

Title
Prebiotic reaction mechanism for adenine formation, metal cluster mediated dinitrogen activation: Computational investigation

by
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Quantum chemical methods have proven to be a powerful tool to study the structure, behavior, and the mechanisms, for the formation of molecules related with interstellar space and Origin of life, and also modeling active sites. This presentation aims to answer two major, albeit unrelated, unsolved puzzles (a) how did biomolecules originate under prebiotic condition starting from abiotic precursors? (b) which is the smallest possible model compound for the reduction of inert molecular nitrogen, and what is the mechanism and degree of activation?

Fundamental building blocks of life have been detected extraterrestrially, even in interstellar space, and are known to form nonenzymatically. Thus, the HCN pentamer, adenine (a base present in DNA and RNA), was first isolated in abiogenic experiments from an aqueous solution of ammonia and HCN in 1960. Although many variations of the reaction conditions giving adenine have been reported since then, the mechanistic details remain unexplored. Our predictions are based on extensive computations of sequences of reaction steps along several possible mechanistic routes. H₂O- or NH₃-catalyzed pathways are more favorable than uncatalyzed neutral or anionic alternatives, and they may well have been the major source of adenine on primitive earth. This presentation is aimed to provide a more detailed understanding of some of the chemical processes involved in chemical evolution, and a partial answer to the fundamental question of molecular biogenesis.

Because of the inertness of molecular nitrogen, its practicable activation under mild conditions remains a fundamental challenge. Nature can do it easily; chemists should be able to achieve comparable success. Lithium metal is exceptional, but it exemplifies the possibilities. Remarkably, lithium is the only metal that reacts slowly with N₂ at room temperature and it even burns in a pure nitrogen atmosphere. The lithium nitride product, (NLi₃)_x, has potential as a hydrogen storage material. Our extensive computations elucidate mechanisms for the ready reactions of N₂ with various Li₂, Li₄, Li₆, and Li₈ model clusters, ultimately leading to NN cleavage. Initial isomeric N₂-Li_n complexes, retaining NN triple bonds, undergo cluster insertion/reduction processes over generally low barriers proceeding through sequentially through NN double and single bonded intermediates to two separated N³⁻ moieties. The overall reactions are highly exothermic (N₂Li₆ and N₂Li₈ products with >3Å N-N bond lengths are 39 and 86 kcal/mol more stable, respectively, than N₂ and the separated Li₆ and Li₈ clusters). The behavior of the relatively simple model complexes reported here suggests the potential for dinitrogen activation by polymetallic systems in which the capability of lithium to reduce dinitrogen is enhanced cooperatively.