

The Laboratory Production of Complex Organic Molecules in Simulated Interstellar Ices

J. P. Dworkin,¹ S. A. Sandford,² M. P. Bernstein,¹ and L. J. Allamandola²

1) NASA-Ames Research Center, Moffett Field CA

2) SETI Institute, Mountain View CA

Abstract

Much of the volatiles in interstellar dense clouds exist in ices surrounding dust grains. Their low temperatures preclude most chemical reactions, but ionizing radiation can drive reactions that produce a suite of new species, many of which are complex organics. The Astrochemistry Lab at NASA Ames studies the UV radiation processing of interstellar ice analogs to better identify the resulting products and establish links between interstellar chemistry, the organics in meteorites, and the origin of life on Earth. Once identified, the spectral properties of the products can be quantified to assist with the search for these species in space. Of particular interest are findings that UV irradiation of interstellar ice analogs produces molecules of importance in current living organisms, including quinones, amphiphiles, and amino acids.

1. Quinones (Bernstein *et al.* 2001)

The polycyclic aromatic hydrocarbon (PAH) naphthalene was exposed to ultraviolet radiation in H₂O ice under astrophysical conditions, and the products were analyzed using infrared spectroscopy and high performance liquid chromatography (HPLC). Our HPLC analyses demonstrate that the UV photolysis of H₂O-naphthalene ices results in a mixture of unprocessed naphthalene and oxidized naphthalene compounds. The oxidized photoproducts include both alcohols and ketones. The main products are the two isomers of naphthalene bearing one hydroxy group (naphthols), and an isomer of naphthalene bearing two carbonyls (1,4-naphthoquinone). In typical simultaneous deposition/irradiation experiments (equivalent to 30 minutes UV per 0.1 μm ice layer), 1-naphthol and 2-naphthol were observed to be produced with approximately 2.5% and 1.4% yields, respectively, relative to naphthalene. 1,4-Naphthoquinone, the next most abundant product, is produced with roughly a 0.4% yield relative to naphthalene. It is interesting that 1,4-naphthoquinones, further functionalized, often with a methyl group and a long isoprene chain, play essential roles in biochemistry. While best known as K vitamins and for their role as blood clotting co-factors, naphthoquinones, such as the menaquinones, also perform key biochemical functions in organisms all across the tree of life. As one example, the Archaea *Thermoproteus tenax* use menaquinones in the reduction of elemental sulfur to H₂S as their main energy source.

2. Deuterium Enrichments in Meteoritic Aromatics (Sandford *et al.* 2001)

There are a number of processes by which interstellar PAHs can become deuterium enriched, including gas phase ion-molecule reactions, gas-grain reactions, and unimolecular photodissociation. In addition, we have recently shown that, in interstellar ices, PAHs can become

enriched in deuterium by the same ice photolysis processes that make the oxidized aromatics. Each of these various processes is expected to leave a distinctly different signature in the distribution of D enrichment in the PAH population. Ion-molecule reactions would be expected to preferentially deuterate the *larger*, while unimolecular photodissociation should D-enrich only the *smallest* ones. In contrast, in D- enriched interstellar ices, ice photochemistry should produce aromatic deuterium enrichments that are *independent* of PAH molecular size, but which should correlate with specific functional groups, namely the alcohols, ketones, and aliphatic rings produced when PAHs are UV irradiated in H₂O-rich ices. Thus, the regiochemistry of PAH D-enrichment in meteoritic materials, and correlation (or lack thereof) with the presence of specific functionalized aromatic compounds could place constraints on the relative contributions of different interstellar processes that acted on presolar PAHs. In light of the recent work of and the work reported above, searches for a correlation of D-enrichment with PAH size and oxidation state in meteoritic organics would be of particular interest.

3. Vesicles (Dworkin *et al.* 2001)

Laboratory simulations studied to identify the types of molecules which could have been generated in pre-cometary ices were conducted by forming a realistic interstellar mixed-molecular ice (H₂O:CH₃OH:NH₃:CO = 100:50:1:1) at ~15 K under high vacuum irradiated with UV from a hydrogen plasma plasma lamp. When the ice was warmed to room temperature there is an oily organic residue which remains. This material was extracted, dried, and analyzed in aqueous media via microscopy. We found that some components of the photochemical product produced water-insoluble fluorescent vesicles under these conditions. The vesicles are roughly 10 - 50 μm in diameter and have apparent internal structures on a 1 μm scale, which are presumably related to phase separations that occur within the organic components of the droplets.

The ready formation of these organic species from simple starting mixtures, the ice chemistry that ensues when these ices are mildly warmed, and the observation that the more complex refractory photoproducts show lipid-like behavior and self-organize into droplets upon exposure to liquid water suggest that extraterrestrial materials could exhibit a far greater range in chemical properties and behavior than previously thought. Given that these materials are readily created under simulated interstellar conditions and that they seem very similar to materials in primitive meteorites, it seems reasonable to seriously consider whether organic material generated in the interstellar medium could indeed have been delivered to the early Earth and contributed to the origin and early evolution of life. Delivery of this material via meteorites, comets, or interplanetary dust particles may have augmented the endogenously generated molecules for the origin or the early evolution of life. For example, since there are only a few known prebiotic synthesis routes for lipids, exogenous material may have been an important source of amphiphilic molecules or, in hydrated environments, vesicle-like structures.

4. Amino Acids (Bernstein *et al.* 2002)

The laboratory ices are comprised primarily of amorphous H₂O ice at 15 K, with 1-10% NH₃, 5-10% CH₃OH, and 1-10% HCN, relative to H₂O. These mixtures are representative of

the composition of interstellar ice mantles in dense clouds and towards protostars. For example, relative to H₂O, NH₃ has been observed at the 10% level in NGC 7538, higher towards GCS3, and CH₃OH has been commonly observed at the 5% level in comets, and higher towards protostellar objects. Thus, H₂O, CH₃OH, and NH₃ are reasonable starting materials because they are among the most abundant molecules frozen onto grains in the dense ISM. In addition, it is reasonable to include HCN since it is abundant in cometary coma and the dense ISM, where the majority of HCN should be frozen onto grains.

The molecules N-formyl glycine, cycloserine (4-amino-3-isoxazolidinone), and glycerol were detected in the organic residue *before* hydrolysis. This is significant as it demonstrates that the amino acids produced are not merely products of hexamethylenetrtramine (HMT) and/or HCN polymer hydrolysis, but exist as free molecules in the residue. After hydrolysis glycine, alanine, serine, glycerol, urea, ethanolamine, and glyceric acid were observed by GC-MS and/or HPLC.

Given that the water on Murchison was probably deuterium depleted, forming deuterium enriched amino acids by parent body aqueous chemistry poses a conundrum. However, low temperature interstellar ices are believed to be deuterium enriched, so deuterium enrichment of meteoritic amino acids would be a logical consequence of photochemistry of already enriched low temperature ices.

Recent detections of slightly non-racemic mixtures of amino acids in meteorites and astronomical observations of circularly polarized radiation (CPR) in OMC-1 have renewed interest in the hypothesis CPR may have led to such enantiomeric excesses. However, only relatively inefficient mechanisms based on selective destruction of a racemic starting population have been demonstrated in the laboratory. The result reported in this paper, of an apparently free racemic chiral molecule from an ice photolysis, now makes it possible to test whether circularly polarized radiation could yield non-racemic mixtures of amino acids by selective *formation* under astrophysically relevant conditions. We are currently exploring this avenue of research.

This demonstration of amino acid formation from an experimental ice simulation suggests that ice photochemistry could have contributed to the amino acids and other compounds (e.g., glycerol, vesicles, and quinones) observed in carbon-rich meteorites. Ice photochemistry potentially provides a single simple explanation for the presence, deuterium enrichment, and enantiomeric excesses of at least some of the amino acids in meteorites. Since our experimental conditions for ice photolysis were designed to simulate the environments of dense interstellar molecular clouds, the birthsites of new stars and planetary systems, the delivery of these materials to the surfaces of newly formed planets may be a universal process. The level of extraterrestrial molecular complexity is just now becoming apparent, and the full implications of this chemical input to the early Earth, and by implication to other habitable planets, are likely to be far reaching.

REFERENCES

- Bernstein, Dworkin, Sandford, & Allamandola 2001, *MAPS*, **36**, 351.
Bernstein, Dworkin, Sandford, Cooper, & Allamandola 2002, *Nature*, **416**, 401.
Dworkin, Deamer, Sandford, & Allamandola 2001, *PNAS*, **98**, 815.
Sandford, Bernstein, & Dworkin 2001, *MAPS*, **36**, 1117.