

Photochemistry and Photophysics of Prebiotic Precursors of Nucleotides

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During the Archean eon (3.8-2.5 billion years ago), the Sun was much less luminous than today. However, the total amount of UV-light reaching the surface of early Earth was much larger due to lack of the ozone layer, and higher Solar activity in the UV range. This prolonged exposure to UV-light was probably a major selective factor at the early stages of abiogenesis that resulted in the remarkable photostability of naturally occurring nucleic acids, and peptides. UV-irradiation could also initiate prebiotically plausible reactions that would otherwise require significant amounts of heat or a specific catalyst. Thus for many decades UV-light has been considered as an important element of experiments targeted at syntheses of biomolecules, or their precursors, from simple feedstock molecules [1, 2].

These synthetic reaction pathways often contain intermediates that had to accumulate in the environment over longer periods of time, and should evince resistance to different environmental conditions of early Earth including intense UV radiation. During our theoretical studies on the photostability of two such intermediates: 2-aminoxazole (AMOX) and 4-aminoimidazole-5-carbonitrile (AICN)—appearing, respectively, in the Sutherland’s synthesis of pyrimidine nucleotides and oligomerization of HCN leading to adenine suggested by Ferris—we observed an interesting mechanism of their non-radiative deactivation that could be described as electron-driven proton transfer (EDPT) [3,4]. More recently we observed this mechanism also in hydrated imidazole and adenine [5]. Although the ring-puckering processes, driven by $\pi\pi^*$ electronic states, remain usually the main deactivation channels, our non-adiabatic molecular dynamics simulations indicate a significant importance of the EDPT mechanism. The latter seems to occur quite commonly in the case of hydrated chromophores with low-lying $\pi\sigma^*$ electronic states. In such case, photoexcitation of the chromophore clustered with several water molecules leads to the ejection of an electron in the direction of the solvent molecules. The electron may be then followed by a proton from an amino, hydroxyl or imino group of the chromophore. Subsequent proton transfers along H₂O wires result in the recombination of the migrating proton with the hydrated electron and eventually may enable photodeactivation via a conical intersection with the electronic ground-state (cf. Fig. 1).

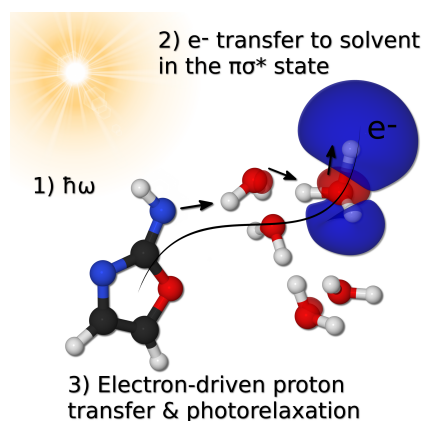


Fig. 1: Electron-driven proton transfer along H₂O wires induces the formation of $\pi\sigma^*/S_0$ state crossing in 2-aminoxazole.

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