Origins of Computational Chemistry

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The question ‘‘How and where did life arise on Earth?’’ constitutes one of the most fascinating in the contemporary science. Over the decades, the RNA-hypothesis became the most common concepts explaining the mystery of life’s primordial beginnings on our planet. It is based on the assumption that there was an ancient life-form in which RNA occupied center stage and performed most jobs in the cell, such as storing genetic information, copying itself, and performing basic metabolic functions. Consequently, the key issue in the origin of life research concerns on finding the synthetic route of RNA building blocks. Studying the origin of life might be therefore considered as a task for chemistry.

In order to understand how the simple molecules present on the early Earth have given rise to the complex systems and processes of contemporary biology it is necessary to use the modern computational chemistry tools to complement the experiments (see Figure 1). This is due to the fact that the major advantage of computations is that they provide information on selected single molecules and chemical reactions. On the contrary, the prebiotic experiments always work with complex mixtures, which often make the interpretation of their results very difficult or even impossible. Thus, computational chemistry may supplement the experiments, providing information from an atomic level insight into the structural aspects, electronic structure changes, energetics, spectroscopic properties and dynamic behavior of the studied systems.

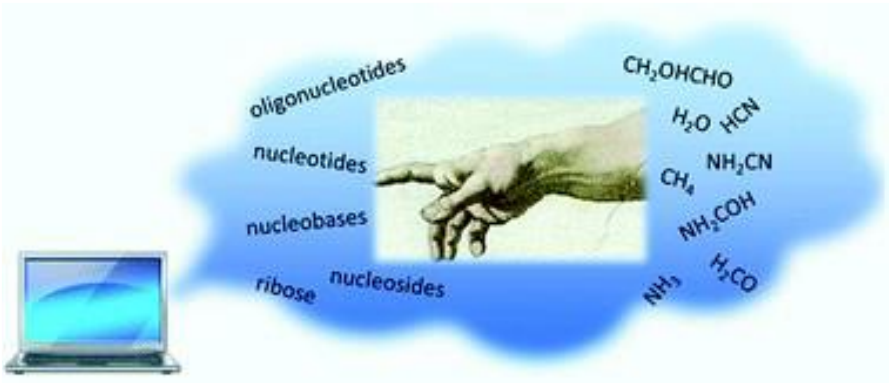

Figure 1. Computational chemistry as a tool for studying the origins of life.

One illustrative example of the synergy between experiment and computer simulations in the origin of life research refers to the important photochemical reaction, demonstrating that the nucleobases (which

together with sugar constitutes the basic building block of RNA) can be synthesized from simple precursor molecules, like HCN (cf. Figure 2).

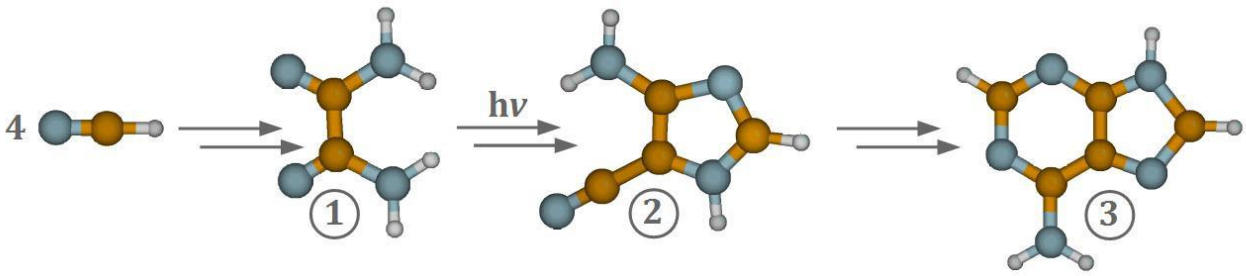

Figure 2. Tetramerization of HCN leads to imidazole

In the above process, HCN polymers (1), which should have occurred on the early Earth, are converted into imidazole (2) due to UV radiation.

It is fair to mention, that although this reaction was experimentally discovered already in 1960's [1] by many years it was not clear how it happened. This is related to the fact that this reaction represents a multistep and complex process and it is very difficult to study its mechanism employing purely experimental methods. However, by using the computational simulations it became possible to trace along all possible reaction routes presented in the figure below (see Figure 3).

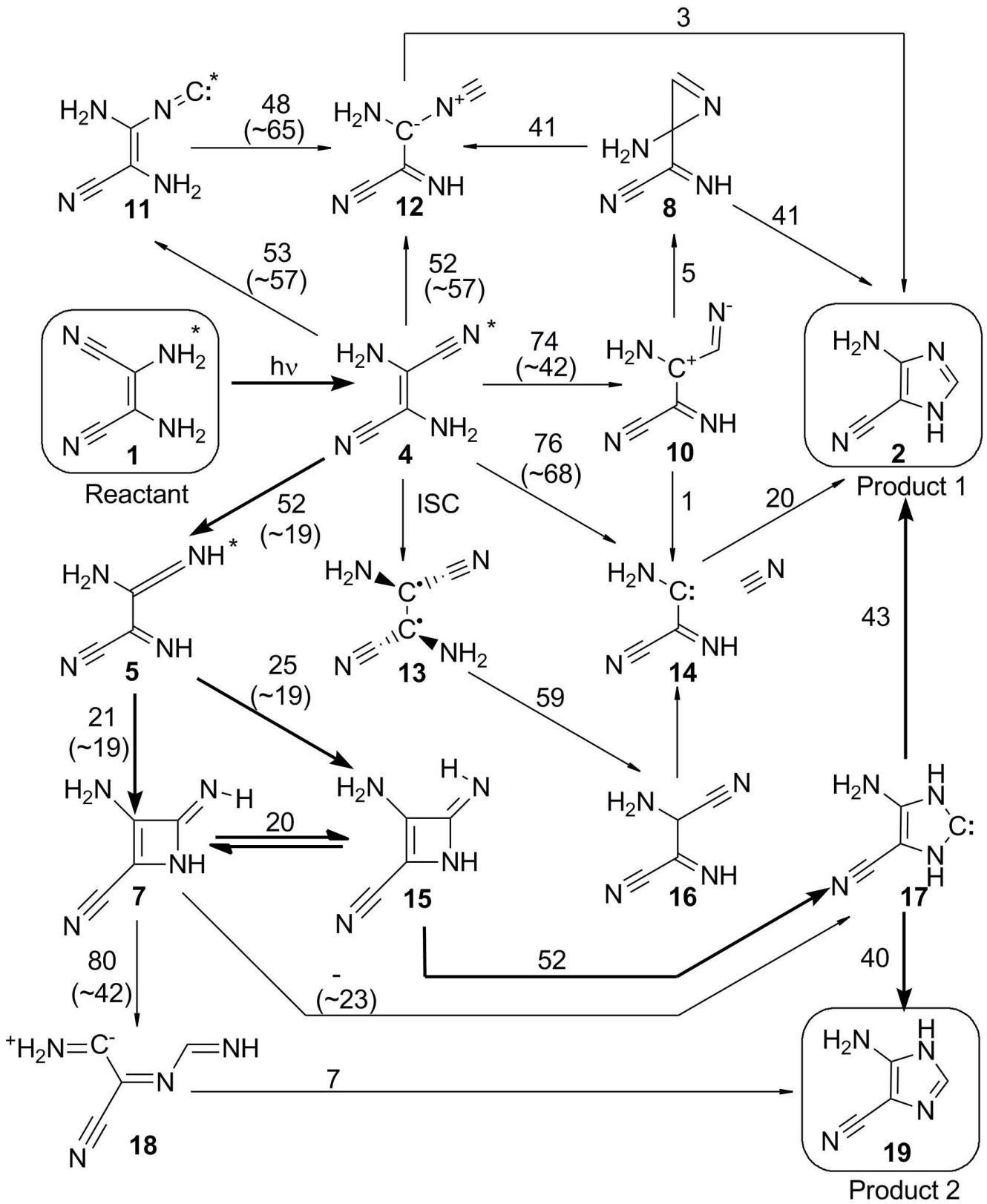

Figure 3. Possible pathways of imidazole synthesis

It seems unbelievable, but the reaction starting in 1 and ending in 2 or 19 might occur by any of the connected arrows. Moreover, the reaction can proceed with the UV energy stored in the nuclei (ground state reaction) or with this energy stored in the electrons (excited state reaction). In order to establish which pathway really happens, the energy needed for each step of the process were computationally determined [1].

These energies (in kcal/mol) are shown near the arrows in the Figure 3 (for excited state reactions they are given in parenthesis). By using the molecular dynamics simulations it has been evaluated how long it takes to dissipate the UV energy to the environment. The data obtained from the molecular dynamic simulations together with a chemical kinetics model leaves no room for doubt that no barrier with more than 30 kcal/mol could be overcome. Thus, it was possible to establish that the reaction can occur only by the steps highlighted in red. So, it seems quite exciting that only by using computer simulations it was possible to explain the mechanism of one of the reaction forming the beginnings of life on Earth, which happens through an excited-state azetene [1]:

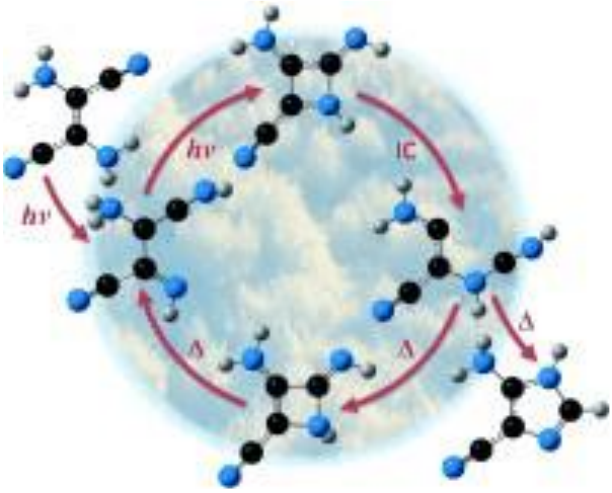

Figure 4. Photochemical steps in the prebiotic

[1] Boulanger, E., Anoop, A., Nachtigallova, D., Thiel, W. and Barbatti, M. (2013), Photochemical Steps in the Prebiotic Synthesis of Purine Precursors from HCN . Angew. Chem. Int. Ed., 52: 8000–8003.

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