A Computational Study of a Prebiotic Synthesis of L-Isoleucine

Nigel Aylward

***Abstract*—** The magnesium ion metalloporphyrin complex is shown to bind the ligands pentdiyne nitrile and pentdiynimine in weak van der Waals complexes on the metal site. When carbon monoxide is also bound to the complex as a high energy compound whose particular structure has been dictated by the magnetic vector of the exciting radiation, photochemical excitation may enable both adducts to combine to give a substituted aziridine-3one. Further photochemical excitation allows the formation of bicyclic and tricyclic adducts. Hydrogenation of this complex allows the opening of the rings to give an aziridine-3one that may easily hydrolyse to the zwitterionic form of L-isoleucine with the correct configuration.

The reactions have been shown to be feasible from the overall enthalpy changes in the ZKE approximation at the HF and MP2 /6-31G* level, and with acceptable activation energies**.**

***Keywords*—** L-isoleucine, prebiotic photochemical synthesis.

I. INTRODUCTION

THE The amino acid L-isoleucine (Ile,I), is an essential amino acid [1], that occurs naturally as the L-isomer [2] and is present in many proteins such as haemoglobin, elastin, wool keratin, myosin and ovalbumin [2]. Isoleucine contains two asymmetric carbon atoms and therefore exists in two racemic forms, DL-isoleucine and DL-alloisoleucine giving four optical isomers. The configuration of normal L-isoleucine is (2S, 3S)-2-amino-3-methyl pentanoic acid [1]-[3]. It has been shown to isomerise to D-alloisoleucine [4]. For isoleucine the α-COOH pKa is 2.4 and a α-NH_2 pKa 9.7 [5]. The biosynthesis of isoleucine is from α-ketobutyric acid followed by transamination [1]. The metabolism of isoleucine leads to succinyl-CoA [1]. (2S,3R,4S)-4-hydroxyisoleucine **is** found in the medicinal herb Fenugreek (*Trigonella foenum-graecum*) [6].

From a prebiotic perspective [7] it is desirable if the reactant molecules formed spontaneously from a supposed prebiotic atmosphere to be inevitably present. It has often been held that the atmosphere of the Earth was originally mildly reducing [1]-[8] implying the presence of concentrations of carbon monoxide, ammonia, water and hydrogen. It is also supposed that pentdiyne nitrile, H-(C ≡ C)$_2$-CN, that has been found in interstellar space [9]-[10] and present on Titan, a moon of Saturn, was also present, possibly formed from the free radical mediated condensation of diacetylene and hydrogen cyanide or by ionic species [11]. It has also been demonstrated that porphin may act as a catalyst for the formation of sugars [12], polyenes [13], and amino acids [14]-[15]-16].

This paper proposes a model for the catalytic photochemically activated formation of L-isoleucine from pentdiynimine, carbon monoxide, water and hydrogen, and the catalyst magnesium porphin.

The reactions described have been deduced as kinetically and thermodynamically viable, but photochemical excitation is required.

II. PROBLEM FORMULATION

This proposed computational study of a plausible synthesis of L-isoleucine involves the calculation of the enthalpy changes for reaction intermediates in the ZKE approximation and the calculation of activation energies at the HF level. These activation energies may all be accessible as the catalyst may absorb appreciable photochemical activation (0.21 h). The computations tabulated in this paper used the GAUSSIAN03 [17] commercial package. The standard calculations at the HF and MP2 levels including zero-point energy corrections at the Hartree Fock level, [18], together with scaling [19], using the same basis set, 6-31G*. are as previously published [7]. Enthalpy changes at the MP2 level not including scaled zero point energies are designated as $\Delta H_{(MP2).}$ The charge transfer complexes are less stable when calculated at the Hartree Fock level [18], and activation energies calculated at the HF level without scaling are less accurate..

If the combined energy of the products is less than the combined energy of the reactants it may show that the reaction is also likely to be spontaneous at higher temperatures. This paper uses the atomic unit of energy, the hartree [17].

1h = 627.5095 kcal.mol-1. 1h = 4.3597482 x 10-18 J

Charges are in units of the electronic charge.

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N. N. Aylward is an affiliate of the School of Chemistry and Molecular Biosciences, University of Queensland, Brisbane, Queensland, Australia. (e-mail: uqnaylwa@uq.edu.au).