A Prebiotic Photochemical Synthesis of Glycerides

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Abstract: - The magnesium ion metalloporphyrin complex is shown to bind the ligands alkyne and carbon monoxide with migration and bridging between the metal ion and nitrogen bound ligands.

The sequence of reactions to form the glyceride acyl bond is:
1. Up to four carbon monoxide molecules may be individually bound to the metal and migrate to the four vacant nitrogen sites to form bridged aziridine-2-one rings.
2. The metal bound alkyne (e.g. propyne) reacts with a peripherally bound carbon monoxide to form a propanone ring compound.
3. The propanone ring ligand isomerises by a hydrogen shift to a 3-methyl butenone ligand with an activation energy of 0.112 h.
4. The 3-methyl butenone ligand forms an acyl bridge to a peripheral carbon monoxide with an activation energy of 0.007 h.
5. The excited state complex is greatly stabilised by protonation, whilst mild hydrogenation at the metal and positively charged carbon atom frees the alkene ester.
6. The activation energy to bond the three carbon monoxide entities bound to the peripheral nitrogen sites is 0.126 h.
7. Mild reduction at the peripheral nitrogen sites frees the mono-glyceride.

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.

Key-Words: - Prebiotic photochemical synthesis, mono-glycerides, carbon monoxide, propyne.

1 Introduction
Glycerol is present in nature esterified on the hydroxyl groups by fatty acids as mono-, di-, or triacyl glycerides [1,2,3]. These glycerides serve primarily to store fuel in the form of fat droplets in cells. The phosphoglycerides contain two fatty acid molecules esterified to the two free hydroxyl groups of glycerol-3-phosphate and an alcohol esterified to the phosphoric acid. They occur mainly in membranes as phosphatidyl ethanolamine and phosphatidyl choline. The polarity of their head groups enables them to spontaneously form micelles, monolayers and bi-layers. They are considered major building blocks of membrane structures such as the liquid-crystalline phosphoglyceride bilayer where they are present as 40-50 % lipid [4]. Naturally occurring triacyl glycerols are by convention named as if they were derived from L-glyceraldehyde [1].

From a prebiotic perspective [5,6] it is desirable if these molecules formed spontaneously from a supposed prebiotic atmosphere to be inevitably present as micellar walls of rudimentary cells. It has been often held that the atmosphere of the Earth was originally mildly reducing [1,7] implying the presence of concentrations of carbon monoxide and formaldehyde [8], the partially reduced substrates of modern photosynthesis. It has also been demonstrated that porphin may act as a catalyst for the formation of sugars [9] and polyenes [10]. This paper proposes a model for the catalytic formation of ester linkages between a nascent glycerol backbone and a preformed alkyne side-chain which has some resemblance to modern photosynthesis in that the catalyst proposed is a metal porphin [5]. The reactions described have been deduced as kinetically and thermodynamically viable, but photochemical excitation is required to form the glycerol backbone.
2 Problem Formulation

The computations tabulated in this paper used the GAUSSIAN98 [11] commercial package. The standard calculations at the HF and MP2 levels including zero-point energy corrections [12], together with scaling [13], using the same basis set, 6-31G* are as previously published [5]. Enthalpy changes at the MP2 level not including scaled zero point energies are designated as $\Delta H_{\text{MP2}}$. The charge transfer complexes are less stable when calculated at the Hartree Fock level [12]. 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 [11].

$1h = 627.5095 \text{ kcal.mol}^{-1}$. 
$1h = 4.3597482 \times 10^{-18} \text{ J}$

3 Problem Solution

3.1 Total Energies (hartrees)

Carbon monoxide may chelate with the magnesium ion of magnesium porphin, which is here taken as a possible catalyst, to form a charge transfer complex where the charge on the ligand is positive and the charge on the porphin molecule is negative. The enthalpy of formation of the complex is small but it appears stable [9].

$$\text{Mg.porphin} + \text{CO} \rightarrow \text{Mg.CO.porphin}$$

(1) 

(2) 

$\Delta H = -0.00919 \text{ h}$

If the Mg.porphin (triplet state) is in the triplet state, the enthalpy change is also favourable, as follows:

$\Delta H_{\text{MP2/6-31g**}} = -0.10388 \text{ h}$

It is postulated that when the complex becomes excited from photolysis according to the equation,

$$\text{Mg.CO.porphin} \rightarrow \text{Mg.porphin.CO}$$

(3) 

$\Delta H = 0.21892 \text{ h}$

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 [9,14,15] at a pyrrole unit. The energy of the product is almost identical to that of the excited reactant, but the excitation energy is more than the activation energy for the transformation [9].

This process of binding a carbon monoxide molecule to the magnesium ion and then migrating the CO group to the periphery may be repeated,

Mg.porphin.CO + CO $\rightarrow$ Mg.CO.porphin.CO [3] 

(4) 

$\Delta H_{\text{MP2/6-31g*}} = -0.06600 \text{ h}$

Mg.CO.porphin.CO $\rightarrow$ Mg.porphin.2CO [4] 

(5) 

$\Delta H_{\text{MP2/6-31g*}} = -0.07007 \text{ h}$

Either of these complexes may form carbon-carbon bonds to give bidentate groups. However, the higher energy complex is that in which both CO groups occupy peripheral ring positions and are bonded, indicated as Mg.porphin.(CO-)₂.

The enthalpy change to form the carbon-carbon bond is low as shown,

$$\text{Mg.porphin.2CO} \rightarrow \text{Mg.porphin.(CO-)₂}$$

(6) 

$\Delta H = 0.01140 \text{ h}$

The activation energy to form the carbon-carbon bond is, 0.126 h, whereas the activation energy to break the bond is 0.032 h, when calculated at the HF level by extending the -CO-CO- bond. A third carbon monoxide group may be added to the third peripheral position by the same mechanism, where the overall reaction is,

Mg.porphin + 3CO $\rightarrow$ Mg.porphin.3CO [6] 

(7) 

$\Delta H = 0.28241 \text{ h}$

This complex may easily bond to form a stable precursor to the glycerol backbone,

Mg.porphin.3CO $\rightarrow$ Mg.porphin.(CO-)₃ [7] 

(8) 

$\Delta H = -0.07935 \text{ h}$

The fourth and last available position may be filled in the same manner to give the highly reactive and unstable quadridentate complex which has gained considerable energy from photolysis.
Mg.porphin + 4CO → Mg.porphin.4CO \[8\]  
\[9\]  
$\Delta H = 0.43206 \text{ h}$

These high energy compounds may relax to form the more stable van der Waals complexes. The initial reactant for the following reactions is taken to be the reactive, Mg.porphin.4CO, with a vacant magnesium ion site for coordination.

The data for some of the more stable of these molecules are given in Table 1, where peripheral carbon monoxide molecules that have fully bonded are represented as Mg.porphin.(CO-)n, etc.

The total energies and zero point energies for the HF and MP2/6-31G* equilibrium geometries are given in Table 1.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>MP2</th>
<th>ZPE (HF)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg.porphin</td>
<td>-1185.12250</td>
<td>0.29262</td>
</tr>
<tr>
<td>(1)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mg.porphin (triplet, 6-31g**)</td>
<td>-1185.10392</td>
<td></td>
</tr>
<tr>
<td>Mg.CO.porphin</td>
<td>-1298.13452</td>
<td>0.29942</td>
</tr>
<tr>
<td>(2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mg.porphin.CO</td>
<td>-1297.93784</td>
<td>0.30434</td>
</tr>
<tr>
<td>(3)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mg.CO.porphin.CO</td>
<td>-1411.03187</td>
<td></td>
</tr>
<tr>
<td>(4)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mg.porphin.2CO</td>
<td>-1411.10194</td>
<td>0.31495</td>
</tr>
<tr>
<td>(5)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mg.porphin.(CO-)2</td>
<td>-1411.09199</td>
<td>0.31658</td>
</tr>
<tr>
<td>(6)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

3.2 The overall stoichiometry for the formation of glycerol 1-butenate.

Although Mg.porphin is here taken as the catalyst for the reaction, the overall stoichiometry to form the glycerol ester, glycerol 1-butenate is as follows,

\[4\text{CO} + \text{CH}_3\text{C}=\text{CH} + \text{H}^+ + \text{H}^- + 3\text{H}_2 \rightarrow \text{HOCH}_2\text{.CH(OH).CH}_2\text{O.CO.CH}=\text{CH.CH}_3 \quad [9] \]

\[\Delta H = -0.79170 \text{ h} \]

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

3.3 The formation of Mg.1-propen-1-yl.porphin.4CO

The high energy complex Mg.porphin.4CO is calculated as being stabilised by the coordination of propyne with the metal ion of the complex, as follows:

\[\text{Mg.porphin.4CO} + \text{CH}_3\text{C}=\text{C.H} \rightarrow \quad (9) \]
The addition of carbon monoxide to alkynes is a classic organic reaction [16], here represented as,

\[ \text{Mg.1-propen-1-yl.porphin.4CO} \rightarrow (10) \]

\[ \Delta H = -0.17227 \text{ hartree} \]

A model of the optimized complex (9), is shown in Fig.1.

**Table 2**

<table>
<thead>
<tr>
<th>Molecule</th>
<th>MP2</th>
<th>ZPE (HF)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg.1-propen-1-yl.porphin.4CO</td>
<td>-1728.50749</td>
<td>0.39912</td>
</tr>
<tr>
<td>Mg.3-methyl-2-oxo-cyclopropan-1-yl.porphin.3CO</td>
<td>-1753.28692</td>
<td>0.38845</td>
</tr>
<tr>
<td>Mg.3-methyl-1-oxo-but-1-en-2-yl.porphin.3CO</td>
<td>-1753.15882</td>
<td>0.38116</td>
</tr>
<tr>
<td>Mg.1-propen-1-yl-carboxylate-.porphin. (CO-)₃</td>
<td>-1753.28445</td>
<td>0.38491</td>
</tr>
<tr>
<td>Mg.1-propen-1-yl-carboxylate-.porphin.CH3.CH=CH.CO.CHO.(CO-)₂⁺</td>
<td>-1753.70635</td>
<td>0.40400</td>
</tr>
<tr>
<td>glycerol 1-butenate (16)</td>
<td>-1754.56471</td>
<td>0.41350</td>
</tr>
<tr>
<td>Mg.3-methyl-2-oxo-cyclopropan-1-yl.porphin</td>
<td>-1414.39852</td>
<td>0.35955</td>
</tr>
<tr>
<td>Mg.3-methyl-1-oxo-but-1-en-2-yl.porphin</td>
<td>-1414.41750</td>
<td>0.37995</td>
</tr>
<tr>
<td>Mg.3-methyl-2-oxo-cyclopropan-1-yl.porphin.CO</td>
<td>-1527.41423</td>
<td></td>
</tr>
<tr>
<td>Mg.3-methyl-1-oxo-but-1-en-2-yl.porphin.CO</td>
<td>-1527.40141</td>
<td></td>
</tr>
</tbody>
</table>

**3.4 The formation of Mg.3-methyl-2-oxo-cyclopropan-1-yl.porphin.3CO.**

The formation of Mg.3-methyl-2-oxo-cyclopropan-1-yl.porphin.3CO can be represented as:

\[ \text{Mg.1-propen-1-yl.porphin.4CO} \rightarrow (10) \]
The enthalpy change for the addition of carbon monoxide is favourable.

\[ \Delta H = -0.05517 \text{ h} \]

The activation energy for the addition reaction of carbon monoxide to a -C≡C- triple bond [5] has been calculated as 0.031 h, and the activation energy to add carbon monoxide to a -C≡N has been given as 0.04 h [17].

Although the Birch reaction is known to be difficult it should be enhanced in this case as the carbon monoxide is already in a high energy complex.

3.5 The formation of the Mg.3-methyl-1-oxo-but-1-en-2-yl.porphin.3CO.

The critical step in this proposed synthesis is a prototropic shift and the opening of the three membered 3-methyl cyclopropanone ring to form a ketenone. A similar opening of a three membered cyclopropenone ring to give an aldehyde [5] had an activation energy of 0.083 h. Here, the activation energy to form the cyclopropanone ring was calculated as 0.102 h, whilst the activation energy to open the ring to give the ketenone was calculated as 0.101 h.

The reaction does require the input of energy, presumably from photolysis.

\[ \text{Mg.3-methyl-2-oxo-cyclopropan-1-yl.porphin.3CO} \rightarrow \]

Fig.1. The potential energy surface for the prototropic shift on molecule, Mg.3-methyl-2-oxo-cyclopropan-1-yl.porphin. The X-axis depicts the stretching of the single -C-CO bond, whilst the Y-ordinate depicts the bending angle H-C-C(CH₃) of the cyclopropanone ring. The minimum for the cyclopropanone ring is at, X=1.4 Å, Y=145 degrees. The saddle points are at X=1.8 Å, Y=70 degrees, and at X=2.3 Å, Y=65 degrees.

3.6 The formation of the Mg.1-propen-1-yl-carboxylate-. porphin. (CO)₃.

The ketenyl complex may form a weak ester linkage,

\[ \text{Mg.3-methyl-1-oxo-but-1-en-2-yl.porphin.3CO} \rightarrow \]

\[ \text{Mg.3-methyl-2-oxo-cyclopropan-1-yl.porphin.3CO} \]

\[ \Delta H = 0.12161 \text{ h} \]
Mg.1-propen-1-yl-carboxylate-. porphin. (CO-)3

The enthalpy change is favourable.

\[ \Delta H = -0.12229 \text{ h} \]

The slightly simpler compound, Mg.3-methyl-1-oxo-but-1-en-2-yl.porphin.CO was used to determine the activation energy to form the ester bond, by stretching the single bond, -C-O-, of the ester grouping, -(C=O)-C-O-. The activation energy to form the bond was found to be minimal, 0.007 h, whilst the energy to sever the bond was 0.021 h.

3.7 The formation of the Mg.1-propen-1-yl-carboxylate-. porphin. CHO.(CO-)2

The glycerol ester complex is considerably stabilised by protonation as shown,

Mg.1-propen-1-yl-carboxylate-. porphin. (CO-)3 + H⁺ →

Mg.porphin.CH₃.CH=CH.CO.CHO.(CO-)₂⁺

\[ \Delta H = -0.40490 \text{ h} \]

3.8 The formation of the neutral Mg.porphin. CH₃.CH=CH.CO.CHO.(CO-)₂

Mild hydrogenation allows the freeing of the alkenyl ester from the magnesium ion.

Mg.1-propen-1-yl-carboxylate-.porphin.CHO.(CO-)₂⁺ + H⁺ →

Mg.porphin.CH₃.CH=CH.CO.CHO.(CO-)₂

\[ \Delta H = -0.42101 \text{ h} \]

The enthalpy change is favourable.

3.9 The formation of Glycerol 1-butenate
Further mild reduction completely frees the glycerol 1-butenate from the catalyst.

\[
\text{Mg.porphin.CH}_2\text{CH} = \text{CH.COCHO.} (\text{CO})_2 + 3\text{H}_2 \rightarrow \text{Mg.porphin} + \text{HOCH}_2\text{CH(OH).CH}_2\text{O.CO.CH=CH.CH}_3
\]

glycerol 1-butenate

The enthalpy change is favourable,
\[\Delta H = -0.16978 \text{ h}\]

4. Conclusion

Carbon monoxide is one of the most abundant molecules in the Universe [18], and in condensed phase readily forms both C-C and C-O bonds [19]. The presence of reactants, carbon monoxide, 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 photochemical directed template for glyceride synthesis.

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

5 Acknowledgements

The advice and support given by Professor Curt Wentrup of Queensland University is gratefully acknowledged.

Appreciation is also expressed to Queensland University of Technology; to Mr. A. Lewis, and Dr. J. Young, M. Barry, and B. Savage, of the Supercomputing Department, and for the APAC facilities at the ANU and QMAS facilities at UQ, and the assistance of Mr.M. Nicholls.

References


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