

PHOTO-IRRADIATION OF PYRIMIDINE IN INTERSTELLAR ICE ANALOGS: SEARCHING FOR NUCLEOBASES. S. N. Milam^{1,2}, M. Nuevo¹, S. A. Sandford¹, J. E. Elsila³, and J. P. Dworkin³, ¹NASA Ames Research Center, M/S 245-6, Moffett Field, CA 94035, Stefanie.N.Milam@nasa.gov, Michel.Nuevo-1@nasa.gov, Scott.A.Sandford@nasa.gov, ²SETI Institute, 515 N. Whisman Rd., Mountain View, CA 94043, ³NASA Goddard Space Flight Center, M/S 691.0, Greenbelt, MD 20771, Jamie.Elsila@nasa.gov, Jason.P.Dworkin@nasa.gov

Introduction: During the last decade, laboratory astrochemistry has shown that complex molecules can be formed under interstellar/circumstellar conditions by vacuum UV irradiation of interstellar ice analogs containing H₂O, CO, CO₂, CH₃OH, NH₃, etc. [1-3]. Some of these species have also been found in meteorites [4-6], indicating that some of these complex molecules may be formed under interstellar/protosolar conditions.

Nucleobases are the building blocks of RNA and DNA, the genetic material used by all living organisms on Earth, and have two main structural forms based on pyrimidine (C₄H₄N₂) and purine (C₅H₄N₄), respectively. Such compounds have been found in carbonaceous chondrites [7,8] and have been determined to have an extraterrestrial origin by their isotopic signatures [9].

The nucleobases have been extensively searched for in the interstellar medium (ISM) for several decades using radio-telescopes [e.g. 10,11]. However, no *N*-heterocycle has yet been detected in the ISM in the gas phase. This suggests that meteoritic nucleobases, and/or their precursors, most likely formed in the solid phase, on the surface of cold interstellar grains via photochemical reactions, and/or in the meteorites' parent bodies (asteroids and comets).

Here, we present recent results of pyrimidine in various ice mixtures and the implications for the formation of nucleobases in such conditions.

Results: Interstellar ice analogs were synthesized at the NASA Ames Research Center's Astrochemistry Laboratory in an evacuated cryogenic chamber described previously elsewhere [12,13]. Details of the experiment and sample preparation are given in Nuevo et al. [14]. Once the sample residue is removed from the vacuum system, it is placed in either H₂O for HPLC or kept dry until derivatization and analysis with GC-MS at NASA Goddard Space Flight Center. Results presented here are based on H₂O: Pyrimidine = 20:1 ice mixtures, though preliminary work has been conducted on NH₃:Pyrimidine = 40:1 and H₂O:NH₃:Pyrimidine = 20:2:1.

Residues were analyzed with either HPLC or GC-MS. Details of these two methods are found in [14]. To verify the presence of given compounds, a series of standards were also analyzed and compared to the sample residues.

IR spectroscopy. A mixture of H₂O:Pyrimidine ~ 20:1 was deposited onto a ZnSe window cooled to 14 K. The ice was then UV irradiated and monitored in incrementing intervals for up to 180 min of exposure and monitored as the sample was warmed to room temperature (Fig. 1). The photodestruction of pyrimidine was monitored via the two strongest features at 1587 cm⁻¹ and 1406 cm⁻¹ (* in Fig. 1). A number of new features became apparent at 2342, 2252, 2167, 2138, and 2090 cm⁻¹ during irradiation and are identified as CO₂, -C≡N (nitrile), OCN⁻, CO, and an isonitrile feature, respectively [15-19].

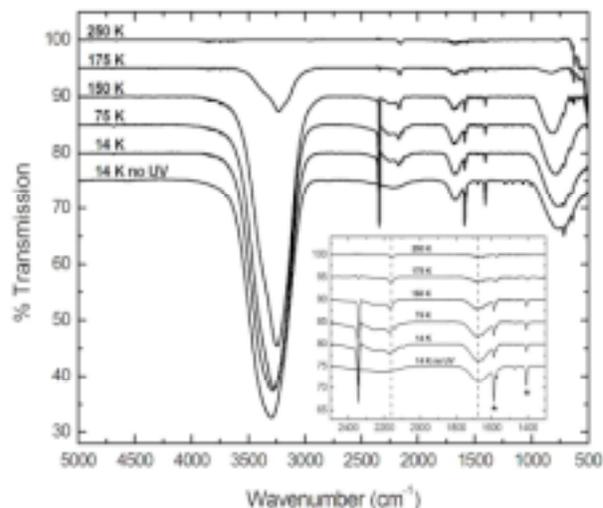


Fig. 1: Infrared spectra of a H₂O:Pyrimidine = 20:1 mixture deposited at 14 K before UV photo-irradiation, and after a 180-min irradiation with the H₂ UV during warm-up at 14, 75, 150, 175, and 250 K.

A photodestruction half-life was determined from the newly derived *A*-values for pyrimidine assuming an optically thin ice and a first order decay. Half-lives for the laboratory, diffuse ISM, dense clouds, and the Solar System (at ~1 AU) could be determined by using appropriate UV fluxes and were determined to be 88 min, 3300 yr, 330 Myr, and 97 hr, respectively. These values are two orders of magnitude longer than gas-phase studies [20] and suggest this species should survive to delivery to a telluric planet more readily in icy bodies than in the gas phase.

HPLC. The total HPLC chromatogram of a H₂O:Pyrimidine = 20:1 mixture irradiated with UV

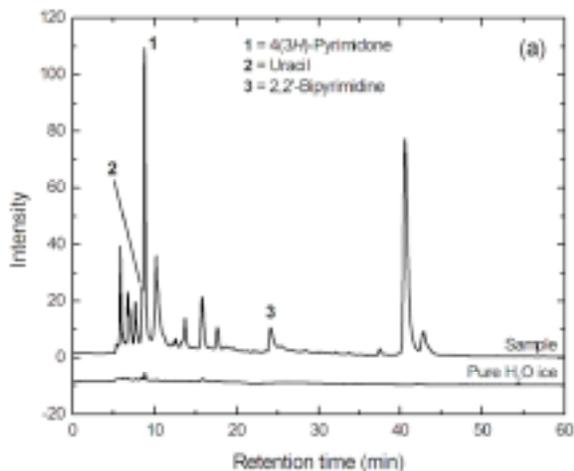


Figure 2: Total HPLC chromatograms of the sample prepared from a UV irradiated H₂O:Pyrimidine = 20:1 mixture, and of a blank experiment where only pure H₂O ice was deposited and UV irradiated during the same time duration.

photons is shown in the top trace of Fig. 2. The bottom trace of Fig. 2, corresponding to a control sample where only pure H₂O ice was deposited and UV irradiated during the same time, clearly shows that no contaminants were present. Only 4(3H)-pyrimidone, a singly-oxidized derivative of pyrimidine, was conclusively identified as an oxidized pyrimidine product in the sample. Its identification was confirmed through a match with the standard. Uracil was tentatively identified in the sample, however, it was a blended feature in this method. Other standards, including oxidized variants of pyrimidine, hydrides, and nitriles were not confirmed in the HPLC samples.

GC-MS. The GC-MS analysis of the extracted residue from a H₂O:Pyrimidine = 20:1 photo-irradiated ice also revealed the presence of multiple compounds not present in the non-irradiated ice control. Figure 3 shows two chromatograms of the same residue using the single-ion mass mode of the GC-MS device for the selected masses $m/z = 269$ (top) and 283 amu (middle), corresponding to the masses of the singly- and doubly-oxidized pyrimidine derivatives, respectively. Uracil was conclusively identified in this residue (peak 2) by comparison of its retention time in the $m/z = 283$ amu single-ion chromatogram (bottom trace).

Conclusions and Future Work: Experiments of H₂O:Pyrimidine ice mixtures have verified the presence of singly- and doubly-oxidized pyrimidine derivatives, including the nucleobase uracil. These results suggest that prebiotic molecules can form in interstellar and/or cometary environments via non-biological processes. The photostability of such compounds is significantly increased when imbedded in

ices. The confirmed species in our mixtures are comparable to those found in carbonaceous chondrites, implying that irradiated ice chemistry may have played a role in the formation of the complex species.

Initial work has been conducted on NH₃:Pyrimidine and H₂O:NH₃:Pyrimidine ices. Preliminary results suggest that the chemistry is consistent. Singly- and doubly-functionalized variants of pyrimidine are found in these ices.

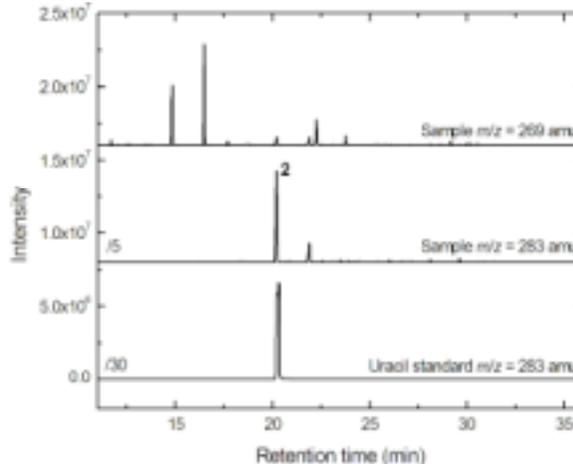


Figure 3: Single-ion GC-MS chromatograms for a residue of a H₂O:Pyrimidine = 20:1 mixture: single-ion chromatogram for $m/z = 269$ amu (singly-oxidized pyrimidines), $m/z = 283$ amu (doubly-oxidized pyrimidine), and the $m/z = 283$ amu trace for the uracil standard.

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