

FORMATION OF NUCLEOBASES FROM THE UV IRRADIATION OF PYRIMIDINE IN ASTROPHYSICAL ICE ANALOGS. S. A. Sandford¹, M. Nuevo^{1,2}, and C. K. Materese¹, ¹NASA Ames Research Center, MS 245-6, Moffett Field, CA 94035, USA (Scott.A.Sandford@nasa.gov), ²BAER Institute, 596 1st St. W, Sonoma, CA 95476, USA.

Introduction: Nucleobases are the informational subunits of DNA and RNA. They consist of *N*-heterocycles that belong to either the pyrimidine-base group (uracil, cytosine, and thymine) or the purine-base group (adenine and guanine). Several nucleobases, mostly purine bases, have been detected in meteorites [1–3], with isotopic signatures consistent with an extraterrestrial origin [4]. Uracil is the only pyrimidine-base compound formally reported in meteorites [2], though the presence of cytosine cannot be ruled out [5,6]. However, the actual process by which the uracil was made and the reasons for the non-detection of thymine in meteorites have yet to be fully explained.

Although no *N*-heterocycles have ever been observed in the ISM [7,8], the positions of the 6.2- μ m interstellar emission features suggest a population of such molecules is likely to be present [9]. In this work we study the formation of pyrimidine-based molecules, including the three nucleobases uracil, cytosine, and thymine from the ultraviolet (UV) irradiation of pyrimidine in ices consisting of several combinations of H₂O, NH₃, CH₃OH, and CH₄ at low temperature, in order to simulate the astrophysical conditions under which prebiotic species may be formed in the interstellar medium, in the protosolar nebula, and on icy bodies of the Solar System.

Experimental: Gas mixtures are prepared in a glass mixing line (background pressure in the low 10⁻⁶ mbar). Relative proportions between mixture components are determined by their partial pressures. Gas mixtures are then deposited on an aluminum foil attached to a cold finger (< 20 K) and simultaneously irradiated with an H₂-discharge lamp emitting UV photons (Lyman α at 121.6 nm and a continuum at ~160 nm). After irradiation, samples are warmed to room temperature, at which time the remaining residues are recovered with water to be analyzed with liquid and gas chromatographies.

Results: Experiments showed that the UV irradiation of pyrimidine mixed in these ices at low temperature leads to the formation of numerous photo-products, some of which consist of pyrimidine that has been further functionalized by new chemical groups added to their edges. Of particular interest for compounds derived from pyrimidine are the nucleobases uracil [10–12], cytosine [11], and thymine [12], as well as a number of their precursors [10–12] (Figure 1). In addition, other species of prebiotic interest such as urea

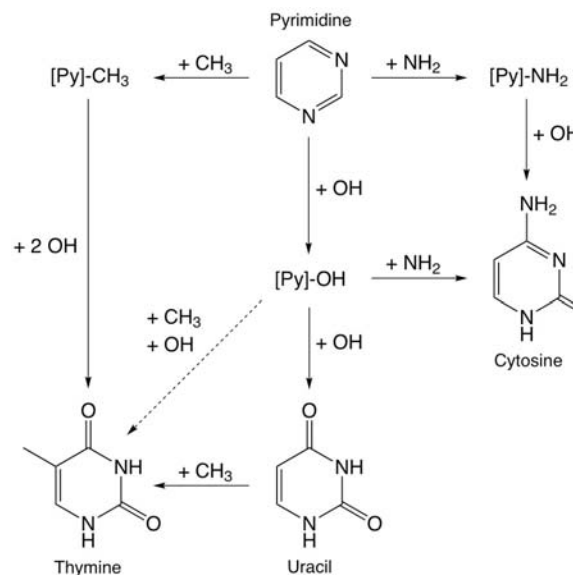


Fig. 1. Pathways leading to the formation of uracil, cytosine, and thymine from the UV photo-irradiation of pyrimidine in H₂O, NH₃, CH₃OH, and/or CH₄ ices [15].

and the amino acids glycine and alanine could also be identified in the same residues [11,12].

However, not all nucleobases are observed to be formed with the same efficiency. Our results show that the oxidation and amination of pyrimidine are efficient processes leading to the formation of uracil and cytosine in all the residues produced from the irradiation of pyrimidine in ices containing H₂O and NH₃. However, the formation of methylated pyrimidine derivatives, including the nucleobase thymine, is significantly more limited, regardless of the carbon source employed (CH₃OH or CH₄) [12]. This observation can be explained by the fact that methylation appears to compete poorly with oxidation under our experimental conditions. In addition, our experiments show that CH₃ groups attached to the pyrimidine ring can be cleaved off more easily than OH or NH₂ groups. Finally, the formation of thymine requires the addition of three groups, as opposed to those of uracil and cytosine, which require the addition of two groups each. Combined these effects result in production yields of thymine that are at least one order of magnitude smaller than those of uracil and cytosine [12].

All these results have been independently confirmed by theoretical quantum computations for the formation of uracil, cytosine, thymine, and their precursors from reactions of condensed-phase pyrimidine in its neutral, cationic, or radical form with OH, NH₂, and/or CH₃ radicals [13,14]. The quantum computations also make it clear that H₂O molecules in the ice play a key role in the chemistry, independent of whether they are supply reactants for the production of the specific molecules in question, by assisting with proton abstraction. Similar laboratory experiments done with and without H₂O in the ices are consistent with this conclusion.

In a scenario in which molecules important for life, such as nucleobases, were formed via astrophysical ice photo-processes and delivered to the primitive Earth via comets and meteorites, our experimental results suggest that the abundance of uracil delivered may have been significantly higher than that of thymine. This is consistent with the detection of uracil and the non-detection of thymine in meteorites. In addition, if the delivery of extraterrestrial nucleobases to Earth played a role in the origin of life, the over-abundance of uracil (an RNA base) over that of thymine (a DNA base) may have contributed to the initial emergence of molecular world dominated by RNA rather than DNA.

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