

ABSTRACT

The TiO₂-catalyzed synthesis of nucleosides in non-aqueous formamide environment via so-called acyclonucleoside intermediates represents an alternative way for the emergence of nucleic acids monomeric units, which could address the the fundamental problem associated with the formation of a β -glycosidic bond between a nucleobase and a sugar moiety. In this computational contribution we present a plausible reaction route for the prebiotic TiO₂-catalyzed synthesis of purine C₂- and C₃-acyclonucleosides in formamide, which does not require photocatalytic or radical chain mechanisms. The maximum computed activation energy along the proposed reaction channel is ~ 32 kcal·mol⁻¹, which is clearly feasible under the experimental conditions of the Saladino synthesis. We show that the rate determining step of the entire reaction path is the deprotonation of the formaldehyde hydrate methylene carbon occurring likely on defective binding sites of an anatase surface. Our calculations thus support the view of Saladino et al. about the catalytic role of the TiO₂ surface in the one-pot synthesis of purine acyclonucleosides in heat formamide solution.