

Thermochemistry of Co(II) Porphyrin-Catalysed Oxidation of Methanol to Formaldehyde

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Abstract: In recent years, much attention has been focused on cobalt catalysis because of its abundance on Earth, low toxicity, and low cost. A lot of work has been focused on catalysis with cobalt porphyrin. A very interesting chemical reaction catalysed by cobalt(II) porphyrin is the Oxidation of methanol to formaldehyde. The formaldehyde formed in this reaction can be used in the synthesis of 1,5-diketones. Herein in this work, A density functional theory calculations at the APFD/SDD level were performed to study the optimised geometry of the intermediate cobalt porphyrin complexes formed in this oxidation reaction, and the thermochemistry parameters for the relevant steps were calculated. The reactions between cobalt(II) porphyrin and methanol, methoxide, and methoxy radical yield complexes *Copor*(CH₃OH), [*Copor*(CH₃O)]⁻, *Copor*(CH₃O), respectively; all of these are exothermic reactions. These complexes produce formaldehyde and complexes in which one hydrogen attaches cobalt porphyrin either to nitrogen or to cobalt to form natural or anion complexes, such as [*Copor*(NH)]⁻, [*Copor*(H)]⁻, *Copor*(NH), *Copor*(H). Of these complexes, the formation of *Copor*(H) (one hydrogen atom forms a bond with a cobalt atom) is the least endothermic. Complexes where hydrogen atoms form bonds with cobalt atoms are more stable than complexes where hydrogen atoms form bonds with nitrogen porphyrin. Hydrogen molecules may be produced from the reaction between *Copor*(NH) and *Copor*(H). Finally, *Copor*(H) can be used as a catalyst in the oxidation reaction of methanol to formaldehyde.

Keywords: Cobalt (II) Porphyrin, Density Functional Theory, Thermochemistry, Oxidation, Methanol

1. Introduction

Organic synthesis based on transition-metal catalysis is a power tool method. In recent years, much attention has been focused on cobalt catalysis [1] because of its abundance on Earth, low toxicity, and low cost. For four-coordinated

cobalt, the square planar geometry is more stable than the tetrahedral one. Although the tetrahedral geometry is sterically more stable, the square planar one is stabilised by the electronic effect [2]. This is because the antibonding orbital $d_{x^2-y^2}$ has high energy, and it is unoccupied in the square planar geometry, as shown in Figure 1.

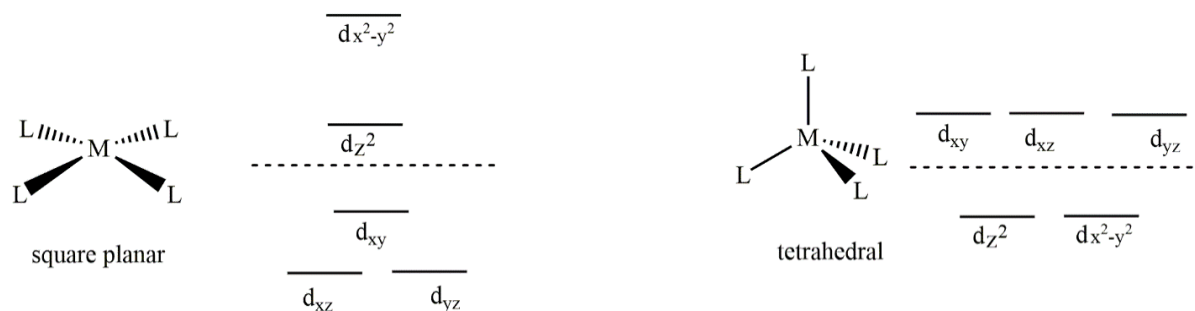


Figure 1. The d orbitals of the square planar and tetrahedral geometries.

The four-coordinated square planar cobalt with its three oxidation states (I, II, III) has versatile applications in catalysed reactions.

For example, planar Co (II)-d⁷ acts as a metalloradical, as shown in Figure 2, and alkyl-Co (III) undergoes homolytic cleavage to an alkyl radical and Co (II) radical, followed by beta hydrogen abstraction to yield an alkene [3].

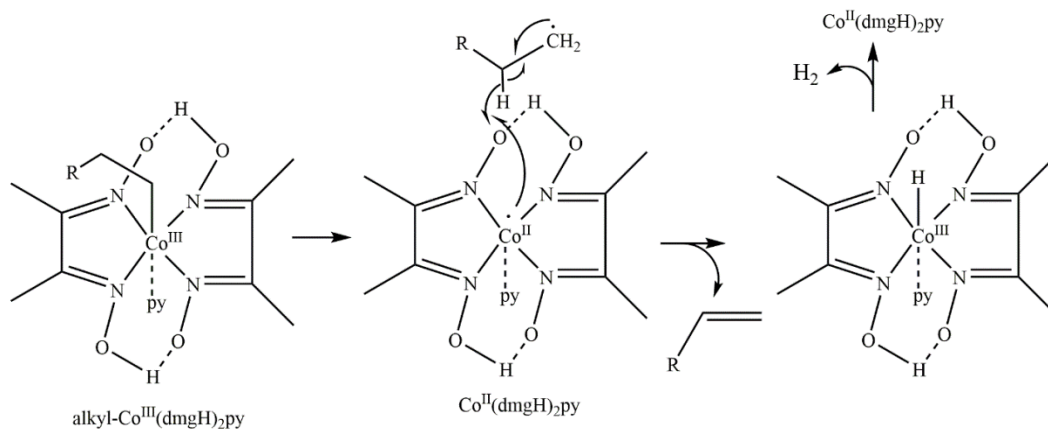


Figure 2. Reaction of the Co (II) radical with an alkyl radical to produce an alkene and hydrogen. (dmgH = dimethylglyoxime, py = pyridine).

Moreover, cobalt (II) porphyrin catalysis is the radical mechanism in the aziridination [4] of olefins, as shown in Figure 3.

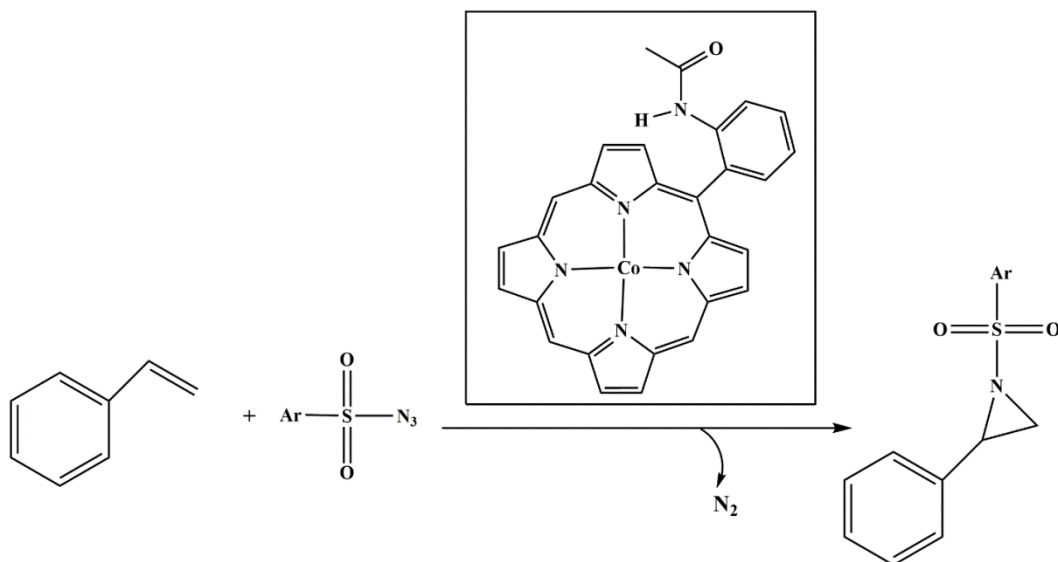


Figure 3. Cobalt (II) porphyrin-catalysed aziridination of styrene.

The intermediate in this reaction is a nitrene radical, as shown in Figure 4. It was found that this intermediate was stabilised by a hydrogen bond, which increases the catalytic efficiency.

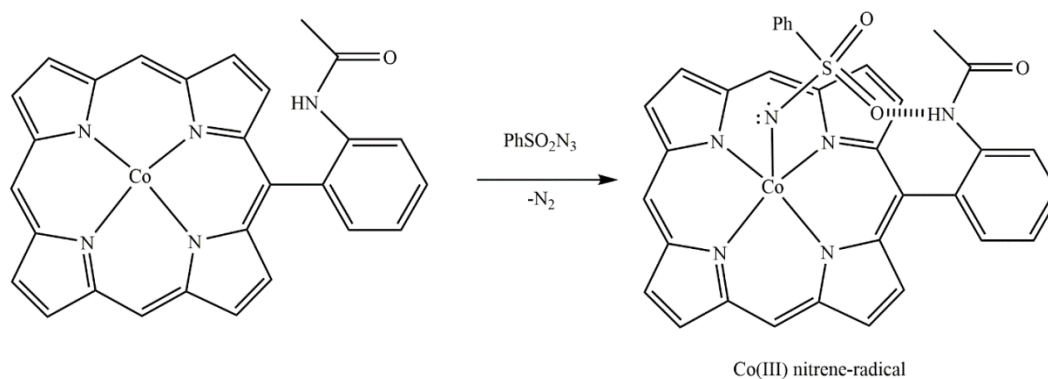


Figure 4. Formation of Co (III) nitrene radicals from the Co(II) porphyrins and PhSO₂N₃.

In Co (I), d^8 complexes in the other hand, the homo d_{z^2} is occupied. These complexes act as nucleophiles and bases. Moreover, the ligand at the axial position increases the nucleophilicity and basicity further. An example of this is using a vitamin B₁₂ catalyst in the addition reaction of alkyl to aldehydes [5] in the presence of CrCl₂, as shown in Figure

5. In this reaction, Co (I) Complex 1 acts as a nucleophile that reacts with alkyl-X to form Co (III) Complex 2. Further, reductive cleavage of 2 yields an alkyl radical and Co (II) Complex 3, which is reduced by CrCl₂ to 1. The alkyl radical is trapped with CrCl₂ to form 4, and alkyl chromium 4 adds an aldehyde to produce a secondary alcohol.

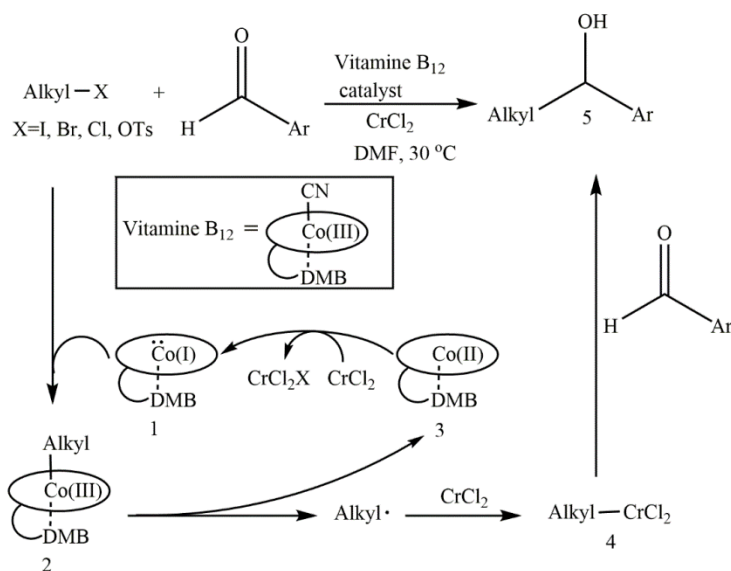


Figure 5. Vitamin B₁₂-catalysed addition of alkyl-X to aldehydes.

In addition, an intensive studies on cobalt porphyrin [6-13] for organic transformations have been reported.

In 2021, Venkatasubbaiah and Chandrasekhar et al. [14] reported a novel cobalt (II) porphyrin-mediated selective synthesis of 1,5-diketones via interrupted-borrowing hydrogen, as shown in Figure 6. Methanol is

used as a C1 source, and the catalyst is a stable, simple bench. The only by-products are the environmentally benign H₂ and H₂O.

Diketones are building blocks for a wide variety of organic compounds. Moreover, they are biologically active and are used to synthesise heterocyclic compounds.

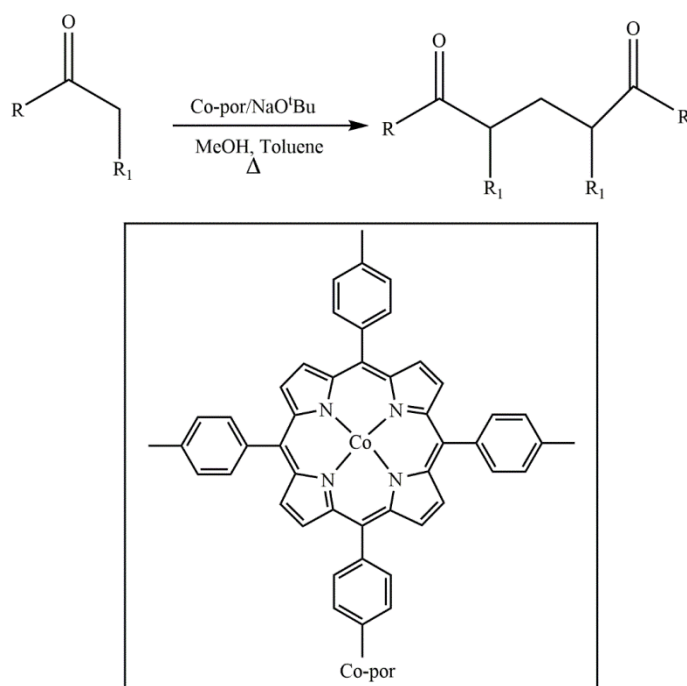


Figure 6. Cobalt(II) porphyrin-catalysed synthesis of 1,5-diketones.

Based on experiments and previous work [15-24], the authors proposed that the intermediate is a protonated cobalt (II) porphyrin methoxide complex, which generates formaldehyde along with a metal hydride. The in-situ formed

formaldehyde condensed with propiophenone to yield an enone. The Michael addition of this enone with propiophenone produces 1,5-diketones exclusively, as shown in Figure 7.

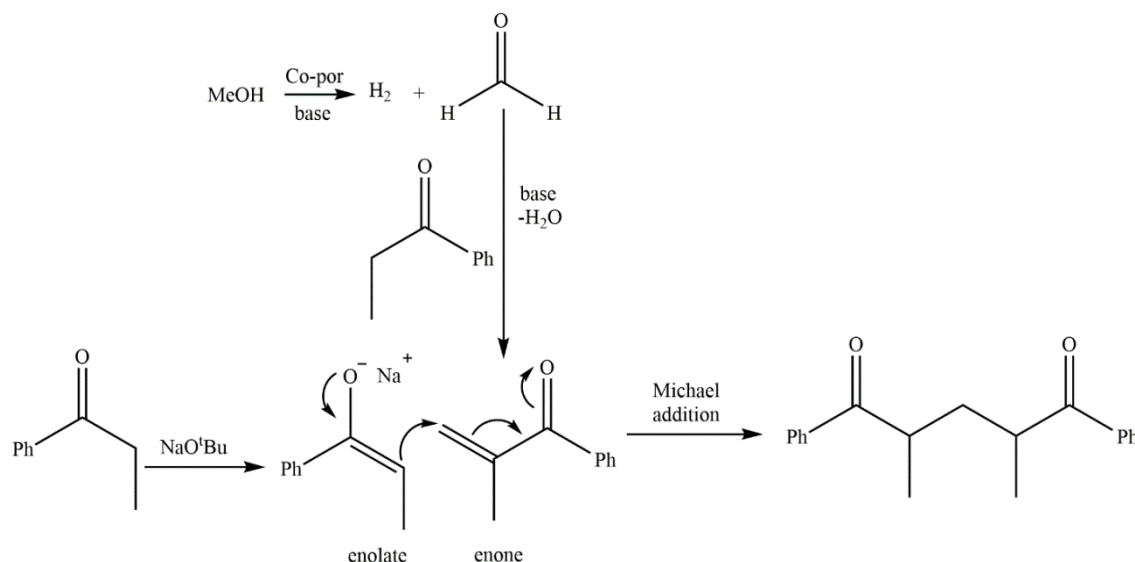


Figure 7. Proposed mechanism for 1,5-diketone production.

However, to the best of the present author's knowledge, the exact structures of the intermediate complexes of cobalt porphyrin were not determined in the oxidation reaction of methanol to formaldehyde. Therefore, this work aims to computationally optimise the complexes produced from the reaction of cobalt (II) porphyrin (*Copor*) with methanol, methoxide, and methoxy radical. And Optimisation of cobalt porphyrin hydrides complexes.

Finally, the thermochemistry calculations for the conversion of methanol to formaldehyde were catalysed by cobalt (II) porphyrin. This work involves a thermodynamical approach that may provide guidance for further kinetics studies.

2. Computational Methods

Density functional theory (DFT) calculations were performed using the Gaussian 16 software [25] and GaussView 6.0 interface [26]. All geometric optimisations and frequency calculations were performed using the Austin-Frisch-Petersson functional with dispersion (APFD) hybrid DFT method. The basis set is SDD, which combines double-zeta with the Stuttgart-Dresden effective core potential basis set.

The keyword Int = Ultrafine was used for higher accuracy; all the stationary points were identified as minima (zero imaginary frequencies). The values of the total energy with thermal correction (ΔE), enthalpy (ΔH), and Gibbs energy (ΔG) were obtained under the standard conditions of 298.15 K and 1 atm in gas phase. The Cartesian coordinates and the thermodynamic parameters of all the calculated structures are provided in the Supplementary Material.

3. Results and Discussion

To study the thermochemical parameters of the intermediates in the oxidation of methanol to formaldehyde, first, the geometry of cobalt (II) porphyrin (*Copor*) was optimised, as shown in Figure 8. As expected, the structure was square planar, and the N4-Co37-N2 angle was 177.8°; Co (II) is d^7 .

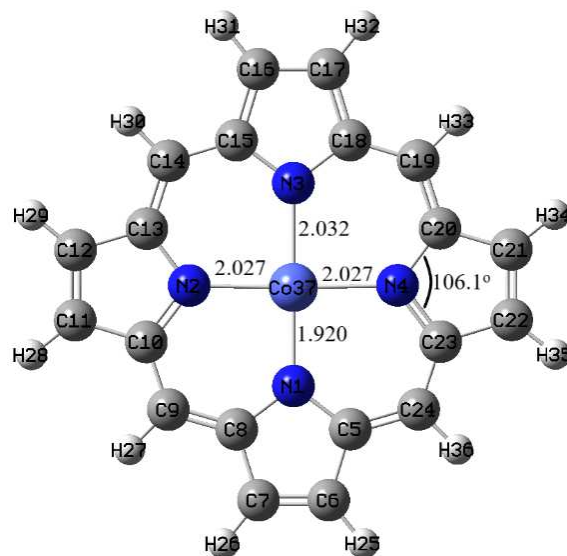
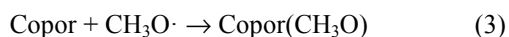
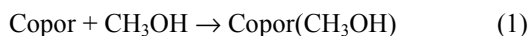


Figure 8. Optimised structure of *Copor* (the bond length is in angstrom).

The next step is to investigate the reaction of cobalt porphyrin with CH_3OH , CH_3O^- , and $\text{CH}_3\text{O}^\cdot$ (equations 1, 2, 3).



The optimised structure of *Copor*(CH₃OH) is shown in

Figure 9. It has a square pyramidal geometry, and Co(II) is d⁷. The cobalt atom is slightly out of the plane of the porphyrin rings, and N4-Co37-N2 is 175°. The length of the Co37-O38 bond is 2.187 Å, and the distance between N3 and H43 is 2.547 Å, indicating hydrogen bond interaction.

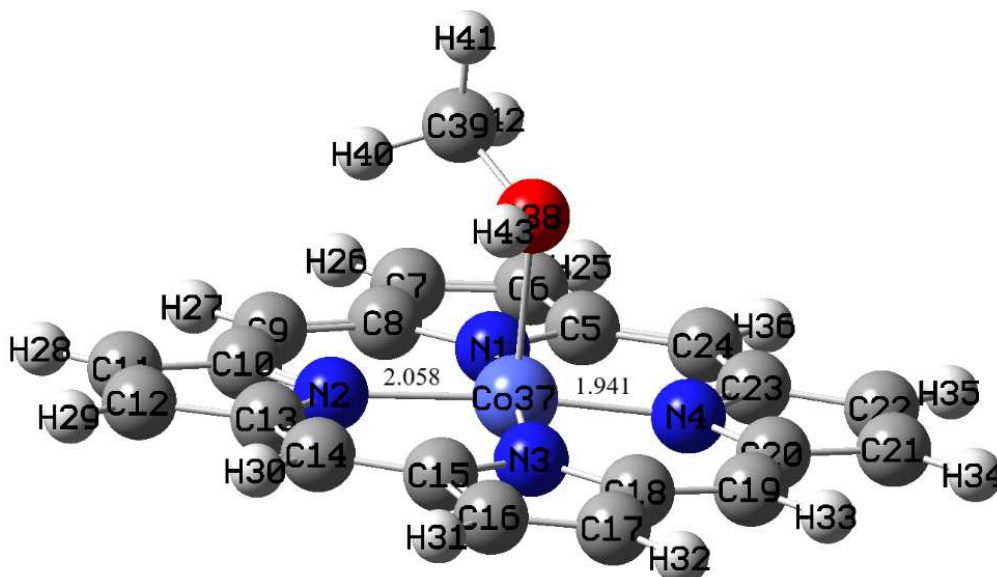


Figure 9. Optimised structure of *Copor*(CH₃OH) (the bond length is in angstrom).

The optimised structures of *[Copor*(CH₃O)]⁻¹ and *Copor*(CH₃O) are given in Figure 10. In the neutral complex, *Copor*(CH₃O), Co(III) is d⁶. In the anion complex, *[Copor*(CH₃O)]⁻¹, Co(II) is d⁷.

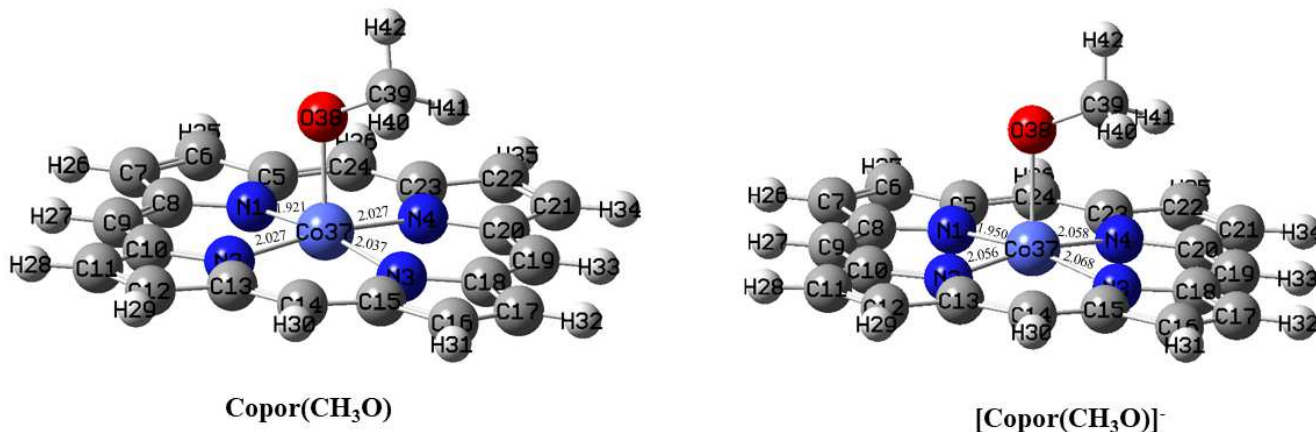


Figure 10. Optimised structures of *[Copor*(CH₃O)]⁻¹ and *Copor*(CH₃O) (the bond length is in angstrom).

The length of the Co37-O38 bond is 2.066 Å in *[Copor*(CH₃O)]⁻¹ and 1.933 Å in *Copor*(CH₃O). Therefore, the Co-O and Co-N bonds are shorter in the *Copor*(CH₃O) complex than in the *[Copor*(CH₃O)]⁻¹ complex. The Co atom is more deviated from planarity in the *[Copor*(CH₃O)]⁻¹ complex. The N4-Co37-N2 angle is 172.1° in *Copor*(CH₃O) and 170.1° in *[Copor*(CH₃O)]⁻¹.

The calculated changes in the total energy with the thermal correction (ΔE), enthalpy at 298 K (ΔH_{298K}), and Gibbs energy at 298 K (ΔG_{298K}) for reactions 1–3 are given in Table 1.

Table 1. Thermochemistry (in kcal/mol) of reactions 1–3.

	ΔE	ΔH _{298K}	ΔG _{298K}
Reaction 1	-60.1	-60.7	-49.9
Reaction 2	-90.8	-91.4	-80.8
Reaction 3	-58.9	-59.5	-46.5

According to the data provided in Table 1, reactions 1–3 are all exothermic and thermodynamically feasible.

Figure 11 indicates that there is a strong interaction between the highest occupied molecular orbital (HOMO) of methoxide and the lowest unoccupied molecular orbital (LUMO) of

Copor. The oxygen atom of methoxide interacts with Co, N1, and C10, which explains the spontaneous reaction.

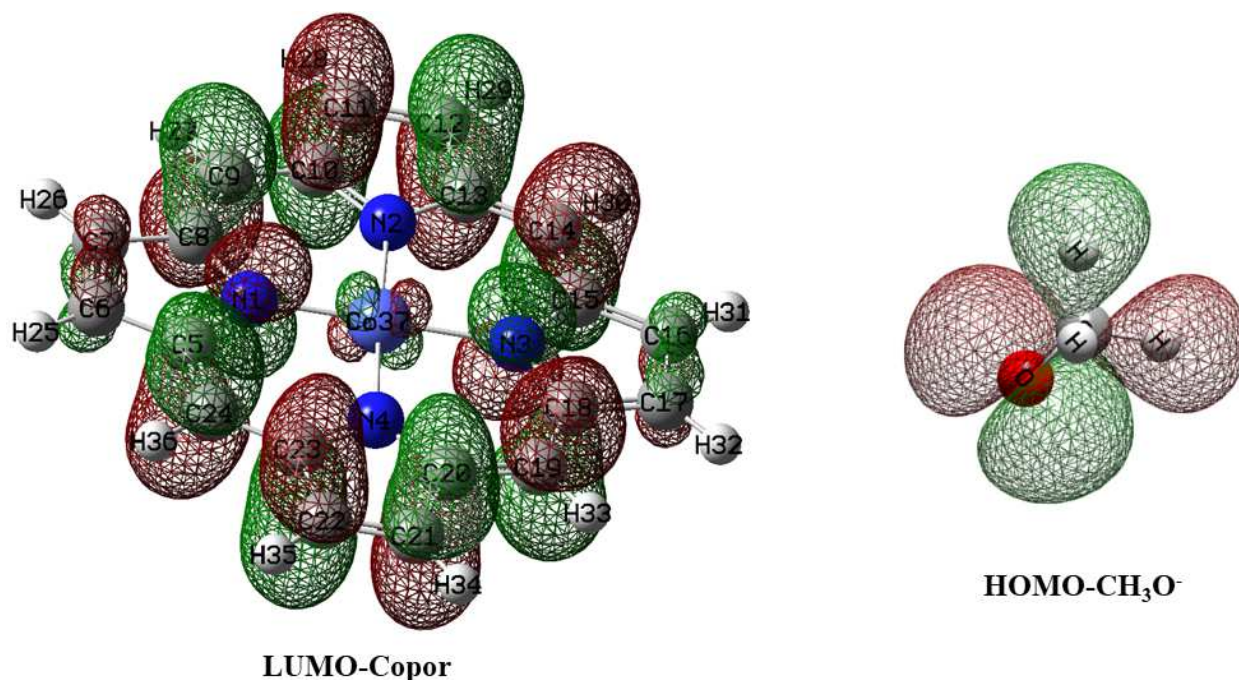


Figure 11. HOMO orbital of CH₃O⁻ and LUMO orbital of *Copor*.

The *Copor*(CH₃OH) complex was compared with its isomer *Copor*(CH₃O)(H), as shown in Figure 12.

Co(IV) in the *Copor*(CH₃O)(H) complex is d⁵, the length of the Co37-O39 bond is 1.878 Å, the length of Co37-H38 is 1.452 Å, and the N4-Co37-N2 angle is 174.2°.

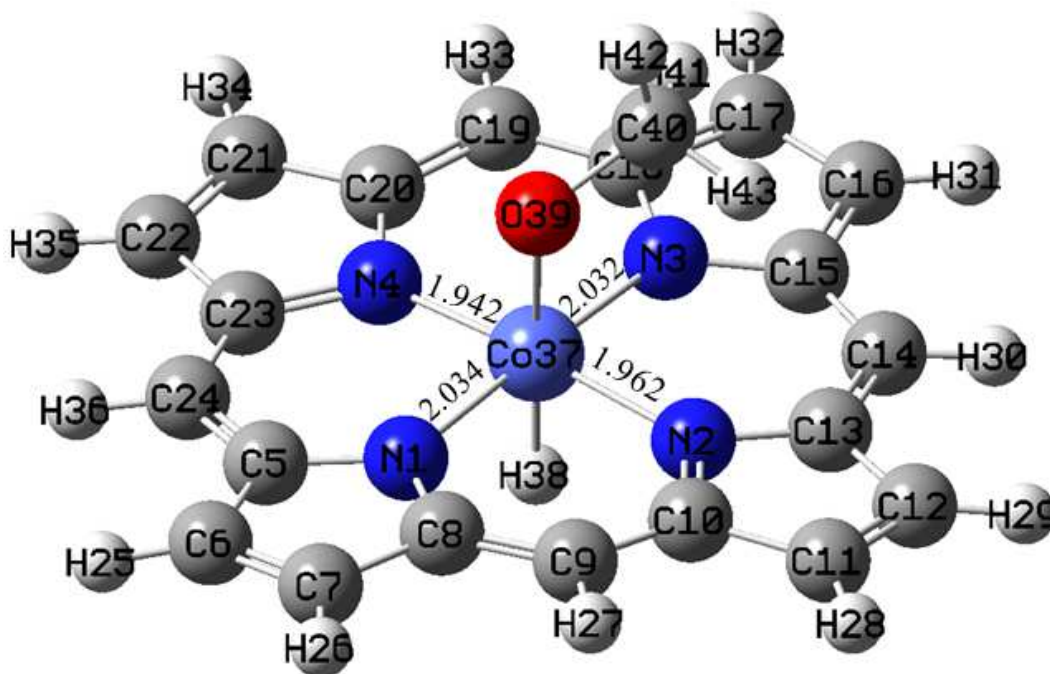


Figure 12. Optimised structure of *Copor*(CH₃O)(H) (the bond length is in angstrom).

The *Copor*(CH₃OH) complex is more stable than *Copor*(CH₃O)(H), and the energy difference, $E(\text{Copor}(\text{CH}_3\text{OH})) - E(\text{Copor}(\text{CH}_3\text{O})(\text{H}))$, is -66.6 Kcal/mol. It can be seen from the electrostatic potential map of [*Copor*(CH₃O)]⁻¹ in Figure 13 that the negative charge is

concentrated on the oxygen atom. Hence, the hydrogen atom prefers to bond with oxygen rather than cobalt, and this explains the higher stability of *Copor*(CH₃OH) compared to that of *Copor*(CH₃O)(H).

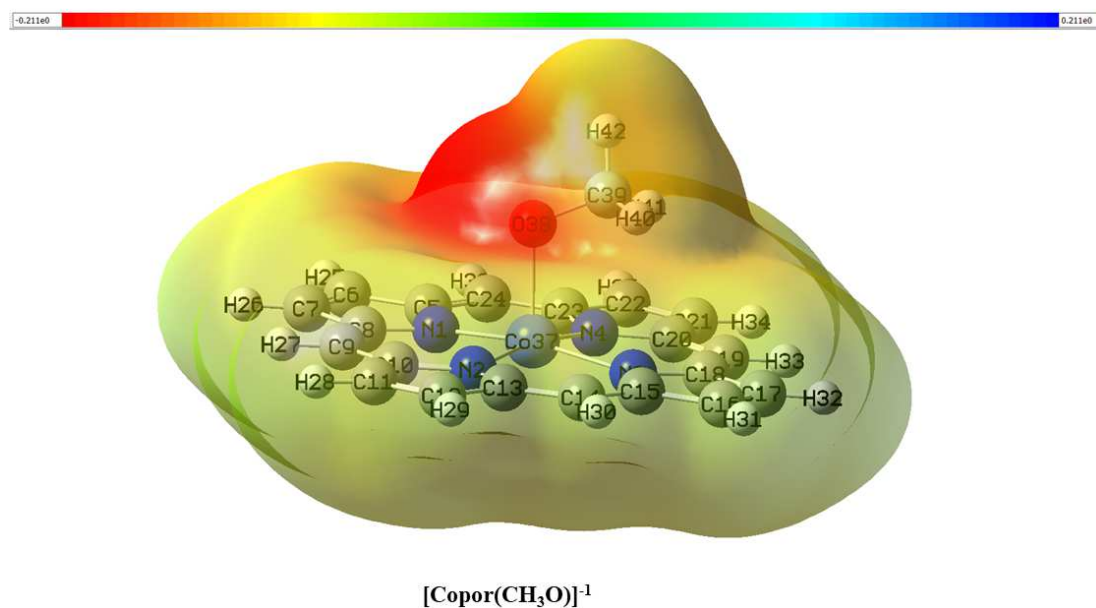


Figure 13. Electrostatic potential map of [Copor(CH₃O)]⁻¹.

The electrostatic potential map of Copor(CH₃OH) is shown in Figure 14. The positive charge is located on H43, which may be connected to the nitrogen of the porphyrin ring.

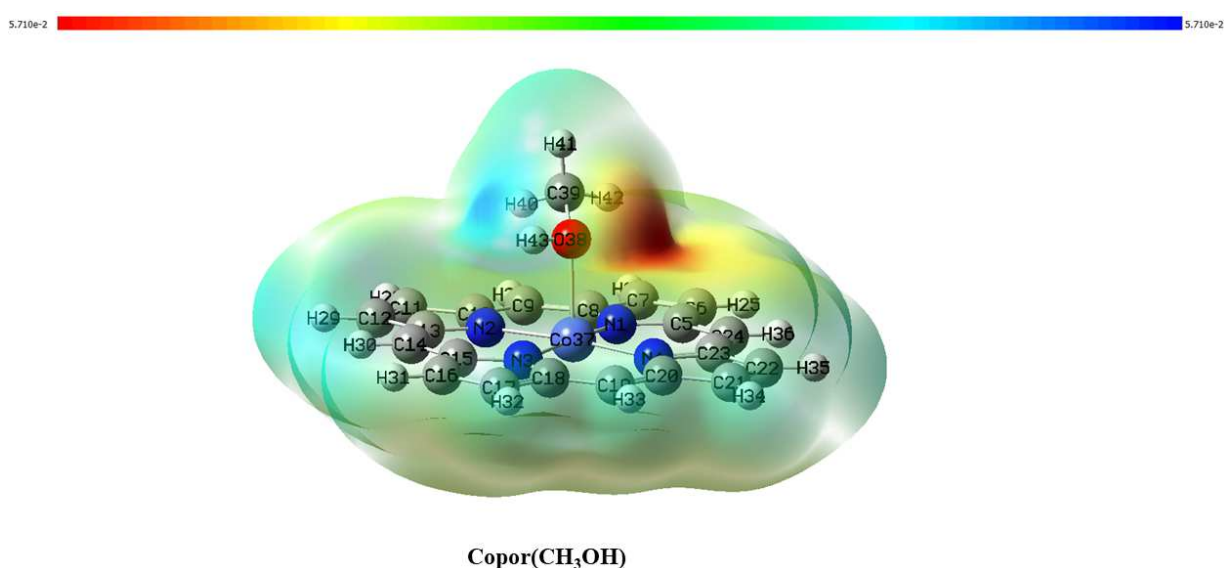
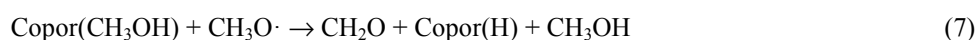
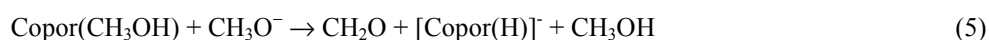
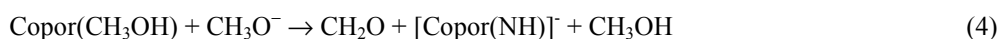


Figure 14. Electrostatic potential map of Copor(CH₃OH).

The next step is to produce formaldehyde from the products of reactions 1–3. Formaldehyde can be formed from the Copor(CH₃OH) complex through these reactions:



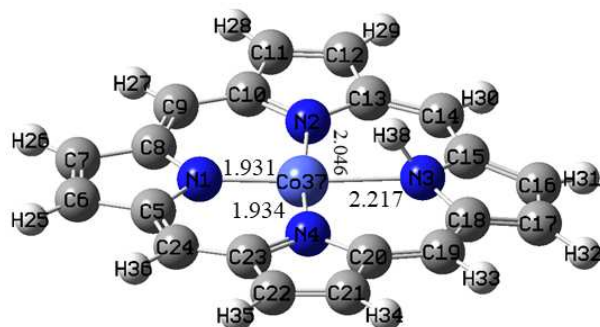
The optimised structures of [Copor(NH)]⁻ and Copor(NH) are shown in Figure 15.

The [Copor(NH)]⁻ complex is Co(0), d⁹. The length of the

N3-H38 bond is 1.028 Å, and the N4-Co37-N2 angle is 171.7°.

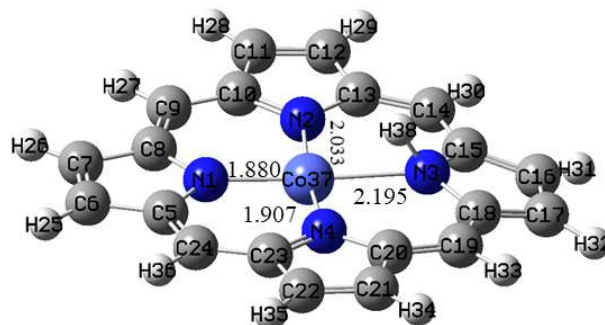
The Copor(NH) complex is Co(I), d⁸. The length of the

N3-H38 bond is 1.062 Å, and the N4-Co37-N2 angle is 173.7°.



[Copor(NH)]⁻

The Co-N bonds are shorter in the neutral complex *Copor(NH)*.

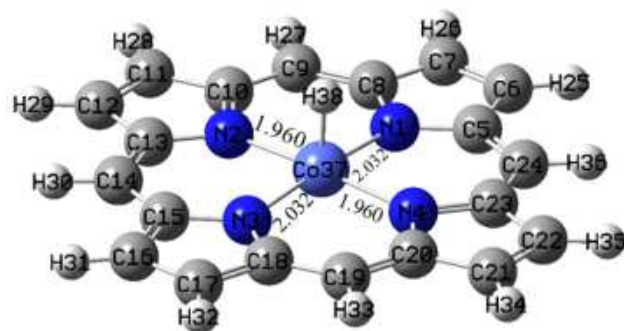


Copor(NH)

Figure 15. Optimised structures of [Copor(NH)]⁻ and Copor(NH) (the bond length is in angstrom).

The optimised structures of [Copor(H)]⁻ and Copor(H) are shown in Figure 16.

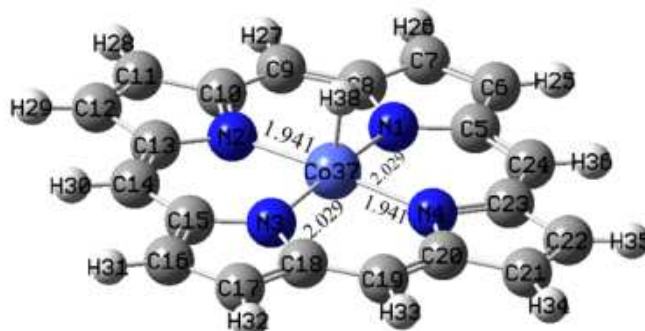
The [Copor(H)]⁻ complex is Co(II), d⁷. The length of the Co37-H38 bond is 1.420 Å, and the N4-Co37-N2 angle is 175.6°.



[Copor(H)]⁻

The *Copor(H)* complex is Co(III), d⁶. The length of the Co37-H38 bond is 1.416 Å, and the N4-Co37-N2 angle is 175.9°.

The Co-N bonds are shorter in the neutral complex *Copor(H)*.



Copor(H)

Figure 16. Optimised structures of [Copor(H)]⁻ and Copor(H) (the bond length is in angstrom).

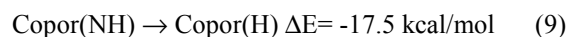
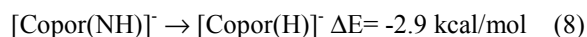
The calculated changes in the total energy with the thermal correction (ΔE), enthalpy at 298 K (ΔH_{298K}), Gibbs energy at 298 K (ΔG_{298K}) for reactions 4–7 are given in Table 2.

Table 2. Thermochemistry (in kcal/mol) of reactions 4–7.

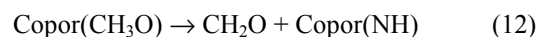
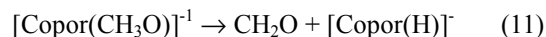
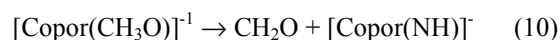
	ΔE	ΔH_{298K}	ΔG_{298K}
Reaction 4	17.3	17.9	6.4
Reaction 5	14.5	15	3.3
Reaction 6	46.7	47.3	37.5
Reaction 7	29.2	29.7	20.1

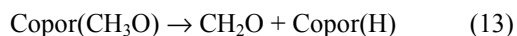
It is clear from Table 2 that the reaction of *Copor(CH₃OH)* with the methoxide ion is thermodynamically more feasible than the reaction with the methoxy radical. Moreover, the complexes in the products where the hydrogen atom forms bonds with cobalt are more stable than those where it forms bonds with nitrogen (equations 8, 9). In the structure of *Copor(NH)* shown

Figure 15, it can be observed that the ring which contains N3 is not in the same plane as the other rings. The length of the Co37-N3 bond in *Copor(NH)* is 2.195 Å longer than that of *Copor(H)*, 2.029 Å, as shown in Figure 16.



Furthermore, the formation of formaldehyde from the [Copor(CH₃O)]⁻¹ and *Copor(CH₃O)* complexes was investigated (reactions 10–13).





The thermochemistry calculations of reactions 10–13 are presented in Table 3.

Table 3. Thermochemistry (in kcal/mol) of reactions 10–13.

	ΔE	ΔH_{298K}	ΔG_{298K}
Reaction 10	48	48.6	37.3
Reaction 11	45.2	45.8	34.2
Reaction 12	45.5	46.1	34.1
Reaction 13	28	28.6	16.7

The reactions 10–13 are endergonic; however, reaction 13

has the lowest ΔG_{298K} .

In the system investigated in this work, no optimised structure contained cobalt(II) porphyrin attached to two hydrogen atoms, one bond to cobalt and the other bond to a nitrogen atom. Moreover, an optimised structure was observed, in which the two hydrogens formed bonds with the cobalt atom to form a *Copor(H)₂* complex, as shown in Figure 17. The *Copor(H)₂* complex has an octahedral geometry, and Co(IV) is d⁵. This complex spontaneously decomposes to cobalt porphyrin (*Copor*) and a hydrogen molecule, as shown in equation 14.

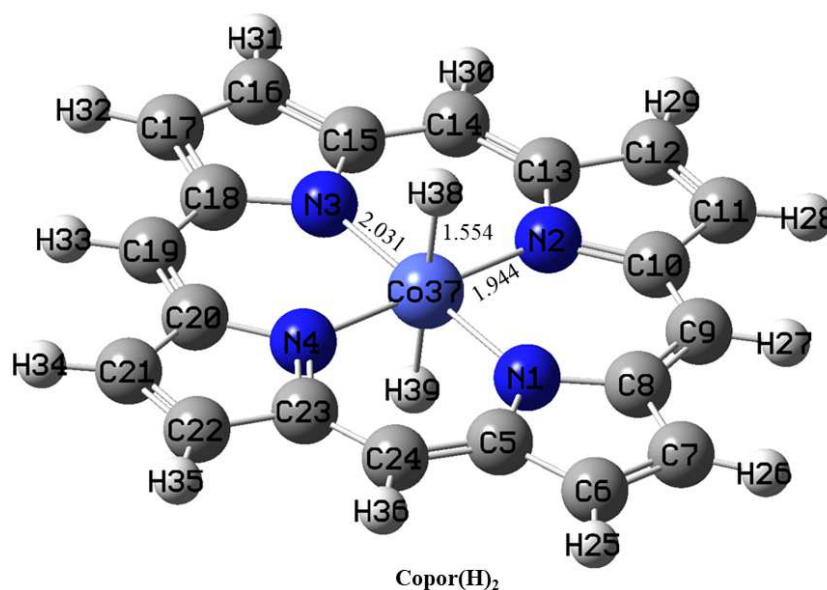
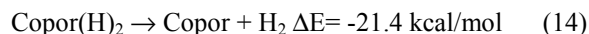


Figure 17. Optimised structure of *Copor(H)₂* (the bond length is in angstrom).

The monohydrogen cobalt porphyrin complexes may be interconverted according to reaction 15.



The last step in the oxidation of methanol to formaldehyde catalysed by cobalt(II) porphyrin is the production of the hydrogen molecule. The formation of H₂ by reactions 16–19 is highly endergonic, as shown in Table 4.

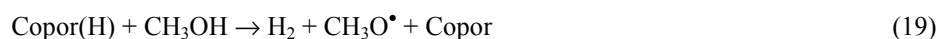


Table 4. Thermochemistry (in kcal/mol) of reactions 16–19.

	ΔE	ΔH_{298K}	ΔG_{298K}
Reaction 16	70.8	71.4	63.7
Reaction 17	73.6	74.2	66.8
Reaction 18	41.4	42	32.6
Reaction 19	58.9	59.5	50.1

If we carefully examine the electrostatic potential maps of *Copor(H)* (Figure 18) and *Copor(NH)* (Figure 19), it can be seen that H38, which forms a bond cobalt in *Copor(H)*, is

negative. In *Copor(NH)*, H38, which forms a bond with nitrogen, is positive. Therefore, if *Copor(H)* reacts with *Copor(NH)*, hydrogen will be formed with a lower ΔE , as

shown in equation 20. If two *Copor(H)* react with each other to produce H_2 , the ΔE will be higher, as shown in equation 21.

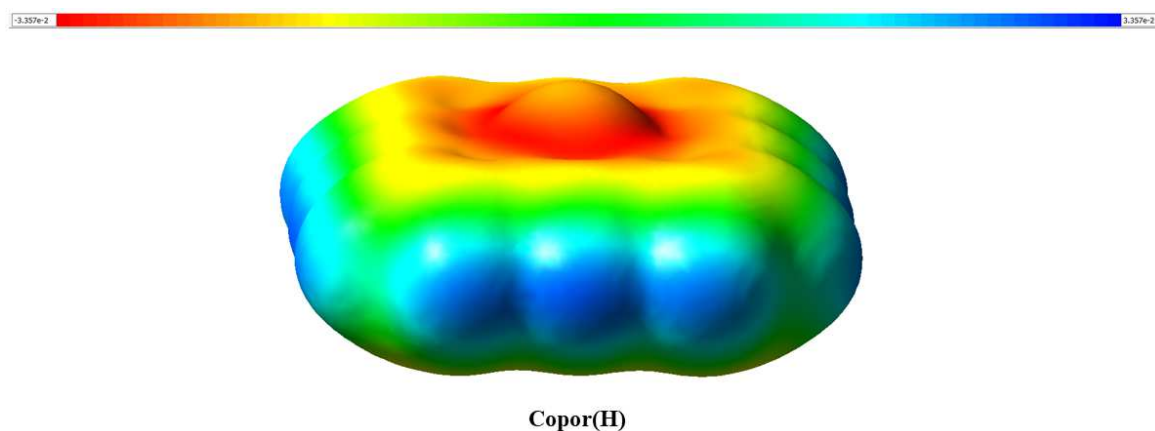
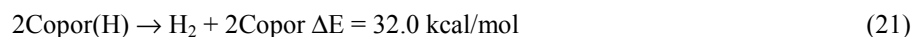
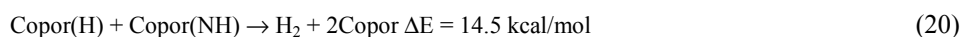


Figure 18. Electrostatic potential map of *Copor(H)*.

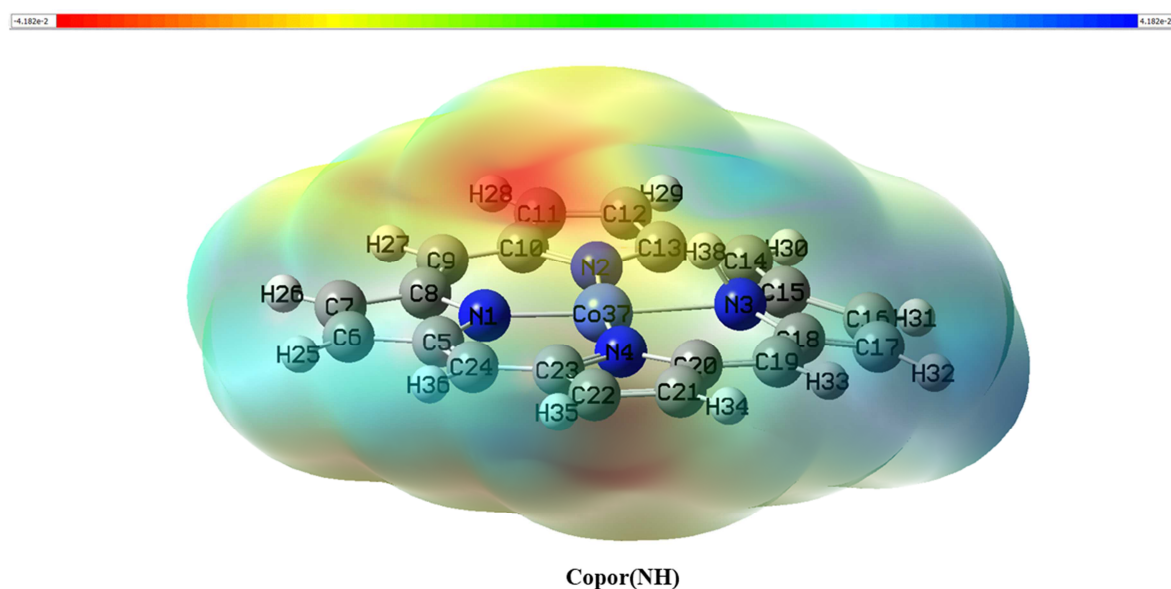
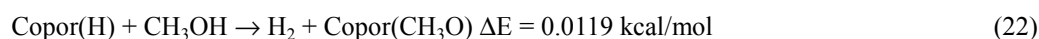


Figure 19. Electrostatic potential map of *Copor(NH)*.

Moreover, *Copor(H)* can react with methanol and produce hydrogen according to reaction 22.



Therefore, if *Copor(CH₃O)* continues to react according to reaction 13, *Copor(H)* will become a catalyst for the oxidation of methanol to formaldehyde.

In summary, according to the thermochemistry calculations, the oxidation of methanol to formaldehyde catalysed by cobalt(II) porphyrin depends on the formation of *Copor(H)* and *Copor(NH)*. If there is a source of methoxy radicals, the subsequent steps will be as follows:

- a) $2\text{Copor} + 2\text{CH}_3\text{O}^\bullet \rightarrow 2\text{Copor(CH}_3\text{O)}$
- b) $2\text{Copor(CH}_3\text{O)} \rightarrow 2\text{CH}_2\text{O} + 2\text{Copor(H)}$
- c) $\text{Copor(H)} \rightarrow \text{Copor(NH)}$
- d) $\text{Copor(H)} + \text{Copor(NH)} \rightarrow H_2 + 2\text{Copor}$

These paths may also be considered:

- a) $2\text{Copor} + 2\text{CH}_3\text{OH} \rightarrow 2\text{Copor(CH}_3\text{OH)}$
 - b) $2\text{Copor(CH}_3\text{OH)} + 2\text{CH}_3\text{O}^\bullet \rightarrow 2\text{CH}_2\text{O} + 2\text{Copor(NH)} + 2\text{CH}_3\text{OH}$
 - c) $\text{Copor(NH)} \rightarrow \text{Copor(H)}$
 - d) $\text{Copor(H)} + \text{Copor(NH)} \rightarrow H_2 + 2\text{Copor}$
- and
- a) $2\text{Copor} + 2\text{CH}_3\text{O}^\bullet \rightarrow 2\text{Copor(CH}_3\text{O)}$
 - b) $2\text{Copor(CH}_3\text{O)} \rightarrow 2\text{CH}_2\text{O} + 2\text{Copor(H)}$
 - c) $2\text{Copor(H)} \rightarrow H_2 + 2\text{Copor}$
- Finally, *Copor(H)* itself, which may be formed from reactions 7, 9, 13, 15 (reversed direction), could be used as the catalyst through the following steps:

- a) $\text{Copor(H)} + \text{CH}_3\text{OH} \rightarrow \text{H}_2 + \text{Copor(CH}_3\text{O)}$
 b) $\text{Copor(CH}_3\text{O)} \rightarrow \text{CH}_2\text{O} + \text{Copor(H)}$

4. Conclusion

This study investigated the steps involved in the oxidation of methanol to formaldehyde.

The first step involved the addition of methanol, methoxide, or a methoxy radical to cobalt(II) porphyrin; all the reactions were exothermic. The geometry of the products ($\text{Copor(CH}_3\text{OH)}$, $[\text{Copor(CH}_3\text{O)}]^-$, $\text{Copor(CH}_3\text{O)}$) was optimised. These products produce formaldehyde and $[\text{Copor(NH)}]^-$, $[\text{Copor(H)}]^-$, Copor(NH) , Copor(H) complexes. All the reactions were endothermic; however, with Copor(H) it was the least endothermic.

The complexes where the hydrogen atom forms a bond with the cobalt atom are more stable than when it forms a bond with the nitrogen atom; Copor(H) is more stable than Copor(NH) , and $[\text{Copor(H)}]^-$ is more stable than $[\text{Copor(NH)}]^-$.

The production of a hydrogen molecule from these complexes is highly endothermic. The best and thermodynamically feasible way for the production of hydrogen is the reaction between Copor(H) and Copor(NH) , which also regenerates the cobalt(II) porphyrin catalyst.

This research also concluded that Copor(H) could be used as a catalyst in the oxidation of methanol to formaldehyde.

This work focused on a thermodynamical approach, and it is hoped that a detailed kinetic mechanism study will be done to reinforce this research.

Conflict of Interest

The author(s) declared no potential conflicts of interest with respect to the research, authorship, and publication of this article.

Supplemental Material

Thermochemistry of Co (II) porphyrin-catalysed oxidation of methanol to formaldehyde:

Cartesian coordinates and thermodynamic parameters at APFD/SDD level in gas phase.

All coordinates are given in ångströms.

All energies are given in hartrees.

Copor

N	0.00185101	-1.9624667	0
N	-2.02633	-0.0047371	0
N	-0.0016482	1.9900195	0
N	2.02620982	-0.0008266	0
C	1.10741476	-2.8021574	0
C	0.68807466	-4.1851098	0
C	-0.6800926	-4.1864826	0
C	-1.1025303	-2.8045169	0
C	-2.4332347	-2.4200764	0
C	-2.8611261	-1.1034464	0
C	-4.2443423	-0.6819594	0

C	-4.2385605	0.6887122	0
C	-2.8520015	1.1030477	0
C	-2.4325467	2.4231197	0
C	-1.1060607	2.8241624	0
C	-0.6883508	4.2097279	0
C	0.68079654	4.2109999	0
C	1.10081258	2.8260944	0
C	2.42830329	2.4277295	0
C	2.84983273	1.1085033	0
C	4.2373602	0.6965238	0
C	4.24559333	-0.6739946	0
C	2.86293913	-1.0981096	0
C	2.43766731	-2.4154658	0
H	1.36584929	-5.0278083	0
H	-1.3561104	-5.0305798	0
H	-3.1855226	-3.2024512	0
H	-5.091697	-1.3538927	0
H	-5.0807375	1.3672654	0
H	-3.1943827	3.1965747	0
H	-1.3653748	5.0531316	0
H	1.35630675	5.0556153	0
H	3.18842331	3.2028568	0
H	5.07803257	1.376924	0
H	5.09386579	-1.3447511	0
H	3.19107832	-3.1967531	0
Co	0	-0.0419951	0

Zero-point correction= 0.283049

Thermal correction to Energy= 0.299390

Thermal correction to Enthalpy= 0.300334

Thermal correction to Gibbs Free Energy= 0.238551

Sum of electronic and zero-point Energies= -1133.047073

Sum of electronic and thermal Energies= -1133.030732

Sum of electronic and thermal Enthalpies= -1133.029788

Sum of electronic and thermal Free Energies= -1133.091571

Copor (CH₃OH)

N	-1.56266	1.163723	-0.26509
N	-1.10676	-1.62911	-0.27878
N	1.701139	-1.1458	-0.17534
N	1.188281	1.640512	-0.20795
C	-1.62561	2.545115	-0.22762
C	-2.99896	2.995868	-0.27352
C	-3.77838	1.872091	-0.34915
C	-2.87949	0.737431	-0.34213
C	-3.31856	-0.57723	-0.39484
C	-2.4832	-1.68398	-0.36598
C	-2.93729	-3.05826	-0.39797
C	-1.81544	-3.84274	-0.32152
C	-0.68083	-2.94393	-0.25106
C	0.638199	-3.37083	-0.17959
C	1.741638	-2.52851	-0.15988
C	3.114621	-2.99102	-0.13993
C	3.908496	-1.87288	-0.15165
C	3.017431	-0.73227	-0.17186
C	3.429958	0.59157	-0.18114
C	2.571576	1.680492	-0.1925
C	3.038794	3.052114	-0.16931
C	1.926041	3.848378	-0.15681
C	0.78283	2.960552	-0.17871
C	-0.53265	3.395315	-0.17575
H	-3.30625	4.032886	-0.25896
H	-4.85613	1.799238	-0.40779
H	-4.38886	-0.74904	-0.45988

H	-3.97225	-3.36457	-0.47039
H	-1.74557	-4.92234	-0.32091
H	0.820999	-4.4414	-0.16355
H	3.413472	-4.03071	-0.12854
H	4.988535	-1.81198	-0.14932
H	4.497317	0.791591	-0.17278
H	4.080359	3.344211	-0.16052
H	1.865481	4.928173	-0.13712
H	-0.71786	4.464744	-0.14875
Co	0.04271	0.074181	-0.16288
O	0.122458	-0.08988	2.016864
C	-1.18748	-0.12269	2.651184
H	-1.81528	-0.90955	2.217485
H	-1.09223	-0.26088	3.735391
H	-1.63854	0.847116	2.443417
H	0.603777	-0.93406	2.113472

Zero-point correction= 0.335009

Thermal correction to Energy= 0.355959

Thermal correction to Enthalpy= 0.356903

Thermal correction to Gibbs Free Energy= 0.285254

Sum of electronic and zero-point Energies= -1248.703238

Sum of electronic and thermal Energies= -1248.682288

Sum of electronic and thermal Enthalpies= -1248.681344

Sum of electronic and thermal Free Energies= -1248.752993

Copor(CH₃O)

N	-0.62183	1.899546	-0.23956
N	-1.96264	-0.57346	-0.22115
N	0.562226	-1.86232	-0.29636
N	1.894963	0.641474	-0.2551
C	0.176924	3.029078	-0.17084
C	-0.63655	4.223345	-0.1402
C	-1.9414	3.813476	-0.16613
C	-1.92438	2.368806	-0.20642
C	-3.07754	1.603059	-0.18373
C	-3.08753	0.21963	-0.17577
C	-4.28011	-0.59675	-0.11626
C	-3.86128	-1.90136	-0.10721
C	-2.41502	-1.87594	-0.16652
C	-1.61933	-3.00872	-0.18484
C	-0.23566	-2.99155	-0.25981
C	0.576515	-4.18677	-0.30664
C	1.882079	-3.77498	-0.36138
C	1.863882	-2.32946	-0.34202
C	3.009873	-1.55005	-0.33836
C	3.014869	-0.1658	-0.28608
C	4.214317	0.642462	-0.24564
C	3.808159	1.949872	-0.17383
C	2.362504	1.935133	-0.17708
C	1.560386	3.061605	-0.13446
H	-0.24321	5.230018	-0.10085
H	-2.84079	4.41389	-0.15057
H	-4.02986	2.122736	-0.14931
H	-5.28961	-0.21025	-0.08296
H	-4.45805	-2.80251	-0.06666
H	-2.11188	-3.97551	-0.14617
H	0.185225	-5.19507	-0.29975
H	2.779657	-4.37672	-0.40711
H	3.96814	-2.05967	-0.36521
H	5.221138	0.247949	-0.26756
H	4.414506	2.84413	-0.12673
H	2.042805	4.032117	-0.07412
Co	-0.0445	0.072206	-0.1035

O	-0.09929	0.227991	1.822574
C	0.697009	-0.75819	2.485239
H	0.293396	-1.77672	2.378933
H	1.745987	-0.75545	2.151417
H	0.683122	-0.49044	3.553648

Zero-point correction= 0.325750

Thermal correction to Energy= 0.345344

Thermal correction to Enthalpy= 0.346288

Thermal correction to Gibbs Free Energy= 0.278304

Sum of electronic and zero-point Energies= -1248.054049

Sum of electronic and thermal Energies= -1248.034455

Sum of electronic and thermal Enthalpies= -1248.033511

Sum of electronic and thermal Free Energies= -1248.101494

[Copor(CH₃O)]⁻¹

N	-0.69652	1.902376	-0.22703
N	-1.97903	-0.64531	-0.21782
N	0.618663	-1.87928	-0.27247
N	1.894438	0.692738	-0.28256
C	0.075712	3.042689	-0.18081
C	-0.77115	4.222071	-0.13532
C	-2.06714	3.77532	-0.14301
C	-2.00701	2.32477	-0.18937
C	-3.1363	1.510612	-0.18306
C	-3.11782	0.12088	-0.19238
C	-4.29509	-0.73131	-0.16473
C	-3.83898	-2.02637	-0.16252
C	-2.38595	-1.95641	-0.19252
C	-1.54419	-3.06504	-0.20129
C	-0.15322	-3.01919	-0.24781
C	0.694732	-4.19801	-0.2916
C	1.99089	-3.74912	-0.3456
C	1.930411	-2.29803	-0.32963
C	3.051812	-1.47407	-0.35961
C	3.027868	-0.08201	-0.33148
C	4.210119	0.764638	-0.3347
C	3.764348	2.062476	-0.27499
C	2.312805	1.999242	-0.24105
C	1.465955	3.10025	-0.18561
H	-0.40592	5.240687	-0.09464
H	-2.98282	4.352438	-0.10876
H	-4.10567	2.002464	-0.15022
H	-5.31741	-0.37492	-0.14044
H	-4.41286	-2.94454	-0.13897
H	-2.0101	-4.04752	-0.176
H	0.332904	-5.21869	-0.28138
H	2.90533	-4.3279	-0.38617
H	4.025422	-1.95756	-0.39458
H	5.229967	0.401746	-0.36783
H	4.345585	2.975854	-0.25147
H	1.923571	4.086014	-0.14389
Co	-0.05523	0.066381	-0.07879
O	-0.07234	0.249339	1.979425
C	0.844031	-0.62472	2.605033
H	0.601582	-1.70482	2.465243
H	1.892934	-0.49966	2.24758
H	0.873658	-0.4562	3.705128

Zero-point correction= 0.318288

Thermal correction to Energy= 0.339108

Thermal correction to Enthalpy= 0.340052

Thermal correction to Gibbs Free Energy= 0.268974

Sum of electronic and zero-point Energies= -1248.130759

Sum of electronic and thermal Energies= -1248.109938
 Sum of electronic and thermal Enthalpies= -1248.108994
 Sum of electronic and thermal Free Energies= -1248.180073

Copor(CH₃O)(H)

N	-2.05094	-0.30886	-0.13827
N	0.291129	-1.88799	-0.25965
N	1.953757	0.38436	-0.20444
N	-0.37939	1.952244	-0.1693
C	-3.0532	0.624441	-0.19936
C	-4.34756	-0.02177	-0.12394
C	-4.10672	-1.3656	-0.00586
C	-2.66758	-1.53193	-0.03052
C	-2.01673	-2.75286	-0.01987
C	-0.64563	-2.90039	-0.15974
C	-0.00357	-4.19162	-0.25932
C	1.333906	-3.95632	-0.43449
C	1.508861	-2.52158	-0.41971
C	2.75424	-1.91338	-0.49139
C	2.954267	-0.55053	-0.36552
C	4.248767	0.094525	-0.34397
C	4.018182	1.434294	-0.16287
C	2.582914	1.602869	-0.09561
C	1.933435	2.82213	-0.0051
C	0.557821	2.96621	-0.07826
C	-0.09003	4.258833	-0.10712
C	-1.43167	4.025219	-0.23282
C	-1.60555	2.589857	-0.25581
C	-2.85364	1.99187	-0.28875
H	-5.29658	0.496216	-0.15104
H	-4.81812	-2.17599	0.077248
H	-2.61723	-3.65358	0.058779
H	-0.52415	-5.13826	-0.20871
H	2.138708	-4.66933	-0.55117
H	3.623461	-2.55098	-0.61731
H	5.193878	-0.42043	-0.45061
H	4.735587	2.24094	-0.09689
H	2.535438	3.721597	0.074084
H	0.431535	5.204417	-0.04754
H	-2.2421	4.739039	-0.29082
H	-3.72463	2.636851	-0.34477
Co	-0.04707	0.039605	-0.11494
H	-0.10544	0.003701	-1.56525
O	-0.12431	-0.12237	1.754499
C	0.990353	-0.59108	2.500499
H	1.867127	0.053439	2.338975
H	0.737719	-0.63444	3.566403
H	1.262905	-1.6009	2.154891

Zero-point correction= 0.331317

Thermal correction to Energy= 0.351644

Thermal correction to Enthalpy= 0.352589

Thermal correction to Gibbs Free Energy= 0.282468

Sum of electronic and zero-point Energies= -1248.596407

Sum of electronic and thermal Energies= -1248.576080

Sum of electronic and thermal Enthalpies= -1248.575135

Sum of electronic and thermal Free Energies= -1248.645256

[Copor(NH)]⁻

N	-2.02111	0.154232	-0.12752
N	0.157276	1.992839	0.080092
N	2.094972	-0.15949	0.232953

N	-0.17486	-1.96302	0.075969
C	-2.95185	-0.8786	-0.15242
C	-4.28597	-0.34159	-0.19864
C	-4.16628	1.034328	-0.17098
C	-2.75937	1.335549	-0.1121
C	-2.23591	2.620561	-0.00845
C	-0.88219	2.924669	0.097227
C	-0.35314	4.256787	0.1929
C	1.026075	4.14381	0.209925
C	1.338254	2.74461	0.129195
C	2.649193	2.258574	0.02421
C	3.017244	0.927626	-0.05917
C	4.264931	0.361028	-0.41448
C	4.157176	-1.03518	-0.38096
C	2.838381	-1.38435	-0.00805
C	2.25143	-2.63292	0.097508
C	0.87749	-2.89414	0.16688
C	0.348969	-4.2251	0.237046
C	-1.0289	-4.12571	0.167271
C	-1.34639	-2.73094	0.056597
C	-2.63753	-2.23179	-0.07645
H	-5.18788	-0.94033	-0.22841
H	-4.95173	1.780066	-0.17617
H	-2.93915	3.449586	0.0012
H	-0.95576	5.156259	0.223316
H	1.765678	4.932916	0.268563
H	3.440629	2.99816	-0.06883
H	5.127536	0.942449	-0.71405
H	4.917903	-1.75539	-0.65413
H	2.909173	-3.49652	0.037206
H	0.956205	-5.11789	0.322199
H	-1.76323	-4.92174	0.175153
H	-3.45625	-2.94634	-0.09319
Co	-0.10186	-0.03363	-0.03374
H	1.763519	-0.10837	1.205204

Zero-point correction= 0.287888

Thermal correction to Energy= 0.305410

Thermal correction to Enthalpy= 0.306354

Thermal correction to Gibbs Free Energy= 0.242806

Sum of electronic and zero-point Energies= -1133.694904

Sum of electronic and thermal Energies= -1133.677383

Sum of electronic and thermal Enthalpies= -1133.676439

Sum of electronic and thermal Free Energies= -1133.739986

Copor(NH)

N	-1.96384	0.329868	-0.0569
N	0.338757	1.953984	0.051908
N	2.047309	-0.34931	0.150856
N	-0.35949	-1.91778	0.04534
C	-2.99027	-0.59684	-0.11037
C	-4.27622	0.061025	-0.18836
C	-4.02821	1.407067	-0.16766
C	-2.59135	1.566095	-0.07987
C	-1.96217	2.798794	-0.00125
C	-0.59178	2.976572	0.072787
C	0.05908	4.269462	0.145688
C	1.405324	4.030199	0.158223
C	1.574327	2.589702	0.092827
C	2.826457	1.99056	0.009755
C	3.056619	0.629489	-0.0506
C	4.281146	-0.04017	-0.32454
C	4.044793	-1.40635	-0.30139
C	2.668102	-1.61311	-0.01452

C	1.977209	-2.80666	0.064949
C	0.594567	-2.93346	0.121948
C	-0.04626	-4.23439	0.181864
C	-1.39285	-4.01512	0.125563
C	-1.57819	-2.58157	0.038816
C	-2.81453	-1.96991	-0.05358
H	-5.22698	-0.45154	-0.24573
H	-4.73414	2.225829	-0.20553
H	-2.58967	3.685471	-0.00175
H	-0.45897	5.218708	0.174264
H	2.219113	4.741576	0.200472
H	3.690454	2.645329	-0.05278
H	5.213205	0.463268	-0.54132
H	4.751357	-2.20055	-0.49926
H	2.558442	-3.72316	0.030635
H	0.485482	-5.17409	0.246992
H	-2.19752	-4.73798	0.136151
H	-3.69785	-2.60123	-0.0742
Co	-0.11929	-0.02606	0.005007
H	1.473993	-0.23358	1.03681

Zero-point correction= 0.291607

Thermal correction to Energy= 0.308444

Thermal correction to Enthalpy= 0.309388

Thermal correction to Gibbs Free Energy= 0.247783

Sum of electronic and zero-point Energies= -1133.622731

Sum of electronic and thermal Energies= -1133.605894

Sum of electronic and thermal Enthalpies= -1133.604950

Sum of electronic and thermal Free Energies= -1133.666555

[C_{op}or(H)]

N	-0.03795	2.030154	0
N	-0.02505	-5.7E-06	1.95817
N	-0.03796	-2.03016	0
N	-0.02505	-5.7E-06	-1.95817
C	-0.02067	2.866598	-1.10708
C	-0.01457	4.256954	-0.68408
C	-0.01457	4.256954	0.684076
C	-0.02067	2.866598	1.107077
C	-0.01189	2.451099	2.415501
C	-0.0155	1.104237	2.810369
C	-0.01464	0.69463	4.177005
C	-0.01484	-0.69463	4.17701
C	-0.01546	-1.10424	2.810376
C	-0.01186	-2.4511	2.415503
C	-0.02066	-2.8666	1.10708
C	-0.01456	-4.25696	0.684077
C	-0.01456	-4.25696	-0.68408
C	-0.02066	-2.8666	-1.10708
C	-0.01186	-2.4511	-2.4155
C	-0.01546	-1.10424	-2.81038
C	-0.01484	-0.69463	-4.17701
C	-0.01464	0.69463	-4.17701
C	-0.0155	1.104237	-2.81037
C	-0.01189	2.451099	-2.4155
H	-0.01013	5.100692	-1.36304
H	-0.01013	5.100692	1.363041
H	-0.00116	3.204136	3.198786
H	-0.01523	1.372651	5.021173
H	-0.0156	-1.37265	5.021179
H	-0.00116	-3.20415	3.198784
H	-0.01012	-5.10069	1.363043
H	-0.01012	-5.10069	-1.36304
H	-0.00116	-3.20415	-3.19878

H	-0.0156	-1.37265	-5.02118
H	-0.01523	1.372651	-5.02117
H	-0.00116	3.204136	-3.19879
Co	0.05088	8.35E-06	0
H	1.471024	-2.9E-05	0

Zero-point correction= 0.284553

Thermal correction to Energy= 0.302064

Thermal correction to Enthalpy= 0.303008

Thermal correction to Gibbs Free Energy= 0.239104

Sum of electronic and zero-point Energies= -1133.699473

Sum of electronic and thermal Energies= -1133.681962

Sum of electronic and thermal Enthalpies= -1133.681018

Sum of electronic and thermal Free Energies= -1133.744923

C_{op}or(H)

N	0.032084	-2.02748	0
N	0.028096	-1.5E-07	1.939375
N	0.032071	2.027475	0
N	0.028096	-1.5E-07	-1.93938
C	0.017409	-2.86235	-1.09906
C	0.009986	-4.24811	-0.68535
C	0.009986	-4.24811	0.685345
C	0.017409	-2.86235	1.099058
C	0.011685	-2.4327	2.413195
C	0.016724	-1.10043	2.788505
C	0.013728	-0.68374	4.172037
C	0.013879	0.683738	4.172037
C	0.016701	1.100433	2.788505
C	0.011665	2.432702	2.413195
C	0.017391	2.862346	1.099058
C	0.00998	4.248108	0.685345
C	0.00998	4.248108	-0.68535
C	0.017391	2.862346	-1.09906
C	0.011665	2.432702	-2.41319
C	0.016701	1.100433	-2.7885
C	0.013879	0.683738	-4.17204
C	0.013728	-0.68374	-4.17204
C	0.016724	-1.10043	-2.7885
C	0.011685	-2.4327	-2.41319
H	0.005376	-5.09177	-1.36207
H	0.005376	-5.09177	1.362073
H	0.001641	-3.18161	3.198953
H	0.012539	-1.36189	5.01461
H	0.012802	1.361892	5.014611
H	0.001649	3.181613	3.198953
H	0.005376	5.091773	1.362073
H	0.005376	5.091773	-1.36207
H	0.001649	3.181613	-3.19895
H	0.012802	1.361892	-5.01461
H	0.012539	-1.36189	-5.01461
H	0.001641	-3.18161	-3.19895
Co	-0.04195	9.7E-07	0
H	-1.45836	8.26E-06	0

Zero-point correction= 0.290795

Thermal correction to Energy= 0.307418

Thermal correction to Enthalpy= 0.308363

Thermal correction to Gibbs Free Energy= 0.246925

Sum of electronic and zero-point Energies= -1133.650421

Sum of electronic and thermal Energies= -1133.633798

Sum of electronic and thermal Enthalpies= -1133.632854

Sum of electronic and thermal Free Energies= -1133.694291

Coppor(H)₂

N	-0.00019	2.030617	0
N	0.000372	9.7E-07	1.944473
N	-0.00018	-2.03062	0
N	0.000372	9.7E-07	-1.94447
C	-0.00063	2.863933	-1.09808
C	-0.00151	4.250899	-0.68518
C	-0.00151	4.250899	0.685177
C	-0.00063	2.863933	1.098077
C	5.51E-06	2.430854	2.411624
C	0.000634	1.099357	2.791256
C	0.001254	0.683594	4.176241
C	0.001151	-0.68359	4.17624
C	0.000648	-1.09936	2.791256
C	1.84E-05	-2.43085	2.411625
C	-0.00061	-2.86393	1.098078
C	-0.00151	-4.2509	0.685177
C	-0.00151	-4.2509	-0.68518
C	-0.00061	-2.86393	-1.09808
C	1.84E-05	-2.43085	-2.41162
C	0.000648	-1.09936	-2.79126
C	0.001151	-0.68359	-4.17624
C	0.001254	0.683594	-4.17624
C	0.000634	1.099357	-2.79126
C	5.51E-06	2.430854	-2.41162
H	-0.00199	5.094687	-1.36169
H	-0.00199	5.094687	1.361687
H	-6.3E-06	3.180216	3.197402
H	0.001654	1.362204	5.018354
H	0.001475	-1.3622	5.018353
H	-1.3E-05	-3.18021	3.197406
H	-0.00199	-5.09469	1.361686
H	-0.00199	-5.09469	-1.36169
H	-1.3E-05	-3.18021	-3.19741
H	0.001475	-1.3622	-5.01835
H	0.001654	1.362204	-5.01835
H	-6.3E-06	3.180216	-3.1974
Co	0.000252	-2.4E-06	0
H	1.554274	8.15E-06	0
H	-1.55535	2.36E-06	0

Zero-point correction= 0.293474

Thermal correction to Energy= 0.310800

Thermal correction to Enthalpy= 0.311744

Thermal correction to Gibbs Free Energy= 0.248590

Sum of electronic and zero-point Energies= -1134.169188

Sum of electronic and thermal Energies= -1134.151863

Sum of electronic and thermal Enthalpies= -1134.150918

Sum of electronic and thermal Free Energies= -1134.214072

Formaldehyde

C	-1.8E-06	0.545407	0
H	0.938455	1.129439	0
H	-0.93843	1.129479	0
O	-1.8E-06	-0.69142	0

Zero-point correction= 0.026867

Thermal correction to Energy= 0.029736

Thermal correction to Enthalpy= 0.030680

Thermal correction to Gibbs Free Energy= 0.005167

Sum of electronic and zero-point Energies= -114.358870

Sum of electronic and thermal Energies= -114.356002

Sum of electronic and thermal Enthalpies= -114.355058

Sum of electronic and thermal Free Energies= -114.380571

Methanol

C	0.682967	-0.0219	3.31E-06
H	1.084787	0.992993	-0.00107
H	1.051372	-0.54531	-0.89544
H	1.051486	-0.54348	0.896462
O	-0.7605	0.121962	4E-07
H	-1.20147	-0.74853	2.38E-05

Zero-point correction= 0.051504

Thermal correction to Energy= 0.054815

Thermal correction to Enthalpy= 0.055759

Thermal correction to Gibbs Free Energy= 0.028736

Sum of electronic and zero-point Energies= -115.559158

Sum of electronic and thermal Energies= -115.555848

Sum of electronic and thermal Enthalpies= -115.554903

Sum of electronic and thermal Free Energies= -115.581926

Methoxide

C	-0.55641	-7.7E-06	-2.8E-05
H	-1.06814	-0.77283	-0.67683
H	-1.06841	-0.19991	1.007602
H	-1.06858	0.97257	-0.33072
O	0.817948	2.61E-05	1.41E-05

Zero-point correction= 0.035130

Thermal correction to Energy= 0.038043

Thermal correction to Enthalpy= 0.038987

Thermal correction to Gibbs Free Energy= 0.012834

Sum of electronic and zero-point Energies= -114.937467

Sum of electronic and thermal Energies= -114.934554

Sum of electronic and thermal Enthalpies= -114.933610

Sum of electronic and thermal Free Energies= -114.959762

Methoxy radical

C	-0.60142	-4.1E-05	0.010374
H	-0.90031	0.001804	-1.05429
H	-1.0221	-0.90773	0.466871
H	-1.02194	0.906314	0.469703
O	0.819106	-1.7E-05	0.006934

Zero-point correction= 0.036990

Thermal correction to Energy= 0.040028

Thermal correction to Enthalpy= 0.040973

Thermal correction to Gibbs Free Energy= 0.013988

Sum of electronic and zero-point Energies= -114.912855

Sum of electronic and thermal Energies= -114.909816

Sum of electronic and thermal Enthalpies= -114.908872

Sum of electronic and thermal Free Energies= -114.935857

Hydrogen molecule

H	0	0	0.372185
H	0	0	-0.37219

Zero-point correction= 0.010134

Thermal correction to Energy= 0.012494

Thermal correction to Enthalpy= 0.013439

Thermal correction to Gibbs Free Energy= -0.001357
 Sum of electronic and zero-point Energies= -1.157532
 Sum of electronic and thermal Energies= -1.155172
 Sum of electronic and thermal Enthalpies= -1.154228
 Sum of electronic and thermal Free Energies= -1.169024

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