A Plausible Route to a Prebiotic Synthesis of L-Histidine

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Abstract: - Possible reactions in a mildly reducing prebiotic atmosphere of ammonia and hydrogen cyanide produce cyanamide, its isomer carbodiimide, and formamidine. Alkynes such as diacetylene may form very weak van der Waals complexes with metal derivatives of porphin that acts as a potent photochemical catalyst. The reactants carbodiimide and the diacetylene adduct with magnesium porphin may react spontaneously to form an iminazole structure. Subsequent reaction with ammonia leads to an aziridine derivative. Prototropic shifts lead to an opening of the ring and finally an imine bound to the catalyst. Carbon monoxide gas may also bind to porphin with either the metal ion or in the form of an aziridine-2one complex. If this has been determined by the magnetic field of the exciting ultraviolet radiation to have a particular orientation and is present as a high energy compound, photochemical excitation may easily lead to the migration of the carbon monoxide from the surface of the porphin ring to the imine group of the iminazole adduct. Subsequent hydrolysis gives the L-histidine which forms the zwitterion.
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: -.L-histidine, diacetylene, carbodiimide, formamidine, cyanamide.

1 Introduction

L-histidine is an essential amino acid [1], found in the hydrolysis products of proteins [2] which occurs naturally [3,4], and in the dipeptides carnosine and anserine [5]. The structure contains an iminazole ring which exhibits prototropy such that the imino-hydrogen atom may reside on either nitrogen atom, but does not lead to isolable isomers [1]. The amino acid has pKa values at 1.82, 9.17 and the iminazole side group pKa at 6.0 [4] is important in enzymatic reactions. The biosynthesis has been established [4].
From a prebiotic perspective [6] 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 [4,7] implying the presence of concentrations of carbon monoxide, ammonia, water and hydrogen. It is also supposed that alkynes such as diacetylene were present as found on Titan, a moon of Saturn [8]. It has also been demonstrated that porphin may act as a catalyst for the formation of sugars [9] and polyenes [10] and many biological molecules [11-14]].
This paper proposes a model for the catalytic photochemically activated formation of L-histidine from the gases, hydrogen cyanide, diacetylene, ammonia, carbon monoxide, hydrogen, and the catalyst magnesium porphin..
The reactions described have been deduced as kinetically and thermodynamically viable, but photochemical excitation is required.

2 Problem Formulation

The computations tabulated in this paper used the GAUSSIAN98 [15] commercial package. The standard calculations at the HF and MP2 levels including zero-point energy corrections [16], together with scaling [17], using the same basis set, 6-31G*. are as previously published [6]. 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 [16], 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 [15].
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)

Diacetylene may chelate with the magnesium ion of magnesium porphin, which is here taken as a possible catalyst, to form an in-plane charge transfer complex where the charge on the ligand is positive, 0.35. 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-$(C\equiv C)_2$-H → Mg.H-$(C\equiv C)_2$-H.porphin
(1) (2) (3)
[1]
$\Delta H = -0.01480$ h

Mg.porphin also forms a stable high energy complex with carbon monoxide in which the carbon monoxide is in a particular orientation on a peripheral pyrrole unit of the porphin [9]. This is also involved in the proposed synthesis, as shown later. The formation requires photochemical activation, which is less than the first ultraviolet excitation of the complex. The enthalpy of formation is positive.

Mg.CO.porphin → Mg.porphin.CO
(4) (5)
[2]
$\Delta H = 0.21892$ h

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 [9,18] at a pyrrole unit.
As the complex, Mg.CO.porphin , has C1v symmetry [9] , there is an allowed transition from the HOMO to the LUMO of energy 0.21 h. The electric vector of the ultraviolet radiation gives an in-plane electric transition moment [19]. The magnetic vector is of equal value [20] . If it is pointing upwards from the plane of the ring with the adduct on its surface then the degeneracy of every molecular orbital is split into a pair from the Zeeman effect [21]. As porphin derivatives are found to be diamagnetic [22], the higher energy orbital of a pair is required to have an angular momentum generating a magnetic moment to oppose the applied field in accordance with Lenz's Law [23]. The transient magnetic field may stretch the Mg-C-O bonding tending to dissociate the complex [24], rather than compress it [9]. When viewed from above it is this surge of electronic charge in the highest energy molecular orbital that should cause reaction of the most counterclockwise –C=N- grouping of a pyrrole unit with the dissociated CO group giving an excited state aziridine-2one complex..

Another major reactant has been assumed to be cyanamide which arises from the condensation of hydrogen cyanide [4]. The enthalpy change is not really favourable, as shown,

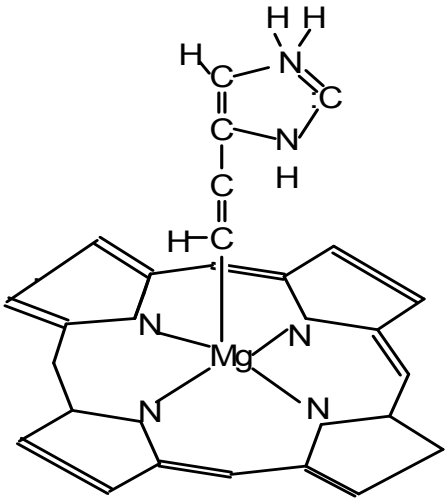
$NH_3 + HCN \rightarrow NH_2\text{-}CN + H_2$
[3]
(6)
$\Delta H = 0.01601$ h

Another might be formamidine,

$NH_3 + H\text{-}CN \rightarrow HN{=}CH\text{-}NH_2$
[4]
(7)
$\Delta H = -0.00102$ h

However, cyanamide does not appear to react favourably with the reactant, Mg.H-$(C\equiv C)_2$-H.porphin. Moreover, the enthalpy change for the formation of an iminazole with formamidine is positive, as shown,

Mg.H-$(C\equiv C)_2$-H.porphin + $HN{=}CH\text{-}NH_2$ →
(3) (7)



Mg.2-(2H-4-iminazoyl) ethynyl.porphin
(8) [5]
$\Delta H = 0.06700$ h

However, an isomer of cyanamide, carbodiimide can be formed relatively easily, especially if ionic species such as the hydronium ion [25] are assumed to have been present in the atmosphere.

The enthalpy change to form the molecule is less than to form cyanamide.as shown,

$$NH_2\text{-}CN \rightarrow HN=C=NH \quad (9) \quad [6]$$
$$\Delta H = 0.01055 \text{ h}$$

The enthalpy change to form carbodiimide from formamidine is also unfavourable,

$$HN=CH\text{-}NH_2 \rightarrow HN=C=NH + H_2 \quad [7]$$
$$\Delta H = 0.02758 \text{ h}$$

The mechanisms to form carbodiimide may involve ionic species such as the hydronium ion and the hydride anion. The enthalpy changes for these reactions are favourable,

$$NH_2\text{-}CN + H_3^+ + H^- \rightarrow HN=C=NH + 2\,H_2 \quad [8]$$
$$\Delta H = -0.55368 \text{ h}$$

$$HN=CH\text{-}NH_2 + H_3^+ + H^- \rightarrow HN=C=NH + 3H_2 \quad [9]$$
$$\Delta H = -0.53664 \text{ h}$$

These are the reactants that will be used in the synthesis of the amino acid, histidine.
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 hartree	ZPE (HF) hartree
Mg.porphin (1)	-1185.12250	0.29262
diacetylene (2)	-153.00240	0.04203
Mg.H-(C≡C)$_2$-H.porphin (3)	-1338.13417	0.32843
Mg.CO.porphin (4)	-1298.13452	0.29942
Mg.porphin.CO (5)	-1297.93784	0.30434
cyanamide, (6)	-148.35090	0.03702
formamidine (7)	-149.52602	0.06303
Mg.2-(2H-4-iminazoyl) ethynyl.porphin	-1487.59936	0.39841
(8) carbodiimide (9)	-148.33864	0.03510
Mg.2-(1H-2-dehydro-4-iminazoyl) ethynyl.porphin (10)	-1486.53508	0.37488
Mg.2-(4-iminazoyl) ethynyl.porphin (11)	-1486.58792	0.37367
Mg.2-amino-2-(4-iminazoyl) ethynyl.porphin (12)	-1542.93260	0.42754
Mg. 3-(4-iminazoyl)-1H aziridinyl.porphin (13)	-1542.93211	0.41973
Mg.2 (4-iminazoyl)-2-ethanimine.porphin (14)	-1543.00390	0.41769
Mg. 2-(4-iminazoyl)-ethanimine.porphin.CO (15)	-1855.82007	0.42231
Mg. 3-(4-iminazoyl)-aziridin-2one.porphin (16)	-1656.01574	0.42940
2-(4-iminazoyl)-ethanimine (17)	-357.85834	0.13187
2-(4-iminazoyl)-1-amino-propionic acid	-547.13849	0.17521
histidine (non zwitterionic)	-547.13849	0.17521
CO	-113.02818	0.00484
H_2O		

	-76.19924	0.02148
NH_3		
	-56.35738	0.03529
H_3^+		
	-1.29643	0.02210
HCN		
	-93.15894	0.01799
H_2	-1.14414	0.01034
H^-	-0.42891	

3.2 The overall stoichiometry for the formation of L-histidine.

Although Mg.porphin is here taken as the catalyst for the reaction, the overall stoichiometry to form the amino acid, L-histidine is as follows,

$NH_2\text{-}CN + H\text{-}(C\equiv C)_2\text{-}H + NH_3 + CO + H_2O \rightarrow$ [10]

$C_6N_3O_2H_9$
histidine (non-zwitterion)
(Fig.7.)

$\Delta H = -0.16965$ h

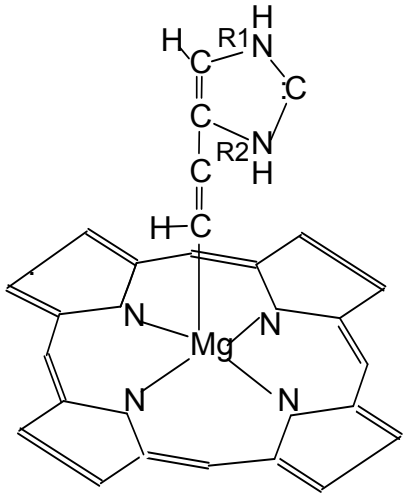
The enthalpy change is negative indicating that this may be the energetically favourable route to the initial formation of the amino acid. The intermediates by which this stoichiometric reaction may have occurred are as follows:

3.3 The formation of Mg.2-(1H-2-dehydro-4-iminazoyl) ethynyl.porphin

The Mg.porphin coordinated diacetylene complex may react with carbodiimide by a 1:3 addition to give an iminazole derivative, as follows:

Mg.H-$(C\equiv C)_2$-H.porphin + HN=C=NH $\rightarrow$

(3) (9)



Mg.2-(1H-2-dehydro-4-iminazoyl) ethynyl.porphin
(10) [11]

$\Delta H = -0.05219$ h

A model of the optimized complex (10), is shown in Fig.1.

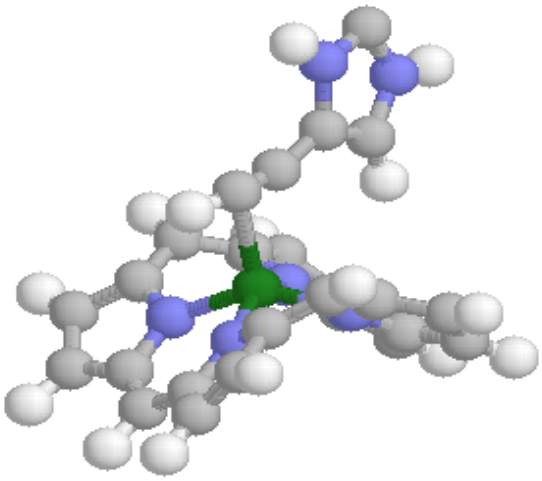


Fig.1. The optimized complex Mg.2-(1H-2-dehydro-4-iminazoyl) ethynyl.porphin

The potential energy surface for the formation of the iminazole is given in Fig.2. The activation energy for the addition has been calculated as 0.090 h, and the activation energy for the reverse reaction as 0.148 h

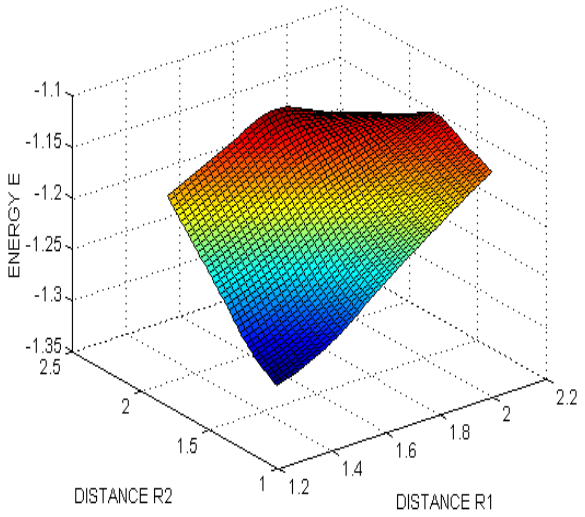


Fig.2. The potential energy surface for the addition of carbodiimide to Mg.H-$(C\equiv C)_2$-H.porphin using the internal coordinates R1 and R2 depicting bond stretches (10). The minimum for the reactants, Mg.H-$(C\equiv C)_2$-H.porphin and carbodiimide is at R1=2.2 A, R2=2.2.4 A. The minimum for the iminazole is at R1=1.4 A, R2=1.4 A. The ordinate is the total energy, -1481+E h.

The data for this molecule and the others involved in the synthesis are given in Table.1.

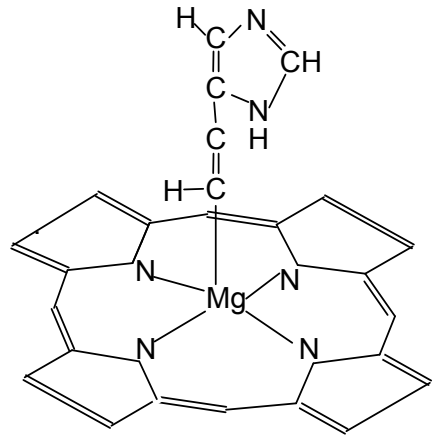
3.4 The formation of Mg.2-(4-iminazoyl) ethynyl.porphin .

The Mg.2-(1H-2-dehydro-4-iminazoyl) ethynyl. porphin may convert to the more stable Mg.2-(4-iminazoyl) ethynyl.porphin by a simple prototropic shift, where the enthalpy change is favourable, as shown.

Mg.2-(1H-2-dehydro-4-iminazoyl) ethynyl.porphin

$\rightarrow$

(10)



Mg.2-(4-iminazoyl) ethynyl.porphin .

(11)

. [12]

$\Delta H = -0.05391$ h

The potential energy surface for the formation of the Mg.2-(4-iminazoyl) ethynyl.porphin is given in Fig.3 .The activation energy for the addition has been calculated as 0.090 h, and the activation energy for the reverse reaction as 0.148 h

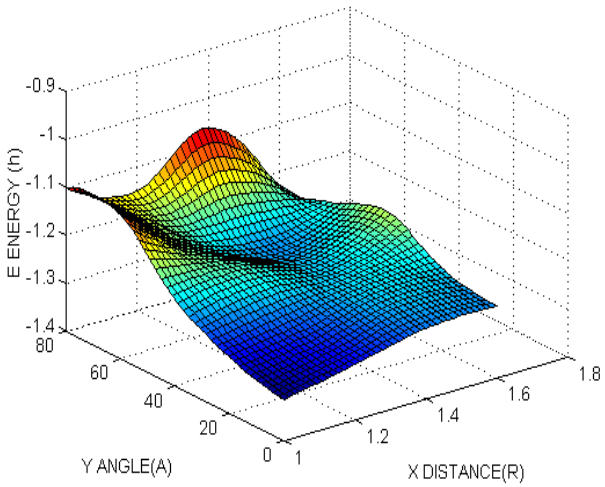


Fig.3. The potential energy surface for the prototropic shift on molecule, Mg.2-(1H-2-dehydro-4-iminazoyl) ethynyl. porphin. The X-axis represents the stretching of the H-N bond. The Y-axis depicts the bending of the angle (110.0 - A) degrees, where A is the angle H-N-C(2). The minimum for the Mg.2-(1H-2-dehydro-4-iminazoyl) ethynyl. porphin is at, X=1.0 A., Y=0.0 degrees, A saddle point is at X=1.4 A., A=40 degrees, The minimum for the Mg.2-(4-iminazoyl) ethynyl.porphin is at X= 1.6 A. A=70.0 degrees, The energy is -1481 + E h.

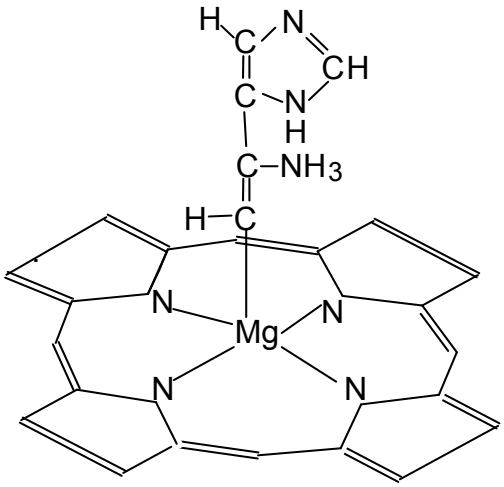
The activation energy for the prototropic shift has been calculated as 0.083 h, and the activation energy for the reverse reaction as 0.130 h .

3.5 The formation of the Mg.2-amino-2-(4-iminazoyl) ethynyl.porphin.

The addition of ammonia to the complex is a rate determining step. At least one of these steps is expected in the synthesis and most of the intermediates would not be expected to attain appreciable concentrations on non-astronomical time scales. Here, the activation energy to form the amino compound was calculated by extending the length of the bond to the ammonia adduct.
The activation energy to add the ammonia was calculated as 0.049 h. The activation energy to dissociate the ammonia as 0.031 h.

Mg.2-(4-iminazoyl) ethynyl.porphin + NH_3
(11)

→



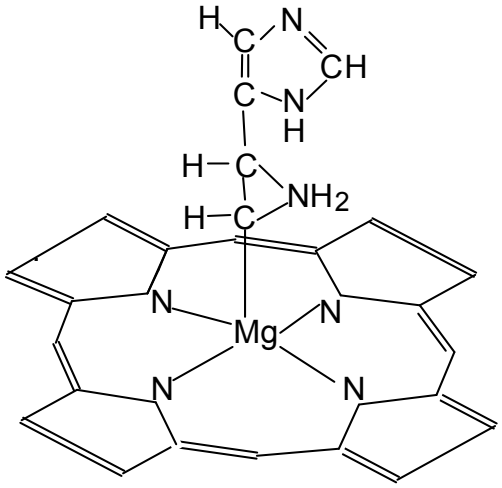
Mg.2-amino-2-(4-iminazoyl) ethynyl.porphin.
(12) [13]

$\Delta H = 0.02919$ h

3.6 The formation of Mg. 3-(4-iminazoyl)-1H aziridinyl.porphin

The charge transfer complex may stabilise with activation to yield the aziridine structure depicted. This involves the first transfer of a hydrogen atom from the complexed ammonia to the iminazole adduct [13].

Mg.2-amino-2-(4-iminazoyl) ethynyl.porphin. →
(12)



Mg. 3-(4-iminazoyl)-1H aziridinyl.porphin
(13) [14]

The enthalpy change is favourable.

$\Delta H = -0.00642$ h

The potential energy surface for the formation of the Mg. 3-(4-iminazoyl)-1H aziridinyl.porphin is given in Fig.4.

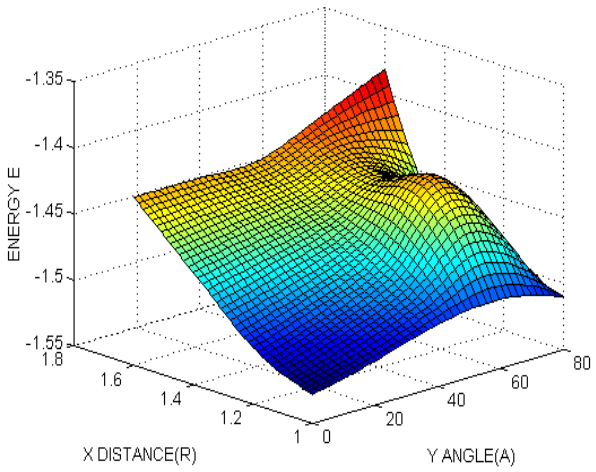


Fig.4. The potential energy surface for the closure of the ring together with the concerted prototropic shift to form the Mg. 3-(4-iminazoyl)-1H aziridinyl.porphin The X-axis depicts the N-H stretch, A. The Y- axis depicts the bending of the angle (110.0 - A) degrees, where A is the angle H-N-C(2). The

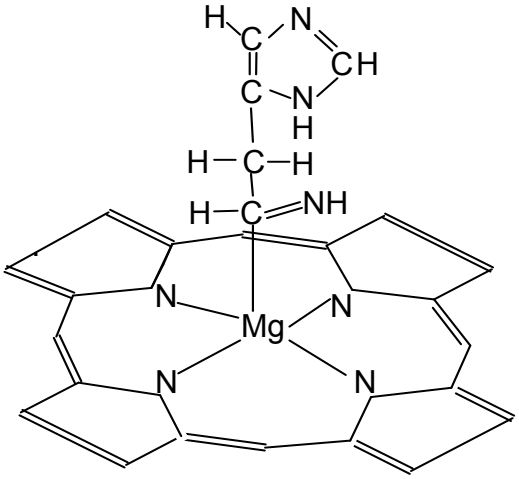
minimum for the Mg.2-(4-iminazoyl) ethynyl.porphin is at, X=1.0 A., Y=0.0 degrees. A saddle point is at X=1.0 A., A=60 degrees, The minimum for the Mg. 3-(4-iminazoyl)- 1H aziridinyl.porphin is at X= 1.0 A. A=80.0 degrees, The energy is -1537 + E h.

The activation energy to form the carbon-hydrogen bond was found to be, 0.031 h, whilst the energy to restore the nitrogen-hydrogen bond was 0.028 h.

3.7 The formation of Mg.2 (4-iminazoyl)-2-ethanimine.porphin

With only moderate activation energy a second hydrogen atom may be transferred from the protonated amino group to form the second carbon-hydrogen bond and opening the aziridine ring [13], as shown.

Mg. 3-(4-iminazoyl)-1H aziridinyl.porphin
(13) →



Mg.2 (4-iminazoyl)-2-ethanimine.porphin (14)
[15]

$\Delta H = -0.07361$ h

The potential energy surface for the formation of the Mg.2 (4-iminazoyl)-2-ethanimine.porphin is given in Fig.5.

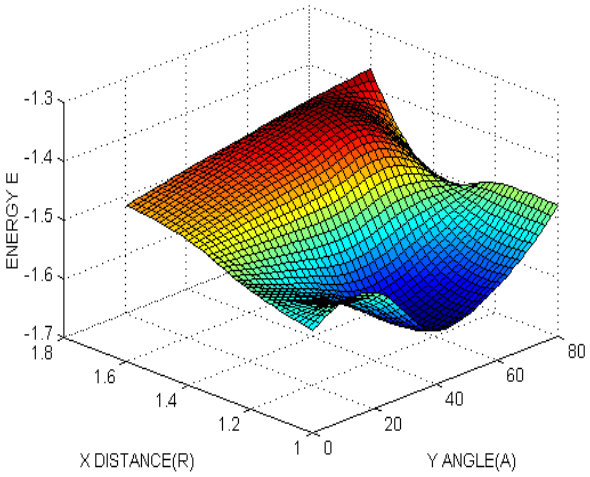


Fig.5. The potential energy surface for the formation of Mg.2 (4-iminazoyl)-2-ethanimine.porphin. The X-axis depicts the N-H stretch, A. The Y- axis depicts the bending of the angle (110.0 - A) degrees, where A is the angle H-N-C(2). The minimum for the Mg. 3-(4-iminazoyl)-1H aziridinyl.porphin is at, X=1.0 A., A=0.0 degrees. A saddle point is at X=1.1 A., A=20 degrees, The minimum for the Mg.2 (4-iminazoyl)-2-ethanimine.porphin. is at X= 1.0 A. A=40.0 degrees, The energy is -1537 + E h.

The activation energy to open the ring was calculated as 0.019 h, whilst that to close it was 0.113 h. These values are comparable to those previously found for the formation of the amino acids serine and threonine [13]. 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.2 (4-iminazoyl)-2-ethanimine.porphin →
(14)
Mg.porphin + 2-(4-iminazoyl)-ethanimine
(17) [16]

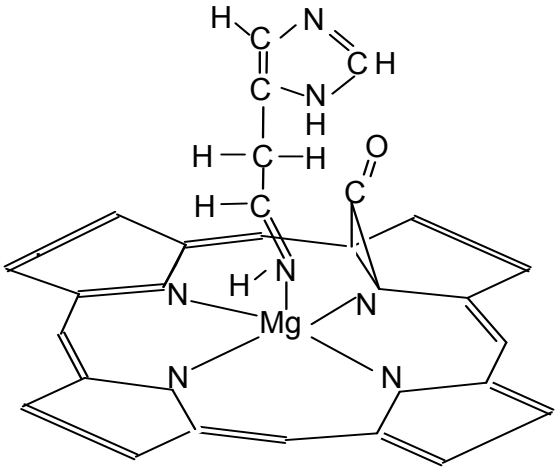
$\Delta H = 0.02912$ h

3.8 The formation of Mg. 2-(4-iminazoyl)-ethanimine.porphin.CO

For the correct formation of the L-isomer the 2-(4-iminazoyl)-ethanimine needs to chelate to the

magnesium ion on a Mg.porphin which has already obtained the correct orientation of a bound carbon monoxide molecule [9], as shown,

Mg.porphin.CO + 2-(4-iminazoyl)-ethanimine
→



Mg. 2-(4-iminazoyl)-ethanimine.porphin.CO
(15) [17]

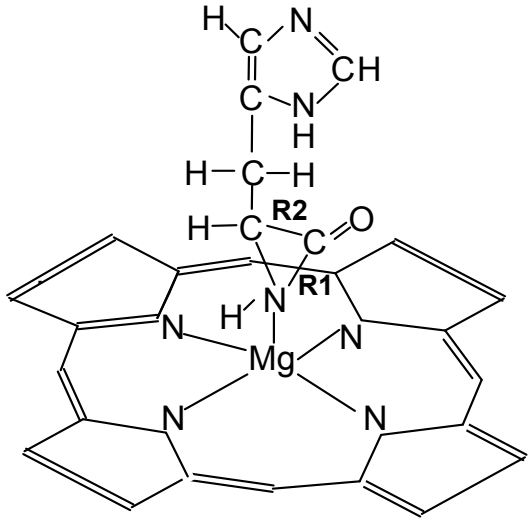
$\Delta H = -0.03626$ h

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

3.9 The formation of Mg. 3-(4-iminazoyl)-aziridin-2one.porphin

The Mg.2- (4-iminazoyl)-ethanimine.porphin.CO may easily rearrange to form Mg. 3-(4-iminazoyl)-aziridin-2one.porphin with an activation energy of 0.028 h and a ring dissociation energy of 0.168 h, as shown.

Mg. (4-iminazoyl)-2-ethanimine.porphin.CO
(15) →



Mg. 3-(4-iminazoyl)-aziridin-2one.porphin
(16) [18]

The enthalpy change is favourable and appreciable,

$\Delta H = -0.18936$ h

The potential energy surface for the formation of the Mg. 3-(4-iminazoyl)-aziridin-2one is given in Fig.6.

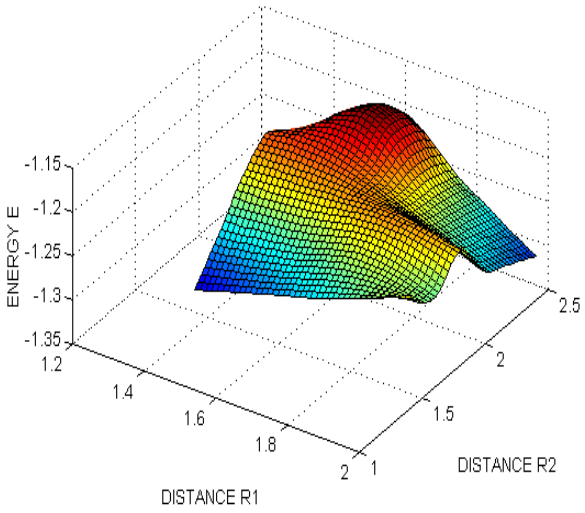
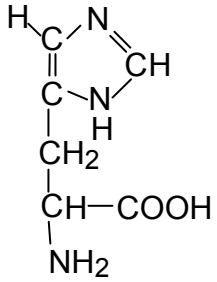


Fig.6. The potential energy surface for the formation of Mg. 3-(4-iminazoyl)-aziridin-2one.porphin. The R1-axis depicts the C-N stretch. The R2 axis depicts the C-C stretch.. The minimum for the Mg.2- (4-iminazoyl)-ethanimine.porphin.CO is at, R1=1.6 A., R2=2.4 A. A saddle point is at R1=2.0 A., R2=1.8 A. The minimum for the Mg. 3-(4-iminazoyl)-aziridin-2one.porphin is at R1= 1.4 A. R2=1.4 A. The energy is -1650 + E h.

4.0 The formation L-histidine.

Hydrolysis of the complex is here depicted as releasing the undissociated acid, Fig.7, from the catalyst. Further formation of the zwitterion may occur.

Mg. 3-(4-iminazoyl)-aziridin-2one.porphin + H_2O → Mg.porphin + L-histidine



L-histidine [19]

Fig.7. The structure of L-histidine

ΔH = -0.03091 h

4. Conclusion

The presence of reactants, hydrogen cyanide, carbon monoxide, ammonia, alkynes and hydrogen in the early Earth's atmosphere together with the catalyst porphin, suggests that thermodynamically and kinetically viable reactions such as those presented here, could have formed a prebiotic photochemically directed template for the synthesis of this unique amino acid.
Further work at a higher accuracy may alter the values given here.

5 Acknowledgements

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