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# Possible interstellar formation glycine from the reaction of $CH_2$=NH, CO and $H_2O$: Catalysis by extra water molecules through the hydrogen relay transport

Authors: Zanele P. Nhlabatsi, Priya Bhasi, Sanyasi Sitha*

**Department of Chemistry, University of Johannesburg, PO Box 524, Auckland Park, Johannesburg, South Africa 2006**

**Abstract:** “How the fundamental life elements are created in the interstellar medium (ISM)?, is one of the intriguing questions related to genesis of life. Using computational calculations, we have discussed the reaction of $CH_2$=NH, CO and $H_2O$ for the formation of glycine. This reaction proceeds through a concerted mechanism with reasonably large barriers for the cases with one and two water molecules as reactants. For the two water case we found that the extra water molecule exhibits some catalytic role through hydrogen transport relay effect and the barrier height is reduced substantially compared to the case with one water molecule. These two cases can be treated as ideal cases for the hot-core formation of the interstellar glycine. With increasing number of water molecules as the reactants, we found that when the numbers of water molecules are three or more than three, the barrier height reduced so drastically that the transition states were more stable than the reactants. Such a situation gives a clear indication that with excess water molecules as the reactants, this reaction will be feasible even in the low temperature conditions existing in the cold interstellar clouds and the exothermic nature of the reaction will be driving force.

*To whom correspondence should be addressed: Email: ssitha@uj.ac.za

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## 1. Introduction:

There exist one fundamental question related to the origin of life and that is "How life is created?" or more technically "How the essential life elements, i.e., the amino acids are formed?"[1,2] To find answers for this question; chemists, biologists, astronomers and geologists are trying with their full potentials by considering all possible angles. Among the various amino-acids, glycine, ($H_2N$-$CH_2$-COOH) is one of the simplest amino acid found in the earth. The era of the astronomical search for glycine begins with the availability of the laboratory spectra for it[3], but its presence in the interstellar medium (ISM) is still controversial[4-6]. On the other side, many amino-acids including glycine have been found on meteorites[7-18]. In a recent discovery glycine is being detected even in comets, as evidenced from the pristine cometary samples reverted back by NASA STARDUST mission[18], which can be treated as a validation for its extraterrestrial origin. On the other hand our knowledge on its formation in the extraterrestrial space through various chemical pathways seems to be either incomplete or inconclusive[19]. To imitate the synthesis in laboratory, there are two most widely exploited approaches can be found in the literature. First one is the Strecker's synthesis[20], and the second one is the Miller experiment[21], where in both the cases it is believed that the key intermediate is the HCHO (formaldehyde). Similar to formaldehyde, another important reactant, Methanimine ($CH_2$=NH) which is isoelectronic with HCHO is also suggested as a potential prebiotic precursor for glycine[22-25]. Starting with this Methanimine, in this work using computational calculations, we have carried out a complete potential energy surface (PES) analysis of $CH_2{=}NH + CO + H_2O \rightarrow$ Glycine reaction. In a recent work, "Discovering chemistry with an ab initio nano reactor"[26] by Wang et al. also indicates the possibility of such a reaction, but without any further discussions. With a detailed potential energy surface analysis, we have shown that the reaction suggested by Wang et al.[26] proceeds through a concerted type of reaction mechanism from $CH_2$=NH, CO and $H_2O$ to give glycine as the end product. Also we have discussed about the cooperative and catalytic role of extra water molecules for this reaction through hydrogen relay transport phenomena. The role of water acting as proton transfer helper was first described by Radom and co-workers[27-29]. But, such phenomena are less investigated for the interstellar formation of Glycine[25, 30-33]. In the recent work by Rimola et al.[33] where they have carried out computational studies on the formation of glycine from the reaction $CH_2$=NH and CO on radical surfaces of water-ice dust particles, indicates a clear catalytic role exhibited by the water molecules of the water-ice cluster. Moreover the work of Rimola et al.[33], they have shown how the defects formed in the water-ices is capable of making the reaction feasible and the mechanism proposed is multi-stepped in nature. The work discussed here shows a concerted type of mechanism for the formation of glycine, also with discussions related to the catalytic role of extra water molecules, which is capable of bring down the reaction barrier drastically.

## 2. Computational Methods:

All the calculations have been carried out using Gaussian software package[34]. We have carried out calculations using various methods like, B3LYP, B3PW91, CBS-QB3, MP2, and also various composite methods which are known for accurate energy predictions, like, G3B3, G3MP2B3, G4 and G4MP2. For the B3LYP method we have also tested the effect of various basis sets. The true minima and the transition states were confirmed from analysis of their frequencies by ensuring that all frequencies were positive for the minimum, with there is only one imaginary frequency for the transition state. We have also carried out the analysis of the displacement vectors for the imaginary frequency to ascertain that the TS is a structurally true TS and also confirmed by the IRC analysis. All the thermodynamic quantities were calculated from the zero point energy (ZPE) corrected energies of the stationary points in the PES. As all the methods predict similar kind of trend, in the main text we have limited our discussion only to B3LYP/6-31++G(3df,3pd) method only with a very little discussions on effects of methodologies and basissets.

## 3. Results and discussions:

### *3.1. PES for $CH_2$=NH + CO + $H_2O$ → Glycine reaction:*

The PES of the termolecular reaction between $CH_2$=NH, CO and $H_2O$ to form glycine is shown in Figure 1. PES for the MP2 method is provided in the supporting information.

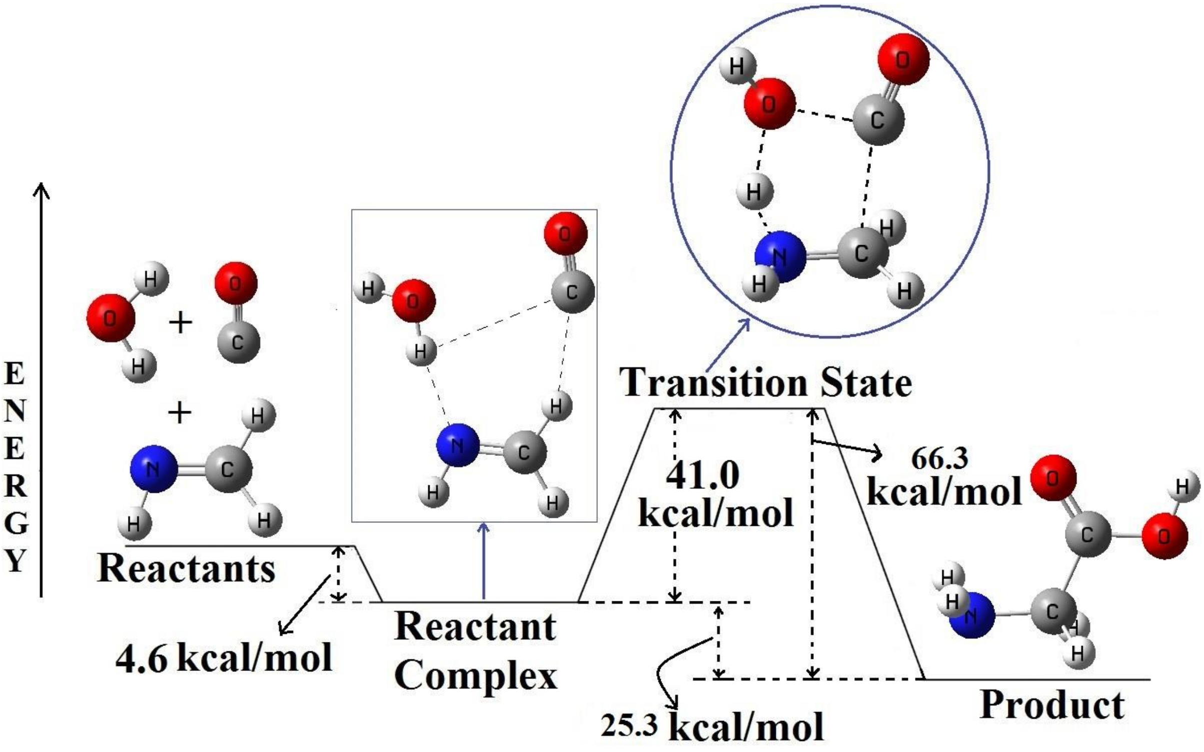

**Figure 1:** B3LYP/6-31++G(3df,2pd) optimized PES for the $CH_2$=NH + CO + $H_2O$ → Glycine, reaction. All the energies are in kcal/mol and the diagram is not to scale.

Analysis of the PES shows that a well synchronized approach of the three reactants first leads to the formation of a stable hydrogen-bonded complex, which ultimately passes through a transition state to reach the product, glycine. Energetics of the PES shows that the complex is around 4.6 kcal/mol more stable than the corresponding reactants. The complex then passes through a transition state, where the TS is 41.0 kcal/mol higher in energy than the complex (36.4 kcal/mol is higher in energy compared to the reactants). Analysis of the product, glycine shows that it is 25.3 kcal/mol more stable compared to the reactant complex or 29.9 kcal/mol more stable compared to the reactants. The PES for the MP2 method shows similar kind of behavior like that of the B3LYP surface with a little difference in the energetics. The exothermic nature of this reaction is a clear indication for the thermochemical feasibility of this reaction ISM, but the reasonably large barrier may act as a bottleneck. We have also investigated the effect of various basissets with the B3LYP method for the PES of this reaction and also the effect of various methodologies for the PES of this reaction. The detailed discussions related to these are provided in the supporting information. As the reactant complex and transition state, are vital to the feasibility of this reaction in the interstellar conditions, a concise discussion about their structures and nature of interactions are shown below.

### *3.1.1. Reactant Complex:*

There are two major possibilities for the approach of the CO+$H_2O$ towards the planar $CH_2$=NH; (1) above or below the plane of the molecule (perpendicular to the $\pi$-cloud of molecule), (2) in-plane from one side of the methanimine. The optimized structure of the reactant-complex is shown in Figure 2(a). Analysis of the reactant-complex shows that approach of the reactants towards $CH_2$=NH is almost in-plane and also is in the same side of the plane. CO molecule is placed in the side of $CH_2$ of the methanimine and makes a hydrogen bonded interaction with one of the H-atom of $CH_2$ unit (C-H-O hydrogen bonding. Hydrogen bond distance is 2.895 Å). On the other hand $H_2O$ molecule is in the NH unit side of the methanimine, where one of the H-atom of the water molecule is interacting with the N-atom of the methanimine and the nature of interaction is hydrogen bonding (O-H-N hydrogen bonding. Hydrogen bond distance is 1.941 Å). Besides these two major interactions there exist so many van der Waals type of interaction in the reactant complex.

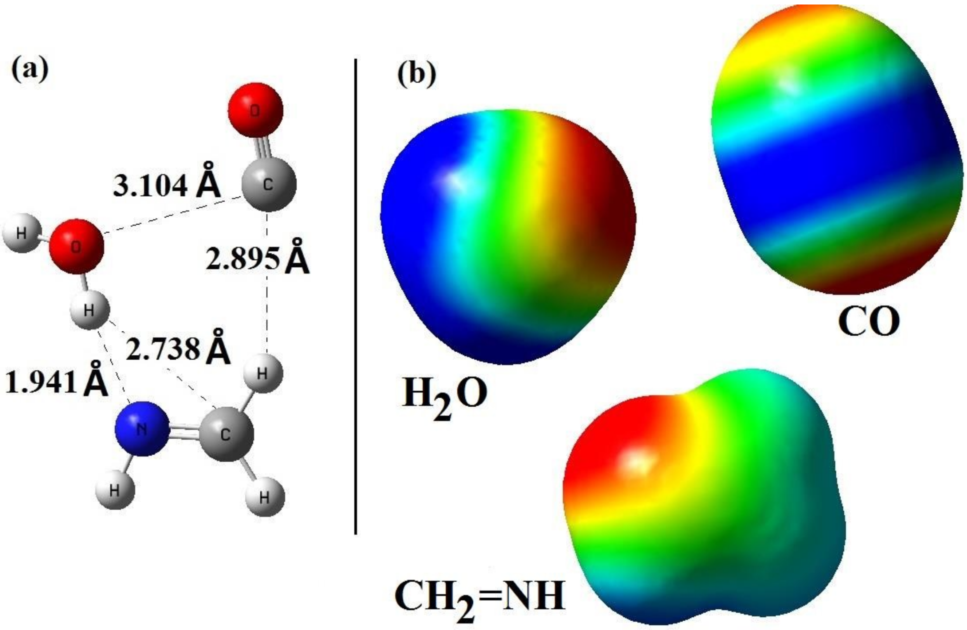

**Figure 2: (a)** B3LYP/6-31++G(3df,2pd) optimized structure of the reactant complex with important interaction distances. **(b)** Computed ESP maps of $CH_2$=NH, CO and $H_2O$ (oriented in the similar fashion like that of the reactant complex) calculated from the B3LYP/6-31++G (3df,2pd) method at 0.001 au electron density surfaces [ESP colour scheme: Red (negative) ----- Positive (blue)].

To study the nature of interaction existing in the complex we have analyzed the electrostatic potential (ESP) maps of the reactants [Figure 2(b)]. Analysis of the ESP maps shows that; (1) for CO: there is a maximum negative potential around the C-atom and a smaller negative potential around the O-atom, which are capable of interacting with positive potential regions of other reactants, (2) For $H_2O$: two ends with H-atoms have positive potentials and region around the central O-atom is having the negative potential, (3) for $CH_2=NH$: except the region around N-atom (showing negative potential) all other regions have positive potentials. Analysis of the geometry of the reactant-complex shows a well synchronized approach of the reactions from electrostatic potential point of view.

### *3.1.2. Transition state:*

Optimized structure of the TS is shown in Figure 3. Analysis of the TS shows that it is a distorted cyclic 5-membered ring and at the TS all the three reactants are arranged in a nonplanar three dimensional way (imaginary frequency: 777.3i $cm^{-1}$).

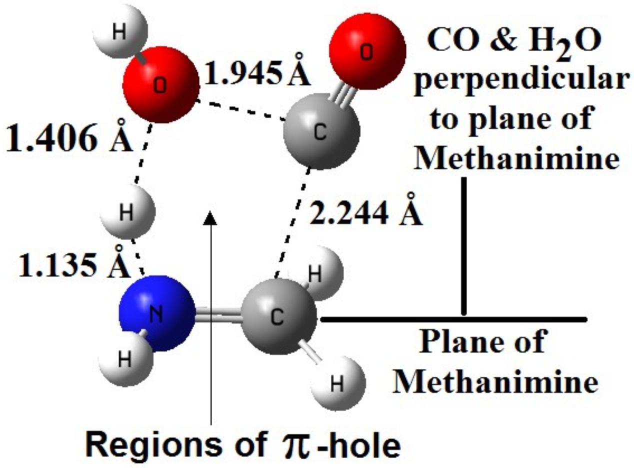

**Figure 3:** B3LYP/6-31++G(3df,2pd) optimized structure of the reactant complex with important interaction distances.

Structure of the TS shows that the molecular structural characteristics of CO and $CH_2$=NH are almost retained in the TS, and at the same time one of the H-O bond in $H_2O$ is largely elongated. Further analysis of the structure of the TS shows that the approach of the CO+$H_2O$ towards the $CH_2$=NH is perpendicular to the plane of $CH_2$=NH (perpendicular to the $\pi$-cloud of $CH_2$=NH). To know the nature of interaction existing at the TS, we have analyzed the ESPs of the reactants again. It can be seen that again the $H_2O$ in the TS is in the side of NH unit of $CH_2$=NH, with one of the H-atom (with positive potential) of $H_2O$ sandwiched between the negative potentials of N-atom of NH and O-atom of $H_2O$. On the other hand the CO and the OH of $H_2O$ are interacting with the $\pi$-hole regions[35] of the $CH_2$=NH rather than interacting with each other. In other word $\pi$-hole regions[35] of the $CH_2$=NH provides a well synchronized positioning of these two reactants in the TS.

### *3.2. Catalysis by an extra water molecule:*

Rimola et al. have carried out computational studies on the formation of glycine on radical surfaces of water-ice dust particles which involves $CH_2$=NH and CO as reactants[33]. In their work they have used a cluster of water molecule where many water molecules are interlinked with each other[33]. Though the mechanism predicted in their work is a step-wise mechanism, but their work clearly indicates the prominent hydrogen transport catalytic effect exhibited by those interlinked water molecules. Similarly, Wang et al. in their recent work also indicated the possible catalytic effect for this reaction , but without any further details on the mechanistic aspect of this reaction[26]. So in this work we have carried out calculations related to PES of the reaction between the $CH_2$=NH, CO and two molecules of $H_2O$ to study the mechanistic aspect of this reaction. In our study we have placed the two water molecules adjacent to each other and at the same time also interlinked with each other. This inter linked system also sometimes can be viewed as a $H_2O$-$H_2O$ binary complex. We have compared our results of the reaction PES consisting of two individual molecules of water with that of the reaction PES for $H_2O$-$H_2O$ binary complex. The potential energy surface of the reaction between $CH_2$=NH, CO, with two water molecules is shown in Figure 4. PES related to $H_2O$-$H_2O$ binary complex for both the MP2 and B3LYP methods are provided in the supporting information.

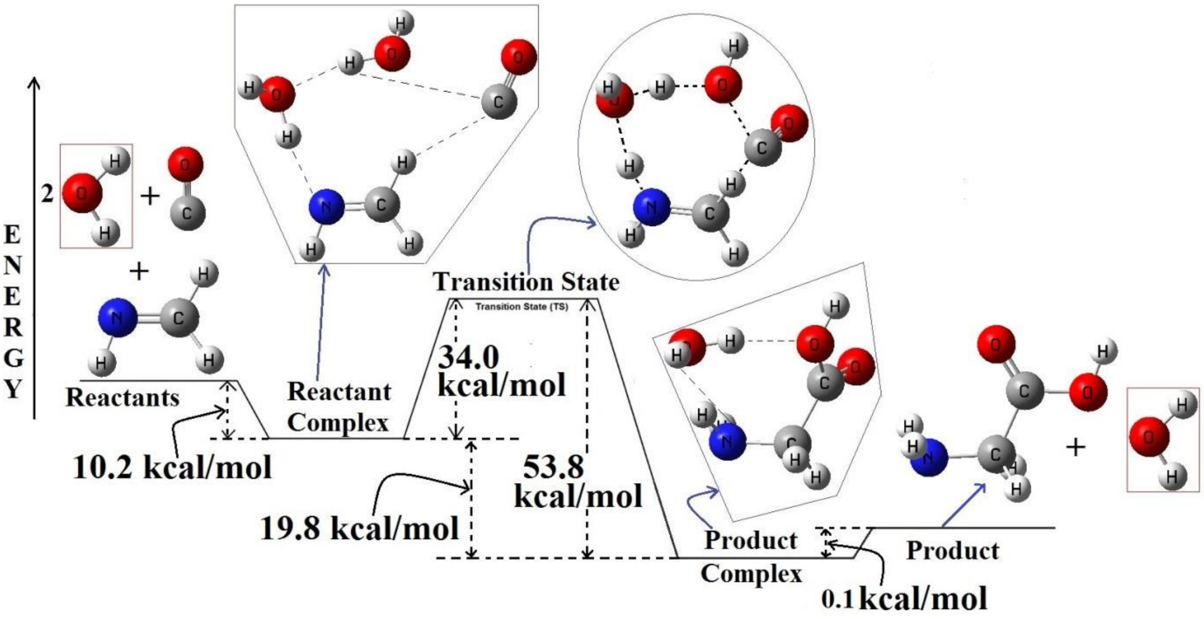

**Figure 4:** B3LYP/6-31++G(3df,2pd) optimized PES for the $CH_2$=NH + CO + $2H_2O$ → Glycine, reaction. All the energies are in kcal/mol and the diagram is not to scale.

Analysis of the potential energy surface shows that a well-coordinated approach of the four reactants leads to the formation of a stable hydrogen bonded reactant-complex (multiple hydrogen bonding situations can be seen in the complex) at the entry channel of this reaction. This complex ultimately passes through a transition state to reach a stable product-complex, an exit channel complex for this reaction. This exit channel complex then endothermically dissociates to give glycine and water as final products. Without any further discussion about the structures of the all the stationary points in the PES we have only discussed the energetics of this reaction PES to account for the extent of catalytic effect by extra water molecule as reactant. More details about the optimized structures of these stationary points can be found in the supporting information. Analysis of the reactant complex shows that it is highly stable (around 10.2 kcal/mol more stable than the corresponding reactants). The extra stability of the reactant complex is coming from the more number of well synchronized H-bonded interactions existing in the complex than the previous case as discussed above for one water molecule. Instead of the two separate water molecules, we have extended our discussions for the $H_2O$-$H_2O$ complex reacting with $CH_2$=NH and CO and this is based on the fact that the binary complex of $H_2O$ also being detected in the ISM[36]. Now, with $H_2O$-$H_2O$ binary complex as one of the reactant, the reactant complex is 7.0 kcal/mol stable compared to the reactants. The loss in the stability is hidden in the $H_2O$-$H_2O$ binary complexation energy.

The complex then passes through a transition state and analysis of the TS shows that it is a distorted cyclic 8-membered ring. At the TS all the four reactants are arranged in a nonplanar three dimensional way. Energetics of the TS shows that it is 34.0 kcal/mol higher in energy than the reactant complex (23.8 kcal/mol higher in energy compared to the reactants). This clearly shows a 7.0 kcal/mol of decrease in energy compared to the uncatalyzed case (~12 kcal/mol compared to the reactants in the un-catalyzed case) and a direct indication of the prominent catalytic activity by the extra water molecule for this reaction[26]. In the TS, the catalytic effect of the extra $H_2O$ molecule can be considered as being facilitated by the relay effect it is exhibiting in transporting the H-atom to the N-atom site of $CH_2$=NH[37]. In the transition state the water molecule close to the N-atom of the $CH_2$=NH acts as the communicator in relay transporting the H-atom from the other water molecule placed close to the CO molecule to the N-atom of the methanimine. Though prominent hydrogen transport is happening in the transition state, the low value of imaginary frequency of the TS clearly gives an indication of negligible chances for the low temperature tunneling mechanism to happen for this reaction[38]. While descending from the TS towards the product in the PES, we observed a product-complex formation (complex between Glycine and water). In the complex the hydrogen bonding complexation of the $H_2O$ seems to be with both $NH_2$ and COOH groups of the glycine. Interestingly we found that the exit channel product complex to be marginally more stable (0.1 kcal/mol) than that the glycine and water alienated. Being a stable complex it might help to prevent the photochemical degradation of glycine, a phenomenon needs separate and further investigations. At the end, under suitable conditions, product-complex will dissociate endothermically to give the glycine and water separated. We have also investigated the effect of various basissets with the B3LYP method for the PES of this reaction and also the effect of various methodologies for the PES of this reaction. The detailed discussions related to these are provided in the supporting information.

### *3.3. Effect of excess water molecules:*

As we have seen in the earlier case of two water molecules, the catalytic effect exhibited by the extra water molecule is very significant in reducing the barrier by an amount of around 12.6 kcal/mol. So to have some preliminary idea about the above mentioned catalytic effect when the water is in excess, we extended our investigation for three and four water molecules. Without going further detail into the PES, we tried to optimize the transition states for these two cases. The optimized structure of the transition states for three and four water molecules are shown in Figure 5. With the limited computational resource available with us, first we optimized both the transition states using B3LYP/6-31G method. Then to compare with our results of the other two PESs as discussed above, we did only the energy calculations at B3LYP/6-31++G(3df,2pd) level, using those optimized geometries. Then the energies were corrected for ZPVE with the zero point energies obtained during the B3LYP/6-31G optimizations.

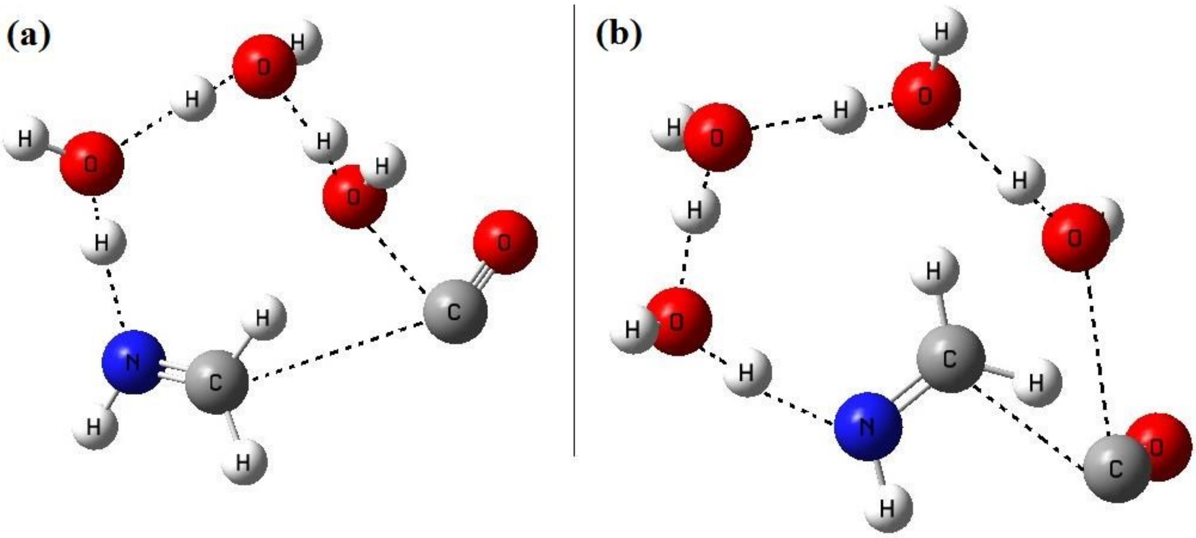

**Figure 5:** B3LYP/6-31G optimized geometries of the transition states, **(a)** with three water molecules as reactants and (b) with four water molecules as reactants.

As it can be seen from the two transition state structures, by adding extra water molecules to the reaction, the relay transport of hydrogen are happening over a longer and longer distances. Besides these the major differences observed are in the structure of the transition state, i.e. the positioning of the CO molecule. For the one $H_2O$ case, the CO and $H_2O$ are in the same side of the plane, and for the two $H_2O$ case, though the CO position is shifted a little bit, the two $H_2O$ molecules and the CO are still in the same side of the plane (this is perpendicular to the molecular plane of the $CH_2$=NH, or we can say, above the molecular plane of the $CH_2$=NH). With the three $H_2O$ and four $H_2O$, the situations are quite similar in the sense that all the $H_2O$ and the CO are above the molecular plane of the $CH_2$=NH. The major differences as stated earlier are with respect to the positions of CO molecules in these two cases. For $3H_2O$, the CO molecule is just above the C-N bond axis of the $CH_2$=NH molecule, whereas for $4H_2O$, the CO molecule is away from the C-N bond axis of the $CH_2$=NH molecule. For the $4H_2O$ case, the 4H2O are in one side and the CO is in the opposite side with respect to the C-N bond axis of the $CH_2$=NH molecule. Thus it can be imagined that this drastic shift in the positions of the CO molecules in these two cases might have some significant effect on the energetics of these two transition states. After comparing the energetics of these two transition states, we found that the results were quite surprising and indicate that both the transition states are now more stable than the reactants. For the case of $3H_2O$ as reactants, the transition state [Figure 5(a)] is around 10.0 kcal/mol below the reactants, and for $4H_2O$, the transition state [Figure 5(b)] is around 13.8 kcal/mol below the reactants. Such a situation gives a clear indication that with excess water molecules as the reactants, will definitely has a significant catalytic effect in making the reaction feasible in the low temperature conditions.

### *3.4. Possible Interstellar Applications:*

Though the interstellar time scale is large, still these kinds of reactions are kinetically less probable owing to the large number of molecules involved in the reaction process. As the reaction proceeds through the formation of a stable complex (a super molecule), the kinetic behavior of the reaction can be expected to be unimolecular. The only problem arises here is the probability of the formation of this super molecule or the stable complex and this largely depends on the molecular composition of the ISM. It is well known that the CO and $H_2O$ are among the most abundant molecules in the ISM (in fact it is believed that CO is the second most abundant molecule in the ISM) besides the hydrogen[39-41]. On the basis of this, along with the large concentrations of the $H_2O$ available in ISM, formation of this complex is fairly probable. Once the complex is formed the reaction will precede towards a unimolecular kinetics pathway to give glycine as an end product.

As extreme temperature conditions are prevailing in the ISM, we tried to explore the possibility of this reaction in both hot-cores and cold interstellar clouds. As part of this we first tried to find whether the reactants are available in those hot-cores and cold interstellar clouds, or not? Methanimine ($CH_2NH$) was first detected in Sgr B2 by Godfrey et al.[22], then subsequently has been found in many other hot core sources[23], and also recently Salter et al. detected it in the ultraluminous infrared galaxy (ULIRG) Arp 200 which is 250 million light years away, with the Arecibo radio telescope; certainly a remarkable discovery[24]. Interestingly, besides the availability in hot cores, $CH_2$=NH was also observed to be present in the quiesceny gas at the so-called "radical-ion peak" along the Orion ridge, where the temperature is about 20K and also expected to be present even at regions of 10K or low temperatures[23]. Availability of CO and $H_2O$ in the through the ISM are well known[39-41]. In the interstellar medium (ISM), hot cores are the dense and warm regions consisting of gases and dusts, which are rich in exotic gas chemistries[40,41]. High temperature in those hot cores (around 200K - 1000K) is capable of facilitating most of the high barrier reactions[40]. Analysis of the PES shows that there is a reasonably large barrier for this reaction for the cases of one and two water molecules. We believe that with the existing condition in the hot-cores of ISM and where water is not in very large excess the reaction might proceed through the paths shown in figures 1 and 4 and the large reaction barriers will not be able to act as a bottleneck to this reaction to happen. On the other hand the feasibility of this reaction in the cold interstellar clouds, where a large amount of water exists as water-ice and the temperature is extremely low, is affirmative only if there are three or more water molecules involved in the reaction. Our preliminary results on the transition state analysis for three water molecules involved in the reaction process shows that, the transition state is even more stable than the reactants. This makes the entire process thermodynamically favourable to happen in the extreme low temperature conditions existing in the cold interstellar clouds. In the low temperature conditions, these transition states being lower in energies comparted to the reactants, the exothermic nature of the reaction will drive the reaction. Moreover though probability of tunnelling can be expected to extremely low[38], but owing to the exhibited prominent proton dynamics, such a phenomenon can't be completely ruled out[37].

## 4. Conclusions:

We have discussed a reaction for the possible interstellar formation of glycine from $CH_2$=NH, CO and $H_2O$ using computation calculations. We have carried out the complete PES analysis for this reaction using various methodologies. Our calculations show that the reaction is having a large barrier height, indicating that such a reaction is only feasible in the hot core regions of the ISM. We have also shown the catalytic role of an extra water molecule in reducing the barrier height, which can further enhance the rate and thus a clear indication that excess water is going to assist the reaction strongly in the hot core regions of ISM. The catalytic role of the extra water molecule is explained by the relay hydrogen transport effect of the water. With the expectations that more number of water molecules as reactants (more than two water molecules) will be able to reduce the barrier significantly to a very low value, we carried out some preliminary investigation for the cases with three and four water molecules as reactants. Our preliminary studies related to finding the transition states for these two cases indicates that the respective transition states were found to be more stable than the reactants. Now with the transition states being lower in energy compared to the reactant, we can predict that this reaction will also be feasible in the cold interstellar clouds, and the exothermic nature of the reaction will be the driving force for this reaction to happen in such extreme low temperature conditions. A more detailed PES analysis of the reactions related to three and four water molecules needs further investigations to have an idea about the complete reaction profile. We hope that this work will be able to contribute to our future understanding of the formation of glycine in the ISM as well as its synthesis in the laboratory.

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**Supplementary Information:** Potential energy surfaces for the MP2 method for the reaction, $CH_2$=NH+CO+1$H_2O$ and $CH_2$=NH+CO+2$H_2O$ are shown in Figures S1 and S2 respectively. Similarly, for the reaction $CH_2$=NH+CO+$H_2O$-$H_2O$ (binary complex) the PESs for B3LYP and MP2 methods are shown in Figures S3 and S4 respectively. Optimized structures with important geometric parameters for MP2 as well as B3LYP methods are shown in Figures S5-S8. Table S1 summarizes the optimized geometries of the TS for the $CH_2$=NH+CO+1$H_2O$ reaction for various methodologies and Table S2 summarizes the optimized geometries of the TS for the $CH_2$=NH+CO+2$H_2O$ reaction case for various methodologies. Table S3 and S4 are related to the effect of various basissets and methodologies respectively for the reaction of $CH_2$=NH, CO with one $H_2O$. Similarly, Table S5 and S6 are related to the effect of various basissets and methodologies respectively for the reaction of $CH_2$=NH, CO with two $H_2O$.

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## TOC Graphics

# Possible interstellar formation glycine from the reaction of $CH_2$=NH, CO and $H_2O$: Catalysis by extra water molecules through the hydrogen relay transport

Authors: Zanele P. Nhlabatsi, Priya Bhasi, Sanyasi Sitha*

Department of Chemistry, University of Johannesburg, PO Box 524, Auckland Park,
Johannesburg, South Africa 2006