

Laboratory Astrochemistry: A Powerful Tool to Understand the Origin of Organic Molecules in the Interstellar Medium, Comets, and Meteorites

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During the past two decades, astrochemistry laboratory simulations have shown that complex organic molecules can be formed under simulated astrophysical conditions from the vacuum ultraviolet (UV) irradiation of ice mixtures containing simple species such as H₂O, CO, CO₂, CH₃OH, and NH₃. These organics include compounds of biological and prebiotic interests such as amino acids—the building blocks of proteins, and nucleobases—the informational subunits of DNA and RNA. Although the presence of amino acids in the interstellar medium (ISM) has not been confirmed by observations to date, they have been detected in meteorites, indicating that biomolecules and/or their precursors can be formed under extraterrestrial, non-biological conditions. Nucleobases have also been detected in meteorites, broadening the variety of complex organic molecules that can be formed in astrophysical environments. Like amino acids, nucleobases and other *N*-heterocycles have not been observed in the ISM. In the following, I will review some of the progress made by laboratory astrochemistry towards understanding the formation of organic species from the UV irradiation of ices at low temperature under astrophysically relevant conditions. This discussion will be focused on the formation of amino acids and other molecules of prebiotic interest such as urea and glycerol. Then, I will present recent studies on the formation of nucleobases and related compounds from the UV irradiation of pyrimidine in H₂O, NH₃, and CH₃OH ices, which show the formation of a large suite of photo-products including the nucleobases uracil and cytosine.

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1. Ices and organics in the Solar System and the interstellar medium

Gas (atoms, molecules, ions) and dust grains (solid particles) in the interstellar medium (ISM) are clumped into clouds and processed by energetic particles, mainly photons (ultraviolet, X-rays, γ -rays) and cosmic rays (high energy protons and other heavier nuclei). Given sufficient mass, the gravitational collapse of these clouds will eventually lead to the formation of stars via several stages of evolution, from diffuse clouds to denser molecular clouds, and finally to protostellar objects surrounded by debris disks.

Dust grains have a typical size of $\sim 0.1 \mu\text{m}$ and are usually made of carbonaceous material [1, 2] or minerals (amorphous or crystalline) [3, 4]. In cold environments such as interstellar dense clouds and inside disks around protostars, grains are coated with a volatile mantle consisting of ices. Here the term "ice" refers to any volatile species that can condense on cold grains, mainly H_2O , CO , CO_2 , CH_3OH , NH_3 , and CH_4 [5–10], but they can also be other more complex organic molecules, including polycyclic aromatic hydrocarbons (PAHs) [11–13]. Icy compounds are usually bound together by Van der Waals interaction and/or hydrogen bonds, and participate actively to the chemical and thermal coupling between the grains and the surrounding gas.

Ices are ubiquitous in the ISM, and present in the (outer) Solar System (Table 1). It first appears that the composition of astrophysical ices is comparable in astrophysical objects and in comets. The most abundant component of astrophysical ices is H_2O . Small carbon- and oxygen-bearing molecules such as CO , CO_2 , and CH_3OH have abundances ranging from a few percent to 30% compared with H_2O . NH_3 is not very abundant, but its photochemistry in the presence of the other ices leads to the formation of new species including OCN^- , observed in many astrophysical ices with detectable abundances [14].

The interaction of the ices with ultraviolet (UV) photons and cosmic rays modifies the chemical structure of the mantle. As more and more complex molecules are formed, an organic refractory layer starts to form on the grains. Experimental simulations have shown that such a refractory material, often called organic residue, can be formed from the irradiation of astrophysically relevant ice mixtures with UV photons or high-energy protons [15–17]. Stable at room temperature, residues can then be analyzed with several techniques.

These complex organic molecules are then probably incorporated into small objects during the formation of the protoplanetary disk and the stellar system, such as comets, asteroids, and interplanetary dust particles (IDPs). The bombardment of planets from comets and asteroids during the heavy bombardment period in the early stages of the formation of our Solar System may have seeded the primitive Earth, as well as other planets, with a broad range of organic molecules, including the ingredients necessary for the emergence of life as we know it [18, 19]. These ingredients are amino acids (the building blocks of proteins), nucleobases (the informational subunits of DNA and RNA), ribose (the carbonaceous backbone of DNA and RNA), as well as other sugars, and lipids (constituents of cell walls). The detection of these compounds in meteorites [20–22] strongly supports an extraterrestrial origin of the building blocks of life.

In the following, I will review what is known about the composition of organic residues formed from the UV irradiation of astrophysically relevant ices. I will discuss the detection and formation of amino acids and nucleobases in these residues, and compare those results with what has been observed in meteorites and collected extraterrestrial materials.

Table 1: Composition and relative abundances of ices in the interstellar medium and comparison with comets. The abundance of H₂O, most abundant ice component, has been set to 100 for all these objects.

	<i>RAFGL 7009S</i>	<i>NGC 7538 IRS9</i>	<i>W33A</i>	<i>Elias 16</i>	<i>Comets</i>
<i>Species</i>	[23]	[24, 25]	[5]	[5]	[5]
H ₂ O	100	100	100	100	100
CO	15	12	8	25	5–3
CO ₂	21	15	13	18	3–20
CH ₃ OH	30	4–12	18	< 3	0.3–5
CH ₄	3.6	2	0.4	–	1
NH ₃	–	13	15	≤ 9	0.1–1.8
OCN [–]	3.7	2	3.5	< 0.5	–

2. Laboratory simulations

Mixtures of the compounds to be studied are prepared in the gas phase in a stainless steel or glass mixing line (background pressure: $\leq 10^{-5}$ mbar). Relative abundances between components are determined by their partial pressures. Gas mixtures are transferred into bulbs, which are then connected to the deposition tube of a vacuum chamber. Vacuum chambers consist of a stainless steel cage pumped to a pressure of a few 10^{-8} mbar and cooled to temperatures as low as 10 K with a closed-cycle He cryocooler. A detailed description of typical vacuum system set-ups can be found in refs. [26–28].

Mixtures are then simultaneously deposited on a cold substrate (infrared-transparent KBr or MgF₂ windows, aluminum, etc.) and irradiated with UV photons or energetic protons. UV photons can be provided either by a microwave-powered H₂-discharge lamp, emitting mainly Lyman- α and a continuum centered around 160 nm [27–30], or by a synchrotron radiation beam (tunable light source), provided by facilities such as former LURE (Orsay, France) [31], recently open SOLEIL (Gif-sur-Yvette, France) [32], or NSRRC (Hsinchu, Taiwan) [26, 33]. UV lamp radiation is a good analog to the light emitted by young stars, whereas UV light from synchrotron can be used to study a given photochemical reaction or pathway at a specific wavelength. Ices can also be bombarded with energetic protons produced by a Van de Graaff accelerator [34]. The deposition/irradiation duration can vary from a few minutes to a few days, with typical experiments lasting 1 to 2 days. After irradiation, samples are usually warmed to room temperature, at which time they are recovered from their substrate and conserved before they are analyzed with different techniques. Some vacuum systems are also equipped with a Fourier-transform infrared (FTIR) spectrometer in order to monitor the composition of the ices during irradiation and warm-up. The infrared (IR) spectra obtained from such experiments can in some cases be directly compared with astronomical data in order to search for the presence of ice components (see, e.g., refs. [35, 36]) and/or the physical conditions in the media where those species are observed.

3. Composition of organic residues

Infrared spectroscopy is a powerful tool to monitor the evolution of the ices during irradiation at low temperature and warm-up to room temperature. UV irradiation of ices induces the breaking

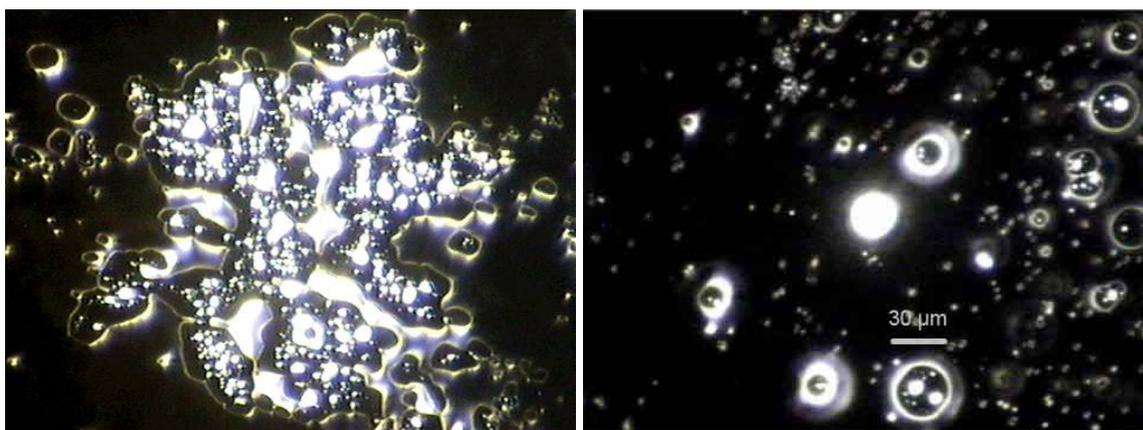


Figure 1: Infrared microscopy images of an organic residue produced from the UV irradiation of an $\text{H}_2\text{O}:\text{CH}_3\text{OH}:\text{NH}_3$ ice mixture. Organic molecules form vesicle-like structures that are soluble in water.

of chemical bonds and/or the ionization of some compounds, leading to the formation of reactive species such as ions and radicals. The mobility of radicals in an ice matrix is usually very limited at low temperature, and only first-opportunity reactions between nearby species can take place at this stage. After irradiation and during warm-up, photo-produced species become more mobile and react with each other to form more complex molecules. IR spectra at low temperature of photolyzed ice mixtures containing H_2O and combinations of CO , CO_2 , CH_3OH , CH_4 , and NH_3 indicate the presence of several families of molecules including alcohols, amines, carboxylic acids, alkanes, and alkenes, as well as species such as H_2CO (formaldehyde), NH_4^+ (ammonium ion), OCN^- (cyanate ion, observed in astrophysical objects, see Table 1), the HCO^\bullet radical, HNCO (isocyanic acid), and organic molecules as complex as NH_2CHO (formamide) [26, 31, 37].

During the warm-up phase, all volatile species (both starting ices and new photo-products), sublime away from the substrate. Some of those volatile compounds can be identified by mass spectrometry, such as carbamic acid, produced from the irradiation of an $\text{H}_2\text{O}:\text{CO}_2:\text{NH}_3$ mixture, and observed to sublime around 250 K [26].

At room temperature, organic residues usually appear oil-like with a flavescent tinge. They are sometimes referred to as "yellow stuff", and are soluble in water [16, 38]. They usually consist of 10–50 μm droplets (Fig. 1), suggesting that a decent fraction of the formed photo-products can self-assemble into vesicle structures [39]. Laser-desorption mass spectrometry of one residue showed a very complex mass spectrum displaying a peak for almost every single mass from 40 to 400 atomic mass units (amu), indicating that this material is very complex and probably macromolecular [40].

IR spectra of organic residues show a number of characteristic bands assigned to molecular families including alcohols, amines, carboxylic acids, alkanes, alkenes, nitriles/isonitriles, ketones, esters, and amides, as well as carboxylate salts [31, 37]. Specific compounds could not be identified in residues, with the exception of hexamethylenetetramine (HMT) [17] and NH_4^+ [41].

More recently, X-ray absorption near-edge structure (XANES) spectra of similar residues have been measured in the carbon, oxygen, and nitrogen edges at the Advanced Light Source (Berkeley, USA) [42]. These measurements confirmed the presence of several families of chemical groups (aromatic and aliphatic CH_x bonds, carboxyls, amides, ketones, nitriles, etc.). This study

also indicated that oxygen and nitrogen atoms are very efficiently incorporated into carbonaceous chains, resulting in a very nitrogen- and oxygen-rich material, with elemental N/C and O/C ratios of 0.1–0.3 and 0.4–0.6, respectively [42]. Compared with XANES measurements of extraterrestrial materials, the N/C and O/C ratios found in organic residues are up to 2 times higher than what was measured in cometary particles returned by Stardust [43, 44], and 2–10 times higher than for organic matter extracted from the Murchison meteorite [45, 46].

However, mass spectrometry as well as IR and X-ray absorption spectroscopies techniques are usually not sufficient to identify specific organic molecules. For this, residues need to be analyzed with chemical techniques such as liquid and gas chromatographies.

4. Amino acids in organic residues

The first organic molecules that were searched for in residues as well as in carbonaceous chondrites were amino acids. Amino acids are the building blocks of proteins for all life on Earth. There are 20 proteinic amino acids, plus 2 additional rare ones—selenocysteine and pyrrolysine—that were found in some proteins. Other non-proteinic amino acids can also be found in biological systems, such as sarcosine or β -alanine [47]. In proteins, amino acids are only present in their enantiomeric form L. This property of homochirality is chemically favored for amino acid polymerization, and gives a particular chiral 3-dimensional structure. D-Amino acids, such as D-alanine and D-aspartic acid, are also found in some biological systems such as bacteria cell membranes [47].

Organic residues produced from the UV irradiation of ice mixtures containing H_2O , CO , CO_2 , CH_3OH , CH_4 , and NH_3 , and analyzed with high-performance liquid chromatography (HPLC) and/or gas chromatography coupled with mass spectrometry (GC-MS) showed the presence of a broad variety of amino acids [27, 29], up to 16 in one sample [30]. These amino acids are mostly detected after acid hydrolysis of the residues, as only very small quantities of free amino acids are present in non-hydrolyzed residues [27], indicating that organic residues consist of either a macromolecular material that can be easily hydrolyzed, or precursors which are more photo-stable to UV photons than the compounds detected after hydrolysis, or both.

Because they are formed from achiral starting compounds under achiral experimental conditions, amino acids detected in residues are racemic, i.e., they have equal amounts of D- and L-enantiomers [29, 30, 48]. In addition, the distribution of amino acids is different from what is observed in biological proteins, as the most abundant amino acid—glycine—is also the simplest, and the abundance of larger amino acids decreases with their molecular weight [27, 48]. Finally, the formation of amino acids from the UV irradiation of astrophysical ice analogs has proven efficient as long as the starting ices contain C, H, N, and O atoms, regardless of the starting carbon source [27]. For example, amino acids have been detected in residues formed from the UV irradiation of a fully inorganic starting mixture $\text{H}_2\text{O}:\text{CO}_2:\text{NH}_3$ [33], as well as from the UV/EUV irradiation of naphthalene (C_{10}H_8), the smallest PAH, in an $\text{H}_2\text{O}:\text{NH}_3$ ice mixture [49]. These characteristics are consistent with non-biological formation pathways, and indicate that the amino acids detected in residues are not due to biological contamination.

Amino acids have been extensively searched for in the ISM in the gas phase (radio astronomy) [50], but none of them have been detected, though the possible detection of glycine is still under debate [51, 52]. In contrast, up to 70 amino acids have been found in carbonaceous

chondrites such as the Murchison and Murray meteorites [20, 53, 54]. These meteoritic amino acids, of which only a small fraction are found in proteins, have isotopic ratios consistent with an extraterrestrial origin [55] and a non-racemic distribution, with enantiomeric excesses of a few percent for proteinic-like α -hydrogenated amino acids [21, 56, 57], and up to 18% for isovaline, a non-proteinic α -methylated amino acid [58, 59].

The origin of this asymmetry in the chiral distribution of amino acids is still a mystery, and a number of theoretical and experimental studies have attempted to reproduce such a result by adding asymmetry to the formation of organic residues from the UV irradiation of ices [31]. Recently, the irradiation of $\text{H}_2\text{O}:\text{CH}_3\text{OH}:\text{NH}_3$ (achiral) ice mixtures with circularly polarized light (CPL) in the UV range has shown that alanine, the smallest chiral proteinic amino acid, was formed with enantiomeric excesses of opposite signs when left or right polarizations of the light were used [32]. Moreover, enantiomeric excesses seem to be directly proportional to the number of polarized photons irradiating the ices. Astronomical observations showed that CPL could be present in the ISM and affect the stereochemistry of carbonaceous molecules formed in astrophysical environments [60, 61].

5. Other molecules of prebiotic interest in organic residues

Although present in all organic residues formed from the UV irradiation of simple astrophysical ice analogs (H_2O , CO , CO_2 , CH_3OH , CH_4 , NH_3 , etc.), amino acids only represent a small fraction of the residue material, with a quantum yield estimated to be of the order of 10^{-4} for the total amount of amino acids [30]. Other molecules of prebiotic interest, in particular DNA- and RNA-like nucleobases, have been searched for in organic residues, with no success.

Nonetheless, molecules such as urea, glycerol, and a number of its derivatives including glyceric amide, glycolic acid, and glyceric acid [62] have been detected in residues. These compounds are known to perform different functions in biological systems, and some of them have been detected in meteorites [22, 63, 64]. The presence of these compounds in residues has been confirmed in other experiments, which also showed the presence of hydantoin [65]. This compound, also detected in meteorites [64, 66], is particularly interesting because its hydrolysis leads to the formation of carbamoyl amino acids (CAAs), which can also be formed from the addition of isocyanic acid (HNCO) to α -amino acids. CAAs are the precursors of *N*-carboxyanhydride amino acids, which can polymerize into poly- and oligopeptides, that is, primitive proteins [67, 68].

Finally, amphiphilic molecules, consisting of a hydrophilic head and a hydrophobic tail, are also present in organic residues (see Fig. 1 and ref. [39]). These compounds have the ability of self-assembling into vesicles. The delivery of amphiphiles via meteorites and comets to the primitive Earth may have led to the formation of the first cell membranes, within which chemical reactions are protected from the outside environment [69].

Future analysis of organic residues will focus on the search for sugar compounds, which are assumed to be present, but whose presence in residues has never been demonstrated, though they have been detected in the Murchison meteorite [22].

6. Formation of nucleobases from pyrimidine in astrophysical ices

Nucleobases, the informational subunits of DNA and RNA, are compounds based on the backbones of two *N*-heterocyclic compounds, namely, pyrimidine and purine. Biological pyrimidine-based nucleobases are uracil (RNA), thymine (DNA), and cytosine (DNA/RNA), whereas biological purine-based nucleobases are adenine and guanine, both found in DNA and RNA. There are also other pyrimidine- and purine-based compounds in the nature including barbituric acid, its derivatives, and caffeine.

Nucleobases have been extensively searched for in the ISM in the gas phase [70–72], but never been detected. Only an upper limit for the column density of pyrimidine of $1.7\text{--}3.4 \times 10^{14} \text{ cm}^{-2}$ could be derived from these observations [71]. More generally, no *N*-heterocyclic molecules have been unequivocally detected so far in the ISM [72], although there are observational indications that they may be present [73]. However, purines have been found in a large number of carbonaceous chondrites including Murchison, Murray, and Orgueil [74–77]. Meteoritic pyrimidines are usually detected with smaller abundances than purines because they are more subject to chemical and photochemical processes. Nonetheless, uracil was found in water extracts of Murchison, Murray, and Orgueil [78]. Finally, the extraterrestrial origin of nucleobases in Murchison has been confirmed by isotopic measurements [79].

Therefore, pyrimidines and purines must be present in astrophysical environments. Since they are not observed in the gas phase, they may be condensed on the surface of cold grains, mixed with ices, together with other aromatic molecules [11, 12]. Moreover, some theoretical studies suggest that pyrimidine and other aromatic compounds could be formed via polymerization of smaller molecules [80]. For this reason, experiments in which pyrimidine is mixed with ices of astrophysical interest and irradiated with UV photons has been and are currently being performed [28, 81].

The UV irradiation of pyrimidine mixed with pure H₂O ice leads to the formation of an organic residue in which several pyrimidine derivatives have been detected, including the nucleobase uracil and its precursor 4(3*H*)-pyrimidone [28]. Theoretical calculations simulating such reactions are in agreement with experimental results, and showed that 4(3*H*)-pyrimidone and uracil are the most stable singly and doubly oxidized derivatives formed, respectively [82]. These calculations also showed that H₂O plays an essential as an ice matrix to stabilize the formation of these photo-products.

The photochemistry of pyrimidine mixed other pure ices such as NH₃ (ammonia), CH₃OH (methanol), or CH₄ (methane) is not as efficient, although a few singly substituted pyrimidine derivatives do form, such as 4-aminopyrimidine in NH₃+pyrimidine mixtures [81], or 4-pyrimidinmethanol in CH₃OH+pyrimidine mixtures (unpublished results). The addition of H₂O in those mixtures not only diversifies the chemistry by oxidizing pyrimidine and its amino derivatives, but it also increases the efficiency of addition of NH₂, CH₂OH, and CH₃ groups to pyrimidine, probably via the same matrix effect as observed for H₂O+pyrimidine mixtures [82]. In H₂O-rich mixtures, identified photo-products include the nucleobases uracil and cytosine, as well as small quantities of non-aromatic species such as glycine, urea, and small amino acids [81]. However, the addition of CH₃ groups to pyrimidine appears to be an inefficient process. Consequently, thymine, the third pyrimidine-based nucleobase, can only form when the number of UV photons per deposited molecule is significantly higher (unpublished results).

Future experiments will focus on the study of the irradiation of pyrimidine in a realistic mixture of astrophysical ice analogs, in order to assess the role of each ice component in the formation of pyrimidine derivatives, including nucleobases and their isomers.

7. Laboratory astrochemistry, extraterrestrial materials, and space missions

IR studies of ice mixture irradiations can be directly compared with IR astronomical observations of a broad range of astrophysical objects from ISO (European Space Agency, ESA) and Spitzer (NASA). For instance, laboratory experiments helped identifying the interstellar bands of OCN^- [83, 84] and NH_3 [35, 36]. On the other hand, techniques used to analyze organic residues produced in the laboratory are usually applicable to the analysis of extraterrestrial materials such as meteorites, IDPs, and samples returned by space missions, for a direct comparison.

For example, cometary grains collected by Stardust from comet Wild 2 and returned to Earth have been analyzed with IR and XANES spectroscopies, as well as liquid and gas chromatographies. Results show that the composition of these grains varies significantly from one to another, displaying a broad range of organic compounds [43, 44, 85]. These measurements can be directly compared with what is observed for IDPs [86] and laboratory organic residues [42], and constrain the conditions in which those materials form in astrophysical environments [87]. NASA is already planning a future sample-return mission (OSIRIS-REx) currently scheduled for launch in 2016 for an encounter with asteroid 1999 RQ36 in 2023.

Similar analyses for the search of organics will probably be performed on the grains returned by Hayabusa from asteroid Itokawa, although mineralogical analysis showed that this S-type asteroid has the same IR characteristic features as LL ordinary chondrites [88], known to be poor in carbonaceous matter. The Japanese space agency (JAXA) is currently working on Hayabusa 2.

Analysis of the fragments of the Almahata Sitta meteorite, collected in Sudan after asteroid 2008 TC₃ entered the Earth's atmosphere [89], showed that this unique ureilite contains organic compounds including amino acids [90, 91]. Almahata Sitta was also found to contain adenine, one of the purine nucleobases [77]. Further analysis of these meteoritic fragments may be conducted in order to identify other organic compounds of prebiotic interest.

Finally, the Rosetta mission (ESA), launched in 2004 [92], will encounter comet Churyumov–Gerasimenko and land the Philae probe on its nucleus in 2014, where several in-situ analytical techniques will be performed. Instruments onboard Philae include a GC-MS instrument which can automatically prepare and run samples [93]. These data will be directly comparable with laboratory measurements of organic residues, meteoritic samples, IDPs, and Stardust grains.

8. Conclusion

Laboratory astrochemistry is a rich, powerful research field in constant evolution. Laboratory experiments can constrain physical and chemical parameters in observed astrophysical environments, while astronomical observations can test laboratory predictions. In addition, analytical techniques used to analyze samples produced in the laboratory are in most cases applicable to the study of extraterrestrial materials such as meteorites, IDPs, and samples returned from Solar

System objects such as comets and asteroids. Direct comparison between these data is a powerful tool to assess the composition, the origin, and the evolution of extraterrestrial matter, as well as the link between astronomical observations and extraterrestrial material collected on Earth. In particular, one of the goals of astrochemistry is to study the evolution and origin of molecules of biological interest, from the astrophysical environments where they form, to their incorporation into Solar System bodies and their delivery to telluric planets such as the primitive Earth.

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