Nucleobase Synthesis via UV-induced oxidation of their precursors in astrophysical ices: A Quantum Chemical Perspective.
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Introduction: Identification of nucleobases in extraterrestrial carbonaceous chondrites, such as Murchison, implies their formation in an abiotic condition, and supports their prebiotic role in early Earth. Physicochemical processes by which these complex molecules are synthesized in icy grains are not well understood. The products of UV photoirradiation of purine and pyrimidine in H_2O, NH_3 and CH_4 ices have been explored using fancy new density functional theory (DFT) methods (ωB97M–V) along with large correlation consistent basis sets, and compared against laboratory experimental results. Mechanisms studied include those starting with neutral pyrimidine and purine, and their cationic counterparts, and then reacting with neutrals and radicals generated by radiation. Reaction mechanisms that involved cations on the purine or pyrimidine proved to be the ones that are most important. The calculations reveal that the formation of nucleobases is energetically and kinetically favorable. The gas phase mechanism of their formation proved ineffective, and the presence of one or several water molecules is necessary in order for the final products to form. Explicit solvent calculations using a polarized continuum model (PCM) established the effect of the ice matrix and product formation preferences. Uracil forms rather easily as oxidation is rather easy in pure H2O ices. The scope of thymine formation in H_2O:CH_4 mixed molecular ices, however, is limited due to the inefficiency of the methylation of pyrimidine, and its oxidized derivatives. Thymine is a minor component of the products in the experimental samples. Amine group addition to purine leading to adenine and guanine in mixed NH_3 and H_2O ices is facile. Although adenine is the most likely monosubstituted photoproduct in mixed H2O:NH3 ice, isoguanine and xanthine are the bi-substituted products. Many of the photoproducts in UV-irradiated H_2O and pyrimidine ice mixtures are found in an experimental study. The results support the scenario in which prebiotic molecules, such as the nucleobase uracil, can be formed under abiotic processes in astrophysically relevant interstellar environments, and on surfaces of icy grains before being delivered to telluric planets such as Earth. But, it constrains the formation of thymine as well as its role in the origin of life.

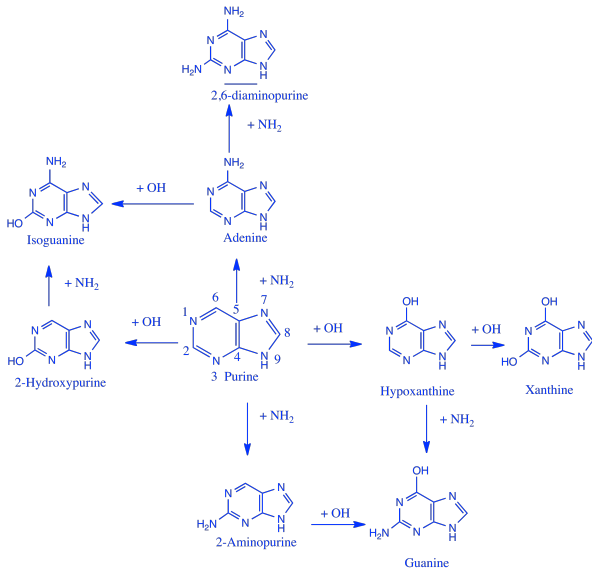

Figure 1. A reaction scheme indicating the amino and hydroxyl group substitutions on the purine ring.

References:

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