

Quantum chemical analysis for the formation of glycine in the interstellar medium

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Abstract Glycine ($C_2H_5NO_2$) was the first amino acid to be detected in space by the stardust space probe in Comet Wild2, and is used by living organisms to make proteins. We discuss three different reaction paths for the formation of glycine in interstellar space from some simpler molecules detected in the interstellar medium. The possibility of the formation of glycine in interstellar space is considered by radical-radical and radical-molecule interaction schemes using quantum chemical calculations with density functional theory at the B3LYP/6-31G (d,p) level. In the chemical pathways we discuss, a few reactions are found to be totally exothermic and barrierless while others are endothermic with a very small reaction barrier, thus giving rise to a high probability of forming glycine in interstellar space.

Key words: astrobiology — astrochemistry — ISM: abundances — ISM: molecules

1 INTRODUCTION

The interstellar medium (ISM) consists of an extremely dilute mixture of ions, atoms, molecules, layered dust grains, cosmic rays and magnetic fields (about 99% gas and 1% dust by mass) (Spitzer 1978). Interstellar dust particles (Thaddeus 2006) might have been a source of prebiotic carbon, hydrogen and nitrogen (Chyba & Sagan 1992; Chyba & Hand 2005), pointing towards the interconnection between interstellar chemistry and the terrestrial origin of life (Jortner 2006). The extent to which amino acids and other key organic molecules are distributed through the universe could contribute to an increased understanding of how widely life itself might be distributed (Woon 2002). The amino acid chemistry of the ISM, comets and meteorites is one of the most intriguing topics of extraterrestrial organic chemistry and astrobiology. The only indisputable evidence for the occurrence of amino acids outside our planet is their detection in carbonaceous chondrites (Cronin 1989; Cronin & Moore 1976; Cronin & Pizzarello 1983; Engel & Macko 1997; Kotra et al. 1979; Kvenvolden et al. 1970; Lattelais et al. 2011; Ponnampereuma 1972; Shimoyama et al. 1979). These organic compounds, i.e. amino acids, are generally believed to have been delivered by meteorites and other small bodies (comets, asteroids, interplanetary dust particles, etc). Their origin is a key point in understanding how life emerged on primitive Earth 3.8 billion years ago (Oró 1961). Bombardment of early Earth by comets and asteroids delivered large amounts of organic materials. This mechanism of delivering organic materials like amino acids could be of general importance for astrobiology since it is likely that terrestrial planets in extrasolar nebulae experienced similar impacts. Hence,

products of extraterrestrial organic chemistry could, in principle, allow prebiotic chemistry to occur throughout the Galaxy (Chyba et al. 1990).

The cold (10–50 K) clouds are composed of interstellar grains and their astronomical infrared vibrational spectra show large amounts of ice grains, which are mainly composed of water but also contain other molecules such as CO, CO₂, CH₃OH, NH₂, CH₂, NH, CH, etc. During the grain evolution, this material will undergo numerous chemical modifications caused by ionic and UV irradiations as well as thermal effects (Dartois 2005). The glycine molecule has been tentatively detected in interstellar space. In 1994, a team of astronomers from the University of Illinois, led by Lewis Snyder, claimed that they had found glycine molecules in space (Mehringer et al. 1994), but this detection was not confirmed by other groups of astronomers.

In 2003, Yi-Jehng Kuan and coworkers from National Taiwan Normal University repeated this discovery of glycine (Kuan et al. 2003) and claimed real detection in three warm, dense, interstellar clouds. They also claimed detection of 27 glycine lines in 19 different millimeter wave bands in hot molecular cores Sgr B2(N-LMH), Orion KL and W51 e1/e2 regions of the ISM. Snyder et al. (2005) used new laboratory measurements and an analysis technique for a glycine asymmetric rotor and concluded that key lines necessary for interstellar glycine identification have not yet been found. They identified some common molecular candidates that should be examined further as more likely carriers of several of the lines reported as glycine. Pilling et al. (2011) also reported the extensive search for glycine (NH₂CH₂COOH) and other amino acids in molecular clouds associated with star-forming regions. Only upper limits have been derived from radio observations. Nevertheless, two of glycine's precursors, formic acid and acetic acid, have been abundantly detected. Although both precursors may lead to glycine formation, the reaction efficiency depends on their abundance and survival in the presence of a radiation field. These facts could promote some favoritism in the reaction pathways in the gas phase and solid phase (ice). Glycine and these two simplest carboxylic acids are found in many meteorites. Recently, glycine was also observed in cometary samples returned by the Stardust space probe. Barrientos et al. (2012) also carried out a theoretical study about the formation of precursors of interstellar glycine through the reaction of neutral hydroxylamine with acetic acid. Thus in the absence of new observational results, glycine has still not been confirmed to exist in the ISM. But its possible existence in dense molecular clouds, abundant with organic molecules, cannot be excluded. Since there is an abundance of the precursors needed for the synthesis, we discuss the possible routes of formation for glycine in the ISM.

Several workers have proposed the mechanism for glycine production in interstellar grains or ices, but this molecule can also be generated in the gas phase via molecular cations (Bernstein et al. 2002; Basiuk & Kobayashi 2002; Blagojevic et al. 2003). An ab initio study on the formation of glycine in a two-step synthetic route has been done by using NH₃, CH₂ and CO₂ (Maeda & Ohno 2004). Largo et al. (2010) performed a quantum chemical study of glycine precursors in interstellar space using acetic acid (CH₃COOH) and the ammonium ion (NH₄⁺). Different theoretical studies have been done that investigated the viability of various pathways in forming amino acids in astrophysical ices (Woon 2001, 2002). Some formation mechanisms for cyanopolyynes require endothermic reactions that could only occur in the vicinity of a source of energy, such as a circumstellar disk, and others involve exothermic reactions that could occur in cold, dense interstellar clouds (Cataldo 2004; Pardo et al. 2004; Freeman & Millar 1983). Many of the relevant rate constants are unknown or estimated, so it is difficult to analyze the effectiveness of the proposed reaction mechanisms (Theodore et al. 2009).

In a continuation of our work on quantum chemical studies for the formation of adenine in the ISM (Gupta et al. 2011), the present work reports quantum chemical calculations for the formation of glycine in the ISM with the help of some simple molecules, which have been detected in interstellar space. Three new reaction paths are considered for the formation of glycine in the ISM starting from some simple molecules, viz. CO, CO₂, CH₃OH, NH₂, CH₂, NH, CH, etc. We have adopted radical-radical and radical-molecule interaction schemes in the gas phase for studying the formation

of glycine. The polarizable continuum model (PCM) is employed to detail the formation of glycine in icy grains.

2 COMPUTATIONAL DETAILS

The geometries of the different species involved in the reaction pathway have been obtained at the B3LYP level of the theory including all the electrons in the calculations. The B3LYP functional is composed of Becke's three-parameter hybrid exchange functional (B3) and the correlation functional of Lee, Yang, and Parr (LYP) yields good results in calculations of molecular structure and energetics. In these optimizations, a 6-31G (d,p) basis set has been employed. The 6-31G (d,p) basis set is widely used in chemistry, because it succeeds in representing experimental data with high reliability (Cramer 2002). Each optimized structure was verified to be a satisfactory point or a transition state by vibrational analysis carried out at the same level [B3LYP/6-31G(d,p)]. All calculations reported in this work were carried out with the Gaussian03W program package. Harmonic frequency calculations were also conducted to identify the stable and transition states. The transition states are those with one negative frequency while the stable states have no negative frequency. All the steps in the reaction path are shown separately in Figure 1 with total energies and the reaction barriers of individual steps given as reactant, product and transition states. The chemical analysis calculates the energy requirement for three paths; all calculations are performed at a temperature of 273.25 K and pressure of 1 atmosphere. It is also concluded that the proposed reactions, which are feasible and exothermic at this temperature and pressure, can also have a high probability of occurrence at low temperature (≈ 100 K) and pressure (≤ 1 atm) in interstellar space. Although the results depend on environmental conditions such as radiation field, temperature and pressure, our study gives qualitative indicators about the formation of glycine in the ISM. The most suitable reaction pathway is exothermic. The PCM as implemented in the Gaussian03W program has been used to include the bulk solvation effect.

3 RESULTS AND DISCUSSION

The different reaction paths leading to the formation of glycine in interstellar space involve several neutral molecules and radicals such as CH_2 (Lambert et al. 1995), NH_2 (van Dishoeck et al. 1993), CO, OH (Ziurys 2006) and CH (Adams 1941). There are mainly two types of radical reactions, viz. (a) bimolecular reactions between radicals and molecules, like addition, displacement, atom abstraction, etc., and (b) unimolecular reactions such as fragmentation and rearrangement. Among these, addition, displacement and rearrangement are most important for the study of interstellar chemistry where radicals are used as either reactants or intermediates. Formation of glycine, in the gas phase as well as in water containing grains (PCM) in the ISM, following different possible reaction paths is considered under the following headings.

3.1 Reaction Path 1

The first reaction path for the formation of glycine is as follows:



This reaction involves three steps, which are shown in Figure 1(a). All the optimized geometries of the reactants, products and transition states involved in reaction 1 are schematically shown in Figure 2 and the electronic energies, zero point vibrational energies (ZPVEs) and total energies of all the molecules, radicals and transition states are given in Table 1.

As the quantum chemical calculations show, the NH_2 radical reacts with CH_2 (carbene like structure) and forms an NH_2CH_2 radical with a reaction energy of $-112.79 \text{ kcal mol}^{-1}$ with ZPVE

a Reaction 1: $\text{NH}_2 + \text{CH}_2 \rightarrow \text{NH}_2\text{CH}_2 + \text{CO} \rightarrow \text{TS} \rightarrow \text{NH}_2\text{CH}_2\text{CO} + \text{OH} \rightarrow \text{NH}_2\text{CH}_2\text{COOH}$			
Step 1	Step 2		Step 3
$\text{NH}_2 + \text{CH}_2$ <u>-94.975243</u> -0.179739 (-112.79) NH_2CH_2 <u>-95.154982</u>	TS <u>-208.434983</u> 0.024421 (15.32) $\text{NH}_2\text{CH}_2 + \text{CO}$ <u>-208.459404</u> $\text{NH}_2\text{CH}_2\text{CO}$ <u>208.468386</u>		$\text{NH}_2\text{CH}_2\text{CO} + \text{OH}$ <u>-284.188447</u> -0.167020 (-104.81) $\text{NH}_2\text{CH}_2\text{COOH}$ <u>-284.355467</u>
b Reaction 2: $\text{NH}_2 + \text{CH} \rightarrow \text{NH}_2\text{CH} + \text{CO} \rightarrow \text{NH}_2\text{CHCO} + \text{OH} \rightarrow \text{NH}_2\text{CHCOOH} + \text{H} \rightarrow \text{TS} \rightarrow \text{NH}_2\text{CH}_2\text{COOH}$			
Step 1	Step 2	Step 3	Step 4
$\text{NH}_2 + \text{CH}$ <u>-94.334457</u> -0.199861 (-125.41) NH_2CH <u>-94.534318</u>	$\text{NH}_2\text{CH} + \text{CO}$ <u>-207.838740</u> -0.052130 (-32.71) NH_2CHCO <u>-207.890870</u>	$\text{NH}_2\text{CHCO} + \text{OH}$ <u>-283.6109310</u> -0.126244 (-79.22) NH_2CHCOOH <u>-283.737175</u>	TS <u>-284.355044</u> 0.117596 (73.79) $\text{NH}_2\text{CHCOOH} + \text{H}$ <u>-284.237448</u> $\text{NH}_2\text{CH}_2\text{COOH}$ <u>-284.358187</u>
c Reaction 3: $\text{CH}_2 + \text{CO} \rightarrow \text{CH}_2\text{CO} + \text{OH} \rightarrow \text{CH}_2\text{COOH} + \text{NH}_2 \rightarrow \text{NH}_2\text{CH}_2\text{COOH}$			
Step 1	Step 2	Step 3	
$\text{CH}_2 + \text{CO}$ <u>-152.419659</u> -0.150683 (-94.55) CH_2CO <u>-152.570342</u>	$\text{CH}_2\text{CO} + \text{OH}$ <u>-228.290399</u> -0.076797 (-48.19) CH_2COOH <u>-228.367196</u>	$\text{CH}_2\text{COOH} + \text{NH}_2$ <u>-284.22721</u> -0.122239 (-76.70) $\text{NH}_2\text{CH}_2\text{COOH}$ <u>-284.349449</u>	

Fig. 1 Steps of formation of glycine and an energy level diagram for different reaction paths. All the energies are in a.u. (energy differences in kcal mol⁻¹ are given in parentheses) and corrected for ZPVE.

Table 1 Electronic (EE), ZPVE and Total Energies of Molecules, Radicals and Transition State Using B3LYP/6-31G (d,p) Theory

Molecules/ TS /Radicals	E.E. (a.u.)	ZPVE (a.u.)	Total Energies (a.u.)
NH_2	-55.878981	0.018977	-55.860004
CH_2	-39.131752	0.016513	-39.115239
CO	-113.309454	0.005032	-113.304422
OH	-75.728482	0.008421	-75.720061
$\text{NH}_2 + \text{CH}_2$	-95.010733	0.035490	-94.975243
NH_2CH_2	-95.205334	0.050352	-95.154982
$\text{NH}_2\text{CH}_2 + \text{CO}$	-208.514788	0.055384	-208.459404
TS	-208.494716	0.059733	-208.434983
$\text{NH}_2\text{CH}_2\text{CO}$	-208.529342	0.060956	-208.468386
$\text{NH}_2\text{CH}_2\text{CO} + \text{OH}$	-284.257824	0.069377	-284.188447
$\text{NH}_2\text{CH}_2\text{COOH}$	-284.435563	0.080096	-284.355467

correction. Mulliken population analysis of a molecule having a net atomic charge on a C atom is -0.201 e.s.u. and on an N atom is -0.478 e.s.u. These atoms can have an electrostatic force of attraction which leads to the formation of the NH_2CH_2 radical. In the second step, this NH_2CH_2 radical reacts with carbon monoxide (CO), which is quite abundant in interstellar space and gives rise to $\text{NH}_2\text{CH}_2\text{CO}$ through a transition state having a reaction barrier of about 15.32 kcal mol⁻¹

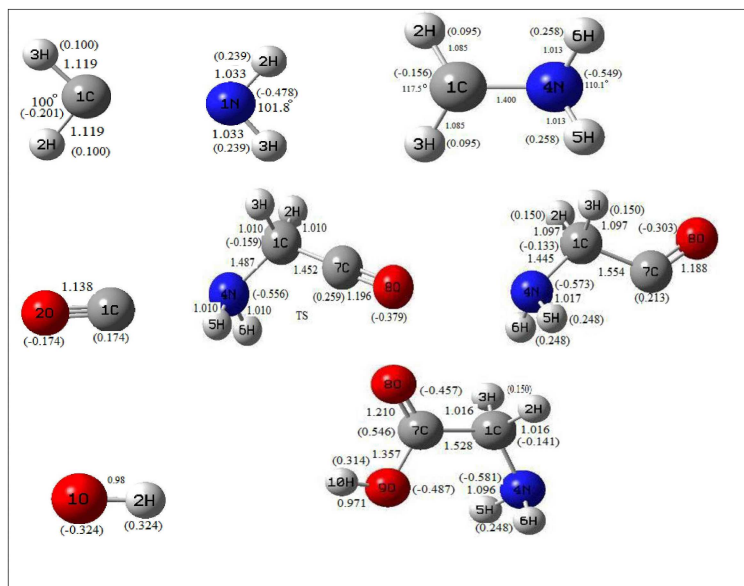
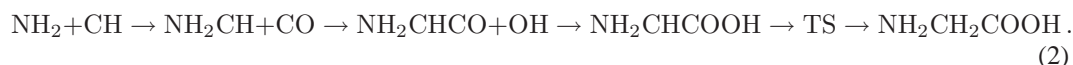


Fig. 2 Optimized geometries of the reactants, products and transition states involved in the formation of glycine in Reaction 1 at B3LYP/6-31G (d,p) (charge densities of each atom are given in parentheses).

with ZPVE which reduces to about $8.40 \text{ kcal mol}^{-1}$ in water containing icy grains. The N atom has a charge of -0.549 e.s.u. in NH_2CH_2 and it reacts with the C atom of CO which has a charge of 0.174 e.s.u. Hence due to a strong electrostatic force of attraction between these two radicals, formation of the $\text{NH}_2\text{CH}_2\text{CO}$ molecule takes place. In the last step, an exothermic reaction between $\text{NH}_2\text{CH}_2\text{CO}$ and the hydroxyl radical (OH) gives rise to glycine with a reaction energy of about $-104.81 \text{ kcal mol}^{-1}$. The charge densities of all atoms with all the geometries are given in Figure 2.

3.2 Reaction Path 2

The second reaction path for the formation of glycine is as follows:



In the above proposed reaction path, glycine formation takes place in four steps. In the first step, an NH_2 radical reacts with a CH radical giving rise to an NH_2CH radical, having reaction energy of about $-125.41 \text{ kcal mol}^{-1}$. Here a negative sign shows that this step is totally exothermic and has no reaction barrier. In the second step, a C4 (Fig. 3) atom from an NH_2CH radical may attach itself to the carbon atom of CO to form an NH_2CHCO radical, with reaction energy of about $-32.71 \text{ kcal mol}^{-1}$. In the third step, NH_2CHCO reacts with a hydroxyl radical (OH) to exothermally form NH_2CHCOOH , having reaction energy $-79.22 \text{ kcal mol}^{-1}$. In the last step, protonation (addition of a hydrogen radical) takes place at the C4 atom of NH_2COOH to form glycine through a transition state with a reaction barrier of about $73.79 \text{ kcal mol}^{-1}$. Mulliken population analysis of NH_2CH gives net atomic charges of -0.101 and -0.490 e.s.u. respectively at C4 and N1. These atoms have a strong electrostatic force of attraction towards each other. In this molecule (NH_2CH), addition of two consecutive CO atoms and OH radicals produces glycine. All the optimized geometries of the involved species are shown in Figure 3 and total energies, ZPVE and electronic energies

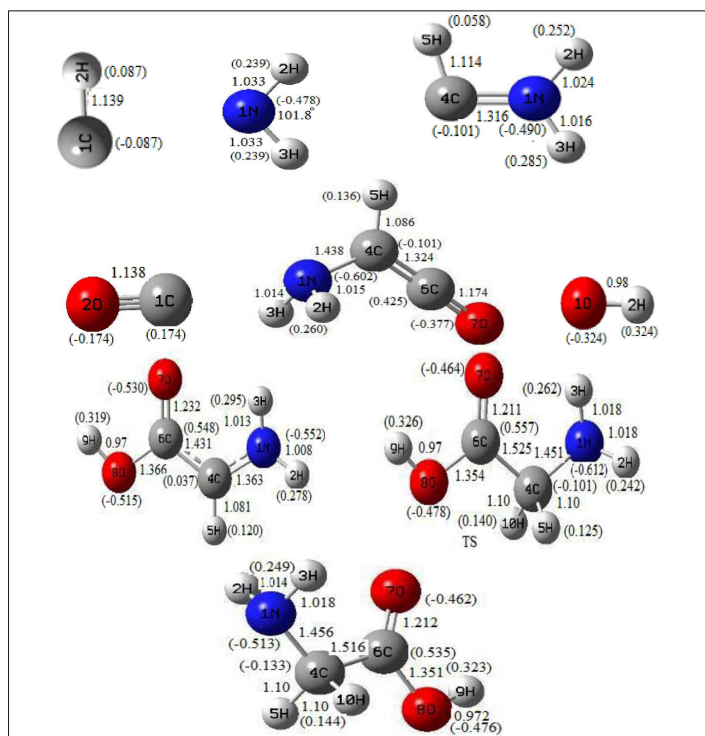


Fig. 3 Optimized geometries of reactants, products and transition states involved in the formation of glycine in Reaction 2 at B3LYP/6-31G (d,p) (charge densities of each atom are given in parentheses).

are given in Table 2. All the steps involved in this reaction are shown in Figure 1(b). This proposed reaction path for the formation of glycine is almost exothermic at every step when a polarizable continuum model is used.

3.3 Reaction Path 3

The third reaction path for the formation of glycine is as follows:



In this reaction, first the addition of CH_2 to CO gives rise to CH_2CO , after which an OH radical attaches itself to CH_2CO to form CH_2COOH . Finally, the NH_2 radical reacts with CH_2COOH and forms the glycine molecule. Since this reaction path is totally exothermic and has no reaction barrier, there is a high probability of forming glycine. This path has three steps which are shown in Figure 1(c) and optimized geometries are given in Figure 4. The electronic energies, ZPVE and total energies of all the species involved in this reaction path are given in Table 3. In the first step of this reaction, CH_2 is attached to CO to form a CH_2CO radical with a reaction energy of about $-94.55 \text{ kcal mol}^{-1}$. In the second step, this CH_2CO reacts exothermically with a hydroxyl radical (OH) to form CH_2COOH , having a reaction energy of about $-48.19 \text{ kcal mol}^{-1}$. In the final step of the reaction, CH_2COOH reacts with the NH_2 radical and forms one of the conformers of glycine with a reaction energy of about $-76.70 \text{ kcal mol}^{-1}$.

Table 2 Electronic (EE), ZPVE and Total Energies of Molecules, Radicals and Transition State Using B3LYP/6-31G (d,p) Theory

Molecules/ TS /Radicals	E.E. (a.u.)	ZPVE (a.u.)	Total Energies (a.u.)
H	-0.500273	0.000000	-0.500273
OH	-75.728482	0.008421	-75.720061
CH	-38.480800	0.006355	-38.474445
CO	-113.309454	0.005032	-113.304422
NH ₂	-55.878981	0.018969	-55.860012
NH ₂ + CH	-94.359781	0.025324	-94.334457
NH ₂ CH	-94.573848	0.039530	-94.534318
NH ₂ CH + CO	-207.883302	0.044562	-207.838740
NH ₂ CHCO	-207.940829	0.049959	-207.890870
NH ₂ CHCO + OH	-283.669311	0.058380	-283.610931
NH ₂ CHCOOH	-283.804245	0.067070	-283.737175
NH ₂ CHCOOH + H	-284.304518	0.067070	-284.237448
TS	-284.434616	0.079572	-284.355044
NH ₂ CH ₂ COOH	-284.438208	0.080021	-284.358187

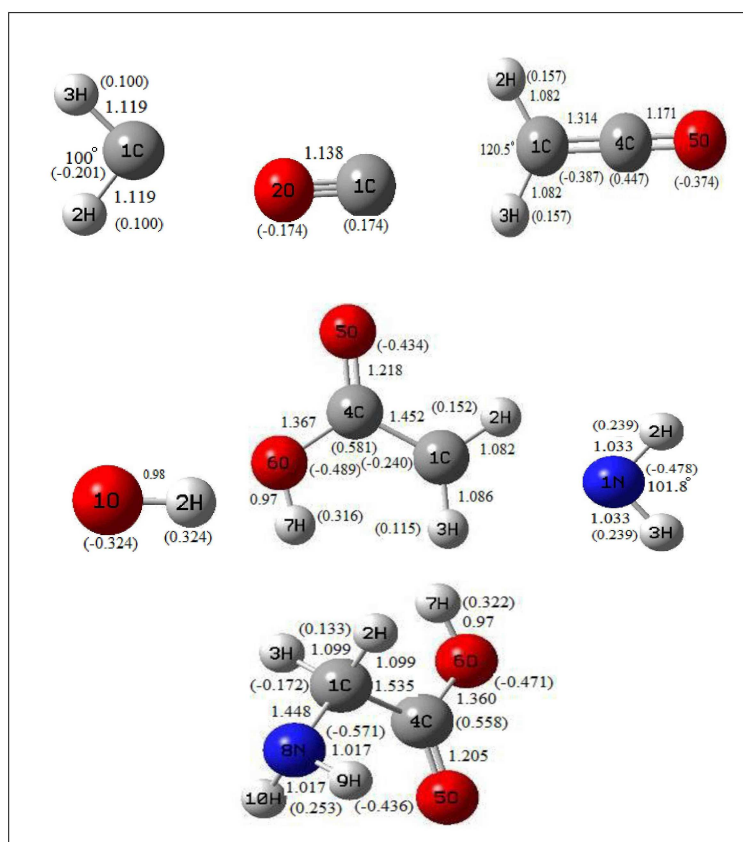
**Fig. 4** Optimized geometries of reactants, products and transition states involved in the formation of glycine in Reaction 3 at B3LYP/6-31G (d,p) (charge densities of each atom are given in parentheses).

Table 3 Electronic (EE), ZPVE and Total Energies of Molecules, Radicals and Transition State Using B3LYP/6-31G (d,p) Theory

Molecules / TS / Radicals	E.E. (a.u.)	ZPVE (a.u.)	Total Energies (a.u.)
CH ₂	-55.878981	0.018969	-55.860012
CO	-113.309454	0.005032	-113.304422
OH	-75.728482	0.008421	-75.720061
NH ₂	-55.878981	0.018969	-55.860012
CH ₂ + CO	-152.441208	0.021549	-152.419659
CH ₂ CO	-152.602024	0.031682	-152.570342
CH ₂ CO + OH	-228.330506	0.040107	-228.290399
CH ₂ COOH	-228.414880	0.047684	-228.367196
NH ₂ COOH + NH ₂	-284.293860	0.066650	-284.227210
NH ₂ CH ₂ COOH	-284.429139	0.079690	-284.349449

4 CONCLUSIONS

The possibility of forming glycine from some simple molecules like NH₂, CH₂ CH and CO, which are known to be abundant in interstellar space, has been explored with quantum chemical methods using radical-radical and radical-molecule interaction schemes, both in the gaseous phase and in grains. The PCM has been adopted to study reactions in the grains. Total energies, ZPVE and EE of all the molecules, transition states and radicals formed during the reaction path were calculated. Geometries of the reactants, products and transition states have been optimized and harmonic frequencies are calculated to identify the stable states. The study of reaction energies and structures of the reactants and products shows that the formation of glycine is possible in the gaseous phase as well as in water ice grains. The reaction paths, both in the gaseous phase and in the solvent, are either totally exothermic or have a very small barrier. Among all three proposed reaction paths, Reaction 2 is found to be more appropriate than the other two. Glycine formed via Reaction 2 is most stable because it possesses the lowest energy among all three reactions. Since the reaction barriers are small enough in all the three proposed reactions, there is a high probability of the occurrence for these reactions in the formation of glycine in the ISM.

Astrophysical Interest: Simulation of the formation and reactions of amino acids and their precursors in the ISM is a difficult task and it is necessary to propose the reactions that can occur at extremely low densities and temperatures. The general problem is finding a viable, thermodynamically feasible mechanism that can account for the formation of amino acids in the ISM. Reaction mechanisms involving several intermediate and transition states can be studied effectively through computation. It is unlikely that amino acids form by the gas phase reactions normally considered for interstellar chemistry; an alternative process is that the molecules are chemically created in the bulk solvation model. In spite of the experimental evidence, very little is known about the reactions through which amino acids form. There is rapidly growing interest in using computational chemistry to study chemical mechanisms and interstellar organic reactions which are difficult to detect and identify experimentally. Quantum mechanical calculations provide a direct tool for understanding systems that are too complex to be observed experimentally and it gives a detailed view of transition-state geometries for predicting the mechanisms of organic chemical reactions. The goal of the present work is to study the feasibility of the formation of the simplest amino acid glycine in the ISM at the B3LYP/6-31G (d,p) level of theory. Harmonic vibrational frequencies and ZPVE corrections were calculated at the same level of theory. Our investigation should explore the detailed mechanisms of the formation of the other amino acids and biological molecules.

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