A Computational Study of a Prebiotic Synthesis of L-Leucine and L-Isoleucine

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Abstract: - The magnesium ion metalloporphyrin complex is shown to bind the ligand pent-1,3-diynein a weak van der Waals complex on the metal site. Photochemical excitation allows the formation of cyclic adducts which may become partially hydrogenated. Subsequent reactionof the adducts withammonia gives amines that easily transform to aziridine derivatives, and ultimately imines bound to the catalyst. 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, reaction occurs to give substituted aziridine-2ones that may easily hydrolyse to the zwitterionic form of the amino acids L-leucine and L-isoleucine.
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.

Key-Words: -Prebiotic photochemical synthesis, L-leucine, L-isoleucine, L-norleucine.

1 Introduction

The amino acids L-leucine (Leu,L) and L-isoleucine (Ile,I), are essential amino acids [1], that occur naturally as the L-isomer [2] and are present in many proteins such as haemoglobin, elastin, wool keratin, myosin and ovalbumin [2]. N-Methylleucine occurs naturally in seeds of Cycascircinalis and Phaseolusvulgaris[3]. Norleucine, α-aminocaproic acidalso has a natural occurrence in an ergot alkaloid[4]. 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 [1]. L-leucine is regarded as hydrophobic [5] with α-COOH pKa, 2.36and an α-NH_2pKa 9.60 [1], for isoleucine the corresponding values are 2.4 and 9.7 [6]. The biosynthesis of leucine is from α-ketovaleric acid [1] and isoleucine from α-ketobutyric acid [1]. The metabolism of L-leucine yields acetyl-CoA in the tricarboxylate cycle [1]. The metabolism of isoleucine leads to succinyl-CoA [1].
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 methyldiacetylene, CH_3-$(C\equiv C)_2$-H, that has been found in interstellar space [9] was also present, possibly formed from the free radical mediated condensation of acetylene and allylene or by ionic species [10]. It has also been demonstrated that porphin may act as a catalyst for the formation of sugars [11],polyenes [12], and amino acids [13-15].
This paper proposes a model for the catalytic photochemically activated formation of L-leucine and L-isoleucine from methyldiacetylene, ammonia, carbon monoxide, hydrogen, and the catalyst magnesium porphin, whilst seeking to explain the meager occurrence of norleucine and ψ-leucine [2].
The reactions described have been deduced as kinetically and thermodynamically viable, but photochemical excitation is required.

2 Problem Formulation

This proposed computational study of a plausible synthesis of L-leucine and 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 [16] commercial package. The standard calculations at the HF and MP2 levels including zero-point energy corrections at the HartreeFock level, [17], together with scaling [18], 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

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HartreeFock level [17], 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 [16].

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

Charges are in units of the electronic charge.

3 Problem Solution

3.1 Total Energies (hartrees)

Methyl diacetylene may chelate with the magnesium ion of magnesiumporphin, which is here taken as a possible catalyst, to form an in-plane charge transfer complex where the charge on the ligand is positive, 0.06. and the charge on the porphin molecule is negative. The enthalpy of formation of the van der Waals complex is small but it appears stable.

Mg.porphin + H-(C≡C)$_2$- CH$_3$→
(1) (2) [1]

Mg.H-(C≡C)$_2$-CH$_3$.porphin (3)

Δ H = -0.02556 h

The adduct has formal charges of -0.59, 0.22, 0.19, -0.23 and -0.50 on the carbons C1-C4, respectfully.

This is the first reactant required in the synthesis.

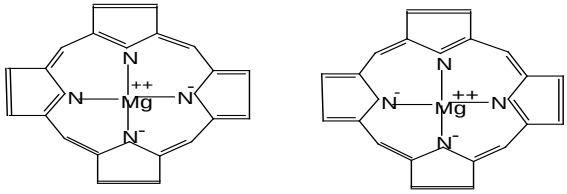
3.2 The asymmetric induction of chirality

Mg.porphin also forms a stable complex with carbon monoxide in which the carbon monoxide is bonded to the magnesium ion, as shown,

Mg.porphin + CO → Mg.CO.porphin
(1) (4) [2]

$\Delta H_{(HF)}$ = -0.00919 h

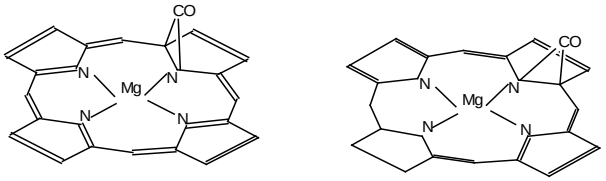
This is the low energy complex [11]. When this complex is photochemically activated, an in-plane electronic transition occurs in which the HOMO may be excited to the LUMO [11]. If the magnetic vector of the radiation is directed perpendicularly upward from the ring when viewed from above, the energy levels of the HOMO and LUMO are each split according to the Zeeman effect [19] and the adduct may dissociate, and rise in height above the ring. The first excitation energy (0.21 h) is greater than the activation energy (0.19668h) and much greater than the bonding energy (-0.02164 h) [11]. The system of conjugated bonds in porphin has been approximated to the particle on a ring quantum mechanical problem [20]. In this model the molecule is described as a cyclic system [21] where the removal of the degeneracy of the orbitals by the magnetic field allows the contributing mesomeric forms [22] to have different energies, as shown in Fig.1.



Mg.porphin (1) Mg.porphin (2)

Fig.1. Mesomeric forms of Mg.porphin in the presence of a magnetic field pointing perpendicularly upwards from the ring towards the observer.

Four transitions may occur[19] of which two are allowed by the selection rules [23]. As the molecule is normally diamagnetic [24] the highest energy HOMO orbital should correspond to that shown as Fig.1(1) . It is postulated that the CO group is able to move through a transition state to the porphin ring where it forms an excited, but stable bridged aziridine-2one ring [11,25-26] at a pyrrole unit with this isomer, as shown, Fig.2(1)



(1) (2)

Fig.2. Isomers of Mg.porphin.CO

This is a higher energy charge transfer complex, where a high proportion of the photochemical energy has been conserved as chemical energy. If the magnetic field reverses the positively charged adduct is compressed down on the ring and less liable to reaction. If the unfavourabe complex Fig.2(2) is formed from atmospherically activated carbon monoxide, then further excitation may lift the adduct from the periphery of the ring and convert it to the more favourable orientation for asymmetric induction. The activation energy

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required to convert the forms Fig.2(1) to Fig.2(2) is < 0.11 h.
This is also involved in the proposed synthesis, as shown later. The formation requires photochemical activation,. The enthalpy of formation is positive.

Mg.porphin + CO → Mg.porphin.CO
(1) (5)
ΔH = 0.21136 h [3]

Mg.CO.porphin→ Mg.porphin.CO
(4) (5) [4]
ΔH = 0.20106 h

These are the reactants that will be used in the synthesis of the amino acids, leucine and isoleucine.
The total energies and zero point energies for the HF and MP2/6-31G* equilibrium geometries for some of these stable molecules are given in Table 1.

Table 1
MP2 /6-31G* total energies and zero point energies (hartrees) for the respective equilibrium geometries

Molecule	MP2	ZPE (HF)
	hartree	hartree
Mg.porphin (1)	-1185.12250	0.29262
Methyl diacetylene(2)	-192.16934	0.06934
Mg.H-(C≡C)$_2$-CH$_3$.porphin(3)	-1377.31505	0.35932
Mg.CO.porphin (4)	-1298.13452	0.29942
Mg.porphin.CO(5)	-1297.93784	0.30434
L-leucine (non-zwitterion)(6)	-440.26501	0.20796
L-isoleucine (non-zwitterion)(7)	-440.26559	0.20794
L-norleucine (non-zwitterion)(8)	-440.26648	0.20817
Mg-1, 2-amino pent-1,3-diyn-1yl.porphin(9)	-1433.62989	0.40324
Mg.1,3-amino pent-1-yne-3-ene-1-yl.porphin (10)	-1433.69366	0.40245
Mg.1,2-methyl bicycle[1.1.0] but-1-dehydro-1-en-4yl.porphin (11)	-1377.22809	0.35678
Mg.1,(2-didehydro-3-dehydro 3-methyl cyclopropenyliden-1yl) methan-1yl.porphin (12)	-1377.21615	0.35551
Mg.1,2-didehydro-3-dehydroethyliden-1yl cyclopropan-1yl.porphin(13)	-1377.21941	0.35513
Mg.1,(2-dehydro-2-methyl cyclopropenyliden-1yl) methan-1yl.porphin(14)	-1378.43219	0.38281
Mg.1,3-methenyl butyn-1-yl.porphin (15)	-1374.59087	0.38431
Mg.1,2-amino 3-methenyl butyn-1-yl.porphin (16)	-1434.86584	0.42952
Mg.1,3-(1-methenyl ethyl) 1H aziridin-2yl.porphin(17)	-1434.86399	0.42924
Mg.1,3-methenyl butanimin-1yl.porphin(18)	-1434.94414	0.42832
3-methenyl butanimine (19)	-249.78846	0.14028
Mg.1,3-methenyl butanimin-1-yl.porphin.CO(20)	-1547.93017	0.43879
Mg.1,(2-methenyl propyl) aziridine-3-one-1-yl.porphin(21)	-1547.94954	0.43870
CO	-113.02122	0.00556
H_2O	-76.19685	0.02298
NH_3	-56.35421	0.03700
H_2	-1.14414	0.01059

3.3 The overall stoichiometry for the formation of L-leucine, L-isoleucine and L-norleucine.

Although Mg.porphin is here taken as the catalyst for the reaction, the overall stoichiometry to form the amino acids, L-leucine, L-isoleucine and L-norleucine are as follows,

H-(C≡C)$_2$-CH$_3$+ NH$_3$ + CO + H$_2$O +2H$_2$→C$_6$H$_{13}$NO$_2$
(2) (6)[5]
L-leucine (non-zwitterion)(6) Fig.3
Δ H = -0.18893 h
L-isoleucine(non-zwitterion)(7)
ΔH = -0.18952 h
L-norleucine(non-zwitterion)(8)
ΔH = -0.19093 h

The enthalpy changesare negative indicating that this may be the energetically favourable route to the initial formation of the amino acids. The intermediates by which these stoichiometric reactions may have occurred are as follows:

3.4 The formation of Mg-1, 2-amino pent-1,3-diyn-1yl.porphin.

The first reaction in this synthesis is probably not the reaction of Mg-1,methyldiacetylene.porphin with ammonia, as shown,

Mg.H-(C≡C)$_2$-CH$_3$.porphin + NH$_3$→
(3) [6]

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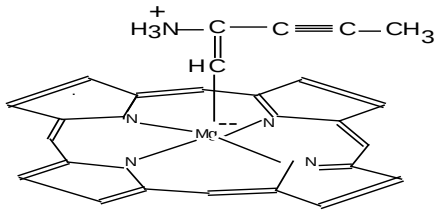


Mg-1, 2-amino pent-1,3-diyn-1yl.porphin.(9)

Although this is the rate determining step in the prebiotic synthesis of most of the amino acids[13-15] this enthalpy change is the largest encountered and implies a large activation energy and the formation of a high energy compound.

$$\Delta H = 0.04553 \text{ h}$$

The activation energies for the forward and reverse reactions were calculated as 0.041 h and 0.001 h, respectively at MP2 accuracy.

There is also a more favourable enthalpy change for the addition of ammonia across the triple bond of the adduct than addition to C2 of the adduct and subsequent reaction to form a cyclic aziridine as shown later,

$Mg.H\text{-}(C{\equiv}C)_2\text{-}CH_3.porphin + NH_3 \rightarrow$

$Mg.H\text{-}C{=}C\text{-}C(NH_2){=}CH\text{-}CH_3.porphin$

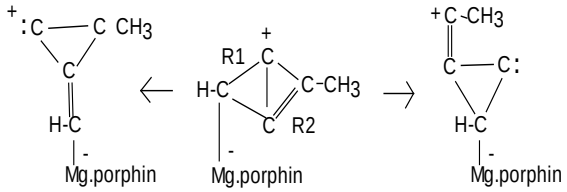
(10) [7]

$$\Delta H = -0.01894 \text{ h}$$

These initial calculations are not favourable for the formation of substantial concentrations of norleucine, 2-amino hexanoic acid, compared to the other isomers. Similarly, the isomer, ψ-leucine , 2-amino-3,3-dimethyl butyric acid, cannot form as there is not any possible alkyne hydrocarbon to react with the catalyst.

3.5 The formation of cyclic isomers of Mg-1,methyl diacetylene.porphin.

Here, it is postulated that the formation of the amino-acids L-leucine and L-isoleucine was initiated by photochemical excitation of the adduct Mg-1,methyldiacetylene.porphin. to forma bicyclic high energy product (11). The activation energy was calculated as 0.085 h. This may dissociate intotwo products of almost identical energy.with bothbeing inter-convertible via the marginally more stable molecule, Mg.1,2-methyl bicycle[1.1.0] but-1-dehydro-1-en-4yl.porphin (11). The following structures depict these molecules.with a stereochemistry determined by the presence of the magnetic field pointing upwards from the porphin ring such that the positive charges of the adduct tended to move counterclockwise whilst the negative charges moved clockwise. For Mg.1,(2-didehydro-3-methyl cyclopropenyliden-1yl) methan-1yl.porphin the adduct retains a positive charge of 0.08 with the only positively charged carbon atom of the adduct (C diradical) being 0.018. For Mg.1,(2-didehydro-3-dehydroethyliden-1yl) cyclopropan-1yl.porphin the adduct has a charge of 0.08 with the only positively charged carbon atom of the adduct (C radical) being 0.057.For each the only carbon atomswith positive charges, 0.018 and 0.057, respectively, move counterclockwise when viewed from above.giving rise to the structures shown.



(12) (11) (13)

$Mg.H\text{-}(C{\equiv}C)_2\text{-}CH_3.porphin \rightarrow$ Mg.1,(2-didehydro-3-dehydro 3-methyl cyclopropenyliden-1yl) methan-1yl.porphin

(12) [8]

$$\Delta H = 0.09551 \text{ h}$$

The activation energy to dissociate the bicyclic complex is 0.041 h and to form the complex 0.002 h.

$Mg.H\text{-}(C{\equiv}C)_2\text{-}CH_3.porphin \rightarrow$ Mg.1,2-didehydro-3-dehydroethyliden-1yl cyclopropan-1yl.porphin

(13) [9]

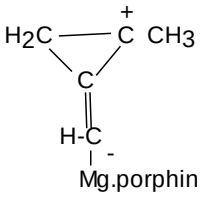
$$\Delta H = 0.09191 \text{ h}$$

The activation energy to dissociate the bicyclic complex is 0.051 h and to form the complex 0.020 h.

3.6 The formation L-leucine from Mg.1,(2-dehydro-2-methyl cyclopropenyliden-1yl) methan-1yl.porphin

The Mg.1,(2-didehydro 3-dehydro 3-methyl cyclopropenyliden-1yl) methan-1yl.porphin is a high energy diradical which would be much stabilized by atmospheric hydrogenation.

Mg.1,(2-didehydro 3-dehydro-3-methyl cyclopropenyliden-1yl) methan-1yl.porphin+ $H_2 \rightarrow$



Mg.1,(2-dehydro-2-methyl cyclopropenyliden-1yl) methan-1yl.porphin(14)[10]

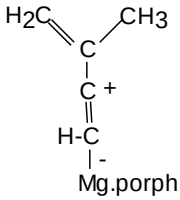
$$\Delta H = -0.05703 \text{ h}$$

The activation energy to form the carbon-hydrogen bond was found to be, 0.036 h, whilst the energy to restore the hydrogen-hydrogen bond was 0.091 h.

3.7 The formation of Mg.1,3-methenyl but-1-yl.porphin

With only moderate activation energy the Mg.1,(2-dehydro-2-methyl cyclopropenyliden-1yl) methan-1yl.porphin may isomerise to give Mg.1,3-methenyl butyn-1-yl.porphin

Mg.1,(2-dehydro-2-methyl cyclopropenyliden-1yl) methan-1yl.porphin(14)→



Mg.1,3-methenyl butyn-1-yl.porphin (15) [11]

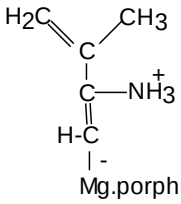
$$\Delta H = -0.09354 \text{ h}$$

The activation energy to open the ring was calculated as 0.024 h, whilst that to close it was 0.103 h.

3.8 The formation of Mg.1,2-amino 3-methenyl butyn-1-yl.porphin

The Mg.1,3-methenyl butyn-1-yl.porphinmay react with ammonia gas at the positively charged C2 of the adduct. This is the rate determining step in the synthesis.

Mg.1,3-methenyl butyn-1-yl.porphin $+NH_3$→



Mg.1,2-amino 3-methenyl butyn-1-yl.porphin (16) [12]

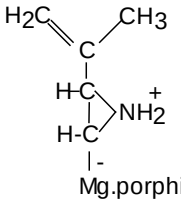
$$\Delta H = 0.02275 \text{ h}$$

The activation energy to add the ammonia was calculated as 0.028 h and 0.036 for the reverse reaction.

3.9 The formation of Mg.1,3-(1-methenyl ethyl) 1H aziridin-2yl.porphin

The Mg.1,2-amino 3-methenyl butyn-1-yl.porphin may cyclise to an aziridine derivative during being activated to transfer a hydrogen atom. The enthalpy change is marginal.

Mg.1,2-amino 3-methenyl butyn-1-yl.porphin →



Mg.1,3-(1-methenyl ethyl) 1H aziridin-2yl.porphin (17) [13]

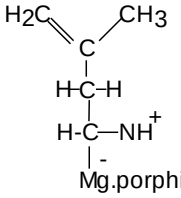
$$\Delta H = 0.00161 \text{ h}$$

The activation energy to form the ring was calculated as 0.099 h, whilst that to close it was 0.093 h.

3.10 The formation of Mg.1,3-methenyl butanimin-1yl.porphin

With only moderate activation energy a second hydrogen may be transferred from the protonated imino group to form the second carbon-hydrogen bond and opening the aziridine ring, as shown.

Mg.1,3-(1-methenyl ethyl) 1H aziridin-2yl.porphin →



Mg.1,3-methenyl butanimin-1yl.porphin (18) [14]

$$\Delta H = -0.08097 \text{ h}$$

The activation energy to open the ring was calculated as 0.109 h, whilst that to close it was 0.205 h.

At the transition state the metal bonding changes from Mg-C to Mg-N. The imine is expected to dissociate to a minor extent with a small vapour pressure, but this requires a small activation energy according to the equation,

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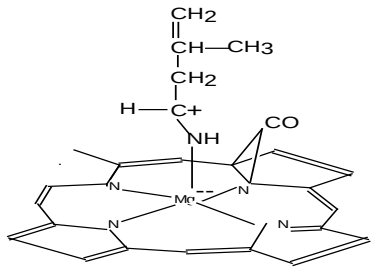
Mg.1,3-methenyl butanimin-1yl.porphin→
Mg.porphin + 3-methenyl butanimine
(19) [15]
ΔH = 0.03726 h

3.11 The formation of Mg.1,3-methenyl butanimin-1-yl.porphin.CO

For the correct formation of the L-isomer the3-methenylbutanimine needs to chelate to the magnesium ion on aMg.porphin which has already obtained the correct orientation of a bound carbon monoxide molecule [11], as shown,

Mg.porphin.CO +3-methenyl butanimine
(5)(19) →



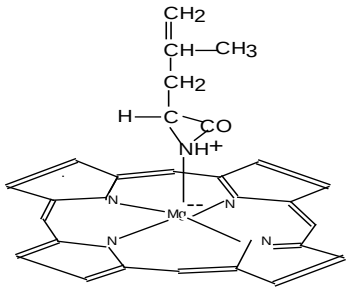
Mg.1,3-methenyl butanimin-1-yl.porphin.CO
(20)[16]
ΔH = -0.20906 h

The enthalpy change is favourable and the activation energy to form van der Waals complexes is usually not significant if they are spontaneous.

3.12The formation of Mg.1,(2-methenyl propyl) aziridine-3-one-1-yl.porphin.

The Mg.1,3-methenyl butanimin-1-yl.porphin.CO may easily rearrange to formMg.1,(2-methenyl propyl) aziridine-3-one-1-yl.porphin.

Mg.1,3-methenyl butanimin-1-yl.porphin.CO
(20) →



Mg.1,(2-methenyl propyl) aziridine-3-one-1-yl. porphin.(21) [17]

The enthalpy change is favourable.
ΔH = -0.01946 h
The activation energy to form the aziridine was 0.093 h and the ring dissociation activation
energy of 0.147 h.

3.13The formation L-leucine.

Hydrolysis and hydrogenation in the reducing environment of the complex, is here depicted as releasing from the catalyst the non-zwitterionic form of L-leucine.Fig.3. Further formation of the zwitterions may occur.

Mg.1,(2-methenyl propyl) aziridine-3-one-1-yl.porphin + H_2O+ H_2→Mg.porphin+L-leucine
(21) (6) [18]
ΔH = -0.07179 h

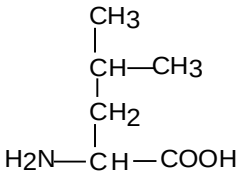
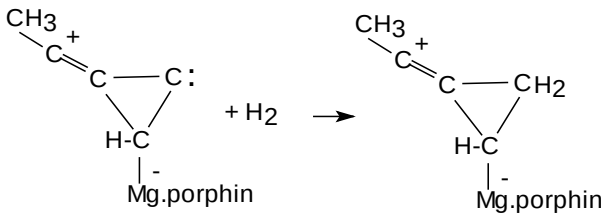


Fig.3L-leucine (non zwitterion) (6)

4. The formation of L-isoleucine.

The proposed synthesis of L-isoleucine starts with the hydrogenation of the other cyclic high energy compound from the photolysis of Mg.H-$(C\equiv C)_2$- CH_3.porphin , Mg.1,(2-didehydro-3-ethyliden-1yl) cyclopropan-1yl.porphin to give Mg.1,2-ethylidenyl cyclopropan-1yl.porphin, and proceeds in an identical manner.

Mg.1,(2-didehydro-3-dehydroethyliden-1yl) cyclopropan-1yl.porphin



(13) (22) [19]
ΔH =-0.05225 h

The activation energy for the addition was calculated as 0.089 h and 0.121 h for the reverse reaction.

The total energies and zero point energies for the HF and MP2/6-31G* equilibrium geometries for some of these stable molecules are given in Table 2.

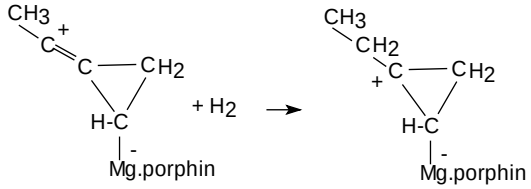
Table 2
MP2 /6-31G* total energies and zero point energies (hartrees) for the respective equilibrium geometries

Molecule	MP2	ZPE (HF) hartreehartree
Mg.1(2-dehydroethylidenyl cyclopropan-1yl.porphin(22)	-1378.42926	0.38084
Mg.1,2-dehydro 2-ethyl cyclopropan-1yl.porphin(23)	-1379.69479	0.40982
Mg.1,2-amino 2-ethyl cyclopropan-1yl.porphin(24)	-1436.02905	0.45425
Mg.1,3-ethyl 3-methyl 1H aziridin-2yl.porphin(25)	-1436.06973	0.45377
Mg.1, 2-methyl butanimin-1yl.porphin(26)	-1436.15250	0.45396
2-methyl butanimine(27)	-250.98865	0.16548
Mg.1,2-methyl butanimin-1-yl.porphin.CO (28)	-1549.14088	0.46451
Mg.1,2-(1-methyl propyl) aziridine-3-one-1-yl.porphin (29)	-1549.15132	0.46429

4.1. The formation of Mg.1,2-dehydro 2-ethyl cyclopropan-1yl.porphin

The Mg.1(2-dehydroethylidenyl cyclopropan-1yl.porphin may undergo a further highly favourable hydrogenation to give Mg.1,2-ethyl 2-dehydro cyclopropan-1yl.porphin.

Mg.1(2-ethylidenyl cyclopropan-1yl.porphin



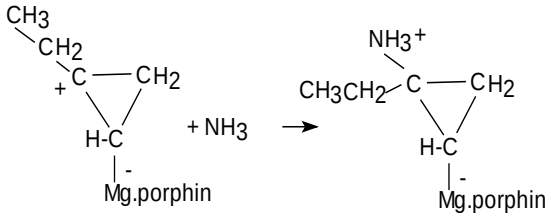
(22) (23) {20]

ΔH =-0.10504 h

The activation energy for the addition was calculated as 0.044 h and 0.176h for the reverse reaction

4.2. The formation of Mg.1,2-amino 2-ethyl cyclopropan-1yl.porphin

The Mg.1, 2-dehydro 2-ethylcyclopropan-1yl.porphin may add ammonia to give Mg.1,2-amino 2-ethyl cyclopropan-1yl.porphin.



(23) (24) [21]

This is the rate determining step where the enthalpy change is comparable to that found for the formation of other amino acids [11-15] and less than that for the formation of norleucine.

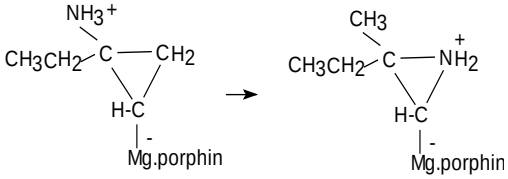
ΔH = 0.02657 h

Also, the activation for the addition is lower, 0.019 h, and for the dissociation, 0.013 h.

4.3 The formation of Mg.1,3-(2-ethyl 2-methyl) 1H aziridin-2yl.porphin

The Mg.1,2-amino 2-ethyl cyclopropan-1yl.porphin may cyclise to an aziridine derivative, Mg.1,3-ethyl 3-methyl 1H aziridin-2yl.porphin, during being activated to transfer a hydrogen atom. The enthalpy change is favourable.

Mg.1,2-amino 2-ethyl cyclopropan-1yl.porphin



(24) (25) [22]

ΔH ==0.04110 h

To determine the activation energy to form an aziridine, the potential energy surface studied involved the stretching of the CH –CH_2 bond of the cyclopropane ring and the stretching of the CH_2 – H(NH_2) bond. The activation for the cyclisation was , 0.121 h, and for the reverse reaction, 0.087 h.

4.4 The formation of Mg.1, 2-methyl butanimin-1yl.porphin

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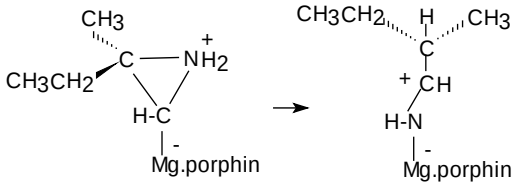
With only moderate activation energy a second hydrogen may be transferred from the protonated imino group to form the second carbon-hydrogen bond and opening the aziridine ring, as shown to give Mg.1,2-methyl butanimin-1yl.porphin



(25) (26) [23]

ΔH =-0.08261 h

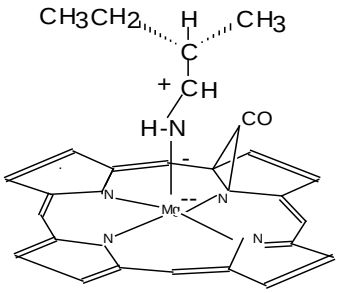
The activation for the ring opening was, 0.087 h, and for the reverse reaction, 0.136 h.
At the transition state the metal bonding changes from Mg-C to Mg-N. The imine is expected to dissociate to a minor extent with a small vapour pressure, but this requires a small activation energy according to the equation,

Mg.1,2-ethyl 2-methyl) butanimin-1yl.porphin
→
Mg.porphin + 2-methyl butanimine
(27) [24]
ΔH = 0.04504 h

4.5 The formation of Mg.1,2-methyl butanimin-1-yl.porphin.CO

For the correct formation of the L-isomer the2-methylbutanimine needs to chelate to the magnesium ion on aMg.porphin which has already obtained the correct orientation of a bound carbon monoxide molecule [11], as shown,

Mg.porphin.CO **+2**-methyl butanimine
(5)(27) →



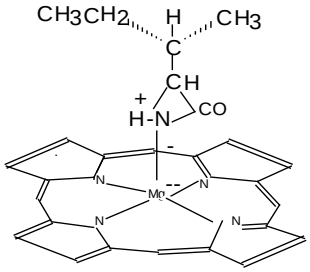
Mg.1,2-methyl butanimin-1-yl.porphin.CO
(28)[25]
ΔH = -0.21912 h

4.6The formation of Mg.1,2-(1-methyl propyl) aziridine-3-one-1-yl.porphin.

The Mg.1,2-methyl butanimin-1-yl.porphin.CO may easily rearrange to formMg.1,2-(1-methyl propyl) aziridine-3-one-1-yl.porphin**.**with an activation energy of 0.105 h and a ring dissociation energy of 0.100 h. The enthalpy change is marginal.

ΔH = 0.01073 h

Mg.1,3-methenyl butanimin-1-yl.porphin.CO
(28) →



Mg.1,2-(1-methyl propyl) aziridine-3-one-1-yl.porphin
(29) [26]

4.7The formation L-isoleucine.

Hydrolysis and hydrogenation in the reducing environment of the complex, is here depicted as releasing from the catalyst the non-zwitterionic form of L-isoleucine.Fig.4.Further formation of the zwitterions may occur.

Mg.1,2-(1-methyl propyl) aziridine-3-one-1-yl.porphin
+ H_2O→Mg.porphin+L-isoleucine
(29) (7) [27]

ΔH = -0.02800 h

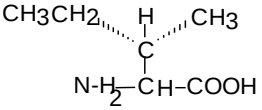


Fig.4L-isoleucine (non zwitterion) (7)

5. Conclusion

This paper suggests that a simple interstellar molecule, methyl diacetylene, may have been induced to isomerise in a surface catalysed photochemically activated reaction where the magnetic field of the radiation induced the stereochemistry. The enthalpy changes and activation energies do appear attainable with this catalyst to produce over time some concentrations of L-leucine and L-isoleucine.
Further work at a higher accuracy may alter the values given here.

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