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REGULAR ARTICLE

Classical dynamics simulations of interstellar glycine formation via $CH_2 = NH + CO + H_2O$ reaction

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Abstract. Formation of simple organic species such as glycine in the interstellar medium and transportation to earth via meteorites is considered to be a possible route for 'Origin of Life' on earth. Glycine formation has been proposed to occur *via* two different pathways involving formaldehyde (HCHO) and methanimine ($CH_2 = NH$) as key intermediates. In the second pathway, which is the topic of this paper, $CH_2 = NH$ reacts with CO and H_2O forming neutral glycine. In a recent article (Nhlabatsi *et al.* in *Phys. Chem. Chem. Phys.* 18:375, 2016), detailed electronic structure calculations were reported for the reaction between $CH_2 = NH$, CO and $(H_2O)_n$, $n = 1, 2, 3$, and 4, forming glycine in the interstellar media. The presence of additional water molecule(s) for this reaction reduces reaction barrier - thus exhibiting a catalytic effect. This effect was described in terms of efficient proton transfer mediated by the additional water molecule through a relay transport mechanism. In the present article, we report *ab initio* classical trajectory simulations for the interstellar formation of glycine for the above mentioned reaction with $n = 1$ and 2. The trajectories were generated *on-the-fly* over a density functional B3LYP/6-31++G(3df,2pd) potential energy surface. Our simulations indicate that the above proposed catalytic effect by the additional water molecule(s) may not be a classical effect.

**Keywords.** Classical *ab initio* dynamics; interstellar glycine.

1. Introduction

It is known today that interstellar media (ISM) contains several complex organic molecules of biological interest.[1,2] The role of amino acids in the 'Origins of Life' on earth has been discussed intensively in the literature.[3–5] It has been proposed that amino acids might have originated in the ISM and reached earth via meteorites.[3,6–11] There exists evidence for the presence of the simplest amino acid glycine (Gly) in meteorites.[12–14] Existence of Gly in ISM is still under discussion[15–17] and our understanding of Gly formation in ISM is not clear.[4] Formaldehyde (HCHO) and methanimine ($CH_2 = NH$) have been suggested[18–24] to be the possible precursors, among others,[25,26] for the formation of Gly in the ISM. Evidences[27] exist for the presence of $CH_2 = NH$ molecule in the ISM and the Gly formation via this molecule is the theme of the present article. The $CH_2 = NH$ molecule reacts with the ISM abundant CO and H_2O molecules and forms neutral Gly.

$$CH_2 = NH + CO + H_2O \rightarrow H_2NCH_2COOH \quad (1)$$
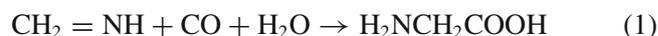
For the above reaction, detailed density functional electronic structure calculations at the B3LYP/6-31++g (3df, 2pd) level of theory (and other methods) were reported by Nhlabatsi *et al.*[28] Reaction 1 is exoergic and proceeds via formation of a stable hydrogen bonded reactant complex involving all three reactants. This *ternary* complex passes through a five-membered transition state forming Gly molecule. The calculations were also performed at MP2 level of theory and the results[28] showed only minor changes to the potential energy profile of the reaction. This work indicated a concerted type of mechanism for the formation of Gly through the $CH_2 = NH + CO + H_2O$ reaction as opposed to a stepwise mechanism proposed earlier by Rimola *et al.,*[29] for the same reaction. Density functional calculations by the latter group showed COOH· radical formation via the $CO + OH·$ reaction which afterwards reacts with the incoming $CH_2 = NH$ to form Gly radical. Here, the OH· radical results from radiative photolysis of water molecules present in the interstellar water-ice

clusters - thus indicating a catalytic role[29] exhibited by the water-ice clusters for the formation of Gly in the ISM. Following this work, Nhlabatsi *et al.*,[28] also investigated the effect of excess water molecules on reaction 1 at the same B3LYP/6-31++g(3df,2pd) level of electronic structure theory. Calculations were carried out for the reactions

$$CH_2 = NH + CO + (H_2O)_n \rightarrow H_2NCH_2COOH \\ + (H_2O)_{n-1} \qquad (2)$$
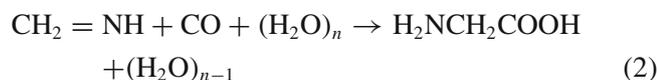
and it was found that all the reactions proceed through formation of a pre-reaction complex involving all the reactant molecules *i.e.*, reactant complexes formed from 4, 5, and 6 reactant molecules for $n = 2, 3,$ and 4, respectively. With increase in n, the barrier height for Gly formation decreases and for $n = 4$, energy of the respective transition state is lower[28] as comparison to the reactants. This decrease in the barrier height with increasing number of water molecules has been viewed as an indicator of catalytic effect by the excess water molecules for reaction 1. This effect was discussed in terms of an efficient proton transfer to the $CH_2 = NH$ reactant molecule by the additional water molecules through a relay transport mechanism.[28] Several earlier studies[30,31] in the literature have also described the ability of water molecules to help transfer proton to a reaction site.

Computational modeling is becoming a very useful tool for studying interstellar chemistry.[32,33] In the present work, we have investigated the dynamics of reaction 1 and reaction 2 (with $n = 2$) using *ab initio* classical trajectory simulations.[34,35] Trajectories were initiated at the rate-controlling transition states at interstellar temperatures and the ensuing dynamics investigated. The calculations were performed at the B3LYP/6-31++g(3df, 2pd) level of theory - the same computational method used by the previous authors[28] in their electronic structure calculations. These studies were about characterizing the potential energy surface of the reactions considered here and our interest is to study these reactions from a dynamics perspective to understand how they actually proceed in ISM. In particular, we are interested to find how the proposed hydrogen relay effect[31] by the excess water molecule helps in glycine formation.

In Section 2 we briefly discuss the potential energy surface for reactions 1 and 2 and present the computational methods and in Section 3 we discuss our simulation results. The article is concluded in Section 4

2. Potential energy surface and computational methodology

On-the-fly classical dynamics simulations[35] reported in this article were performed at density functional theory (DFT) B3LYP/6-31++g(3df,2pd) level of electronic structure theory. This method was chosen because previous work[28] showed that the features of the potential energy surface for reaction 1 were captured in this theory. Further, an appreciable number of *ab initio* classical trajectories can be generated due to the relatively low computational cost requirements for DFT methods. The simulations were performed for reaction 1 and to further investigate the catalytic effect of the excess water molecules, calculations were repeated for reaction 2 with $n = 2$. For discussion purposes, we represent reaction 1 and reaction 2 with $n = 2$ as **1W** and **2W** reaction, respectively, for the remainder of the article.

The potential energy profiles for **1W** and **2W** reactions at B3LYP/6-31++g(3df,2pd) level are presented in Figure 1. In comparison to the previous work,[28] there are small changes to the basis set we have used and the energies computed. Overall reaction profile remains the same in both the studies though a few kcal/mol difference in energies exist. Complete details of the basis set used, computed energies and geometries of all the stationary points are given in the supplementary information. As can be seen in Figure 1, reaction **1W** proceeds via formation of a stable reactant complex (RC) involving all three reactants (R) and a five membered transition state (TS) with a barrier height of 40.4 kcal/mol (measured from RC). For reaction **2W**, the RC is a hydrogen bonded complex involving four reactant molecules ($CH_2 = NH + CO + 2H_2O$). Afterwards the RC passes through a TS with a barrier height of 34.0 kcal/mol (with respect to the RC) and forms the product Gly molecule. Note that the overall barrier height for the reaction reduces from 32.9 to 18.3 kcal/mol by the addition of one extra water molecule. For reaction **2W**, a post-reaction complex (PC) also exists in the exit channel of the reaction profile which is stable by 2.2 kcal/mol as compared to the products Gly + H_2O.

For the dynamics simulations the classical trajectories were launched from the respective TSs for the **1W** and **2W** reactions. Initial conditions were chosen from a Boltzmann distribution (including zero-point vibrational energies) sampled[36] at the transition states. Reaction coordinate had a fixed temperature and the reaction coordinate momentum was set to positive for 50 % of the trajectories and negative for the rest of the trajectories. To simulate the ISM conditions the samplings were done at two different temperatures *viz.*, a higher temperature of T = 1000 K (mimicking conditions of hot-core media) and a lower temperature T = 40 K (cold interstellar clouds). Rotational energy was not added in any of the simulations and the trajectories were propagated by a 6th order Symplectic integrator[37,38] to 1 ps total integration time with an integration stepsize of 1 fs. The trajectories were stopped before reaching the total integration time in case the starting TSs dissociated back to reactants and the fragments reached a distance of 10 Å. The simulations were carried out using the
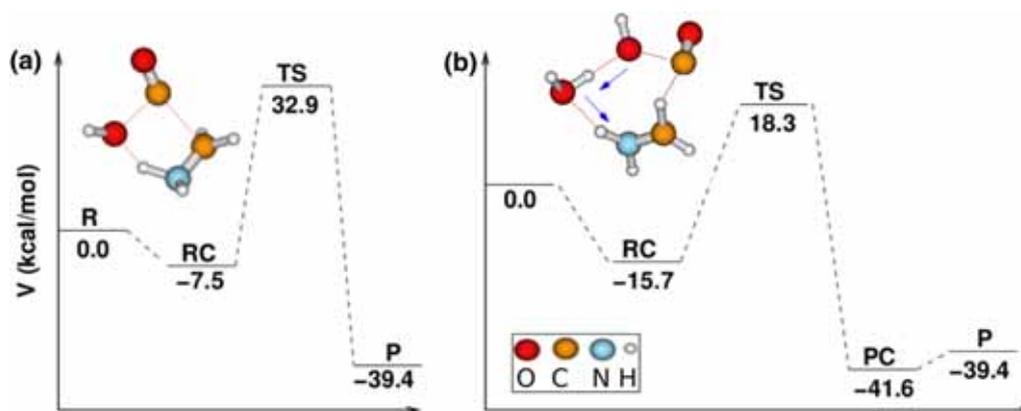
Figure 1. Potential energy profiles for the (a) **1W** and (b) **2W** reactions. Energies are relative with respect to the energy of the reactants and are computed at the B3LYP/6-31++g(3df,2pd) level of electronic structure theory. For both the reactions, geometry of the corresponding transition states are shown. In the **2W** transition state, the blue arrows indicate the directions for the proton relay transport required for product formation.

general chemical dynamics program VENUS[39,40] coupled with the electronic structure theory package NWChem.[41] To integrate one trajectory for 1 ps, it takes approximately 14 and 18 hours for reactions **1W** and **2W** reactions, respectively, on a DELL PRECISION 16 core workstation.

3. Results and Discussion

Trajectory simulations were performed for the **1W** and **2W** reactions at two different temperatures, T = 1000 K and 40 K. An ensemble of 80 classical trajectories were generated for each reaction at two different temperatures amounting to a total of (4 × 80) 320 trajectories. The total energy of each trajectory was conserved within ± 0.1 kcal/mol. The completed trajectories were classified into two groups: (1) forming the Gly product (forward) and (2) dissociating towards the reactants side (backward). No other reaction event was seen in any of the trajectories. Summary of the trajectory results are presented in table 1 and detailed discussions given below.

3.1 *High temperature simulations*

Trajectories were initiated at the transition state for reaction **1W** with Boltzmann distribution of vibrational energies sampled[36] at T = 1000 K for the modes orthogonal to the reaction coordinate and the reaction coordinate itself had a fixed temperature of T = 1000 K. The average total energy of the trajectories under these conditions was 64.7 kcal/mol and the average reaction coordinate energy was 2.4 kcal/mol. Visualization of the normal modes of the transition state for reaction **1W** shows that the reaction coordinate motion involves transfer of the proton from H_2O to the N atom of methanimine.

Table 1. Summary of trajectory events following barrier excitation for the **1W** and **2W** reactions at two different temperatures, T = 1000 K and 40 K. A total of 80 trajectories were generated for each of the simulation conditions.

Simulation condition	Forward[a]	Backward[b]
1W (T = 1000 K)	39/80	41/80
2W (T = 1000 K)	21/80	59/80
1W (T = 40 K)	12/80	68/80
2W (T = 40 K)	0/80	80/80

[a] Forms Gly and Gly + H_2O for reactions **1W** and **2W**, respectively.
[b] Forms the reactants $CH_2 = NH + CO + (H_2O)_n$, $n = 1$ (**1W**) and 2 (**2W**).

For reference, the geometry of the transition state is shown in Figure 1. Out the the total 80 trajectories, 39 trajectories formed the product Gly (forward reaction) and rest of the trajectories showed dissociation of the transition state (backward) to form the reactants $CH_2 = NH + CO + H_2O$. The results of this simulation that approximately 50% of the trajectories formed the product Gly is in consistent with the transition state theory[42] prediction that reactive systems pass through the transition region only once without recrossing the barrier. It is to be noted that the product Gly molecules will have sufficient energy to recross the barrier in those trajectories. Snapshots of typical trajectories forming product Gly molecule and dissociating towards the reactants are shown in the supplementary information. Note that 2 out of 39 reactive trajectories in this simulation showed proton transfer from the −OH group to the carbonyl oxygen atom after the product glycine formation *i.e.*, $H_2NCH_2CO^\dagger OH \rightarrow H_2NCH_2COO^\dagger H$.
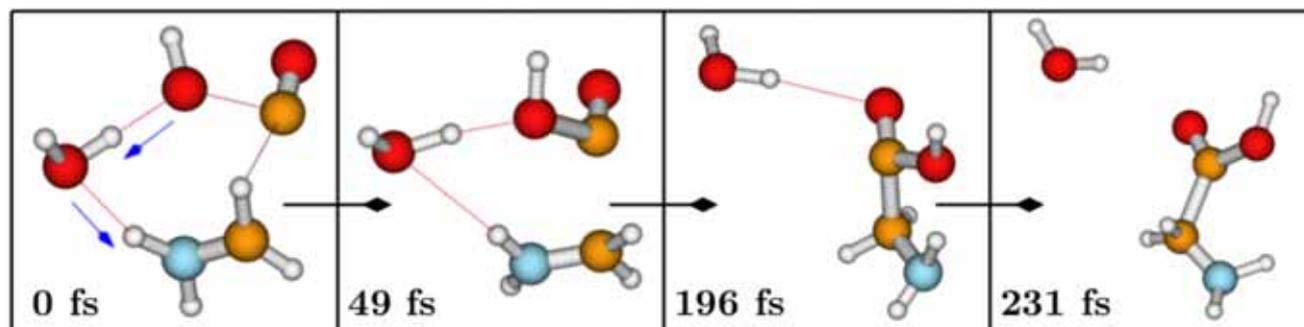
Figure 2. Snapshots of a typical trajectory forming the product Gly for the **2W** reaction. The blue arrows shown in the 0 fs frame indicate the directions for the proton relay transport through the second additional water molecule. Color coding for the atoms can be seen in Figure 1.

To investigate the proposed catalytic effect[28] by additional water molecule(s) on reaction 1, the simulations were repeated at T = 1000 K for reaction 2 with $n = 2$ *i.e.*, one extra water molecule present. Simulation conditions were kept the same as the previous one. The average total and the reaction coordinate energy in the trajectories in this simulation was 85.1 kcal/mol and 2.0 kcal/mol, respectively. Out of the 80 trajectories launched from the transition state, 21 formed the products Gly + H_2O and the rest dissociated to form the reactants $CH_2 = NH + CO + 2H_2O$. Note that the simulation conditions involve directing half of the trajectories towards the product side and the rest towards the reactants. However, we did not observe the expected proportion of trajectories ($\approx 50\%$) forming the products. Several trajectories recross the barrier immediately after the launch and go towards the reactants side. Clearly, the thermal rate constant for this reaction through the trajectory calculations is smaller than the transition state theory prediction. Snapshots of a typical trajectory forming Gly molecule is shown in Figure 2 and the transfer of the protons can be seen in the figure. Out of the 21 trajectories that formed the products, 6 trajectories entered the product complex (Gly...H_2O) and stayed for a short duration before dissociating as Gly + H_2O.

In comparison to the **1W** reaction, the fraction of trajectories forming the reaction products for the **2W** reaction is quite low. In the previous work,[28] it was proposed that the additional water molecule acts as a proton relay transport medium and thus an effective catalyst in promoting reaction 1. Further it was indicated that a tunneling mechanism for this proton transfer process may not be occurring based on the low frequency of the reaction coordinate at the transition state. The computed reaction coordinate frequency is $522\,cm^{-1}$ (B3LYP/6-31++G(3df,2pd)) and the reaction coordinate motion involves proton transfer from first H_2O molecule to the N-atom of methanimine with simultaneous transfer of a proton from the second water molecule to the

first water molecule (Figure 1). The dynamics simulations performed here show that under similar conditions, the **2W** reaction shows a low probability ($\approx 26\,\%$) of forming product Gly molecule as compared to the **1W** reaction (observed probability for product Gly formation $\approx 50\%$). Hence, the proton relay transport effect - proposed to enhance reaction 1 - may not be entirely, if not at all, a classical phenomena. The transition state for **2W** reaction seems to be not favoring the product Gly formation in a purely classical sense. It is possible that the concerted proton transfer process - the proton relay transport - that is necessary for the proposed catalytic effect shown by the additional water molecule(s) for reaction 1 might be a quantum mechanical tunneling effect.[43] Such a concerted proton transfer through a chain of water molecules by tunneling is known in the literature.[44–47] To understand the feasibility of Gly formation through the methanimine route in the cold ISM, the simulations for reactions **1W** and **2W** were repeated at a lower temperature of T = 40 K and the results are presented below.

3.2 *Low temperature simulations*

In the second set of simulations, 160 trajectories were launched from the transition states corresponding to reactions **1W** and **2W** (80 trajectories each). The simulation conditions were the same as the previous set except the energies were chosen from a Boltzmann distribution at T = 40 K. The average reaction coordinate energy in the trajectories was 0.08 and 0.1 kcal/mol, for reactions **1W** and **2W**, respectively. The results of the simulation are summarized in table 1 and it is clear that these simulation outcomes are different from the previous ones at T = 1000 K. For the **1W** reaction, only 12 out of 80 trajectories formed product Gly molecule and none of the trajectories showed product formation for the **2W** reaction (with one additional water molecule) wherein *all* the trajectories dissociated towards the reactants side.

Lowering the reaction temperature from 1000 K to 40 K drastically reduces glycine formation through reactions 1 and 2. Note that the trajectory initial condition sampling scheme involves directing 50% of the trajectories towards products and the rest towards the reactants. It is surprising that not even a single trajectory shows product formation when an additional water molecule is present in the system. Clearly, the transition state for **2W** reaction is not favorable (at least classically) to form product Gly molecule. As mentioned earlier, the relay transport mechanism for this reaction, if at all operative, might be a purely quantum mechanical effect[46] particularly at low temperatures.

To investigate further into the nature of these reactions, a smaller amount of trajectories were initiated from the respective reactant complexes (RC). As mentioned in section 2, potential energy surface for these reactions involve formation of stable RCs. The RCs for the **1W** and **2W** reactions are five and seven membered rings, respectively, and involve several non-bonded interactions such as hydrogen bonds and van der Waals type forces. The corresponding equilibrium geometries of these RCs are given in the supplementary information. Unimolecular barrier height for the complexes to form product Gly is 40.4 and 34.0 kcal/mol, for **1W** and **2W** reactions, respectively, and note that the presence of one additional water molecule brings down the barrier by 6.4 kcal/mol. The RCs were sampled with a Boltzmann distribution of normal mode energies[36] at a temperature of T = 1000 K. For each case, 30 trajectories were initiated and propagated to 1 ps total integration time or until the distance between individual species (after dissociation of the complex) reached a distance of 10 Å. The average total energy in the trajectories was 69.1 and 91.8 kcal/mol for **1W** and **2W** reactions, respectively. Despite the fact that the amount of energy available in the trajectories is sufficient to surmount the forward transition state barrier to form the products, none of the trajectories showed Gly formation in both the cases. All the trajectories dissociated to form the reactants, $CH_2 = NH$, CO, and $(H_2O)_n$. For the **2W** reaction, the RC is stable by 15.7 kcal/mol with respect to the reactants and the reaction is exoergic by 39.4 kcal/mol (see Figure 1). Though the reaction is thermodynamically favorable, the reaction probability from a dynamics perspective is poor.

4. Conclusion

On-the-fly classical chemical dynamics simulations of glycine formation in the ISM via the $CH_2 = NH$ + CO + H_2O reaction is presented. The calculations

were performed at the density functional B3LYP/6-31++G(3df,2pd) level of electronic structure theory. The trajectories were launched from the five membered transition state for this reaction and the initial vibrational energies were chosen from a 1000 K Boltzmann distribution. Results of this simulation showed that ≈50% of trajectories form the product glycine molecule and the rest dissociated to form the reactants - an observation in consistent with the predictions of transition state theory. In a previous work,[28] electronic structure calculations showed that presence of extra water molecules for this reaction reduces the barrier height for product formation thus indicating a possible catalytic effect by the additional water molecule(s). This was proposed[28] to take place through a relay effect in efficiently transferring a proton to the N atom of $CH_2 = NH$ moiety by the additional water molecule. To this end, we performed trajectory simulations for this reaction in presence of one additional water molecule with similar initial conditions and the results showed that a large fraction of the trajectories dissociate to form the reactants and only a small amount of trajectories (≈26%) form product glycine molecule. These trajectory averages indicate that the proposed proton relay transport effect may not be happening classically at least with the current simulation conditions. Further, several publications in the literature[44–47] show a tunneling mechanism for such transport of proton through network of water molecules. It is to be noted that in the present work we have not attempted to establish the tunneling mechanism in these reactions. Simulations were also repeated for both the considered reactions at a lower temperature of 40 K and the probability for glycine formation further reduces (15% for **1W** reaction and zero for **2W** reaction) in these simulations. These reactions involve the formation of reactant complexes/transition states with three or more reactants which requires a well-coordinated approach of the reactants. Further, the reactions considered here are gas phase reactions involving neutral species and hence rate of these reactions are expected to be low as compared to ion-molecule reactions in the gas phase. In summary, rate of the $CH_2 = NH + CO + H_2O$ reaction for the formation of glycine in the ISM might be low and facilitated by quantum mechanical tunneling[43] rather than the classical barrier crossing phenomena.

Supplementary Information (SI)

Details of the basis set used in the calculations (Table S1), computed energies and geometries of the stationary points for the **1W** (Figure S1) and **2W** (Figure S2) reactions are given. Snapshots of a typical trajectory forming product glycine for the **1W** reaction is given in Figure S3. Further, snapshots

of two typical trajectories dissociating to form reactants, one each for **1W** and **2W** reactions are given in Figures S4 and S5, respectively, and the data for this article can be accessed at www.ias.ac.in/chemsci.

Acknowledgements

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