiation for 24h before complete sublimation and analysis of the volatile compounds by GC-MS. This method has provided evidences for the identification of 33 volatile organic compounds among hundred detected, including alcohols, aldehydes, ketones, esters, ethers and carboxylic acids (Abou Mrad et al. 2016). GC-MS allows for the first time the direct quantification of carbon chains (from 2 to 4 carbons), and shows that their abundances decrease with the increase of their carbon chain length. The molecular richness (several chemical functions, 19 atom compounds, chiral molecules) obtained from pure methanol is more diverse than suggested by previous studies. The results obtained from pure methanol ices can be viewed as an important first step for understanding the influence of other ice components on the chemical reactivity. Indeed, the study of binary (H_2O:CH_3OH, CH_3OH:NH_3), and ternary ice analogs (H_2O:CH_3OH:NH_3), VUV-processed and warmed, confirms this method as a very promising tool to investigate the behaviour of the protoproducts in complex ices (role of water, influence of nitrogen chemistry etc...(Abou Mrad et al. 2017). These type of data highlights the correlation between the solid phase composition and volatile abundances in the gaseous phase, which is obviously of high interest considering cometary science.

Finally, we also point out the important molecular diversity found by analysing the residues formed on the window after VUV-photoprocessing and sublimation of ice analogues. For instance, from an ice of H_2O, NH_3 and CH_3OH (3:1:1) deposited at 77 K and simultaneously irradiated during 73 hours and then warmed up to 300 K, a material, soluble in polar solvents (like water) is obtained. This material retrieved from the vacuum has been analysed by High Resolution Mass Spectrometer (FT-Orbitrap). More than thousands of molecules were detected with masses up to 4.000 Da (Danger et al. 2013)). The molecular diversity and group distribution (e.g. CHNO > CHO > CHN in abundance) observed in such residue is convincingly similar to the one extracted from some primitive carbonaceous meteorites, and questions the link between astrophysical ices and the soluble organic matter found in meteorites (Danger et al. 2016). This experiment also demonstrates for the first time the possibility of forming an insoluble material by over-irradiating the soluble one at 300 K in vacuum. The comparison with some astrophysical objects shows an interesting correlation with the insoluble organic matter of some meteorites, which raises the question of the possible relationship between soluble and insoluble organic matter found in meteorites (de Marcellus et al. 2017). Furthermore, the investigation of the impact of ice composition on the molecular content of organic residue allowed to demonstrate the role played by NH_3 and H_2O in their formation (Fresneau et al. 2017). Finally, a direct correlation between ice composition, residue content and gas phase composition can be drawn from these different experiments.

4 Conclusions

In conclusion, although the solid-state chemistry is very difficult to decipher, we have presented a few complementary examples for which original experimental laboratory protocols are able to reveal qualitatively and quantitatively important steps of the complex chemistry leading to the formation of more and more complex organic compounds.

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