A Computational Study of a Prebiotic Synthesis of Menaquinone, Phylloquinone, and Vitamin K Analoges

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Abstract: - Ab initio applied computing is used to determine the viability of a plausible mechanism for the formation of vitamin K from planetary and interstellar gases that contain the necessary essential elements in prebiotic chemistry before the advent of life on Earth. The immutable laws of chemical thermodynamics and kinetics enable the intermediates in the synthesis to be characterized and the activation energies to be established. The planetary molecules propyne, ethyne, carbon monoxide, hydrogen, and water are invoked in a synthesis of menaquinone, a naphthoquinone precursor of the vitamin K series of molecules. The enthalpy change was -0.43 h. This is followed by the formation of oligomers of the gases propyne and ethyne which serve as side-chains for the analogs of vitamin K where the enthalpy change was -0.21 h for the 2-methyl butane side-chain. For vitamin K (n=1), the total enthalpy change was -0.63 h. The additional presence of hydrogen cyanide gas and magnesium ions enables the surface-catalyzed, photochemically activated synthesis of the catalyst, magnesium metalloporphyrin. The activation energies for the formation of intermediates on the surface of the catalyst are less than the first excitation energy, 0.21 h. Finally, the menaquinone derivative and the 2-methyl butane or 2-methyl butene oligomer derivatives are combined to give specific analogs of vitamin K. The reactions are 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, menaquinone, phylloquinone, Vitamin K1, Vitamin K2, Mg.porphin.

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1 Introduction

Vitamin K is a group of structurally similar, 2-methyl-1,4-naphthoquinone derivatives, which belong to the group of natural quinones comprising the classes anthraquinones, naphthoquinones and benzoquinones [1], with at least five accompanying biosynthetic pathways, [2]. The substituent of the napthoquinone defines the exact vitamin K, [3].

There are two natural forms of vitamin K homologues, plant-derived vitamin K1 such as phylloquinone and the bacterium-derived vitamin K2, Figure 1. For example, vitamin K1 (phylloquinone) has a 3-phytyl substituent while vitamin K2 contains repeating unsaturated isoprene units at the 3 position. The menaquinones may be denoted as MK-n, (menaquinone-n, MK-n), [4], where n is the number of repeating isoprene units. The other form of vitamin K encountered is 2-methyl-1,4-naphthoquinone (vitamin K3 or menadione) which lacks substitution at the 3 position. Although biologically active in vivo this compound is not found in nature, [5], [6].

The vitamin K1 series of molecules, Figure 1, such as phylloquinone occur primarily from plants, especially leafy green vegetables such as spinach, brussels sprouts and broccoli, and animal products such as chicken, mollusks and cheese. The Vitamin K2 series, Figure 1, is present in bacteria, [5], which can also convert vitamin K1 into vitamin K2, [7]. . Vitamin K_2 is primarily from animal-sourced foods, with poultry and eggs much better sources than beef, pork or fish, [8]. Vitamin K is found in the tissues of all animals, [5].

It is essential for the biosynthesis of the enzyme proconvertin in the liver which catalyzes a step in the sequence of reactions involved in the formation of prothrombin, [9], the precursor of thrombin, [10], a proteolytic enzyme that accelerates the conversion of fibrinogen into fibrin, the insoluble protein constituting the fibrous portion of blood clots. Analogs of Vitamin K are used to assist blood clotting whilst antagonists are used to prevent blood clotting, [10]. The molecules are napthoquinone derivatives that may function as coenzymes in the

electron transport system in animals where they can be reversibly reduced to quinols, [11]. Deficiency of vitamin K may also weaken bones, and may promote calcification of arteries, [12], [13], [14]. Both K1 and K2 are cofactors for the enzyme γ-glutamyl carboxylase, which converts glutamic acid (Glu) to a new amino acid γ-carboxyglutamic acid (Gla), in vitamin K-dependent proteins during their biosynthesis, [15], [16]. These γ-carboxyglutamic acid residues have a high affinity for positively charged calcium ions, [17]. MK-4 has the selective ability to cause differentiation of neural progenitor cells NPCs, derived from mouse cerebrum into neuronal cells. Vitamin K homologues also have been reported to play a role in preventing oxidative injury to developing oligodendrocytes and neurons, [18], [19]. Vitamin K (VK) has an important part in ageing, [20], [21], [22]. The organic synthesis is accomplished, [23] and the biosynthesis, [24].

From a prebiotic perspective, [25], 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, [5], [26], implying the presence of concentrations of carbon monoxide, ammonia, water, and hydrogen. It is also supposed that the napthoquinone residue was formed from the gases ethyne, propyne, carbon monoxide and water, whilst the variable long-chain side-chains in the different series were also formed from the oligomerization of the gases ethyne and propyne. The structure of these molecules strongly suggests a copolymerization. This paper describes the initial formation of the napthoquinone derivative, and the subsequent addition of the side-chain oligomers of ethyne and propyne. The copolymerization is described as requiring the Mg.porphin catalyst with photochemical activation. These reactions are assumed to occur mainly in the liquid phase, [27].

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 the vitamin K analogs 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 GAUSSIAN09, [28].

The standard calculations at the HF and MP2 levels including zero-point energy corrections at the Hartree Fock level, [29], together with scaling, [30], using the same basis set, 6-31G*, are as previously published, [25]. 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, [29], 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, [28].

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

Mullikan charges are in units of the electronic charge.

3 Problem Solution

3.1 Total Energies (hartrees)

The initial reactants in this proposed prebiotic synthesis of vitamin K compounds are the simple gases, propyne, ethyne, carbon monoxide, water, and hydrogen.

For these molecules to copolymerize it is here postulated that a catalyst is desirable, taken to be Mg.porphin, [31], [32]. The immutable laws of chemical thermodynamics and kinetics then dictate unequivocally that feasible reactions will occur provided the physical conditions are conducive to chemical reactions.

Some of the reactions that may be expected in the gaseous and liquid phases are given here as forming the initial reactant molecules to synthesize compounds collectively called vitamin K analogs. Here the compounds will be limited to phylloquinone and its simple derivatives where the side-chain extension is just n=1 to 3, as shown in Figure 1.Vitamin K2 represents a group of molecules with a varying number of isoprene units as side-chains. Each molecule can be named MK-n, which represents the number of isoprene units it contains, [12].

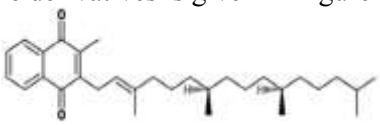
The reactants are expected to have been present at some concentration over eons predicated on the Earth's atmosphere being mildly reducing at some time past.

The intermediates by which these could form vitamin K are listed in Table 1. The catalyst for the formation of the alkyne copolymers is Mg.porphin.

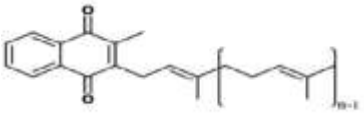
Table 1. MP2 /6-31G* total energies and zero point energies (hartrees) for the respective equilibrium geometries

Molecule	HF hartree	MP2 hartree	ZPE (HF) hartree
propyne (1)	-116.24181	0.06010	
Mg.porphin (2)	-1185.12250	0.29262	
Mg.1,2-dehydro 4-methyl-pent-1.3-diene.porphin (3)	-1417.6182	0.41981	
Mg.1,porphin.2-dehydro 4-methyl-pent-1.3-diene (4)	-1417.59302	0.43597	
Mg.1,CO.porphin.2-dehydro 4-methyl-pent-1.3-diene (5)	-1530.61235	0.41980	
Mg.1,1-carbonyl 3-dehydro 5-methyl-hex-2.4-diene.porphin (6)	-1530.64911	0.41854	
Mg.1,porphin.1-carbonyl 3-dehydro 5-methyl hex-2.4-diene (7)	-1530.64162	0.42353	
Mg.1,7-carbonyl 9-dehydro 11-methyl 1,3,5,8,10-penta diene dodecane.porphin (8)	-1761.81844	0.53021	
Mg.1,porphin.7-carbonyl 9-dehydro 11-methyl 1,3,5,8,10-penta diene dodecane (9)	-1761.82962	0.53981	
cis isomer of Mg.1,porphin.7-carbonyl 9-dehydro 11-methyl 1,3,5,8,10-penta diene dodecane (10)	-1761.42438	0.53272	
Mg.1,porphin.2-(1-carbonyl 3-dehydro 5-methyl hex-2,4-dien-1yl).cyclohex-3,5-diene-1yl (11)	-1761.82588	0.53201	
Mg.1,propyn-1yl.porphin.2-(1-carbonyl 3-dehydro 5-methyl hex-2,4-dien-1yl).cyclohex-3,5-dien-1yl.(12)	-1877.95859	0.60048	
Mg.1,3-(1-carbonyl-2-(cyclohex 3,5-dien-N-2yl)) -4-didehydro-6-methyl 1,5-hept-diene-1yl.porphin (13)	-1878.04640	0.60931	
Mg.1,2-methyl 3-(1-didehydro 3-methyl but 2-en -1yl) 4-keto 9.10 dihydro. napthalene.porphin. (14)	-1878.18966	0.60353	
Mg.1,2-dehydro 2-methyl 3-(3-methyl but 2-en -1yl) 4-keto napthalene.porphin (15)	-1878.41087	0.61127	
4-hydro 4-hydroxy 3,methyl 2-(3-methyl but-2-ene) 1-napthaquinone (16)	-768.47556	0.32220	
2-methyl 3-(3-methyl but-2-ene) 1,4 napthaquinone (17) menaquinone	-767.31923	0.29854	
phylloquinone (18)	-963.13714	0.44772	
2-methylbutane	-196.99336	0.17139	
2-methylbutene	-195.79496	0.14578	
1,4 napthoquinone	-533.50568	0.13218	
1,4 dihydroxy napthoquinine	-534.58088	0.15354	
4-hydro 4-hydroxy 1,4 napthaquinone	-534.66201	0.15584	
ethyne	-77.06680	0.02945	
$H^{\cdot}$	-0.49823		
CO	-113.02122	0.00566	
$OH^{\cdot}$	-75.52257	0.00911	
OH^{-}	-75.51314	0.00816	
H2O	-76.19685	0.02045	
H_2	-1.14414	0.01056	

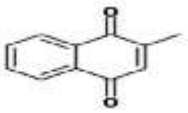
The standard numbering nomenclature for naphthalene derivatives is given in Figure 1.



K1 Series (phylloquinone)



K2 series, MK-n (menaquinone, n=1)



2-methyl-1,4-naphthoquinone (vitamin K3 or menadione)

Fig. 1: The standard numbering for naphthalene.

Vitamin K series. 2-methyl-1,4-naphthoquinone with polyisoprenyl side chain at position 3 for the K2 series and saturated side-chain for the K1 series.

These complexes are integral reactants in the proposed synthesis. The energies of the stable complexes to form the menaquinone and 2-methyl butane oligomers are shown in Table 1.

3.2 The Overall Stoichiometry for the Formation of the Vitamin K1, Series (n=1)

Initially vatamin K1 analogue (n=1), Figure 2, is synthesized, where the stoichiometry is given as,

$$CO + 4CH_3\text{-}C \equiv C\text{-}H + 4H\text{-}C \equiv C\text{-}H + H_2O \rightarrow C_{21}H_{26}O_2$$

K1

$$\Delta H = -0.63040 \text{ h}$$

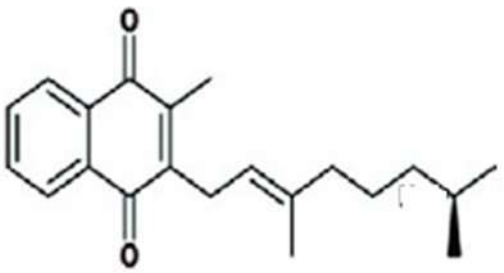


Fig. 2: vitamin K1 series (n=1)

To save computer time the molecule is split into the napthalene derivative, menaquinone, Figure 3,

and the side-chain substituent alkane, 2-methyl butane, Figure 4.

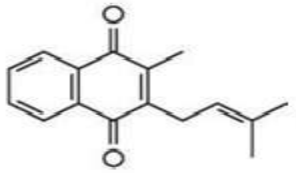


Fig. 3: Menaqinone (n=1)

The overall stoichiometry to form the menaquinone, MK (n=1), Figure 3, is as follows,

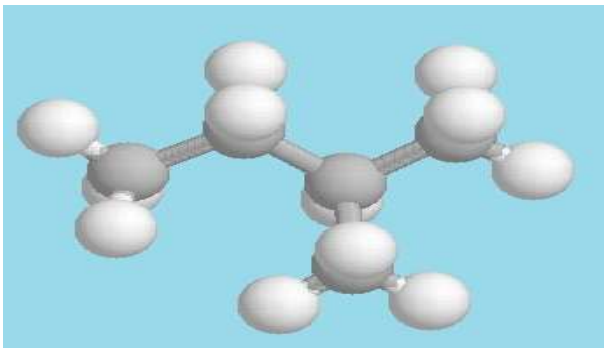
$CO + 3CH_3\text{-}C \equiv C\text{-}H + 3H\text{-}C \equiv C\text{-}H + H_2O \rightarrow C_{16}H_{16}O_2 + 2H_2$,

$\Delta H = -0.44360$ h

The overall stoichiometry to form the 2-methyl butane, Figure 4, is as follows,

$H\text{-}C \equiv C\text{-}H + CH_3\text{-}C \equiv C\text{-}H + 3H_2 \rightarrow C_5H_{12}$

$\Delta H = -0.20776$ h



$CH_3\text{-}CH_2\text{-}CH(CH_3)\text{-}CH_3$

Fig. 4: 2-methyl butane

Finally the two are combined according to the equation,

menaquinone + 2-methylbutane → vitamin K1 (n=1) + H_2

$\Delta H = -0.63040$ h

It is assumed that the enthalpy changes involved in the synthesis of these two simpler molecules are the same as those involved in the formation of the vitamin K1 (n=1) molecule.

The enthalpy change is negative indicating that this may be the energetically favourable route to the initial formation of the vitamin K1 series. The intermediates by which these stoichiometric reactions may have occurred are as follows:
Molecules are numbered consecutively.

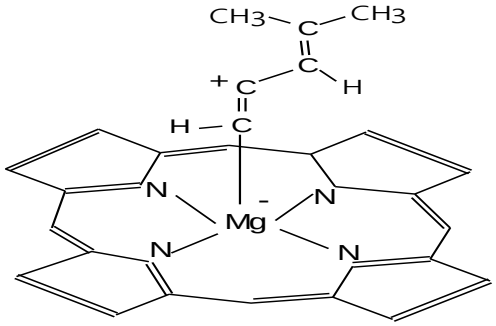
Subsections depict alternatives in the sequence of the reaction mechanism.

A standard numbering of the atoms in the napthalene molecule is shown in Figure 1.

3.3 The Formation of Mg.1,2-dehydro 4-methyl-pent-1.3-diene.porphin

The prebiotic photochemically activated , surface catalysed synthesis of Mg.1,2-dehydro 4-methyl-pent-1.3-diene.porphin has been described, [33], where the catalyst was taken as Mg.porphin, [25], the same catalyst is used in this synthesis of vitamin K where the initial reactant is the gas propyne. Here, those first reactions are summarized and represented here as,

2 $CH_3\text{-}C \equiv C\text{-}H$ + Mg.porphin →
(1) (2)



Mg.1,2-dehydro 4-methyl-pent-1.3-diene.porphin
(3)

$\Delta H = -0.07948$ h

The reaction appears marginally feasible having been excited photochemically on the surface catalyst..

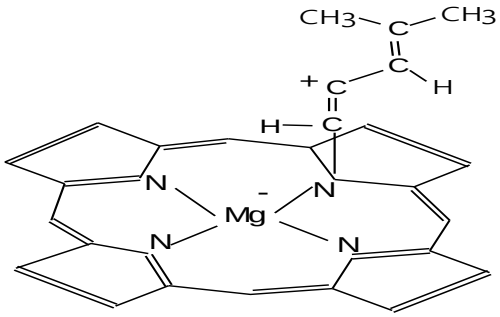
The activation energy in these charge transfer reactions or the formation of van der Waals complexes is always achievable as the catalyst can absorb considerable photochemical activation, 0.21 h, [33]

At this stage in the synthesis of vitamin K analogues very long side-chains from 1 to 50 isoprenyl groups may be added, [34], and hydrogenated with various sterically specific side-chains. These are postponed until later.

3.4 The Formation of Mg.1,porphin.2-dehydro 4-methyl-pent-1.3-diene

The Mg.1,2-dehydro 4-methyl-pent-1.3-diene. porphin may be excited to an alternative energy state, as,

Mg.1, .porphin .2-dehydro 4-methyl pent-1.3-diene (3) →



Mg.1, .porphin. 2-dehydro 4-methyl-pent-1.3-diene. (4)

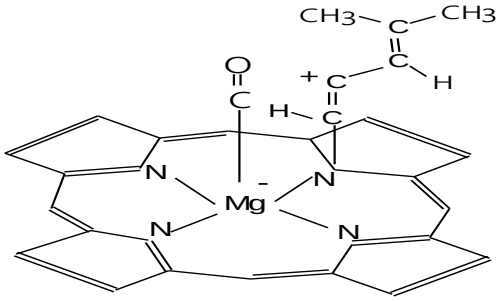
$\Delta H = 0.11318$ h

At HF level the activation energy for the addition was the same as the enthalpy change.

3.5 The Formation of Mg.1,CO.porphin.2-dehydro 4-methyl-pent-1.3-diene

Further condensation may result in a carbon monoxide molecule being added to the magnesium binding site, as,

CO + Mg.1,porphin.2-dehydro 4-methyl-pent-1.3-diene →



Mg.1,CO.porphin.2-dehydro 4-methyl-pent-1.3-diene (5)

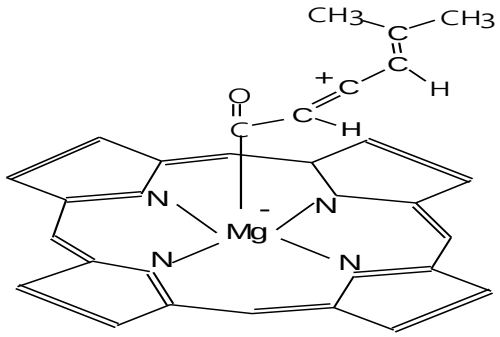
$\Delta H = -0.01744$ h

The addition reaction is favourable without activation energy, [35].

3.6 The formation of Mg.1,1-carbonyl 3-dehydro 5-methyl-hex-2.4-diene.porphin.

The two adducts may coallesce, as,

Mg.1,CO.porphin. 2-dehydro 4-methyl-pent-1.3-diene →



Mg.1,1-carbonyl 3-dehydro 5-methyl-hex-2.4-diene.porphin (6)

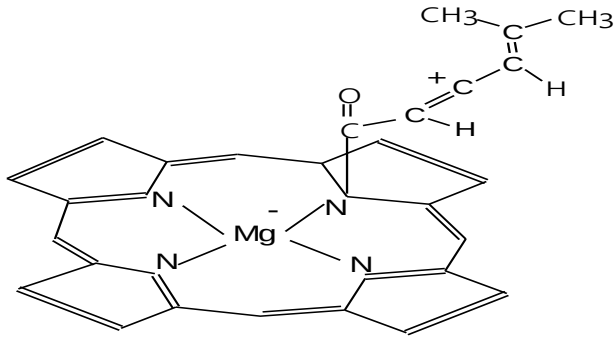
$\Delta H = -0.03788$ h

No activation energy was recorded for this favourable reaction.

3.7 The formation of Mg.1,porphin.1-carbonyl 5-methyl-pent-2.4-diene

The Mg.1,1-carbonyl 2-dehydro 5-methyl-hex-2.4-diene.porphin may be excited to a higher energy state as,

Mg.1,1-carbonyl 3-dehydro 5-methyl-hex-2.4-diene.porphin →



Mg.1,porphin.1-carbonyl 3-dehydro 5-methyl-hex-2,4-diene (7)

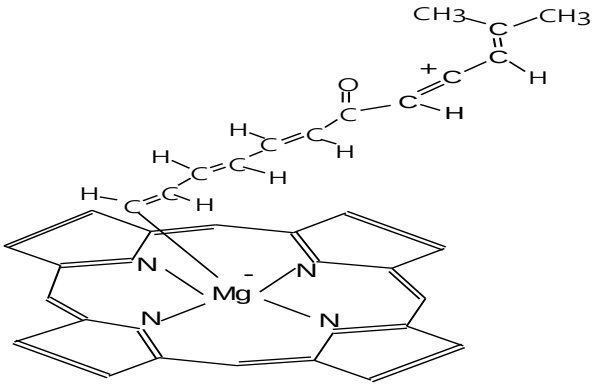
$\Delta H = 0.01193$ h

The activation energy was the same as the enthalpy change.

3.8 The Formation of Mg.1,7-carbonyl 9-dehydro 11-methyl 1,3,5,8,10-penta diene dodecane. porphin

At this stage in the synthesis it is desirable to add an oligomer of three ethyne units, [36], to save on computer time as,

Mg.1,porphin.1-carbonyl 3-dehydro 5-methyl-hex-2.4-diene + 3 H-C ≡ C-H →



Mg.1,7-carbonyl 9-dehydro 11-methyl 1,3,5,8,10-penta diene dodecane.porphin (8)

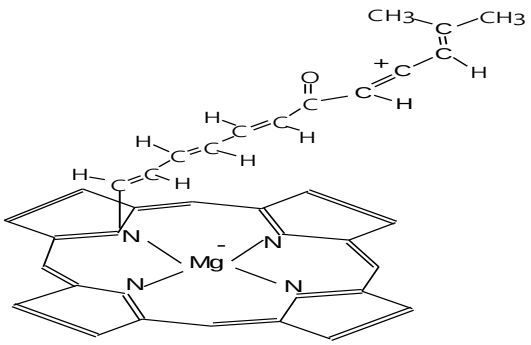
$$\Delta H = 0.03986 \text{ h}$$

The activation energy was the same as the enthalpy change.

3.9 The Formation of Mg.1,porphin. 7-carbonyl 9-dehydro 11-methyl 1,3,5,7,9-penta diene dodecane.

The Mg.1,7-carbonyl 9-dehydro 11-methyl 1,3,5,8,10-penta diene dodecane.porphin
may be excited to a higher energy state as,

Mg.1,7-carbonyl 9-dehydro 11-methyl 1,3,5,8,10-penta diene dodecane.porphin
→



Mg.1,porphin.7-carbonyl 9-dehydro 11-methyl 1,3,5,8,10-penta diene dodecane (9)

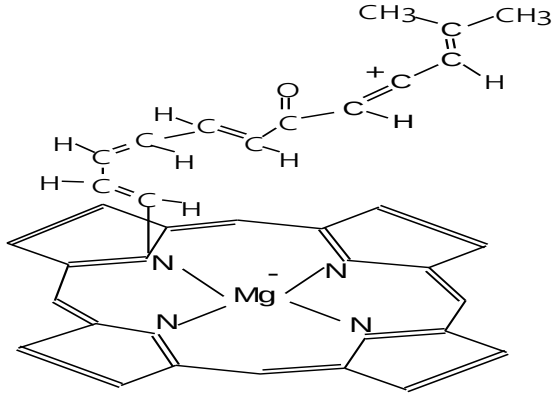
$$\Delta H_{(HF)} = -0.00163 \text{ h}$$

No activation energy was recorded for the formation of this isomeric state.

3.10 The Formation of a cis isomer of Mg.1,porphin.7-carbonyl 9-dehydro 11-methyl 1,3,5,8,10-penta diene dodecane

The Mg.1,porphin.7-carbonyl 9-dehydro 11-methyl 1,3,5,8,10-penta diene dodecane
may be excited by radiation to undergo three consecutive cis rotational energy changes which requires activation energy, [36], as,

Mg.1,porphin.7-carbonyl 9-dehydro 11-methyl 1,3,5,8,10-penta diene dodecane →



A cis isomer of Mg.1,porphin.7-carbonyl 9-dehydro 11-methyl 1,3,5,8,10-penta diene dodecane (10)

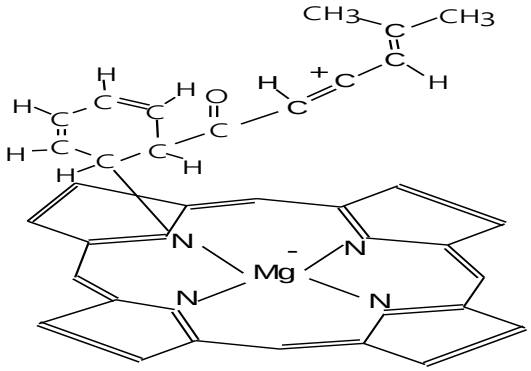
$$\Delta H_{(HF)} = 0.397922 \text{ h}$$

This requires three separate rotational activation energies provided by the catalyst.

3.11 The Formation of Mg.1,porphin.2-(1-carbonyl 3-dehydro 5-methyl hex-2,4-diene-1yl).cyclohex-3,5-dien-1yl

The cis isomer of Mg.1,porphin.7-carbonyl 9-dehydro 11-methyl 1,3,5,8,10-penta diene dodecane may be excited for ring closure to occur and be bonded at the excited higher energy adduct site as,

cis isomer of Mg.1,porphin.7-carbonyl 9-dehydro 11-methyl 1,3,5,8,10-penta diene dodecane →



Mg.1,porphin.2-(1-carbonyl 3-dehydro 5-methyl hex-2,4-diene-1yl).cyclohex-3,5-dien-1yl (11)

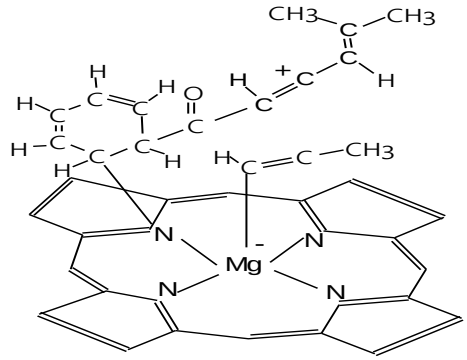
$$\Delta H = -0.40212 \text{ h}$$

.

3.12 The Formation of Mg.1,propyn-1yl.porphin.2-(1-carbonyl 3-dehydro 5-methyl hex-2,4-diene-1yl).cyclohex-3,5-dien-1yl

The Mg.1,porphin.2-(1-carbonyl 3-dehydro 5-methyl hex-2,4-diene-1yl).cyclohex-3,5-dien-1yl may add a propyne adduct on the vacant Mg.porphin site as,

Mg.1,porphin.2-(1-carbonyl 3-dehydro 5-methyl hex-2,4-diene-1yl).cyclohex-3,5-dien-1yl + propyne →



Mg.1,propyn-1yl.porphin.2-(1-carbonyl 3-dehydro 5-methyl hex-2,4-diene-1yl).cyclohex-3,5-dien-1yl. (12)

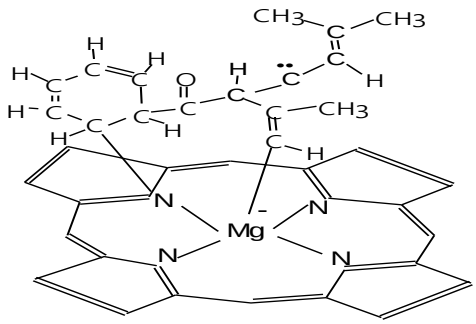
$$\Delta H = 0.11655 \text{ h}$$

These charge transfer complexes form spontaneously, [35].

3.13 The Formation of Mg.1,3-(1-carbonyl-2-(cyclohex-3,5-dien-N-2yl))-4-didehydro-6-methyl 1,5-hept-dien-1yl

Further bonding may occur between the di-ene groups to produce a diradical as**,**

Mg.1,propyn-1yl.porphin.2-(1-carbonyl 3-dehydro 5-methyl hex-2,4-diene-1yl).cyclohex-3,5-dien-1yl →



Mg.1,3-(1-carbonyl-2-(cyclohex 3,5-diene-N-2yl))-4-didehydro-6-methyl 1,5-hept-dien-1yl.porphin (13)

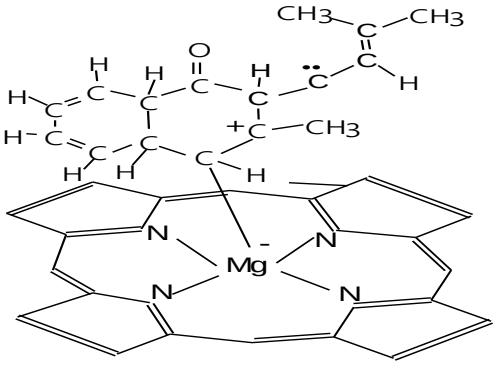
$$\Delta H = -0.07989 \text{ h}$$

The activation energy was calculated as 0.0 h, as they spontaneiously coalesce.

3.14 The Formation of Mg.1,2-dehydro 2-methyl 3-(1-didehydro 3-methyl but 2-ene-1yl) 4-keto 9.10 dihydro napthalene.porphin

Further condensation may occur to form a napthalene derivative as,

Mg.1,3-(1-carbonyl-2-(cyclohex-3,5-diene-N-2yl)-4-didehydro-6-methyl 1,5-hept-diene-1yl →



Mg.1,2-methyl 3-(1-didehydro 3-methyl but 2-en-1yl) -4-keto 9.10 dihydro napthalene.porphin. (14)

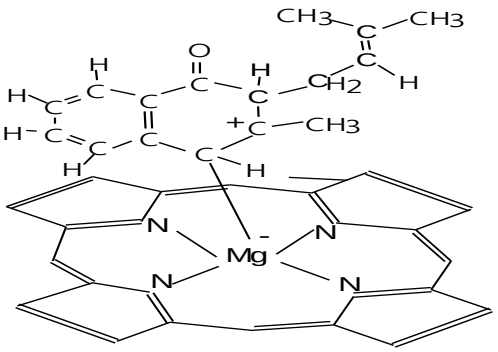
$$\Delta H = -0.14847 \text{ h}$$

The activation energy for the condensation was negligible.

3.15 The Formation of Mg.1,2-methyl 3-(3-methyl but 2-ene-1yl) 4-keto napthalene .porphin

Further isomerization may occur as,

Mg.1,2-methyl 3-(1-didehydro 3-methyl but 2-en-1yl) napthalen 4-keto 9.10 dihydro.porphin ->



Mg.1,2-dehydro 2-methyl 3-(3-methyl but 2-ene-1yl) 4-keto napthalene.porphin (15)

$$\Delta H = -0.24636 \text{ h}$$

The activation energy to add molecular hydrogen to the di-radical is zero.

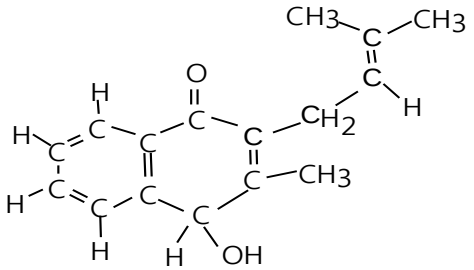
3.16 The Formation of 3-methyl 2-(3-methyl but-2-ene) 4-hydro 4-hydroxy 1-napthaquinone

The nascent vitamin K may be released from the catalyst by the presence of hydrogen and hydroxyl radicals, [37],

$$H_2O \rightarrow H^{\cdot\cdot} + OH^{\cdot\cdot}$$

$$\Delta H = 0.16472 \text{ h}$$

Mg.1,2-dehydro 2-methyl 3-(3-methyl but 2-ene-1yl) 4-keto napthalene.porphin + $H^{\cdot} + OH^{-} \rightarrow H_2$ + Mg.porphin +



4-hydro 4-hydroxy 3-methyl 2-(3-methyl but-2-ene) 1-napthaquinone (16)

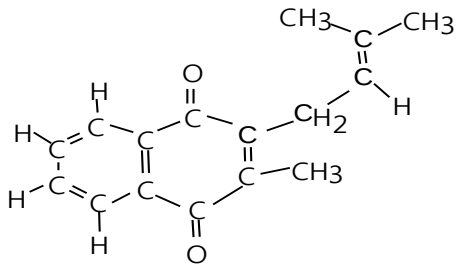
$$\Delta H = -0.25840 \text{ h}$$

The activation energy and enthalpy change for this reaction are assumed to arise from the first excitation of the Mg.porphin catalyst, 0.21 h.

3.17 The Formation of 2-methyl 3-(3-methyl but-2-ene) 1,4 napthaquinone

The napthalene derivative may be oxidised by the presence of hydrogen and hydroxyl radicals to lose a hydrogen molecule as,

3-methyl 2-(3-methyl but-2-ene) 4-hydro 4-hydroxy 1-napthaquinone $\rightarrow H_2$ +



2-methyl 3-(3-methyl but-2-ene) 1,4 napthaquinone (17)

$$\Delta H = 0.00055 \text{ h}$$

The activation energy was the same as the enthalpy change.

3.18 The Formation of Vitamin K1 (n=1)

For the explicit formation of this vitamin K1 (n=1) analoque it is assumed that the enthalpy changes recorded for the above, menaquinone and 2-methylbutane are the same as those for the formation of vitamin K1 (n=1). Here the two molecules are bonded with the exclusion of a hydrogen molecule, according to the equation,

menaquinone + 2-methylbutane $\rightarrow$ vitamin K1 (n=1) + H_2

$$\Delta H = -0.63060 \text{ h}$$

3.19 The Formation of Phylloquinone

The K1 (n=3) vitamin K1, Figure 1, which occurs naturally may be formed by the same sequence of reactions according to the equation,

menaquinone + 3 2-methylbutane $\rightarrow$ 3 H_2 + vitamin K1 (n=3)
phylloquinone (18)

$$\Delta H = -0.90906 \text{ h}$$

3.20 The formation of vitamin K analoques

This polymerization method may also be used to calculate the energies of the K2 series using 2-methylbutene, as,

n 2-methylbutene $\rightarrow$ (2-methylbutene)n + n H_2

3.20.1 The Formation of Reduced Vitamin K-1 Analoges

The order of the enthalpy change in the reduction of 2-methyl 3-(3-methyl but-2-ene) 1,4 napthoquinone may be studied using the simpler compound, 1,4-napthoquinone, as,

1,4-napthoquinone + $H_2 \rightarrow$ 1,4-napthoquinol

$$\Delta H = -0.00055 \text{ h}$$

3.20.2 The Formation of Reduced Vitamin K-1 Analoges

The enthalpy change in the reduction of 2-methyl 3-(3-methyl but-2-ene) 1,4 napthoquinone .may also proceed to produce a semi reduced 1,4-napthoquinone as,

1,4-napthoquinone + H_2 → 4-hydro 4-hydroxy - napthoquinone

$$\Delta H = -0.02146 \text{ h}$$

4 Conclusion

The present biochemistry is via the shikimic acid pathway, [38], which is sequentially demanding and requires multistep enzyme activation. The postulated prebiotic synthesis is much simpler, just a simple copolymerization, and requires just the ancient catalyst, metalloporphin, [39], itself reasonably formed from diacetylene cyanide, [25] together with the most prevalent gases in the Universe, [40], and interstellar hydrocarbynes and water, [41], [42].

The wide range for the length of the side chains in the vitamin series K1 and K2 series does suggest they arose from copolymerization of simple alkyne gases of ancient atmospheres that were mildly reducing. The enthalpy changes and activation energies calculated do confirm this as much as possible. An experiment would be useful to see if vitamin K was indeed formed.

Further work may concentrate on why certain vitamins have specific stereochemistry that is preserved in present biochemistry and how the length of the side chain affects the reduction of the 1,4 quinones. The existence of this molecule in hydrogen transport reactions and its widespread occurrence in biochemistry suggest it is of extreme antiquity

Further work at a higher accuracy may alter the values given here.

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