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Ice world: the origin of nucleobases in ice-liquid water coexistence conditions.

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Abstract

We could define the *ice world* as the chemical evolution in the range between freezing point of water and the limit of stability of liquid brines, ≈273 to 210 K. In this environment, the synthesis of nitrogen heterocycles using urea as nitrogen source and methane as precursor of active intermediates is favorable from a prebiotic chemistry standpoint, leading to a mixture dominated by pyrimidines and hydantoins. Hence, the synthesis in ice matrix constitutes an experimental model for the study of origin of nucleobases in Solar System bodies.

1. Introduction

Despite the research into the photochemical transformations in ice from an astrochemical point of view, the study of the chemistry in the range of stability of the ice–water interface has not received much attention. This may be due to the scarcity of the defined conditions in the Solar System during the epoch of active prebiotic chemistry or the difficulties for demonstrating that these cold conditions existed in Hadean Earth. The evidence for a liquid water subsurface ocean on Saturn's moon Europa[1] and the possible presence of water-ammonia eutectic brines or even a subsurface ocean in other outer giant planet satellites such as Titan[2] rekindled the interest in liquid water prebiotic chemistry. Moreover, the subsequent proposed steps for the emergence of cellular life have a limited temperature range, and a hot prebiotic Earth was regarded to be an unlikely environment for the origin of life by some authors[4]. Miller and Orgel stated in 1974 that the emergence of biological organization could only occur at temperatures below the melting point of the polynucleotide structure. After observing the instability of organic compounds in the prebiotic stages, these authors concluded that a temperature of 273 K would have been beneficial and that temperatures near the eutectic point of NaCl solutions (251.3 K) would have been even better [5]. The low temperatures in planetary surface ices could be more conductive to the origin and the preservation of molecules that could be relevant for the emergence of life. In 1994, in one of the first explorations of the idea of an *ice world*-based origin of the life raw materials, Bada *et al*. [6] suggested that ice formations on early Earth could have preserved organic compounds against hydrolysis or photochemical degradation. Under plausible planetary conditions, the presence of liquid water at T<273 K within an ice matrix creates a potential reactor where the synthesis or polymerization of molecules of biological interest could occur. Within this context, we proposed a model of prebiotic synthesis in icy environments that could favor the origin of nucleobases.

2. Methodology

The experimental setup and methods was detailed previously [7], [8]. Briefly, pure water or urea water solution in a sealed reactor under primordial methane containing or acetylene containing atmosphere, was subjected to freeze-thaw cycles in a temperature range between 5ºC and the urea-water eutectic point (-21ºC). The system was energized by means of spark discharges or ultraviolet irradiation (254 and 185 nm). Reaction products were separated and identified using gas chromatography-mass spectrometry.

3. Results

The sparking on a freezing dilute urea solution under a nitrogen/methane atmosphere leads to the formation of and cytosine, uracil as the main identified pyrimidines, in addition to adenine (Figure 1). The experiments showed that using the freeze-thaw conditions, the observed sequence of pyrimidine yield obtained was cytosine > uracil > 2,4-diaminopyrimidine > 2,4,6-trihydroxy pyrimidine.

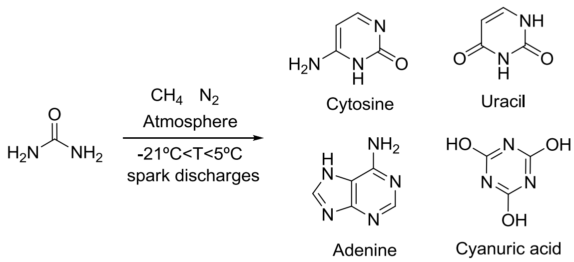

Figure 1. Origin of nitrogen bases in urea water-ice solution under methane atmosphere.

The formation of cytosine as the main pyrimidine suggests that the low temperature conditions could reduce the rate of deamination to uracil and favour subsequent chemical evolution steps. In our analysis of the gas mixture obtained after sparking a CH_4/N_2 mixture, the main product was acetylene, followed by unsaturated hydrocarbons and HCN, but no cyanoacetylene was found. To test if acetylene could be a precursor of nucleobases, ice-water urea system under pure acetylene atmosphere were irradiated with ultraviolet radiation. The reaction products (Figure 2) contained hydantoins, pyrimidines and purines, including uracil, uric acid, xanthine, guanine and adenine. The highest yields corresponded to 5-hydroxyhydantoin,2-oxo-4,5-dihydroxyimidazolidine, hydantoin, uracil, parabanic acid and uric acid. Additionally, cytosine, 6-methyluracil and iso-orotic and orotic acids were found in significant quantities. The presence of urea inhibits the formation of acetylene photopolymers.

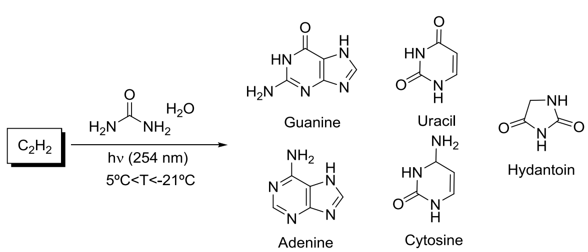

Figure 2: Acetylene as precursor of nucleobases.

Analysis of the reaction products suggests that hydantoin was a product of direct synthesis from acetylene derived glyoxal and urea. 5-hydroxyhydantoin was a product of both direct synthesis from glyoxylic acid and urea, and, in lesser extent, from photodegradation of purines and pyrimidines. The mechanism of formation of purines is unclear, and the formation of ureido derivatives of carboxylic acids could be implicated. The water-ice matrix played a dual role as a protective medium and a source of radicals for the photo-oxidation of purines and pyrimidines.

4. Summary and Conclusions

The ice is a favorable matrix for the origin of nucleobases and other organic molecules of prebiotic interest, from precursors available in primordial conditions, as urea and acetylene or methane. The principal difference with prebiotic chemistry in hot conditions is that, in ice free environment, the atmospheric precursors tend to the formation of tholins and photopolymers and the inhibition of synthesis of nucleobases, which seems to be strongly favored in the zone of coexistence of ice and liquid water solutions enriched in organic solutes.

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