A Computational Study of a Prebiotic Synthesis of α-Tocopherol, Vitamin-E and Tocols

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Abstract: - The prebiotic synthesis of α-tocopherol and the tocols is postulated as a copolymerization of the planetary gases propyne, ethyne and carbon monoxide on a magnesium ion metalloporphyrin complex where the ligands are bonded on the metal or nitrogen pyrrole sites as a two site catalyst. The order of addition of the monomers to form the chroman residue of α-tocopherol is 2 ethyne, propyne, carbon monoxide, 2 ethyne, carbon monoxide leading to bonding on the catalyst to give a chroman derivative. The phytyl side-chain is formed from the successive addition of propyne and ethyne monomers where the isoprenoid residues formed are subsequently hydrogenated. The separation of the catalyst is facilitated by hydrogen radicals to give α-tocopherol. 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, α,β,γ,δ-tocopherol, ε,ζ,η-tocols, Mg.porphin.

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1 Introduction

Tocopherals are natural products derived from chroman, Figure 1, that are essential dietary factors associated with reproduction, [1]. The structure of α-tocopherol is representative of the group which contains β, γ, and δ-tocopherol, Figure 4, which differ only in the position and number of methyl groups on the benzenoid ring, [2]. The same configurations exist for the tocotrienols, except that the hydrophobic side chain has three carbon-carbon double bonds whereas the tocopherols have a saturated side chain, [3]. They are isolated from vegetables and seed-germ oils, [4]. The key-step in the industrial synthesis of (all-rac)-α-tocopherol (synthetic vitamin E) is the condensation reaction of trimethylhydroquinone with the C20 building block isophytol, [5], [6], [7]. Enzymatic synthesis has been achieved, [8], and the synthesis of isophytol from farnesene using genetic engineering, [9]. The biosynthesis has been illucidated, [10], [11].

Vitamin E (tocochromanols) are clearly established as essential compounds in vertebrate species, [12]

Whilst natural α−Tocopherol has a single stereoisomer RRR- α−tocopherol, tocotrienols possess only the chiral stereocenter at C-2, and naturally occurring tocotrienols exclusively possess the (2R,3′E,7′E) configuration, [13].

Tocochromanols are widely used in feed additives, medicine, food, cosmetics, and other fields exerting their influence on physiological functions based on its antioxidation properties, including improving the body's immunity, fertility, possessing anti-cancer and anti-inflammatory properties, heart protection, and nerve protection, [14], [15], [16], [17]. Vitamin E is an antioxidant, protecting polyunsaturated lipophilic molecules from peroxidation, [18], [19], by free radicals such as hydroxyl or oxygen radicals leading to free radical chain-reactions. It also has biochemical and therapeutical aspects, [20], [21]. Vitamin E is an enzyme activity regulator for protein kinase C (PKC), which plays a role in smooth muscle growth, [22].

From a prebiotic perspective, [23], it is desirable if the reactant molecules were present from a supposed prebiotic atmosphere often held to have been originally mildly reducing, [4], [24], implying the presence of concentrations of carbon monoxide, ammonia, water and hydrogen. It has also been demonstrated that porphin present from the time of photosynthesis, [25], may act as a catalyst for the formation of sugars, [26] and terpenes, [27].

This paper proposes a model for the catalytic photochemically activated copolymerization of the simple gases, propyne, ethyne and carbon monoxide

where the order of addition to form the chroman residue is 2 ethyne, propyne, carbon monoxide, 2 ethyne, carbon monoxide .Initiation of the polymerization occurs with the addition of propyne to the catalyst whilst termination and separation of the catalyst is spontaneous. The synthesis of this biochemical vitamin is postulated to be an example of a general mechanism for the prebiotic synthesis of poly unsaturated fatty acids and terpenes formed over a considerable period of time.

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 α-tocopherol 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 and scaling, [29], are as previously published, [23]. The charge transfer complexes are less stable when calculated at the Hartree Fock level, [30], 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}.$1h = 4.3597482 \times 10^{-18}$ J
Mulliken charges are in units of the electronic charge.

3 Problem Solution

3.1 Total Energies (hartrees)

The initial reactants are deemed to be the simple interstellar and planetary gases propyne, ethyne, carbon monoxide and hydrogen, [31], formed from elementary hydrocarbons such as methane and propane, [32], [33], [34].

The intermediates required in this copolymerization and the energies of the stable complexes are shown 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
propyne (1)	-116.24181	0.06010
Mg.porphin (2)	-1185.12250	0.29262
Mg.1,2-dehydro 4-methyl-penta-1.3-dien-1-yl.porphin (3)	-1417.59302	0.43597
Mg.1,porphin.2-dehydro 4-methyl-penta-1.3-dien-N1-yl porphin (4)	-1417.69182	0.41981
Mg.1,ethynyl.porphin.2-dehydro 4-methyl penta-1,3-dien-N1-yl (5)	-1494.65328	0.44469
Mg.1,3-dehydro 1-didehydromethyl -5-methyl hexa-2,4-dien-1-yl (6)	-1494.63846	0.44477
Mg.1,3-dehydro 1,5-dimethyl hexa-2,4-dien-1-yl.porphin (7)	-1495.94765	0.47258
Mg.1,porphin 3-dehydro 1,5-dimethyl hexa-2,4-dien-1-yl.porphin (8)	-1495.91438	0.46288
Mg.1,ethynyl.porphin 3-dehydro 1,5-dimethyl hexa-2,4-dien-1-yl.porphin (9)	-1572.98448	0.50631
Mg.1,5-dehydro-3,7-dimethyl-octa-1,4,6-trien-1yl.porphin (10)	-1573.12584	0.50303
Mg.1,porphin.5-dehydro-3,7-dimethyl-octa-1,4,6-trien-1yl (11)	-1572.97938	0.50983
Mg.1,propynyl.porphin.5-dehydro-3,7-dimethyl-octa-1,4,6-trien-1yl (12)	-1689.15483	0.56873
Mg.1,6-dehydro 1-didehydroethyl- 4,8-dimethyl nona 2,5,7-trien-1-yl.porphin (13)	-1689.41858	0.56640
Mg.1,porphin. 6-dehydro 1-(1-didehydroethyl)- 4,8-dimethyl nona 3,5,7-trien-1-yl (14)	-1689.30770	0.57224
Mg.1,carbonyl.porphin.4-dehydro 1-(1-didehydroethyl) -4,8-dimethyl nona-2,5,7-trien-1yl (15)	-1802.19923	0.57899
Mg.1, 6-dehydro 1-oxo- 2,6,10-trimethyl undeca-2,4,7,9-tetraen-1yl.porphin (16)	-1802.49088	0.58620
Mg.1,porphin.6-dehydro 1-oxo-2,6,10-trimethyl undeca-2,4,7,9-tetraen-1yl (17)	-1802.46823	0.58960
Mg.1,ethynyl.porphin.6-dehydro1-oxo-2,6,10-trimethyl undeca-2,4,7,9-tetraen-1yl (18)	-1879.50606	0.61897
Mg.1,7-dehydro 1-didehydromethyl-2-oxo-3,7,11-trimethyl dodeca 3,5,8,10-tetraen-1yl.porphin (19)	-1879.41356	0.62096

Mg.1,porphin.7-dehydro 1-didehydromethyl-2-oxo-3,7,11-trimethyl dodeca 3,5,8,10-tetraen-1yl.porphin (20) -1879.44501 0.61825
Mg.1,ethynyl.porphin.7-dehydro 1-didehydromethyl-2-oxo-3,7,11-trimethyl dodeca 3,5,8,10-tetraen-N1-yl (21) -1956.51343 0.64344
Mg.1,7-dehydro 1,2-didehydromethyl-3-oxo-4,8,12-trimethyl trideca-4,6,9,11-tetraen-N1-yl. porphin. (22) -1956.46672 0.65293
Mg.1, porphin.8-dehydro 1,2-didehydromethyl-3-oxo-4,8,12-trimethyl trideca 4,6,9,11-tetraen-N1-yl.porphin (23) -1956.44701 0.65204
Mg.1,carbonyl.porphin.8-dehydro 1,2-didehydromethyl-3-oxo-4,8,12-trimethyl trideca-4,6,9,11-tetraen-N1-yl**.** (24) -2069.72987 0.66033
Mg.1,9-dehydro 1,4-dioxo.2,3-didehydromethyl-5,9,13-trimethyl tetradec-5,7,10,12-tetraen-1-yl.porphin (25) -2069.59578 0.66033
Mg.1,porphin.9-dehydro 1,4-dioxo.2,3-didehydromethyl-5,9,13-trimethyl tetradeca-5,7,10,12-tetraen-1-yl. (26) -2069.63917 0.66033
Mg.1,porphin.2-(3-dehydro 3,7-dimethyl-octa-1,4,6-trien-1yl) 5,6-didehydromethyl 1,4-dioxo cyclohexane N1-yl (27) -2069.59573 0.660327
5,6-(didehydromethyl) 2-(3,7-dimethyl octa-1,4,6-trien-1yl) 1,4-dihydroxy cyclohexane (28) -2069.44254 0.65988
2-methyl 2-(4-methyl penta-1,3-dien-1yl) 5,7,8-trimethyl 6-hydroxy chroman. (29) -883.40972 0.42449
2-methyl 2-(4-methyl pentan-1yl) chroman (30) -889.54152 0.48761
Mg.porphin^{--} -1185.00997 0.28821
3,7-dimethyl octane -392.81513 0.30136
2-methylbutane -196.99336 0.17139
2-methylbutene -195.79496 0.14578
H$^{\cdot}$ -0.49823
OH$^{\cdot}$ -75.52257 0.00911
OH^{-} -75.51314 0.00885
H_2O -76.19685 0.02298
H_2 -1.14414 0.01059

3.2 The Overall Stoichiometry for the Formation of the α-tocopherol

Although Mg.porphin is here taken as the catalyst for the reaction, the overall stoichiometry to form α-tocopherol, Figure 1, from the primary reactants is given as:

$$5CH_3\text{-}C \equiv C\text{-}H + 6H\text{-}C \equiv C\text{-}H + 2CO + 9H_2 \rightarrow C_{29}H_{50}O_2$$

α-tocopherol

$$\Delta H = -1.06648 \text{ h}$$

The enthalpy change is negative indicating that this may be the energetically favourable route to the initial formation of the vitamin E, Figure 1.

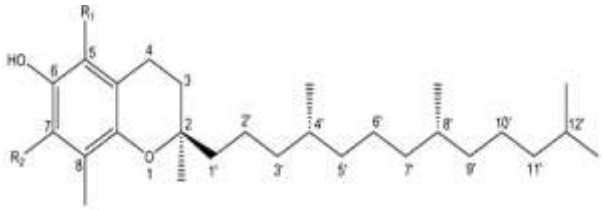


Fig. 1: Atom numbering in α-tocopherol

To save computer time the molecule is split into the chroman derivative, 2-methyl 2-(4-methyl pentan-1yl) chroman, Figure 2, and the side chain substituent alkane, 3,7-dimethyl octane, Figure 3.

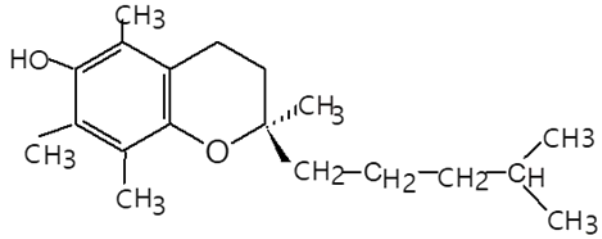


Fig. 2: 2-methyl 2-(4-methyl pentan-1yl) chroman

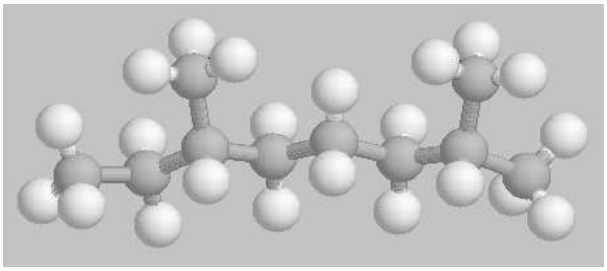


Fig. 3: 3,7-dimethyl octane

The overall stoichiometry to form the 2-methyl 2-(4-methyl pentan-1yl) chroman is as follows:

$$3\ CH_3\text{-}C \equiv C\text{-}H + 4\ H\text{-}C \equiv C\text{-}H + 2CO + 5H_2 \rightarrow C_{19}H_{30}O_2$$

$$\Delta H = -0.67415 \text{ h}$$

The overall stoichiometry to form the 3,7-dimethyl octane, Figure 3, is as follows:

$$2\ H\text{-}C \equiv C\text{-}H + 2\ CH_3\text{-}C \equiv C\text{-}H + 5H_2 \rightarrow C_{10}H_{22}$$

$$\Delta H = -0.41555 \text{ h}$$

Finally, the two are combined according to the equation,

2-methyl 2-(4-methyl pentan-1yl) chroman + 3,7-dimethyl octane → tocopherol + H_2

$$\Delta H = --1.06648 \text{ h}$$

The enthalpy change is negative indicating that this may be the energetically favourable route to the initial formation of the tocopherol series.

The intermediates by which these stoichiometric reactions may have occurred are as follows.

Molecules are numbered consecutively.

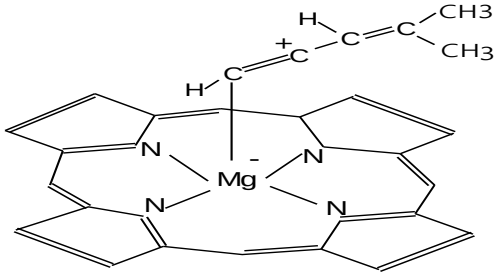
Subsections depict alternatives to give some of the many variations of the α-tocopherol structure.

A standard numbering of the atoms in the tocopherol structure is given in Figure 1.

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

The prebiotic photochemically activated, surface catalyzed synthesis of Mg.1,2-dehydro 4-methyl-penta-1.3-diene.porphin has been described, [27], where the catalyst was taken as Mg.porphin, [23], [26]. The same catalyst is used in this synthesis of vitamin E where the initial reactant is the gas propyne. Here, those first reactions are summarized and represented here as:

2 CH_3-C ≡ C-H + Mg.porphin →
(1) (2)



Mg.1,2-dehydro 4-methyl penta-1,3-dien-1-yl.porphin (3)

$$\Delta H = -0.07948 \text{ h}$$

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

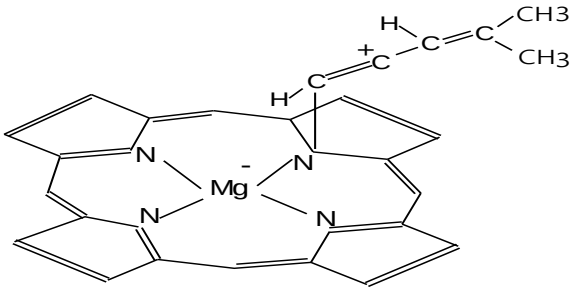
The activation energy in these charge transfer reactions or the formation of van der Waals complexes is always achievable as the catalyst can absorb considerable photochemical activation, 0.21 h, [26].

At this stage in the synthesis of vitamin E analogues the long side-chains of from 1 to 3 isoprenoid groups may be added, [35], and hydrogenated to produce various sterically specific side-chains. These are postponed until later.

3.4 The formation of Mg.1,porphin.2-dehydro 4-methyl penta-1,3-dien-N1-yl

The Mg.1,2-dehydro 4-methyl penta-1,3-dien-1-yl.porphin may be excited to a higher energy state as,

Mg.1,2-dehydro 4-methyl penta-1,3-dien-1-yl.porphin →



Mg.1,porphin.2-dehydro 4-methyl penta-1,3-dien-N1-yl (4)

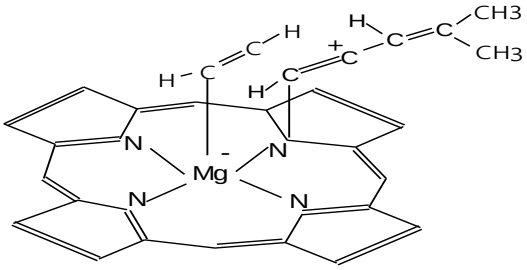
$$\Delta H = 0.11318 \text{ h}$$

Here the activation energy is the same as the enthalpy change, [35].

3.5 The Formation of Mg.1,ethynyl.porphin. 2-dehydro 4-methyl penta-1,3-dien-N1-yl

The Mg.1,porphin.2-dehydro 4-methyl penta-1,3-dien-N1-yl may add a further ethyne as,

H-C ≡ C-H + Mg.1,porphin.2-dehydro 4-methyl penta-1,3-dien-N1-yl →



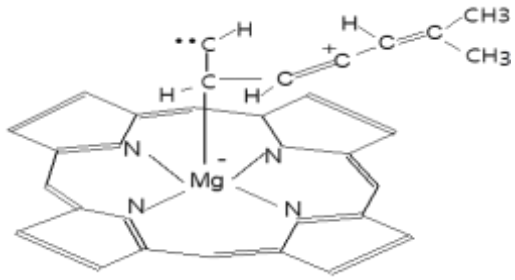
Mg.1,ethynyl.porphin.2-dehydro 4-methyl penta-1,3-dien-N1-yl (5)

$$\Delta H = -0.01192 \text{ h}$$

The activation energy to form these van der Waals's complexes is either zero or very marginal, as here.

3.6 The fORMATION of Mg.1, 3-dehydro 1-didehydromethyl -5-methyl hexa-2,4-dien-1-yl

The Mg.1,ethynyl.porphin.2-dehydro 4-methyl penta-1,3-dien-N1-yl adducts may coalesce as,
Mg.1,ethynyl.porphin.2-dehydro 4-methyl penta-1,3-dien-N1-yl →



Mg.1,3-dehydro 1-didehydromethyl -5-methyl hexa-2,4-dien-1-yl (6)

$$\Delta H = 0.01489 \text{ h}$$

Although an asymmetric centre is created here as R at C1 it is later converted to a transient carbonium ion. The ethyne adduct here depicted later provides the C2 of the chroman ring, yet to be formed, and also the C2-methyl substituent of the chroman ring system.

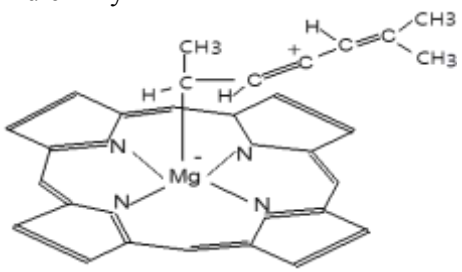
3.6.1 The Formation of γ, δ, and η-tocols

Failure of the ethyne adduct to bond as shown above, but to be incorporated with both ethyne C atoms bonded to adjacent monomers may lead to the absence of a methyl group at C2 of the tocol, [35].

3.7 The Formation of Mg.1, 3-dehydro 1,5-dimethyl hexa-2,4-dien-1-yl.porphin

The Mg.1,3-dehydro 1-didehydromethyl -5-methyl hexa-2,4-dien-1-yl may be hydrogenated as,

H_2 + Mg.1,3-dehydro 1- didehydromethyl -5-methyl hexa-2,4-dien-1-yl →



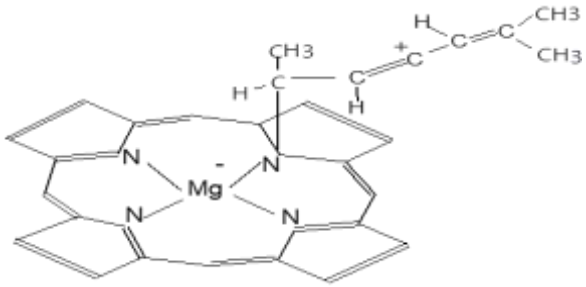
Mg.1,3-dehydro 1,5-dimethyl hexa-2,4-dien-1-yl.porphin (7)

$$\Delta H = -0.14972 \text{ h}$$

This hydrogenation is exothermic without activation energy.

3.8 The Formation of Mg.1,porphin 3-dehydro 1,5-dimethyl hexa-2,4-dien-1-yl.porphin

The Mg.1,3-dehydro 1,5-dimethyl hexa-2,4-dien-1-yl.porphin may be excited to a higher energy state as,
Mg.1,3-dehydro 1,5-dimethyl hexa-2,4-dien-1-yl.porphin →



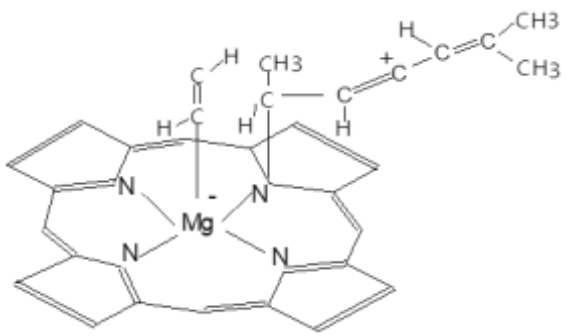
Mg.1,porphin 3-dehydro 1,5-dimethyl hexa-2,4-dien-1-yl.porphin (8)

$$\Delta H = 0.024635 \text{ h}$$

The activation energy was the same as the enthalpy change.

3.9 The Formation of Mg.1,ethynyl.porphin 3-dehydro 1,5-dimethyl hexa-2,4-dien-1-yl.porphin

The Mg.1,porphin 3-dehydro 1,5-dimethyl hexa-2,4-dien-1-yl.porphin may add a further ethyne as,
Mg.1,porphin 3-dehydro 1,5-dimethyl hexa-2,4-dien-1-yl.porphin + H-C ≡ C-H →

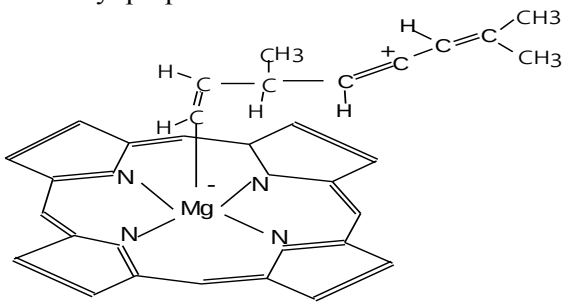


Mg.1,ethynyl.porphin 3-dehydro 1,5-dimethyl hexa-2,4-dien-1-yl.porphin (9)

$$\Delta H = 0.00914 \text{ h}$$

3.10 The Formation of Mg.1,5-dehydro-3,7-dimethyl-octa-1,4,6-trien-1yl.porphin.

The Mg.1,ethynyl.porphin 3-dehydro 1,5-dimethyl hexa-2,4-dien-1-yl.porphin adducts may coalesce as,
Mg.1,ethynyl.porphin 3-dehydro 1,5-dimethyl hexa-2,4-dien-1-yl.porphin →



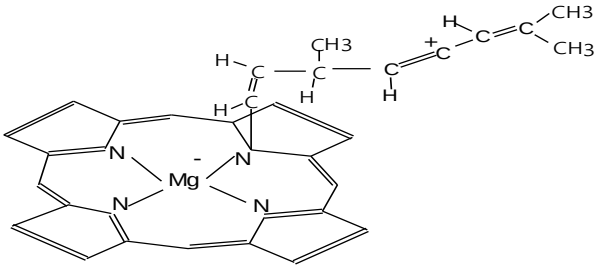
Mg.1,5-dehydro-3,7-dimethyl-octa-1,4,6-trien-1yl.porphin (10)

$$\Delta H = -0.14428 \text{ h}$$

This reaction is without activation energy.

3.11 The Formation of Mg.1,porphin.5-dehydro-3,7-dimethyl-octa-1,4,6-trien-1yl.

The Mg.1,5-dehydro-3,7-dimethyl-octa-1,4,6-trien-1yl.porphin may be excited to a higher energy state as,
Mg.1,5-dehydro-3,7-dimethyl-octa-1,4,6-trien-1yl.porphin →



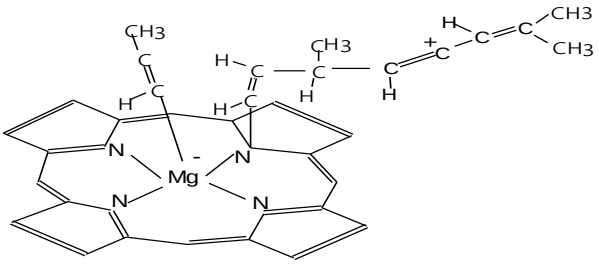
Mg.1,porphin.5-dehydro-3,7-dimethyl-octa-1,4,6-trien-1yl (11)

$$\Delta H = -0.14251 \text{ h}$$

This reaction is without activation energy.

3.12 The Formation of Mg.1,propynyl.porphin.5-dehydro-3,7-dimethyl-octa-1,4,6-trien-1yl.

The Mg.1,porphin.5-dehydro-3,7-dimethyl-octa-1,4,6-trien-1yl may add a propyne adduct as,
CH_3-C ≡ C-H + Mg.1,porphin.5-dehydro-3,7-dimethyl-octa-1,4,6-trien-1yl →

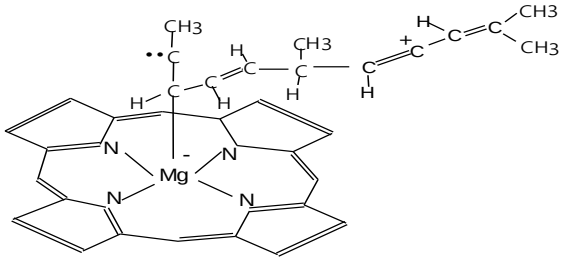


Mg.1,propynyl.porphin.5-dehydro-3,7-dimethyl-octa-1,4,6-trien-1yl (12)

$$\Delta H = 0.07529 \text{ h}$$

3.13 The formation of Mg.1, 6-dehydro 1-didehydroethyl- 4,8-dimethyl nona 2,5,7-trien-1-yl.porphin

The Mg.1,propynyl.porphin.5-dehydro-3,7-dimethyl-octa-1,4,6-trien-1yl adducts may coalesce as,
Mg.1,propynyl.porphin.5-dehydro-3,7-dimethyl-octa-1,4,6-trien-1yl →



Mg.1, 6-dehydro 1-didehydroethyl- 4,8-dimethyl nona 2,5,7-trien-1-yl.porphin (13)

$$\Delta H = -0.26582 \text{ h}$$

The reaction is recorded as without activation energy.

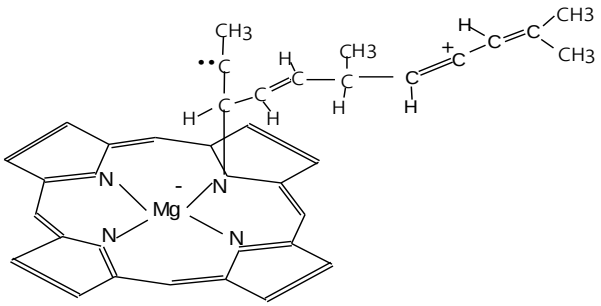
3.13.1 The Formation of γ and δ-tocopherol.

Failure to add a propyne monomer at this stage in the syntheses, and the addition of ethyne in its place may lead to an absence of a methyl group at C5 of the tocol, [35].

3.14 The Formation of Mg.1,porphin. 6-dehydro 1-(1-didehydroethyl) 4,8-dimethyl nona 2,5,7-trien-1-yl.

The Mg.1, 6-dehydro 1-(1-didehydroethyl)- 4,8,-dimethyl nona 2,5,7-trien-1-yl.porphin may be excited to a higher energy state as,

Mg.1, 6-dehydro 1-(1-didehydroethyl)- 4,8,-dimethyl nona 3,5,7-trien-1-yl.porphin →



Mg.1,porphin.6-dehydro 1-(1-didehydroethyl) 4,8-dimethyl nona 3,5,7-trien-1-yl (14)

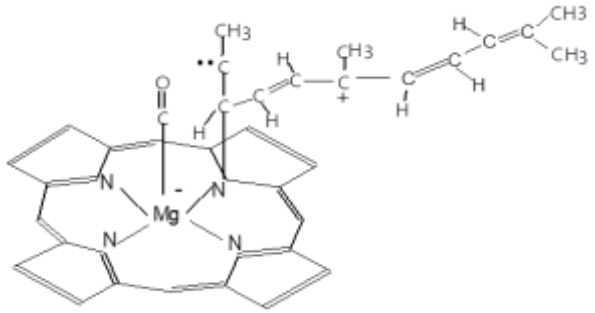
$$\Delta H = 0.11608 \text{ h}$$

The activation energy is the same as the enthalpy change.

3.15 The Formation of Mg.1,carbonyl. porphin. 4-dehydro 1-(1-didehydroethyl) -4,8-dimethyl nona-2,5,7-trien-1yl

The Mg.1,porphin. 6-dehydro 1-(1-didehydroethyl) -4,8-dimethyl nona-2,5,7-trien-1yl may add a carbonyl adduct as,

CO + Mg.1,porphin. 6-dehydro 1-(1-didehydroethyl)- 4,8-dimethyl nona-2,5,7-trien-1yl .→



Mg.1,carbonyl.porphin. 4-dehydro 1-(1-didehydroethyl) 4,8-dimethyl nona-2,5,7-trien-1yl (15)

$$\Delta H = 0.13075 \text{ h}$$

It is also inferred here that prototropic shifts may occur along the side-chain where the enthalpy change of the adduct in this excited state is sufficient to provide the activation energy, 0.101 h. This does result in a closer distance between the charges of the charge transfer complex.

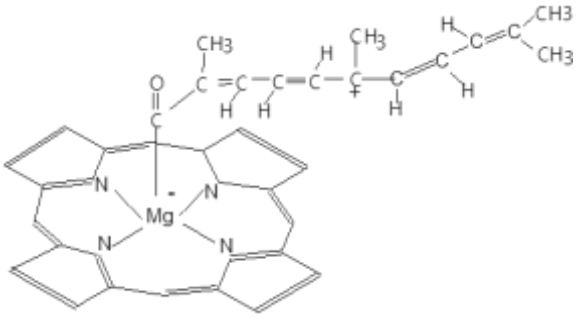
3.15.1 The Formation of ε, ζ and η-tocopherol

Failure to add a carbon monoxide monomer at this stage in the syntheses may give rise to the tocol analoque ε, ζ and η -tocol derivatives, [35], Figure 5.

3.16 The Formation of Mg.1,6-dehydro 1-oxo-2,6,10-trimethyl undeca-2,4,7,9-tetraen-1-yl.porphin

The Mg.1,carbonyl.porphin. 4-dehydro 1-(1-didehydroethyl) -4,8-dimethyl nona-2,5,7-trien-1-yl adducts may coallesce as,

Mg.1,carbonyl.porphin. 4-dehydro 1-(1-didehydroethyl) -4,8-dimethyl nonan-2,5,7-trien-1-yl →



Mg.1, 6-dehydro 1-oxo 2,6,10-trimethyl undeca-2,4,7,9-tetraen-1yl.porphin (16)

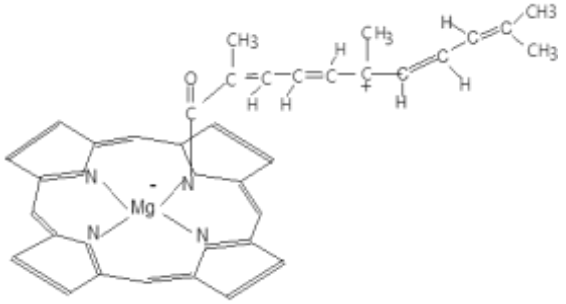
$$\Delta H = -0.28523 \text{ h}$$

The reaction is without activation energy.

3.17 The Formation of Mg.1,porphin.6-dehydro 1-oxo-2,6,10-trimethyl undeca-2,4,7,9-tetraen-1yl.

The Mg.1,6-dehydro 1-oxo-2,6,10-trimethyl undeca-2,4,7,9-tetraen-1yl.porphin may be excited to a higher energy state and undergo prototropic shifts as,

Mg.1,6-dehydro 1-oxo-2,6,10-trimethyl undeca-2,4,7,9-tetraen-1yl.porphin →



Mg.1,porphin.6-dehydro 1-oxo-2,6,10-trimethyl undeca-2,4,7,9-tetraen-1yl (17).

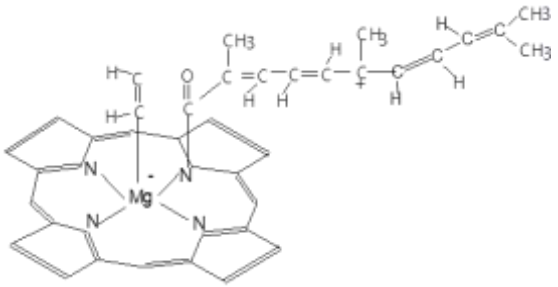
$$\Delta H = 0.02567 \text{ h}$$

The activation energy is the same as the enthalpy change.

3.18 The Formation of Mg.1,ethynyl. porphin.6-dehydro 1-oxo-2,6,10-trimethyl undeca-2,4,7,9-tetraen-1yl.

The Mg.1,porphin.6-dehydro 1-oxo-2,6,10-trimethyl undeca-2,4,7,9-tetraen-1yl may add another ethyne molecule as adduct as,

H-C ≡ C-H + Mg.1,porphin.6-dehydro 1-oxo-2,6,10-trimethyl undeca-2,4,7,9-tetraen-1yl.
→



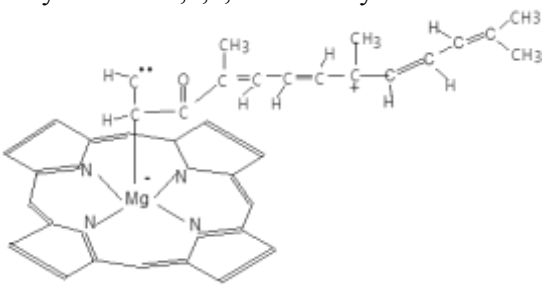
Mg.1,ethynyl.porphin.6-dehydro 1-oxo-2,6,10-trimethyl undeca-2,4,7,9-tetraen-1yl (18)

$$\Delta H = 0.02889 \text{ h}$$

This was the small activation energy.

3.19 The Formation of Mg.1,7-dehydro 1-didehydromethyl-2-oxo-3,7,11-trimethyl dodeca-3,5,8,10-tetraen-1yl.porphin

The Mg.1,ethynyl.porphin.6-dehydro 1-oxo-2,6,10-trimethyl undeca-2,4,7,9-tetraen-1yl adducts may coalesce as,
Mg.1,ethynyl.porphin.6-dehydro 1-oxo-2,6,10-trimethyl undeca-2,4,7,9-tetraen-1yl. →



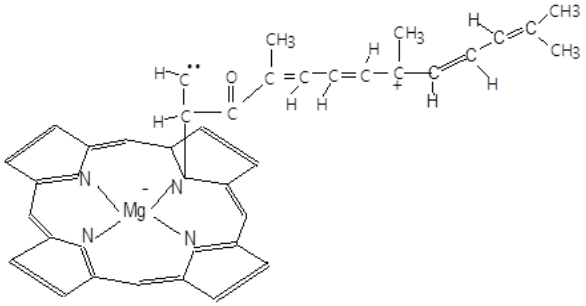
Mg.1,7-dehydro 1-didehydromethyl-2-oxo-3,7,11-trimethyl dodeca 3,5,8,10-tetraen-1yl.porphin (19)

$$\Delta H = 0.09428 \text{ h}$$

This was also the activation energy.

3.20 The Formation of Mg.1,porphin.1-didehydromethyl-2-oxo-3,7,11-trimethyl dodeca-3,5,8,10-tetraen-N1-yl.

The Mg.1,7-dehydro 1-didehydromethyl-2-oxo-3,7,11-trimethyl dodeca 3,5,8,10-tetraen-1yl.porphin may be excited to a higher energy state as,
Mg.1,7-dehydro 1-didehydromethyl-2-oxo-3,7,11-trimethyl dodeca 3,5,8,10-tetraen-1yl.porphin →



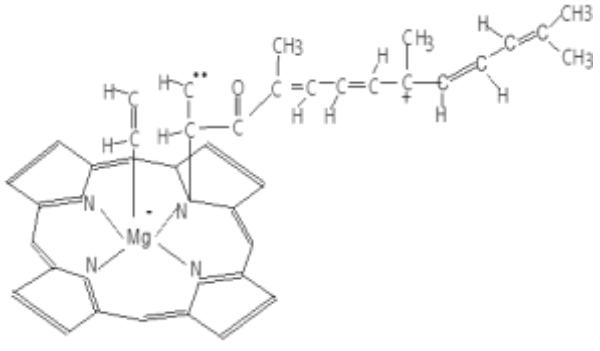
Mg.1,porphin.7-dehydro 1-didehydromethyl-2-oxo-3,7,11-trimethyl dodeca 3,5,8,10-tetraen-1yl.porphin (20)

$$\Delta H = -0.03387 \text{ h}$$

No activation energy was recorded.
The hydrogenation was postponed until later to gauge the reactivity.

3.21 The Formation of Mg.1,ethynyl. porphin.7-dehydro 1-didehydromethyl-2-oxo-3,7,11-trimethyl dodeca-3,5,8,10-tetraenen-N1-yl.

A second ethyne may be added as adduct as,
H-C ≡ C-H + Mg.1,porphin.7-dehydro 1-didehydromethyl-2-oxo-3,7,11-trimethyl dodeca 3,5,8,10-tetraen-1yl.porphin →



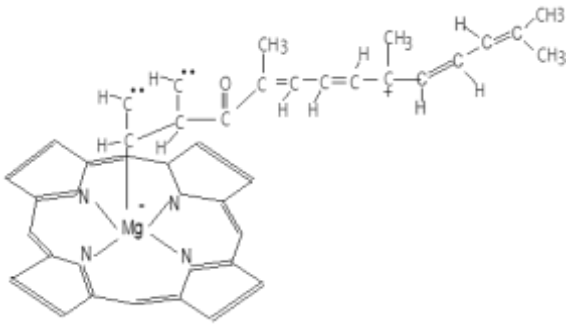
Mg.1,ethynyl.porphin.7-dehydro 1-didehydromethyl-2-oxo-3,7,11-trimethyl dodeca 3,5,8,10-tetraen-N1-yl (21)

$$\Delta H = -0.00542 \text{ h}$$

3.22 The Formation of Mg.1,8-dehydro 1,2-didehydromethyl-3-oxo-4,8,12-trimethyl trideca-4,6,9,11-tetraen-N1-yl.porphin.

The Mg.1,ethynyl.porphin.7-dehydro 1-didehydromethyl-2-oxo-3,7,11-trimethyl dodeca 3,5,8,10-tetraen-N1-yl may coalesce as,

Mg.1,ethynyl.porphin.7-dehydro 1-dehydromethyl-2-oxo-3,7,11-trimethyl dodeca 3,5,8,10-tetraen-N1-yl →



Mg.1,8-dehydro 1,2-didehydromethyl-3-oxo-4,8,12-trimethyl trideca-4,6,9,11-tetraen-N1-yl.porphin. (22)

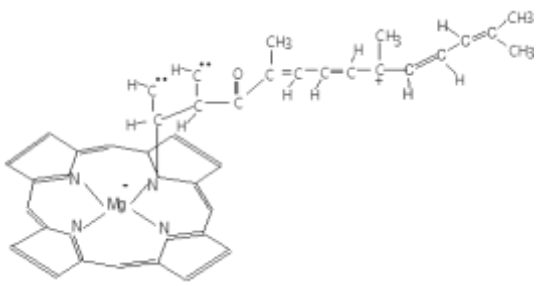
$$\Delta H = 0.05516 \text{ h}$$

The activation energy was the same as the enthalpy change.

3.23 The Formation of Mg.1, porphin.8-dehydro 1,2-didehydromethyl-3-oxo-4,8,12-trimethyl trideca-4,6,9,11-tetraen-N1-yl.

The adduct may be excited to a higher energy state as,

Mg.1,porphin.8-dehydro 1,2-didehydromethyl-3-oxo-4,8,12-trimethyl trideca 4,6,9,11-tetraen-N1-yl. →



Mg.1, porphin.8-dehydro 1,2-didehydromethyl-3-oxo-4,8,12-trimethyl trideca 4,6,9,11-tetraen-N1-yl. (23)

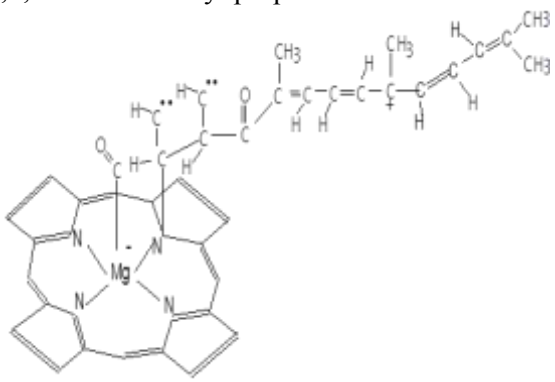
$$\Delta H = 0.01891 \text{ h}$$

The activation energy was the same as the enthalpy change.

3.24 The Formation of Mg.1,carbonyl. porphin.8-dehydro 1,2-didehydromethyl-3-oxo-4,8,12-trimethyl trideca-4,6,9,11-tetraen-N1-yl.

A further carbonyl group may be added to the Mg.1,porphin.8-dehydro 1,2-didehydromethyl-3-oxo-4,8,12-trimethyl trideca-4,6,9,11-tetraen-N1-yl.porphin as,

CO + Mg.1,porphin.8-dehydro 1,2-didehydromethyl-3-oxo-4,8,12-trimethyl trideca 4,6,9,11-tetraen-N1-yl.porphin →



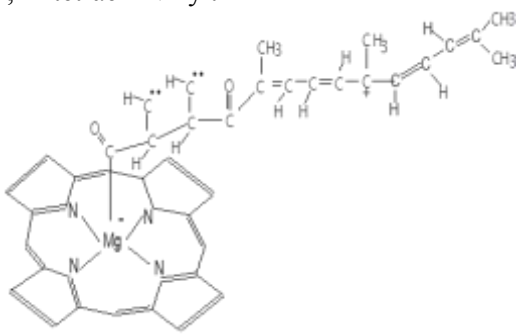
Mg.1,carbonyl.porphin.8-dehydro 1,2-didehydromethyl-3-oxo-4,8,12-trimethyl trideca-4,6,9,11-tetraen-N1-yl**.** (24)

$$\Delta H = -0.25920 \text{ h}$$

3.25 The Formation of Mg.1,9-dehydro 1,4-dioxo.2,3-didehydromethyl-5,9,13-trimethyl tetradeca-5,7,10,12-tetraen-1-yl.porphin

The adducts on the catalyst may coalesce as,

Mg.1,carbonyl.porphin.8-dehydro 1,2-didehydromethyl-3-oxo-4,8,12-trimethyl trideca-4,6,9,11-tetraen-N1-yl**.** →



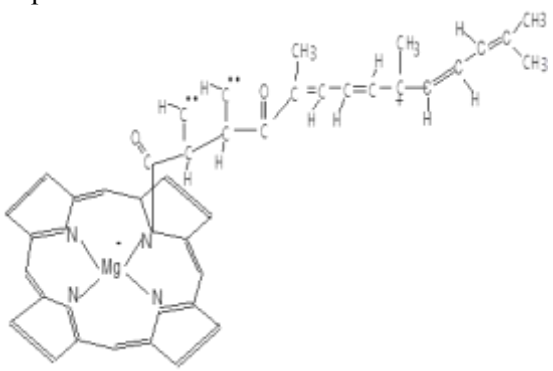
Mg.1, 9-dehydro 1,4-dioxo.2,3-didehydromethyl-5,9,13-trimethyl tetradeca-5,7,10,12-tetraen-1-yl.porphin (25)

$$\Delta H = 0.13413 \text{ h}$$

3.26 The Formation of Mg.1,porphin.1,4-dioxo.2,3-didehydromethyl-5,9,13-trimethyl tetradeca-5,7,10,12-tetraen-1-yl.

The Mg.1,9-dehydro 1,4-dioxo.2,3-didehydromethyl-5,9,13-trimethyl tetradeca-5,7,10,12-tetraen-1-yl.porphin may be excited to a higher energy state as,

Mg.1,9-dehydro 1,4-dioxo.2,3-didehydromethyl-5-9,13-trimethyl tetradeca-5,7,10,12-tetraen-1-yl.porphin →



Mg.1,porphin.9-dehydro 1,4-dioxo.2,3-didehydromethyl-5,9,13-trimethyl tetradeca-5,7,10,12-tetraen-1-yl. (26)

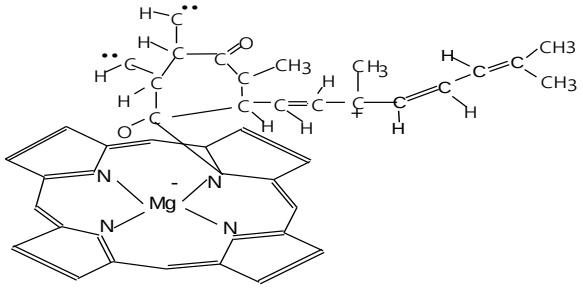
$$\Delta H = -0.04344 \text{ h}$$

No activation energy was recorded for this transition.

3.27 The Formation of Mg.1,porphin.2-(3-dehydro 3,7-dimethyl-octa-1,4,6-trien-1yl) 5,6-didehydromethyl 1,4-dioxo cyclohexane N1-yl

The Mg.1,porphin.9-dehydro 1,4-dioxo.2,3-didehydromethyl-5-9,13-trimethyl tetradeca-5.7.10.12-tetraen-1-yl may cyclize as,

Mg.1,porphin.1,4-dioxo.2,3-didehydromethyl-5-9,13-trimethyl tetradeca-5.7.10.12-tetraen-1-yl.porphin →



Mg.1,porphin.2-(3-dehydro 3,7-dimethyl-octa-1,4,6-trien-1yl) 5,6-didehydromethyl 1,4-dioxo cyclohexane N1-yl (27)

$$\Delta H = 0.21708 \text{ h}$$

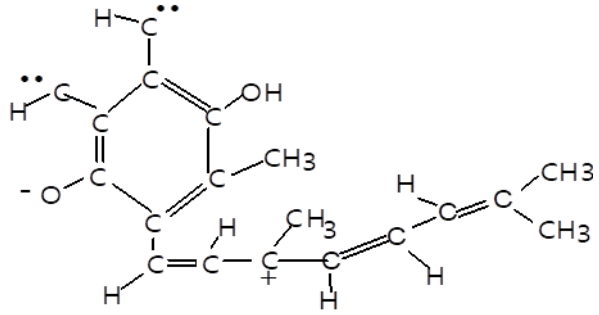
The activation energy for cyclisation was the same as the enthalpy change.

3.28 The Formation of 5,6-didehydromethyl) 2-(3,7-dimethyl octa-1,4,6-trien-1yl) 1,4-dihydroxy cyclohexane

The Mg.1,porphin.2-(3-dehydro 3,7-dimethyl-octa-1,4,6-trien-1yl) 5,6-didehydromethyl 1,4-dioxo cyclohexane N1-yl may separate from the catalyst as a neutral molecule as.

Mg.1,porphin.2-(3-dehydro 3,7-dimethyl-octa-1,4,6-trien-1yl) 5,6-didehydromethyl 4,6-dioxo cyclohexane N1-yl →

$Mg.porphin^{--} + 2H^{+} +$



5,6-(didehydromethyl) 2-(3,7-dimethyl octa-1,4,6-trien-1yl) 1,4-dihydroxy cyclohexane (28)

$$\Delta H = -0.49000 \text{ h}$$

The reaction is more favourable if mediated with hydrogen or hydroxyl radicals [36].

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

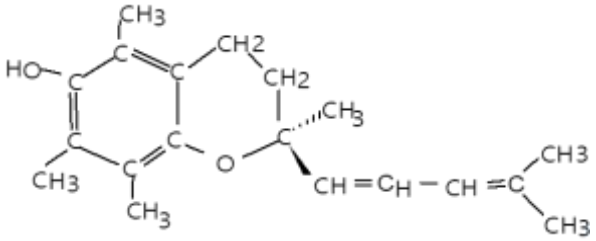
$$\Delta H = 0.16472 \text{ h}$$

The cis bonding of the C2 substituent ensures a favourable orientation for further cyclization as shown below and establish the asymmetry of the C2 carbon atom of the chroman as R. The activation energy was 0.010 h.

3.29 The Formation of 2-methyl 2-(4-methyl penta-1,3-dien-1yl) 5,7,8-trimethyl 6-hydroxy chroman.

The 5,6-(didehydromethyl) 2-(3,7-dimethyl octa-1,4,6-trien-1yl) 1,4-dihydroxy cyclohexane may cyclize and hydrogenate as,

5,6-(didehydromethyl) 2-(3,7-dimethyl octa-1,4,6-trien-1yl) 1,4-dihydroxy cyclohexane + $3H_2$ →



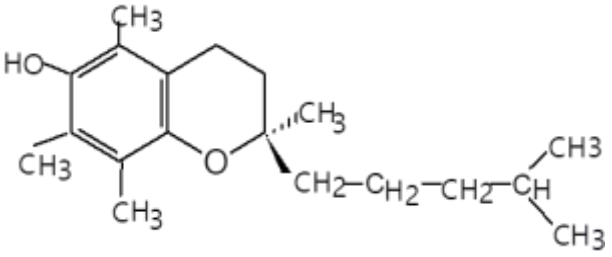
2-methyl 2-(4-methyl penta-1,3-dien-1yl) 5,7,8-trimethyl 6-hydroxy chroman.(29)

$$\Delta H = -0.29567 \text{ h}$$

3.30 The Formation of 2-methyl 2-(4-methyl pentan-1yl) chroman

This 2-methyl 2-(4-methyl penta-1,3-dien-1yl) 5,7,8-trimethyl 6-hydroxy chroman may be fully hydrogenated as,

2-methyl 2-(4-methyl penta-1,3-dien-1yl) 5,7,8-trimethyl 6-hydroxy chroman + $2H_2$ →



2-methyl 2-(4-methyl pentan-1yl) chroman (30)

$$\Delta H = -0.10635 \text{ h}$$

The α-tocopherol may be constituted as before.

3.31 The Formation of α-tocopherol.

Finally, the chroman is combined with the alkane, 3,7-dimethyl octane, according to the equation,

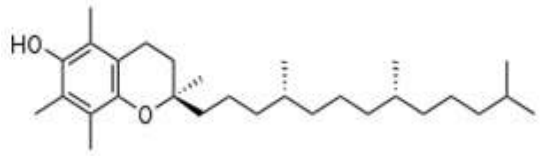
2-methyl 2-(4-methyl pentan-1yl) chroman + 3,7-dimethyl octane → tocopherol + H_2

$$\Delta H = -1.06648 \text{ h}$$

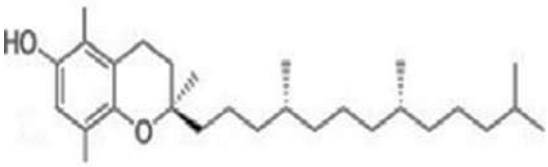
3.31.1 The Formation of Tocols

The postulated synthesis is the formation of a specific tocol, α-tocopherol, formed from the bonding of the, ethyne, propyne, carbon monoxide and hydrogen facilitated by the catalyst Mg.porphin. The energy changes in coordinating each of these gases is minimal implying they all have comparable probabilities of binding to the catalyst. However, propyne may be a stronger nucleophile than ethyne, and ethyne may be in greater concentration. A copolymerization is expected with a full range of different oligomers leading to a range of different tocols, Figure 4 and Figure 5 where one or both of the alkyne carbon atoms may contribute to the sequence of backbone carbon atoms in the oligomer.

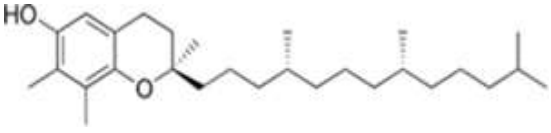
Table 2, depicts the source of the tocol numbered carbon atoms leading to some documented tocols, [35]. Ethyne is represented as e, propyne as p, and carbon monoxide as co.



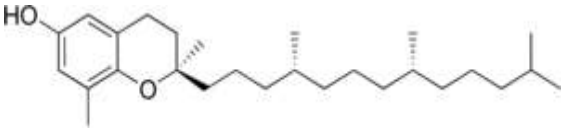
α-tocopherol



β-tocopherol



γ-tocopherol



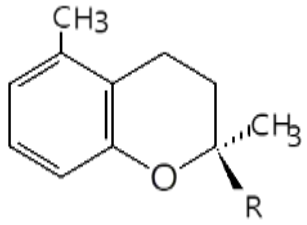
δ-tocopherol

Fig. 4: A representation of the structure of tocols

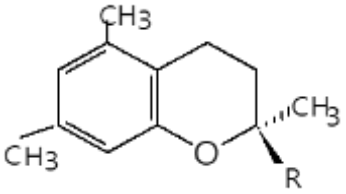
Table 2. Tocol oligomer sequence data. Tocol atom number (At) and alkyne source, ethyne (e), propyne (p) and carbon monoxide (co)

Tocol	At. No. 2	At. No. 3	At. No. 4	At. No. 5	At. No. 6	At. No. 7	At. No.8
α	e	e	e	p	co	e	e
β	e	e	e	p	co	p	P
γ	e	e	e	e	co	e	e
δ	e	e	e	e	co	p	P
ε	p	p	e	p	p	e	e
ζ	p	p	e	p	p	p	P
η	p	p	e	e	e	p	P

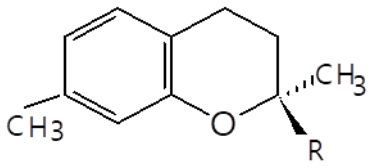
A further range of different tocols are depicted in, Figure 5.



, ε-tocol



ζ-tocol



η-tocol

Fig. 5: A representation of tocols. R-phytyl side-chain

4 Conclusion

Predicated on a planetary atmosphere containing simple gases such as propyne, ethyne, carbon monoxide and a mildly reducing atmosphere containing hydrogen gas the laws of chemical thermodynamics and kinetics would appear sufficient for the formation of vitamin E analoques on its surface, provided in addition that the gases ethyne and hydrogen cyanide would yield by free radical reactions diacetylene cyanide, that has been postulated as being a feasible source of the molecule porphin and its analoques, [23], to synthesize the photchemically activated surface catalyst Mg.porphin, itself of extreme antiquity, [25]. However, the limited range of activation energies involved in the long sequence of the copolymerization would indicate the probable formation of a large range of tocopherols and associated trienols. All of these mentioned and many with extended phytyl side chains are shown to have been accessible from the polymerizations.

The purpose of this work is indicate the expectation of such molecules being found on planets that have the required reactant molecules and physical conditions for this chemistry, and the subsequent incorporation of such molecules into later molecular development and biochemistry where the original morphological structure may be expected to be maintained, but sophisticted incorporation into biochemical structures being evolved over very large time frames. The occurrence of this molecule in the present biochemistry of plants and in cyanobacteria and algae giving a protective function against photooxidative damage in photosystem II, [37], [38] does suggest that this may have occurred during the history of the chemistry of the Earth.

The structure of these molecules strongly suggests they arose from a copolymerizations, and this sequence does support that conclusion.

Research work may determine the exact utilization of the absolute symmetry of the phytyl side chains.

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

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