Mechanisms for the abiotic synthesis of uracil and thymine via UV-induced oxidation of pyrimidine in astrophysical ices

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Abstract: Identification of nucleobases in carbonaceous chondrites such as Murchison supports their role in the origin of life in early Earth. Physicochemical processes and mechanisms involved in the formation of these complex large molecules in icy grains, and in their possible formation in the interstellar medium, are thus far unknown to us. The UV photo-irradiation of pyrimidine in pure H_2O and mixed H_2O and CH_4 ices has been explored using second-order Møller-Plesset Perturbation theory (MP2) and density functional theory (DFT) methods and compared with experimental results. Mechanisms studied include those starting with neutral pyrimidine or cationic pyrimidine radicals, and then reacting with OH and CH_3 radicals. The *ab initio* calculations reveal that the formation of some key species, including the nucleobase uracil, are energetically favored over others. The presence of one or several water molecules is necessary in order to abstract a proton, which leads to the final products. Formation of many of the photoproducts in UV-irradiated H_2O and pyrimidine ice mixtures is established in an experimental study. Our quantum chemistry calculations, however, suggest that a condensed-phase environment is necessary in order for proton abstraction reactions to occur. Uracil is predicted by our calculations to be the most favored, and has been identified by chromatography techniques. The scope of thymine formation, however, is limited because of the inefficiency of the methylation of pyrimidine, and its oxidized derivatives, in a mixed ice. 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 surface 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.