

**THE FORMATION OF NUCLEOBASES FROM THE UV IRRADIATION OF PURINE IN
ASTROPHYSICAL ICES AND COMPARISONS WITH METEORITES.**

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Introduction: *N*-heterocycles have been identified in meteorites and their extraterrestrial origin is suggested by isotopic ratio measurements [1]. Although small *N*-heterocycles have not been detected in the interstellar medium (ISM), recent experiments in our laboratory have shown that the irradiation of the aromatic molecules like benzene (C₆H₆) and naphthalene (C₁₀H₈) in mixed molecular ices leads to the formation of *O*- and *N*-heterocyclic molecules [2]. Among the class of *N*-heterocycles are the nucleobases, which are of astrobiological interest because they are the information bearing units of DNA and RNA. Nucleobases have been detected in meteorites [3–5], with isotopic signatures that are consistent with an extraterrestrial origin [1]. Three of the biologically relevant nucleobases (uracil, cytosine, and guanine) have a pyrimidine core structure while the remaining two (adenine and guanine) possess a purine core. Previous experiments in our laboratory have demonstrated that all of the biological nucleobases (and numerous other molecules) with a pyrimidine core structure can be produced by irradiating pyrimidine in mixed molecular ices of several compositions [6–8].

In this work, we study the formation of purine-based molecules, including the nucleobases adenine and guanine, from the ultraviolet (UV) irradiation of purine in ices consisting of mixtures of H₂O and NH₃ at low temperature. The experiments are designed to simulate the astrophysical conditions under which these species may be formed in dense molecular clouds, protoplanetary disks, or on the surfaces of icy bodies in planetary systems.

Experimental: Gas mixtures were prepared in bulbs attached to a glass line. The relative proportions of each component were established using partial pressures. An evacuated sample tube containing pure purine was prepared separately, attached to the vacuum chamber, and wrapped with heat tape and a thermocouple to monitor temperature. The gas mixtures from the bulbs, along with the purine from the heated sample tube, were deposited on an aluminum foil attached to a cold finger (<20 K). The combined ices formed from the gases and purine were 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, and refractory residues are recovered for derivatization and analysis using gas chromatography coupled with mass spectroscopy.

Results: The UV irradiation of our ice mixtures results in the formation of refractory residues containing functionalized purines. This included the nucleobases adenine and possibly guanine, in addition to hypoxanthine, isoguanine, several aminopurines, and 2,6-diaminopurine. While adenine is one of the most abundant photoproducts in these UV-irradiation experiments, guanine appears to be produced with very low to undetectable levels of abundance. One possible explanation of this may just be that guanine production is far less favorable than alternative structural isomers. However, guanine has a propensity to form strong hydrogen bonds with itself and other molecules, which greatly reduces its solubility in most solvents and thereby makes it more difficult to derivatize and detect with the GC-MS. In this case, guanine may be being produced but not be amenable to detection by GC-MS. This same chemical behavior would have represented a significant difficulty in the inclusion of guanine into early RNA and DNA, and it has been suggested that the compound hypoxanthine may have originally been used to pair with cytosine instead of guanine [9]. In this regards, it is interesting to note that hypoxanthine is abundant in the photoproducts found in our experiments, with an abundance comparable to that of adenine.

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