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Possible interstellar formation of Glycine through a concerted mechanism: A computational study on the reaction of CH_2=NH, CO_2 and H_2

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Abstract: Glycine being the simplest amino acid and also having significant astrobiological implications; intensive investigations have been carried out in the past, starting from its detection in the interstellar medium (ISM), to analysis of meteorites and cometary samples, to laboratory synthesis as well as computational studies, on the possible reaction paths. In this present work quantum chemical calculations have been performed to investigate possible interstellar formation of glycine via two different paths;(1) in a two-step process via a dihydroxy carbene intermediate and (2) through a one-step concerted mechanism, starting from the reactants like, CH_2=NH, CO, CO_2, H_2O and H_2. For the two reactions representing the carbene route, it was observed that the formation of dihydroxy carbene from either CO + H_2O or $CO_2 + H_2$ are highly endothermic with large barrier heights, whereas the subsequent step of interaction of this carbene with CH_2=NH to give glycine is exothermic as well as barrier less. Based on this observation it is suggested that the formation of glycine via the carbene route as a least favourable or even unfavourable path. On the other hand the two reactions, CH_2=NH + CO + H_2O and CH_2=NH + CO_2 + H_2 representing the concerted paths were found to be favourable in leading to the formation of glycine. After an extensive study on the first concerted reaction in our previous work (***Phys. Chem. Chem. Phys. 2016,18, 375-381***), in this work a detailed investigation has been carried out for the second concerted reaction, CH_2=NH + CO_2 + H_2 which can possibly lead to the interstellar formation of glycine. It was observed that this reaction proceeds through a large barrier and at the same time the transition state shows prominent hydrogen dynamics, indicating a tunnelling possibility for this reaction. Based on these observations possible formation of glycine via this reaction in hot-cores and in cold interstellar clouds has been proposed. The cold-core possibility of this reaction is argued on the basis of phenomenon of tunnelling assisted by a van der Waals' complex.

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1. Introduction:

One of the intriguing questions associated with the genesis of life is related to the formation of essential life elements, i.e., the amino-acids[1-2]. 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 glycine begins with the availability of the laboratory spectra for it[3] and since then astronomers have been searching for the glycine for decades, but without any precise conclusions[4-6]. This is in spite of the fact that many amino-acids including the glycine have been found on meteorites and even in comets, and moreover the distinct isotopic signature of those amino acids are indicative of their extraterrestrial origin[7-18]. One of the key discovery is the detection of glycine in the pristine cometary samples reverted back by NASA STARDUST mission[18]. These interesting discoveries put forward a most obvious question on “how these complex molecules are formed in the interstellar medium?” To find an answer to this, many experimental as well as theoretical studies have been carried out in the past and various reaction paths have been proposed for the interstellar formation of glycine[19-33]. In a recent study “***Discovering chemistry with an ab initio nano-reactor***” Wang et al. have shown that the formation of glycine is possible via numerous pathways[34]. This study deals with a highly accelerated first-principle molecular dynamics simulation of the classic Urey-Miller experiment, where the initial reactants were H_2, CO, H_2O, NH_3 and CH_4[34]. As shown in their study, there are two competing channels for the formation of Glycine from CO, H_2O and CH_2=NH (Methanimine)[34].

Reaction 1: $$CO + H_2O \xrightarrow{Step-1} HO - \ddot{C} - OH \xrightarrow[+CH_2 = NH]{Step-2} Glycine$$

Reaction 2: $$CH_2 = NH + CO + H_2O \longrightarrow Glycine$$

Reaction 1 shows that the first step is the formation of a dihydroxy carbene from the reaction between CO and H_2O, which in the subsequent step (step-2) reacts with CH_2=NH to give glycine as the end product. On the other hand, as shown in reaction 2, CO, H_2O and CH_2=NH react with each other through a concerted reaction mechanism to produce glycine directly. Similar to the above two proposed reaction channels, we have proposed two more reaction channels which are not studied in the work of Wang et al.[34] and are shown below.

Reaction 3: $$CO_2 + H_2 \xrightarrow{Step-1} HO - \ddot{C} - OH \xrightarrow[+ CH_2 = NH]{Step-2} Glycine$$

Reaction 4: $$CH_2 = NH + CO_2 + H_2 \longrightarrow Glycine$$

Reaction 3 is very much similar to the reaction 1, where in the first step formation of a dihydroxy carbene happens to be from the reaction between CO_2 and H_2 and the second step is same as reaction 1. On the other hand, though reaction 4 proceeds through a concerted mechanism to form glycine as the end product like that of the reaction 2, but the initial reactants are CO_2, H_2 and CH_2=NH instead. In our previous work using computational calculations we have already studied the detailed mechanistic aspect of the reaction 2 and proposed the interstellar feasibility of this reaction[35]. Analysis of reactions 1 and 3 shows that, the first step in both the reactions is the formation of dihydroxy carbene. A search of the earlier literature showed few studies related to the dissociation of this carbene, where some cases leads to H_2O + CO and some other cases leads to H_2 + CO_2[36-39]. So, in this work we have carried out the computational studies of the potential energy surfaces of [H_2O + CO] and [H_2 + CO_2] leading to the formation of dihydroxy carbene. The second step for both the reaction 1 and 3, is the formation of glycine from the interaction of the dihydroxy carbene with methanimine. A search of the earlier literature showed that mass spectral fragmentation of glycine leads to the CH_2=NH and dihydroxy carbene combinations[40]. So in this work we have carried out computation studies on the potential energy surface of [CH_2=NH + :C$(OH)_2$] leading to the formation of glycine. On the other hand we were not able to find any studies related to the formation of glycine via reaction 4 in a concerted way. So, to know whether such a reaction is feasible of not, we found some interesting evidences. Interestingly some of the works by Miller it has been shown that glycine is the only amino acid formed from the CO and CO_2 model atmospheres[41]. In their prebiotic synthesis experiments they have shown that, when the H_2/CO_2 ratio is < 1.0, the yields reduce drastically[42]. Besides these works of Miller[41-43], three recent works, one, "***Low energy fragmentation of protonated glycine***" of Rogalewicz et al.,[44] second, "***Soft x-ray ionization induced fragmentation of glycine***" by Itala et al.[45] and the third one "***X-ray induced irradiation effects in glycine thin films: A time-dependent XPS and TPD study***" by Tzvetkov et al.[46] also suggest the formation of CO_2 as well as H_2 from the fragmentations of glycine. So, in this work we have carried out computational calculations for the potential energy surface of the reaction and discussed its interstellar feasibility.

2. Computational Methods:

All quantum-chemical calculations have been performed using Gaussian 09 package and the geometries of all the stationary points in the PES have been visualized using GaussView program.[47] In this work, all DFT (density functional theory) calculations were performed by using the B3LYP exchange–correlation functionalities theoretical level,[48,49] using 6-31++G(d,p) basis set, unless otherwise mentioned. Harmonic vibrational frequencies were computed to evaluate the zero-point vibrational energy (ZPVE) corrections, which have been included in all the reported energies in this work. It is notable that no imaginary frequencies were found for all the minima in the PES at all of the theoretical levels investigated in this work. At the same time transition states were confirmed from the analysis of their frequencies, by ensuring that only one imaginary frequency for each of those transition states. We have also carried out analysis of the displacement vectors for the imaginary frequencies of those transition states, to ascertain that the transition states were structurally true transition states, and also confirmed them from their IRC (intrinsic reaction coordinates) analysis[50]. As reaction 4 is crucial to this study, so only for this reaction calculations using various methods like, B3LYP[48-49], X3LYP[51], B3PW91[48,52], HF, O3LYP[53], CBSQB3[54], MP2[55,56], MP2(Full)[55,56] and various composite methods which are known for accurate energy predictions, like, G3[57], G3B3[58], G3MP2[59], G3MP2B3[58] have also been carried out. When computed data for various methods were analysed it was observed that they all predict a similar kind of behaviour in the PES.

3. Results and Discussions:

3.1. Formation of Glycine via the carbene route:

Both reactions 1 and reaction 3 represent the formation of glycine via dihydroxy carbene route. In case of reaction 1, this carbene is formed from the reaction of CO with H_2O and in case of reaction 3, it is formed from the reaction of CO_2+H_2. The second step in both the reactions is the subsequent reaction of this dihydroxy carbene with CH_2=NH to give glycine. The computed PESs for all these steps involved in the reactions 1 and 3 are shown in Figure 1.

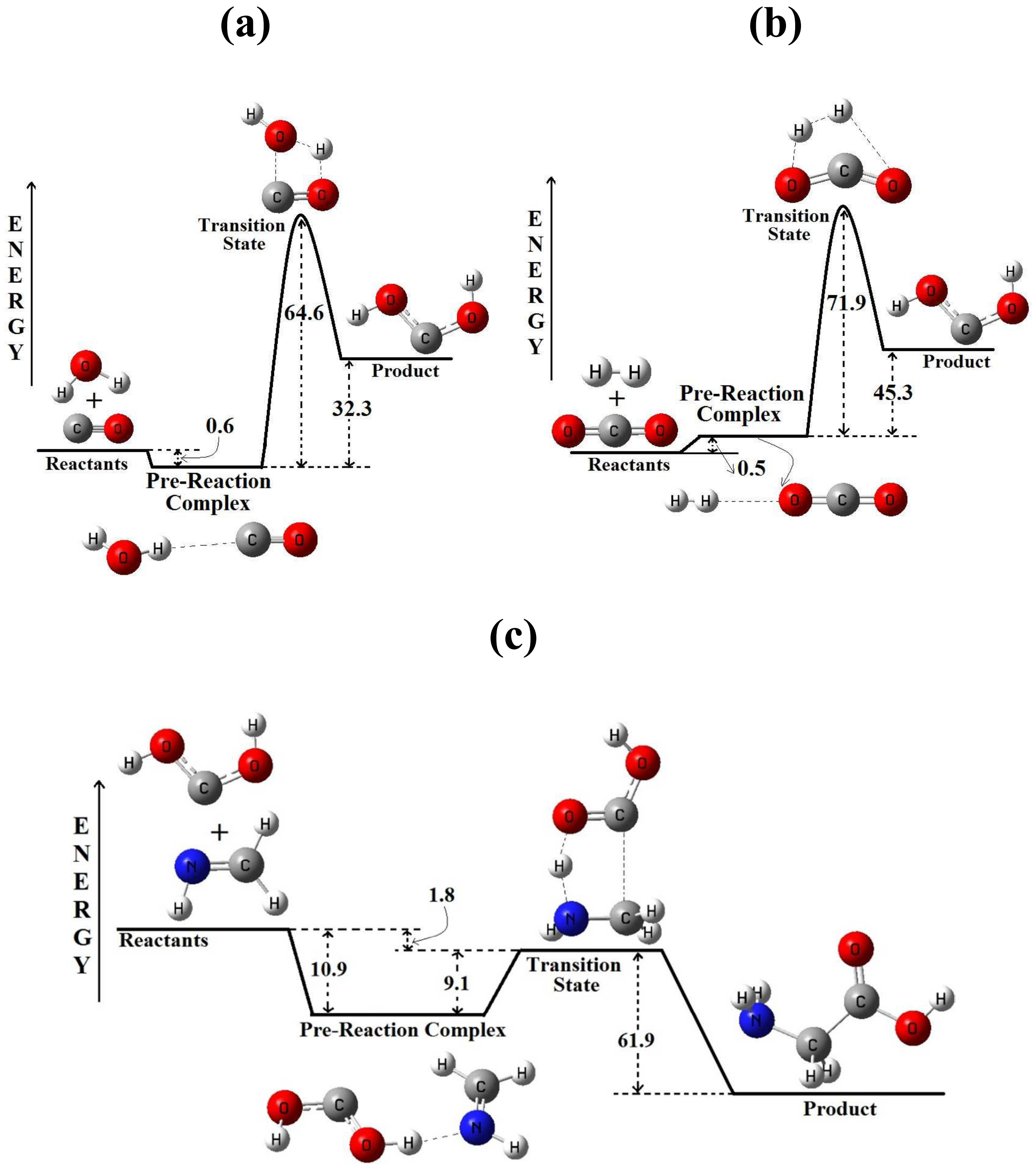

Figure 1: PES of the reactions, (a) CO + H_2O → :C(OH)$_2$, (b) CO_2 + H_2 → :C(OH)$_2$, and (c) :C(OH)$_2$ + CH_2=NH → Glycine, calculated using B3LYP/6-31++G(d,p) method. All the energies reported here are ZPVE corrected and are in the units of kcal/mol. Diagram is not to scale.

Optimized geometries of all the stationary points in these PESs are provided in the supporting information. Analysis of the PESs shows that the formation of dihydroxy carbene, either from the CO + H_2O [Figure 1(a)] or from CO_2 + H_2 [Figure 1(b)] reactions, is endothermic in nature. In the former case, the product dihydroxy carbene is 31.7 kcal/mol higher in energy compared to the reactants, and in the latter case, the dihydroxy carbene is 45.8 kcal/mol higher in energy compared to the reactants. Two barriers in these two reaction surfaces were also located, and it was observed that the barrier of transformation from CO + H_2O and CO_2 + H_2 leading to the formation of dihydroxy carbene are 64.0 kcal/mol and 72.4 kcal/mol respectively with respect to their respective reactants. Also worth to mention here is that both the reaction passes through the formations of pre-reaction complexes in their respective reaction paths. In the case of CO + H_2O leading to the formation of dihydroxy carbene, the pre-reaction complex is 0.6 kcal/mol stable than the reactants and at the same time the nature of interaction existing in this pre-reaction complex can be considered as a hydrogen bonded type of interaction a favourable Keesom type of interaction (the distance between the H-atom of H_2O and the C-atom of CO is 2.369 Å). Whereas in the case of CO_2 + H_2 leading to the formation of dihydroxy carbene, the pre-reaction complex is seems to be 0.5 kcal/mol higher in energy than the reactants and the destabilizing nature of interaction (distance between the H-atom of the H_2 and the O-atom of the CO_2 is 2.992 Å) in this pre-reaction complex can be attributed to the non-existent dipole moments of these two interacting molecules. Analysis of the reaction step leading to the formation of glycine from the interaction of the dihydroxy carbene with CH_2=NH [Figure 1(c)] shows that the reaction passes through the formation of stable complex (10.9 kcal/mol stable compared to the reactants. The stability of the pre-reaction complex can be attributed to the strong hydrogen bonding interaction between the H-atom of the dihydroxy carbene and N-atom of the CH_2=NH. The nature of the H-bonding is very strong as can be evidenced from the small H-bond distance of 1.711 Å) and a low lying transition state (the transition state is 1.8 kcal/mol below the reactants). Though the transition state of the reaction is below the reactants, presence of a pre-reaction complex in its reaction path shows that the reaction is not truly barrierless. This reaction step was found to be exothermic in nature, where the product, glycine was found to be 63.7 kcal/mol more stable than the reactants. By analysing the energetics, we can say that enothermic nature of the reactions along with large barrier heights, leading to the formation of the dihydroxy carbene can put a question mark on the possibility of the formation of glycine via the carbene route. Detailed investigations on the feasibility of glycine formation via this carbene route can be found in the section 3.3.

3.2. Formation of Glycine via concerted mechanism:

Reactions 2 and 4 represent the formation of glycine via a concerted mechanism. In our previous work we have carried out a thorough computational study on the reaction 2 (formation of glycine from CO + H_2O + CH_2=NH) and discussed its interstellar significance[35]. So, this work is only focused on the reaction 4, which represents the formation of glycine via concerted mechanism from the reaction of CO_2 + H_2 + CH_2=NH.

3.2.1. PES of the reaction, CH_2=NH +H_2 + CO_2 → Glycine:

Computed PES for the reaction 4, i.e. the reaction of CO_2 + H_2 + CH_2=NH leading to the formation of glycine is shown in Figure 2. As this reaction is central to this study, investigations have been carried out to know the effect of various basissets on the PES and the results discussed here are from the B3LYP/6-31++G(3df,3pd) method [a comparison of the effects of various basissets on the PES of this reaction is provided in the supporting information]. Also, if required the B3LYP/6-31++G(d,p) results for this reaction can be compared directly with the results of the reactions 1 and 3. Besides the effects of various basissets, an effort has been made to evaluate the effect of various methods on the PES of this reaction (discussed in the section 3.2.3).

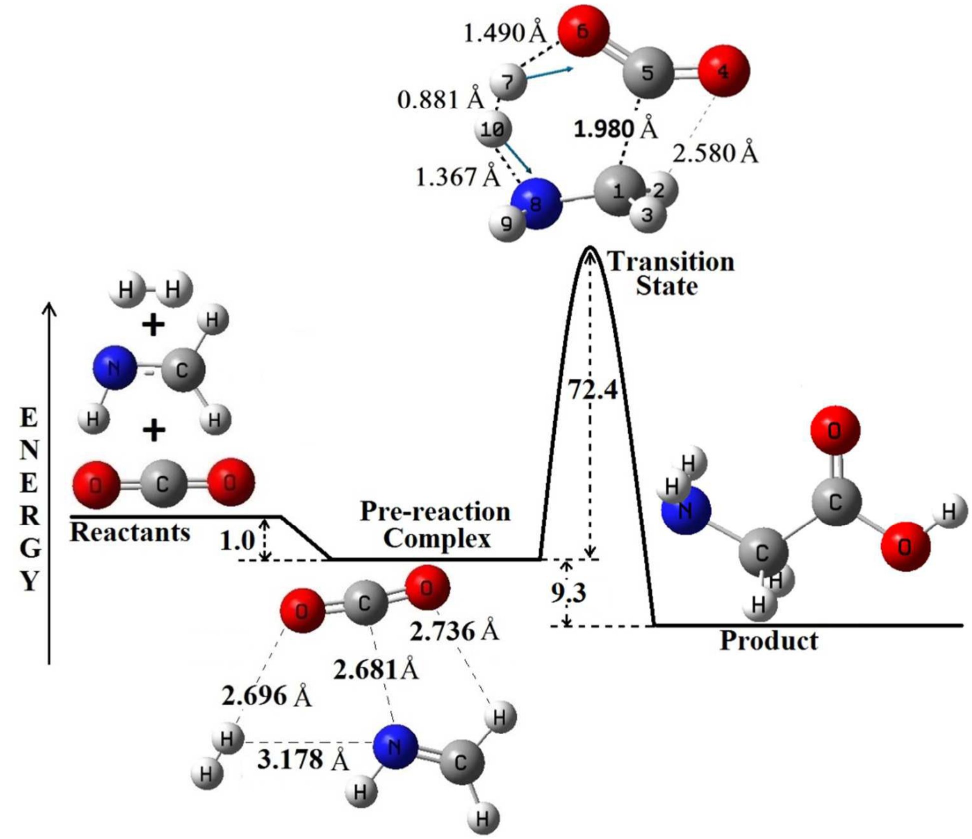

Figure 2: PES for the reaction, $CH_2{=}NH + CO_2 + H_2 \rightarrow$ Glycine, calculated using B3LYP/6-31++G(3df,3pd) method. All the energies reported here are ZPVE corrected and are in the units of kcal/mol. Diagram is not to scale.

Analysis of the PES shows that interaction of the reactants first leads to the formation of a marginally stable pre-reaction van der Waals' complex (vdw-complex), which subsequently passes through an energetically large barrier to reach the product, glycine. Analysis of the structures of the reactants show that CH_2=NH has a fully planar structure (Linear structures of CO_2 and H_2 are well known). Analysis of the structure of the vdw-complex shows that linearity of CO_2 is still conserved and there exist many van der Waals types of interactions between the reactants. Analysis of the structure of the transition state (TS) indicates that it is a 6-membered cyclic transition state. As this TS central to this reaction a detailed discussion related to the structure as well as existing nature of interactions is provided in the section 3.2.2. Analysis of the product structure indicates a three dimensional structure for glycine. Structures of all the stationary points are provided in the supporting information. Energetically, the pre-reaction complex was found to be 1.0 kcal/mol stable compared to the reactants (3.1 kcal/mol in MP2 method. See Supporting information), indicating a marginally stable vdw-complex. At the same time TS was found to be 71.4 kcal/mol higher in energy than the reactants (72.4 kcal/mol above the pre-reaction complex). This is a clear indication that the forward reaction proceeds through a very large barrier and presence of such a large barrier in the reaction path leading to the formation of glycine, might act as a bottleneck to this reaction. Interstellar feasibility of this reaction is discussed in details in the section 3.3. Analysis of the product shows that it is only 10.3 kcal/mol more stable compared to the reactants (9.3 kcal/mol more stable with respect to the pre-reaction complex), indicating that the reaction is reasonably exothermic in nature. Thus, we can say that at the time when the exothermic nature of the reaction predicts the thermodynamic feasibility of this reaction, the large activation energy puts a question mark on the kinetics of this reaction.

3.2.2. Structure and nature of interactions in the TS for the reaction 4:

Structure of the TS (Figure 2) shows a well synchronized placing of the reactants, where the C-atom of the CO_2 is close to the C-atom of the CH_2=NH, and at the same time H_2 is in the close proximity of both CO_2 and CH_2=NH. In the TS, while the geometry of the H_2 molecule is almost intact (a slight increase in the bond distance compared to the reactant H_2), CO_2 and CH_2=NH show some structural deviations. In the TS, interestingly CO_2 is now has a slightly bent structural arrangement rather than its original linear structure. On the other hand, in the TS, CH_2=NH is no more planar, rather the CH_2-unit of the molecule shows some pyramidality. Further analysis of the structure of the TS shows that the approach of the CO_2 + H_2 towards the CH_2=NH is perpendicular to the CH_2=NH molecular plane (perpendicular to the π-cloud of CH_2=NH). To know the nature of interaction existing in the TS, electrostatic potentials of the reactants were analyzed and the ESP maps for the reactants are shown in Figure 3.

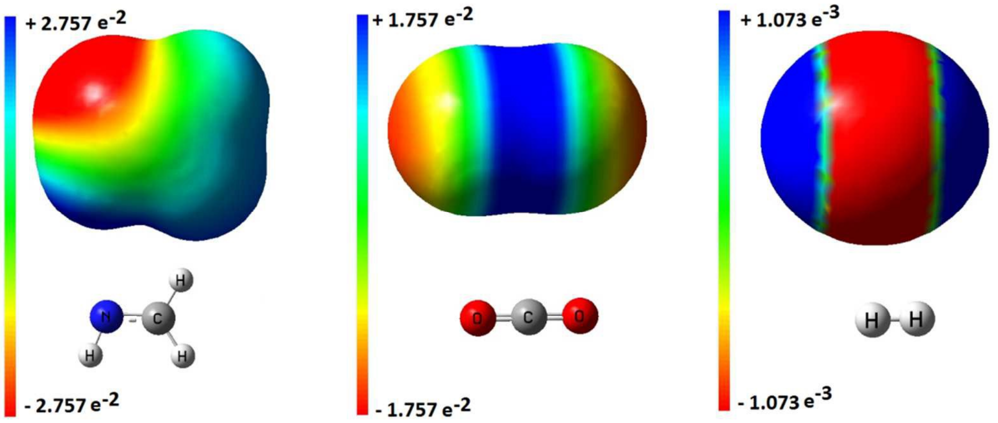

Figure 3: Computed ESP maps of CH_2=NH, CO_2 and H_2 calculated from the B3LYP/6-31++G (3df,3pd) method at 0.001 au electron density surfaces. Quantitative values of electrostatic potentials are also in au.

Analysis of the ESP maps shows that: (I) For H_2: two ends have positive potentials and the central bond region is having the negative potential, (II) for CO_2: two Oxygen ends have negative potentials and the central C-atom has positive potential, (3) for CH_2=NH: except the region around N-atom (showing negative potential) all other regions have positive potentials. Fitting these ESP maps with the TS structure shows a well synchronized approach of the H_2+CO_2 towards CH_2=NH, where: (i) For H_2, while one of the H-atom is interacting with the N-atom of CH_2=NH, the other H-atom is interacting with one of the O-atom of the CO_2. (ii) For CO_2, interestingly which shows bent structure (might have arisen due to reduce in bond order, thus reducing the positive potential in the central carbon region), the other O-atom interacting with the H-atom of the CH_2-unit of the CH_2=NH (exhibiting a kind of CHO hydrogen bonding type of interaction and the hydrogen bond distance is 2.580 Å). Thus it can be said that the bent structure of the CO_2 and pyramidality of the CH_2-unit of the CH_2=NH, facilitates a well synchronized electrostatic approach of the reactants towards each other.

3.2.3. Effects of temperature of the transition state:

To account for the effect of temperature on the transition state calculations have been carried out using B3LYP/6-31++G(d,p) optimized geometry of the transition state. Without further geometric optimization we have carried out only the thermal energy corrections to the transition state energies at various temperatures (taking the optimized geometry obtained in the above method, single point energy and thermochemistry calculations have been carried out at the same level of theory using various temperature conditions). Results related to these calculations are shown in Table 1.

Table 1: Results of effect of temperature (in Kelvin) on activation energy of the $CH_2=NH + CO_2 + H_2 \rightarrow$ Glycine reaction. Thermal energy corrected total energies (E_T = Sum of the electronic and thermal energies) are in Hartrees and relative energies are in kcal/mol calculated using the B3LYP/6-31++G(d,p) method.

Temperature	E_T	Relative Energy
20	-284.238432	-3.2
50	-284.238137	-3.0
100	-284.237548	-2.6
150	-284.236793	-2.2
200	-284.235840	-1.6
250	-284.234679	-0.8
298.15	-284.233360	0.0
350	-284.231723	+1.0
400	-284.229944	+2.1
450	-284.227983	+3.4
500	-284.225855	+4.7
550	-284.223577	+6.1
600	-284.221162	+7.7

Analysis of the results from the Table 1 shows that compared to the room temperature condition, the barrier height getting reduced smoothly when approaching the lower temperature conditions. At 20 K the barrier height is reduced only by 3.2 kcal/mol and may not be considered as a significant. On the other hand when approaching the higher temperature conditions, the barrier height is becoming larger and larger continuously. At 600 K the barrier height is increased by 7.7 kcal/mol compared to the standard room temperature condition. In the light of this observation for the higher temperature conditions, one can say that the limiting value of the barrier height has not yet reached.

3.2.4. Effects of various methods on the PES of the reaction 4:

To account for the accuracies in the energetics, calculations have been carried out on the PES of the reaction 4 using various methodologies and the results are shown in Table 2. Based on our observations related to effect of various basissets on the B3LYP method, during the calculations using various methods, where required a basisset like, 6-31++G(3df,2pd) was used. Analysis of the results shows that all the methods predict more or less similar trend in the energetics of the reaction surface except for the Hartree-Fock method.

Table 2: Results of effect of various methods on the potential energy surface of the $CH_2=NH + CO_2 + H_2 \rightarrow$ Glycine reaction. Where $\mathbf{\Delta E_1 = E_{TS} - E_{REACTANTS}}$, $\mathbf{\Delta E_2 = E_{TS} - E_{PRODUCT}}$ and $\mathbf{\Delta E_3 = E_{REACTANTS} - E_{PRODUCT}}$. All the energies reported here are ZPVE corrected and are in the units of kcal/mol.

Methods	ΔE_1	ΔE_2	ΔE_3	**Methods**	ΔE_1	ΔE_2	ΔE_3
HF	110.7	117.6	6.9	**Full MP2**	70.8	85.9	15.1
B3LYP	70.4	80.1	9.7	**CBS-QB3**	75.5	91.4	15.9
X3LYP	67.9	81.1	13.2	**G3**	75.8	87.5	11.7
O3LYP	73.0	78.3	5.3	**G3MP2**	76.7	86.7	10.0
B3PW91	67.0	81.2	14.2	**G3B3**	76.5	87.9	11.4
MP2(FC)	71.7	85.1	13.4	**G3MP2B3**	77.3	87.1	9.8

For HF method which doesn’t account for electron correlations, the deviations are large and the barrier height of 110.7 kcal/mol for the forward reaction seems to be highly overestimated. Among the DFT methods O3LYP methods predicts a slightly large barrier approximately 2.5 kcal/mol higher compared to B3LYP method. On the hand X3LYP and

B3PW91 methods predict a slightly lower in barrier height by approximately 2.5 and 3.5 kcal/mol respectively compared to B3LYP method. Analysis of the results from MP2 methods shows that while full MP2 method predicts a similar barrier like that of B3LYP method, the frozen core approximation of MP2 predicts the barrier to be approximately 1.3 kcal/mol higher compared to B3LYP method. But, on the other hand the MP2 methods predict a comparatively more exothermic nature of the reaction like that of the X3LYP and B3PW91 methods, compared to the B3LYP method. Analysis of the results of the complete basisset method, CBS-QB3 shows that the reaction is more exothermic in nature and proceeds through a comparatively larger barrier (around 5 kcal/mol higher) as compared to the B3LYP method. Results from various composite methods show that the barrier height is larger compared to B3LYP method (approximately 5.5 kcal/mol higher for G3 and 7.0 kcal/mol higher for G3MP2B3 methods). Analysis of all these results gives a clear indication that the trend is similar and also the reaction proceeds through a large barrier definitely.

3.3. Interstellar possibility of the glycine formation:

As extreme temperature conditions are prevailing in the ISM, we tried to explore the possibility of formation of the glycine in both hot-cores as well as cold interstellar clouds, via the carbene route and via the concerted route. 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[60,61]. High temperature in those hot cores can facilitate most of the high barrier reactions and sometimes even the endothermic reactions[60]. On the other hand interstellar clouds have varied properties depending on the temperature of the gas cloud, but are usually have extremely low temperatures[2]. Occasionally gas clouds are found close to a very hot star which heats the gas to about 10,000 Kelvin and thus can facilitate many high energy barrier reactions as well as endothermic reactions, which are practically impossible in the low temperature conditions[62]. At the same time, in the coldest and densest regions of the interstellar medium one can find clouds whose cores contain molecular gases, primarily molecular hydrogen (H_2) gas and these molecular clouds have temperatures of only about 10 Kelvin[2,62].

3.3.1.: Interstellar feasibility of glycine formation via the carbene route:

As discussed earlier, reactions 1 and 3 represent the interstellar formation of the glycine via the carbene route. In both the reactions the first step is the formation a dihydroxy carbene. For both the reactions the second step is same, where the generated carbene react with CH_2=NH to give glycine. In both the reactions it was found that the second step is highly exothermic in nature and also at the same time, located pre-reaction complex and the transition state being lower in energy than the reactants. Such a situation can make the reaction very much feasible in both hot-cores as well as cold interstellar clouds. But, the real problem arises in the first steps of both the reactions. As shown in Figure 1(a) and (b), for both the reactions formation of the dihydroxy carbene highly endothermic in nature and also are associated with large reaction barriers. As reactions with a barrier or any endothermic reactions are completely forbidden to happen in the interstellar clouds, where the temperatures are extremely low[2]; one can say that the formation of the dihydroxy carbene in those cold interstellar clouds will definitely not happen either via the CO + H_2O reaction or via the CO_2 + H_2 reaction. But, on the other hand owing to the prominent hydrogen dynamics exhibited by all the transition states in the carbene route and in the light of some recent studies related to possibility of tunnelling in endothermic reactions at very low temperature condition (powered by Tunnelling Ready States)[63-65], possible formation of glycine via the carbene route assisted by tunnelling needs a separate investigation to give it a second thought. But, at this stage one can say that formation of glycine through the carbene route via the reactions 1 and 3 seems impossible in the cold interstellar clouds. With the hope that presence of other molecules in these reaction paths might be able to bring some changes to the course of these reactions, we have tried to introduce the water molecule in the reaction path in order to know whether it is going to reduce the barrier heights for the reactions shown in Figure 1(a), (b) and (c) or even the nature of these reactions. After many attempts with various possible input geometric orientations of the reactants, we were not able to locate any transition states in the reaction potential energy surfaces of these three reactions. As we have not carried out similar investigations with any other molecules rather than water, hence a definite conclusion can't be made at this stage on the role of other molecules on these routes of formation of Glycine.

On the other side, in the extreme high temperatures of the hot-cores or in the gas clouds which are close to a very hot star, the feasibility of this reaction can be expected. But, analysis of the dissociation reactions of the dihydroxy carbene [reverse reactions in Figure 1(a) and (b)] to CO + H_2O and CO_2 + H_2 shows that they are 32.3 kcal/mol and 26.6 kcal/mol respectively. This gives very clear indication that the dihydroxy carbene will have very short life time and sometimes being highly unstable it might readily dissociate back to the reactants. With this stability issue associated with the dihydroxy carbene, we can say that formation of glycine via the carbene route is still doubtful even in the hot-cores of the interstellar medium.

3.3.2.: Interstellar feasibility of formation of glycine via the concerted route:

As discussed earlier, reaction 2 and 4 represent the interstellar formation of the glycine via the concerted mechanism. From these two concerted paths leading to the formation of glycine, reaction 2, where CO and H_2O are involved is already discussed in great details in our previous work[35]. There we have shown the possible interstellar formation of glycine via this route in both hot-cores as well as in cold interstellar clouds[35]. We have also discussed the catalytic role of the water molecules to show how this reaction behaves like a barrierless reaction in the presence of excess water and thus making it possible to happen in the cold interstellar clouds[35]. So, in this work we have discussed only the fate of the reaction 4 in the drastic interstellar conditions. Though the interstellar time scale is large, still the reactions where large numbers of molecules are involved in the reaction process can be expected to be kinetically less probable. As the reaction 4, proceeds through the formation of a stable pre-reaction vdw-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 and this largely depends on the molecular composition of the ISM. It is well known that hydrogen covers around 90% of the universe by number density and 75% by mass density[66]. Also, it is well known that CO_2 is one of the most abundant molecules in the ISM besides CO and H_2O[67,68]. Though CO_2 is not quite evenly distributed in the ISM, but a large abundance of CO_2 can be found in many hot cores[67] as well as colder regions of ISM as CO_2-ice[68]. Methanimine (CH_2NH) was first detected in Sgr B2 by Godfrey et al.[69], then subsequently has been found in many other hot core sources[70], 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[71]. 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[70]. On the basis of this, along with the large concentrations of the H_2 and CO_2 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 discussed earlier, reaction 4 leading to the formation of glycine proceeds through a very high barrier, which we believed can act as a bottleneck to the possibility of the reaction in the ISM. But, owing to the availability of all the three reactants in the hot-core regions[69-71,66-67], powered by the high energies of the hot cores[60], the reaction can be expected to be very much feasible. Thus one can say that the formation of glycine in the hot-core regimes of the ISM is quite feasible. On the other hand, as the reaction 4 proceeds through a very high barrier, this large barrier height can act as a bottleneck to this reaction to happen in the extremely low temperature conditions existing in the interstellar clouds. Also as discussed in the section 2.2.3., the decrease in the barrier height at lower temperature is not at all significant and thus eliminating the classical way of approaching the product by climbing the barrier. The only way this reaction will be possible at such low temperatures, if there is an operative tunnelling mechanism. To analyse the possibility tunnelling mechanism, our first check was the imaginary frequency of the TS. It is known that, one can have some qualitative information about the width of a barrier from its imaginary frequency[72], where the lower value of the TS imaginary frequency is associated with a gentler and broader barrier, and the higher value of imaginary frequency corresponds to a sharper and narrower barrier[72]. The value of imaginary frequency of the TS here was found to be around 1600i cm^{-1}. This indicates that the barrier might not be as sharper as expected. We believe that this might be due to the simultaneous proton dynamics arising from the two H-atoms. Analysis of the displacement vectors related to vibrations due to the imaginary frequency shows that two concurrent movements of H-atoms with almost sole contributions to the vibrational coefficients and that to in partially opposite vectorial directions. Such a situation might have some effect on widening the barrier to a little extent. Nevertheless owing to the considerably large value of the imaginary frequency (1600i cm^{-1}) arising from the protuberant movements of the two light H-atoms, one can happily advocate for the effects of tunnelling, especially at very low temperatures[72].

Though the above discussion related to the imaginary frequency of the TS advocates for a tunnelling phenomenon to happen in the low temperature conditions, but it is generally believed that presence of an entry channel weakly bound complex might be able to facilitate the process further [72,73]. As mentioned by Smith et al., existence of such a pre-reaction complex can manifest itself in terms of the negative temperature dependence, i.e. show the significant deviation from the Arrhenius behaviour at extremely low temperatures[73]. The vdw-complex shown in the PES of the reaction 4 (Figure 2) may not play a significant role while dealing with high temperature conditions for the reaction, but its presence will have a vital effect in extremely low temperature conditions and probably could help in facilitating the tunnelling to happen for this reaction. Though the reaction is having a very large barrier, the prominent effect of tunnelling will be able to make this reaction feasible and thus the formation of the glycine in the low temperature regime of the ISM through this concerted mechanism will possible happen. In this work qualitatively we predicted about the possibility of tunnelling from the quantitative value of the imaginary frequency of the transition state. Due to unavailability of the required computing softwares to carry out the kinetics calculations, we were unable to exactly confirm our qualitative prediction about the possibility of tunnelling. But, in view of the prominent proton dynamics, a tunnelling possibility can be advocated for this reaction at low temperature conditions.

It is generally believed that in the ISM, $CH_2=NH$ on hydrogenation reaction produces Methylamine, CH_3-NH_2[70]. This methyl amine then subsequent reaction with CO_2 produces methylammonium methylcarbamate ([$CH_3NH_3^+$] [CH_3NHCOO^-]), which after UV irradiation evolve into ([$CH_3NH_3^+$] [$NH_2CH_2COO^-$]), a glycine salt precursor, instead of glycine[74]. Though this proposed multiple-step process was not able to produce glycine as an end product, still starting with the same reactants, for the first time we were able to show a single-step reaction for the formation of glycine in the ISM. Moreover we have shown the universality of this reaction irrespective of the divergent temperature conditions existing in the ISM. Owing to the interstellar conditions, we believe that single-step reactions have advantages over the multi-step processes and hope this finding will have much more interstellar significance. Moreover with the hope that presence of other molecules in this reaction path might be able to bring some changes to the course of this reaction, we have tried to introduce the water molecule in the reaction path in order to know whether it is going to reduce the barrier height for the reactions 4. After many attempts with various possible input geometric orientations of the reactants, we were not able to locate any transition state in the reaction potential energy surface of this reaction. As we have not carried out similar investigations with any other molecules rather than water, hence a definite conclusion can’t be made at this stage on the role of other molecules on this route of formation of Glycine.

4. Conclusions:

In conclusion, in this work, using computational calculations, we have analyzed two different routes, (1) via a carbene intermediate, and (2) via a concerted reaction path for the possible interstellar formation of glycine. Based on the analysis of the potential energy surfaces for those reactions which proceed though the carbene intermediate paths, it has been suggested that the formation of glycine via this route seems impossible in the interstellar medium. The background for these suggestions comes from the endothermic natures of the reactions steps leading to the formation of this dihydroxy carbene. On the other hand one of the reactions studied in this work, CH_2=NH + CO_2 + H_2 → Glycine, which proceeds through a concerted mechanism, has been suggested as favorable path for the interstellar formation of glycine. It was found that this reaction is having a very large energy barrier and has been proposed that it will be very much feasible in the hot-core regions of ISM. At the same time, by the analysis of the nature of the barrier for this reaction, from its imaginary frequency and also the prominent proton dynamics it is exhibiting, we have advocated for the tunneling to happen. With the aid from an entry channel vdW-complex and the proposed tunneling to happen, the reaction is also suggested to form glycine easily in the colder regions of ISM, thus demonstrating its universality. The reaction though exothermic in nature, owing to the lower value of enthalpy of formation, a detailed kinetics calculations/experiment will probably be able to give an exact picture of the rate constant for this reaction for the hot-core formation of glycine. On the other hand, for the kinetics related to low temperature formation of glycine, where tunnelling plays a vital role, the simultaneous movement of the two H-atoms in the TS for this case can be viewed as a correlated many body tunnelling type[75] and also need further experimental as well as computational investigations.

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Supplementary Information: Optimized geometries for the reactants, TS, and product for the reaction 4 are shown in Figure S1 (for B3LYP method), Figure S2 (For MP2 method) and Potential energy surface for the MP2 method is shown in Figure S3. Thermodynamic data for effect of various basissets for B3LYP method on the PES of reaction 4 are shown in Table S1. Geometries of TS for various methods are shown in Table S2 (and effect of basissets in Table S3) and also the optimized Cartesian coordinates of the stationary points are provided. Besides reaction 4, optimized geometries of the stationary points for reaction 1 and 3 are also provided.

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TOC Graphics

Possible interstellar formation of Glycine through a concerted mechanism: A computational study on the reaction of CH_2=NH, CO_2 and H_2

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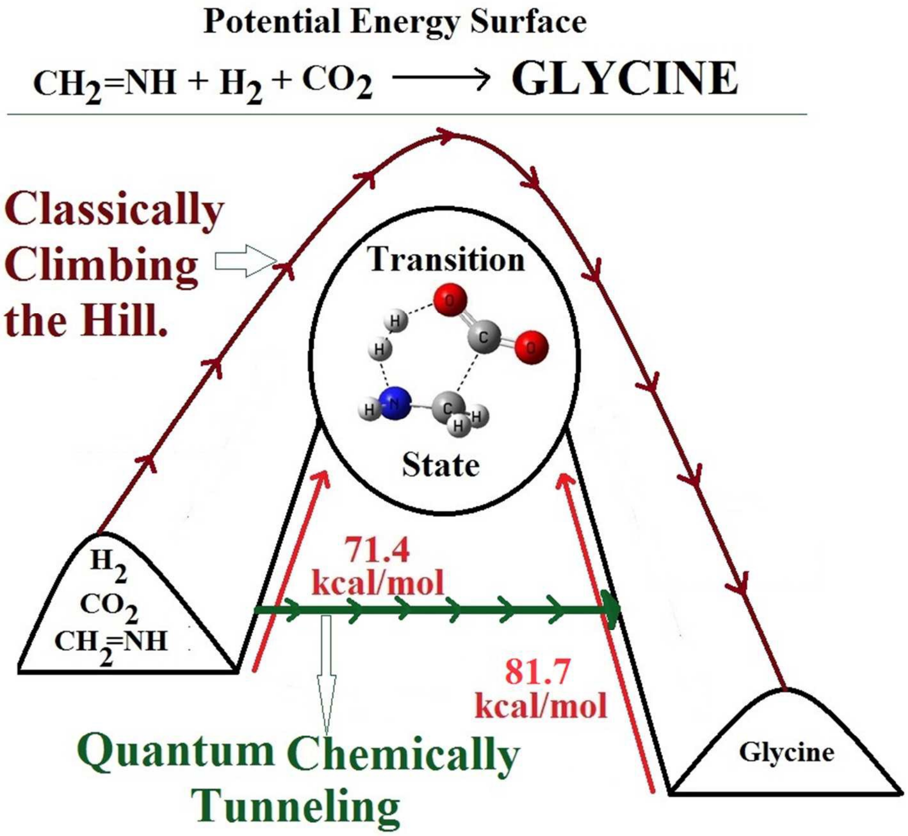

Computational studies on the reaction of CH_2=NH, CO_2 and H_2 shows the possible interstellar formation of glycine both in hot-cores and cold interstellar clouds.