

Aldehydes and sugars from evolved precometary ice analogs: Importance of ices in astrochemical and prebiotic evolution

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Evolved interstellar ices observed in dense protostellar molecular clouds may arguably be considered as part of precometary materials that will later fall on primitive telluric planets, bringing a wealth of complex organic compounds. In our laboratory, experiments reproducing the photo/thermochemical evolution of these ices are routinely performed. Following previous amino acid identifications in the resulting room temperature organic residues, we have searched for a different family of molecules of potential prebiotic interest. Using multidimensional gas chromatography coupled to time-of-flight mass spectrometry, we have detected 10 aldehydes, including the sugar-related glycolaldehyde and glyceraldehyde—two species considered as key prebiotic intermediates in the first steps toward the synthesis of ribonucleotides in a planetary environment. The presence of ammonia in water and methanol ice mixtures appears essential for the recovery of these aldehydes in the refractory organic residue at room temperature, although these products are free of nitrogen. We finally point out the importance of detecting aldehydes and sugars in extraterrestrial environments, in the gas phase of hot molecular clouds, and, more importantly, in comets and in primitive meteorites that have most probably seeded the Earth with organic material as early as 4.2 billion years ago.

glyceraldehyde | glycolaldehyde | astrochemistry | precometary ices | prebiotic evolution

In dense molecular clouds, interstellar ices are by far the most abundant molecular fraction in the solid state compared with the gas-phase molecules. They are observed in the midinfrared range around protostars, from which planets, but also much debris, such as comets and asteroids, eventually form. Their composition is dominated by H₂O, followed by CO, CO₂, CH₃OH, NH₃, CH₄, and some less abundant molecules, although their respective abundances can vary from one (type of) source to another (1). Ices are subjected to various energetic processes such as cosmic rays and UV irradiation (2) as well as thermal reactions, which initiate a rich solid-state chemistry from diffusion within the bulk of reactive species such as ions and radicals, which ultimately recombine to form new and more complex molecules. This molecular complexity is difficult to trace in astrophysical settings and to characterize in the solid state by in situ infrared spectroscopy alone because of the presence of the dominant simple ice species as well as the deep and broad silicate feature along the line of sight that hide minor features expected from complex molecules. However, in warmer regions such as hot molecular cores, icy mantles can sublimate, and complex molecules become more easily detectable and identifiable by radio astronomy due to their rotational spectra (3). Detected gas-phase molecules are thus more complex than those observed in the solid phase, but models show that an important initial solid-state (ice) chemistry is usually required to

explain the measured abundances, which cannot result from gas-phase reactions alone (4, 5).

Laboratory experiments that simulate the photochemical evolution of simple interstellar ices (including C, H, O, and N elements) lead to the production of a complex semirefractory organic residue after warming up to room temperature (6, 7), which is often considered as an analog of precometary matter. Such residues display a macromolecular structure, including a large variety of chemical functions such as alcohols, amines, amides, esters, carboxylic acids, etc. (8, 9). Among the numerous individual molecules detected in these residues, hexamethylenetetramine (HMT) is a dominant species (10–13), although it seems not to have any direct prebiotic implication (14). On the other hand, several molecules of potential prebiotic interest have been found, such as amino and diamino acids (14–18), hydantoin (19), urea and glycolic acid (6, 20), lipid precursors (21), quinones when polycyclic aromatic hydrocarbons are irradiated in water ice (22), and even nucleobases—however, only when pyrimidine is added to the initial ice mixture (23–25). The presence of sugars, in particular those included in nucleotides that are the building blocks of nucleic acids, has never been reported in these residues.

In this study, we report the first to our knowledge detection of aldehydes in room temperature organic residues, including glycolaldehyde and the chiral glyceraldehyde. We discuss their potential implications for prebiotic chemistry within an astrophysical

Significance

In molecular clouds out of which stars and planetary systems form, simple solid-state molecules made in large part of H₂O, CO, CO₂, CH₃OH, and NH₃ are abundantly present. In these environments, energetic and thermal processes on these ices, which can be simulated in the laboratory, lead to complex organic matter. Possibly at the origin of the organic matter in our Solar System and incorporated into planetesimals, this material may be considered as a potential source for prebiotic chemistry on telluric planets, following a process that may be quite universal. The composition of these laboratory-evolved ices includes potentially prebiotic species such as amino acids and, as presented in this paper, aldehydes and sugars.

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Table 1. Aldehydes and sugar-related molecules identified in simulated precometary organic residues

#C ^a	Compound	<i>R</i> ₁ ^b [min]	<i>R</i> ₂ ^c [sec]	MS fragmentation/ ¹³ C sample		MS fragmentation/ ¹² C standard	
				[M ⁺]	Other important ions, <i>m/z</i>	[M ⁺]	Other important ions, <i>m/z</i>
1	Formaldehyde	17.08	1.80	226 ^d	196, 181	225	195, 181
2	(<i>Z</i>)-Acetaldehyde	20.35	1.94	241 ^d	211, 181	239	209, 181
	(<i>E</i>)-Acetaldehyde	21.20	1.92	241 ^d	211, 181	239	209, 181
	(<i>Z</i>)-Glycolaldehyde	41.81	2.24	329 ^e	314, 181, 132, 104, 73	327	312, 181, 130, 103, 73
	(<i>E</i>)-Glycolaldehyde	42.14	2.32	329 ^e	314, 181, 132, 104, 73	327	312, 181, 130, 103, 73
	(<i>Z</i>)-Glyoxal	72.12	5.21	450 ^f	420, 255, 253, 237, 181	448	418, 253, 251, 235, 181
	(<i>E</i>)-Glyoxal	74.54	5.14	450 ^f	420, 255, 253, 237, 181	448	418, 253, 251, 235, 181
3	(<i>Z</i>)-Propanal	25.49	1.94	256 ^d	239, 226, 239, 181	253	236, 223, 181
	(<i>E</i>)-Propanal	25.99	1.94	256 ^d	239, 226, 181	253	236, 223, 181
	(<i>E,Z</i>)-Propenal	25.98	2.20	254 ^d	237, 224, 181	251	234, 221, 181
	(<i>E,Z</i>)-Propenal	26.66	2.33	254 ^d	237, 224, 181	251	234, 221, 181
	(<i>Z</i>) Lactaldehyde	46.39	2.54	344 ^e	329, 181, 73		
	(<i>E</i>) Lactaldehyde	46.81	2.54	344 ^e	329, 181, 73		
	(<i>Z</i>) Glyceraldehyde	51.47	2.55	431 ^g	417, 328, 251, 220, 181, 147, 104, 73	429	414, 326, 248, 218, 181, 147, 103, 73
	(<i>E</i>) Glyceraldehyde	52.89	2.44	431 ^g	417, 328, 251, 220, 181, 147, 104, 73	429	414, 326, 248, 218, 181, 147, 103, 73
	(<i>Z</i>)-Methylglyoxal	71.12	3.84	465 ^f	435, 284, 268, 181	463	432, 281, 265, 181
	(<i>E</i>)-Methylglyoxal	74.54	4.14	465 ^f	435, 284, 268, 181	462	432, 281, 265, 181
4	(<i>Z</i>) Butyraldehyde	31.65	1.99	271 ^d	241 ^h , 181	267	239 ^f , 181
	(<i>E</i>) Butyraldehyde	31.74	2.04	271 ^d	241 ^h , 181	267	239 ^f , 181

Data were obtained from a VUV-irradiated ice mixture at 78 K containing water, ¹³C-labeled methanol, and ammonia, H₂O:¹³CH₃OH:NH₃, in molar composition of 12:3:5:1. After water extraction of the residue at room temperature, the aldehydes were derivatized to form 1-(*O*-pentafluorobenzyl) oxime derivatives and identified by enantioselective GC×GC–TOFMS analysis.

^aQuantity of carbon atoms. ^bGC×GC retention time, first dimension. ^cGC×GC retention time, second dimension. ^dMolecular ion *m/z* value of 1-(*O*-pentafluorobenzyl) oxime (PFBO) derivatives. ^eMolecular ion *m/z* value of PFBO trimethylsilyl ether derivatives. ^fMolecular ion *m/z* value of di-PFBO derivatives. ^gMolecular ion *m/z* value of PFBO-bis(trimethylsilyl) ether derivatives. ^hMcLafferty rearrangement.

scenario that emphasizes the central role of extraterrestrial ice photo/thermochemistry as an ubiquitous phenomenon in protostellar media and protoplanetary disk environments (26).

Results

Ten different aldehydes, ranging from one to four carbon atoms (Table 1), were detected in the organic residue resulting from the processing of an initial H₂O:¹³CH₃OH:NH₃ (12:3.5:1) ice mixture: formaldehyde (H₂CO), glycolaldehyde (CH₂OHCHO), acetaldehyde (CH₃CHO), propanal (CH₃CH₂CHO), propenal (CH₂CHCHO), lactaldehyde (CH₃CHOHCHO), glyceraldehyde (CH₂OHCHOHCHO), glyoxal (OCHCHO), methylglyoxal [CH₃C(O)CHO], and butyraldehyde [CH₃(CH₂)₂CHO]. Our analysis of aldehydes in the organic residues uses a definitive means of detection, 2D gas chromatography, coupled to time-of-flight mass spectrometry (GC×GC–TOFMS). All of these aldehydes—some of them exhibiting additional functional groups (Fig. 1)—were identified as their *O*-pentafluorobenzyl oxime (PFBO) and *O*-pentafluorobenzyl oxime-trimethylsilyl ether (PFBO-TMS) derivatives, respectively, using aqueous-phase derivatization with *O*-(pentafluorobenzyl)hydroxylamine (PFBHA). Nine out of ten aldehydes were identified by their mass fragmentation patterns, along with the chromatographic elution time in both dimensions of individual PFBHA-TMS–reacted authentic standard injections. Due to the lack of a lactaldehyde reference standard, the structural elucidation of lactaldehyde is solely based on the interpretation of its mass spectrum and its predicted retention time.

For glyceraldehyde, the mass spectrum of the detected molecule is displayed just above the mass spectrum of the corresponding standard (Fig. 2). We remind the reader here that organic residues were made with ¹³C only, whereas standards are composed of ¹²C. Thus molecular ions and fragments containing one or more carbon atom(s) are shifted accordingly and lead to unambiguous detections.

In the homologous series of aldehydes detected in the organic residues, the lower-molecular-weight members are usually more abundant (Fig. 3)—the exception here of formaldehyde may be due to its higher volatility and its gradual loss while heating the vacuum chamber up to room temperature after forming in the ices. The abundances of aldehydes (Fig. 3A) and hydroxyaldehydes (Fig. 3B) are decreasing with increasing carbon number, as previously observed for amino acids in such ice simulation experiments (13, 17). Three different samples were analyzed in this study: one containing ammonia (H₂O:¹³CH₃OH:NH₃ = 12:3.5:1, with a simultaneous deposition and irradiation time of 67.5 h) and two without ammonia (H₂O:¹³CH₃OH = 3:1, one made during 65 h and one during 91 h, resulting in a higher quantity of organic residue for the second one). Relative aldehyde abundances for the two samples without ammonia follow

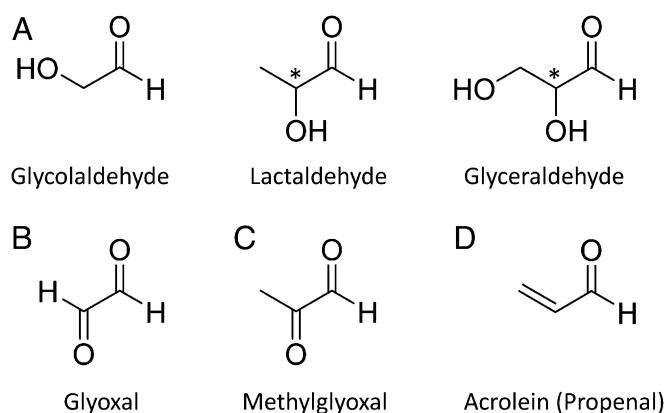


Fig. 1. Selected aldehydes identified at room temperature in simulated precometary organic residues: (A) hydroxyaldehydes, (B) dialdehyde, (C) ketoaldehyde, and (D) an unsaturated aldehyde.

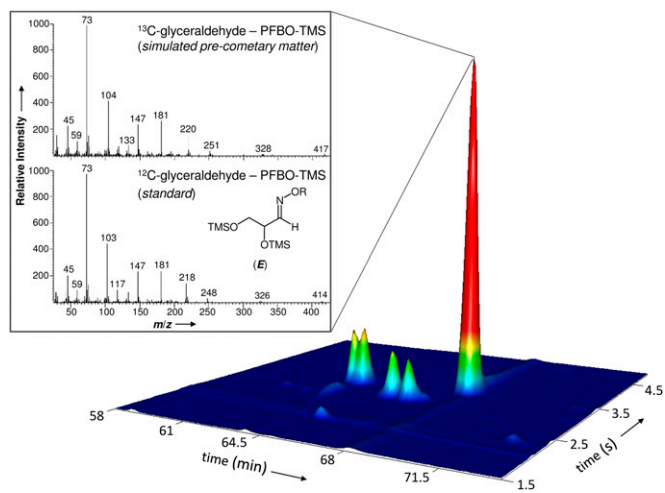


Fig. 2. Glycerinaldehyde detected in simulated precometary organic residues. Identification of glycerinaldehyde as *O*-pentafluorobenzyl (*R*) oxime bis(trimethylsilyl) ether (PFBO-TMS) in laboratory organic residues using multi-dimensional gas chromatography. The corresponding external glycerinaldehyde standard shows identical retention times and ^{12}C isotopic signatures in its mass spectra. The mass fragmentation reveals that glycerinaldehyde formed in the residue is entirely composed of ^{13}C -isotopes provided by the $^{13}\text{CH}_3\text{OH}$ reactant present in the original ice mixture. Note that all aldehyde derivatives, except formaldehyde PFBO, can form *syn* (*Z*) and *anti* (*E*) stereoisomers of the oximes because the carbon nitrogen double bond (imine) formed during derivatization prevents rotation.

the trend of the total experiment duration (the global amount of organic residue), although not strictly proportional to it (Fig. 3). Interestingly, the abundances of the simple aldehydes (formaldehyde, acetaldehyde, propanal, and butyraldehyde) are lower in the absence of ammonia in the initial ice mixture. Even more striking, the hydroxyaldehydes, including glycolaldehyde, lactaldehyde, and glycerinaldehyde, are completely absent in the samples without ammonia (Figs. 3 and 4). In contrast, the abundances of the dialdehydes, glyoxal and methylglyoxal, are reduced in the presence of ammonia, an effect that we do not explain at this stage.

Astrophysical Discussion

Six out of the ten molecules in Table 1 have been detected in extraterrestrial environments, which include protostellar media but also Solar System objects such as comets and asteroids, including meteorites on the Earth's surface. Formaldehyde is actually ubiquitous, observed in many places of the interstellar medium (3, 27), but also in the gas originating from comets (28) and in meteorites (29). Acetaldehyde, propanal (propionaldehyde), and propenal (acraldehyde) are detected in the hot molecular core Sagittarius B2 (30, 31), the well-known "Large Molecular Heimat" (LMH) of radio astronomers, as well as, for the first two, in meteorites (29). Butyraldehyde has been reported in the Murchison meteorite as well (29). Additionally, Cooper et al. (32) identified several sugars, sugar alcohols, and sugar acids, some of them with up to six carbon atoms, in the Murchison and Murray meteorites. Because of the prebiotic importance of sugar-related molecules, the following discussion will focus on glycolaldehyde and glycerinaldehyde.

Glycolaldehyde has been detected in emission and/or in absorption by radio astronomy toward the galactic center source, Sagittarius B2(N) (33–37), in the hot molecular core, G31.41+0.31 (38), and in the solar-type protostellar binary, IRAS 16293–2422 (39). However, glycolaldehyde has never been detected in Solar System objects, for which only an upper limit could be determined in the Hale–Bopp comet (40, 41), as well as in the

C/2012 F6 and C/2013 R1 comets (42). Glycerinaldehyde has been searched for in the interstellar medium by Hollis et al. (31) toward Sgr B2 (*N*-LMH), but no lines were detected. Note, however, that aldehydes of higher molecular weights are more difficult and uncertain to search for because of the intrinsic complexity of their rotational spectra associated with the likely presence of several conformers/tautomers.

In the laboratory, only glycolaldehyde has been detected, in the ice phase. An infrared study of glycolaldehyde and its tentative identification in a proton-irradiated CO:CH₃OH 100:1 ice mixture was reported in 2005 by Hudson et al. (43). In 2009, Öberg et al. (44) reported the formation of acetaldehyde and minor contributions of glycolaldehyde in UV-irradiated CH₃OH-rich ice analogs. Bennett et al. (45) provided an upper limit for the formation rate of glycolaldehyde during ion bombardment of pure CH₃OH ice. IR spectroscopy and mass spectrometry allowed Bennett and Kaiser (46) to establish the formation of glycolaldehyde in CH₃OH:CO ices irradiated with energetic electrons.

The first formation mechanism speculated for glycolaldehyde was an interstellar equivalent of the formose reaction in solid or gas phase based on the polymerization of formaldehyde (35). Recently, Woods et al. (47, 48) considered several different reaction mechanisms in solid or gas phase, most of them previously suggested in the literature (33, 38, 46, 49, 50), and, from a theoretical point of view, studied their effectiveness at 10 K. To our knowledge, no formation mechanism in extraterrestrial conditions has been proposed for glycerinaldehyde or higher-mass aldehydes, although the speculative "interstellar formose reaction" may again apply.

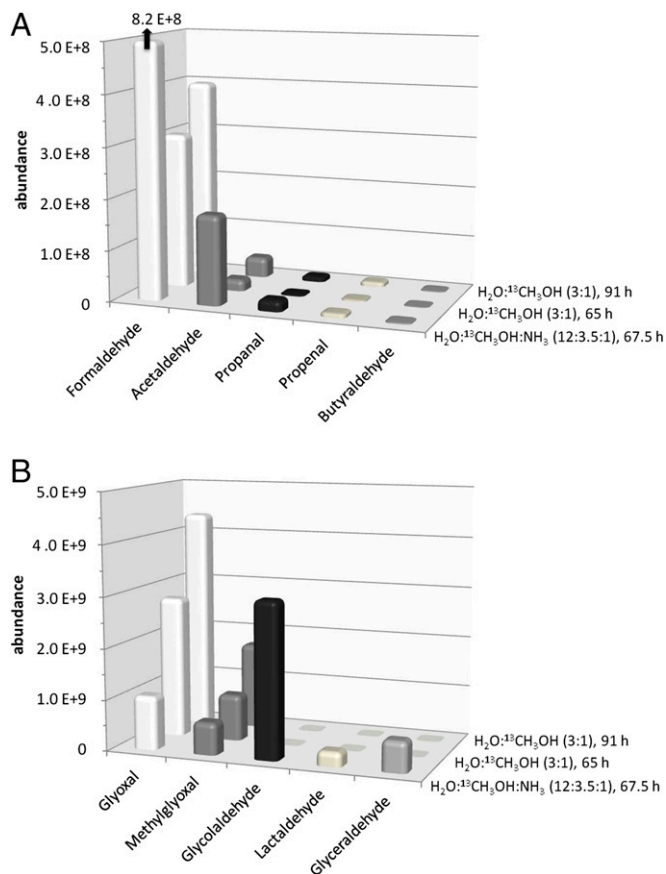


Fig. 3. Abundances of (A) aldehydes and (B) dialdehydes, keto- and hydroxyaldehydes in the room temperature samples with and without ammonia in the initial ice mixtures.

asteroids and have then been delivered at the same moment and location on the early Earth.

Finally, the search for glyceraldehyde, for which spectroscopic data exist in the millimeter range (66), should be attempted with the new Atacama Large Millimeter Array (ALMA) in the various astronomical gas-phase environments where glycolaldehyde is already detected. However, the lack of positive detection of the simplest amino acid, glycine, in the gas phase (67) underscores the lack of stability against cosmic or UV irradiation of such complex molecules in this gas phase. This was shown in laboratory experiments (68) for various amino acids in rare gas matrices, proxy for gas-phase media, and glyceraldehyde may well be similarly unstable in the gas phase of molecular clouds. Molecular complexity does need the protection offered by the solid-state environment (69). In fact, much more significant for prebiotic inference, glycolaldehyde and glyceraldehyde should be searched for in comets and in the Soluble Organic Matter (SOM) of the less possibly aqueously altered carbonaceous chondrites, such as the “Paris” meteorite (70). These proposed detections must be seen as the next step for supporting a scenario in which chemically evolved cosmic ices played a major role in the feeding of organic materials to the primitive solar nebula.

Conclusions

In this paper, we show that the UV irradiation of astrophysically relevant ice mixtures leads to the detection of a new family of molecules, the aldehydes, within the room temperature organic residues. Our results show that the formation of a large range of aldehydes in the solid phase of dense molecular clouds is likely. Among them, two are of particular importance for prebiotic processes: glycolaldehyde and glyceraldehyde are indeed chemical intermediates in ribonucleotide synthesis.

By changing the initial ice composition we observe the apparently essential role of NH_3 in stabilizing light aldehydes within the refractory organic residues. This phenomenon could have been of a fundamental importance to allow these molecules to remain trapped in grains and later be incorporated into small Solar System bodies, from which meteorites found on the Earth originate. The recovery of these aldehydes in comets and in primitive chondrites may constitute a test, bridging our experimental simulations to the SOM of meteorites, linking molecular clouds’ ice chemistry to primitive materials in the solar nebula and further playing a significant role in prebiotic chemistry at the surface of telluric planets.

Finally, the reported data will be of importance for the Rosetta mission that landed on a cometary nucleus in November 2014 (71) to perform in situ measurements of cometary ices,

particularly with the Cometary Sampling and Composition (COSAC) instrumentation, which contains a GC-MS device specifically designed for the characterization of organic molecules.

Materials and Methods

The experimental setup has already been described in detail elsewhere (e.g., ref. 72). In brief, it consists of a high-vacuum chamber (10^{-7} mbar), in which an infrared (IR) transparent MgF_2 window is cooled down to 78 K. A gas mixture, previously prepared in an independent stainless steel gas line pumped down to about 5.10^{-6} mbar, is then injected into the chamber where it condenses on the cold MgF_2 substrate to form a thin film of “ices.” These ices are, simultaneously to their deposition, irradiated by UV photons using a H_2 microwave-discharge lamp (73). In our experiments the ratio of UV photons to deposited molecules is around 1. The entire experiment (deposition rate, ice mixture, and effect of UV photolysis) is monitored by IR spectroscopy.

For this study, we prepared one mixture composed of H_2O , $^{13}\text{CH}_3\text{OH}$, and NH_3 in relative proportions 12:3.5:1, qualitatively representative of interstellar/precometary ices. We also made mixtures without ammonia ($\text{H}_2\text{O}:^{13}\text{CH}_3\text{OH} = 3:1$), to examine the effect of a different ice mixture on the chemical composition of the final residues. Methanol, our unique source of carbon, was labeled with ^{13}C to avoid any confusion with potential biological contamination in the handling and analysis processes of the samples. H_2O (water, liquid) was purified by using a Millipore Direct Q5 system, $^{13}\text{CH}_3\text{OH}$ (methanol, liquid) was purchased from Aldrich (99.9% purity), and NH_3 (ammonia, gas) was purchased from Messer (99.98% purity). The ratios between the components were determined by their partial pressures in the gas line, measured by an absolute pressure gauge (Baratron).

Note that the physicochemical state of the initial sample (temperature and ice composition) is used as a template of preaccretionary ices and not fully representative of interstellar conditions. At 78 K, enhanced diffusion of reactants allows for a faster chemical evolution than at 10 K without significantly affecting the nature of the organic residue, as noted by Muñoz Caro and Schutte (8). For the initial ice composition, we observe that CO and CO_2 do appear during the photochemical process and are thus part of the icy molecular chemical reservoir.

After a total of 65–91 h of deposition and simultaneous irradiation, the samples were slowly warmed up to room temperature (about 0.15 K min^{-1}), then removed from the vacuum chamber and kept under argon atmosphere in special sample holders for storage and transportation until their analysis at the Université de Nice-Sophia Antipolis, Institut de Chimie de Nice, Nice, France.

Samples were water-extracted from their substrate, derivatized, and then analyzed by 2D gas chromatography–time-of-flight mass spectrometry (GCxGC–TOFMS) using a LECO Pegasus IV D system. [Supporting Information](#) provides the detailed procedure.

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