

Hydro-chemical study of the evolution of interstellar pre-biotic molecules during the collapse of molecular clouds

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Abstract One of the stumbling blocks for studying the evolution of interstellar molecules is the lack of adequate knowledge about the rate coefficients of various reactions which take place in the interstellar medium and molecular clouds. Some theoretical models of rate coefficients do exist in the literature for computing abundances of complex pre-biotic molecules. So far these have been used to study the abundances of these molecules in space. However, in order to obtain more accurate final compositions in these media, we have calculated the rate coefficients for the formation of some of the most important interstellar pre-biotic molecules by using quantum chemical theory. We use these rates inside our hydro-chemical model to examine the chemical evolution and final abundances of pre-biotic species during the collapsing phase of a proto-star. We find that a significant amount of various pre-biotic molecules could be produced during the collapse phase of a proto-star. We thoroughly study the formation of these molecules via successive neutral-neutral and radical-radical/radical-molecular reactions. We present the time evolution of the chemical species with an emphasis on how the production of these molecules varies with the depth of a cloud. We compare the formation of adenine in interstellar space using our rate-coefficients and using those obtained from existing theoretical models. Formation routes of the pre-biotic molecules are found to be highly dependent on the abundances of the reactive species and the rate coefficients involved in the reactions. The presence of grains strongly affects the abundances of the gas phase species. We also carry out a comparative study between different pathways available for the synthesis of adenine, alanine, glycine and other molecules considered in our network. Despite the huge abundances of the neutral reactive species, production of adenine is found to be strongly dominated by the radical-radical/radical-molecular reaction pathways. If all the reactions considered here contribute to the production of alanine and glycine, then neutral-neutral and radical-radical/radical-molecular pathways are both found to have a significant part in the production of alanine. Moreover, radical-radical/radical-molecular pathways also play a major role in the production of glycine.

Key words: ISM: clouds — astrochemistry — stars: formation

1 INTRODUCTION

According to the CDMS catalog (<http://www.astro.uni-koeln.de/cdms/molecules>), approximately 165 molecules have been detected in the interstellar medium (ISM) or circumstellar shells. The significance of interstellar dust on the formation of complex interstellar molecules is well recognized after the discovery of more than 20 molecules in interstellar ice, especially around star forming regions (Boogert & Ehrenfreund 2004, Gibb et al. 2004 etc.). Increasing experimental evidence also points to the importance of surface processes (Ioppolo et al. 2008, Öberg et al. 2009 etc.) and suggests incorporating the grain surface processes into related theories. Indeed, a number of attempts have been made to appropriately model interstellar grain chemistry over the years (e.g., Chakrabarti et al. 2006a,b; Das et al. 2008b; Das et al. 2010; Cuppen & Herbst 2007).

At the same time, an understanding of the origin of life is a long standing problem and researchers are curious to know whether various pre-biotic molecules could also be formed in the ISM. It was suggested that during the collapse phase of a proto-star, some basic elements of life such as amino acids and some of the bases of DNA could be produced (Chakrabarti & Chakrabarti 2000a,b; hereafter CC00a and CC00b respectively). It is expected that there might be some strong connection between nitrile chemistry and prebiotic chemistry. Motivated by detections of nitriles in Titan's atmosphere, cometary comae, and the ISM, Hudson & Moore (2004) reported laboratory investigations of low-temperature chemistry of acetonitrile, propionitrile, acrylonitrile, cyanoacetylene, and cyanogen. They performed a few experiments on different nitriles to produce low-temperature photo and radiation products of nitriles. Blagojevic et al. (2003) reported their experiment on the formation of gas phase glycine and β -alanine, as well as acetic and propanoic acid, from smaller molecules in interstellar environments. The effects of fluxes of charged particles and electromagnetic radiation also play an important role in the chemical composition of interstellar clouds (Das et al. 2012). Complex pre-biotic molecules might thus be formed due to very complex and rich chemical processes inside the molecular cloud. The production of amino acids, nucleotides, carbohydrates and other basic compounds possibly starts from molecules like HCN, cyano compounds, aldehyde, and ketones (Orgel 2004; Abelson 1966), which could lead to the origin of life in conditions of the primitive earth. Using an effective (gas-grain) reaction rate, CC00ab proposed the oligomerization of HCN to produce adenine and other complex molecules.

In the present paper, we perform quantum chemical calculations to derive rate coefficients for the formation of several pre-biotic molecules such as adenine, alanine, glycine, glycolic acid and lactic acid. Obtained rate coefficients from the quantum chemical calculations are directly implemented into our hydro-chemical code to model the associated chemical evolution during the collapse phase of a proto-star.

The plan of this paper is the following. In Section 2, the models and the computational details are discussed. Different computational results are presented in Section 3, and finally in Section 4, we draw our conclusions.

2 METHODS AND COMPUTATIONAL DETAILS

2.1 Quantum Chemical Calculations

Density functional theory (DFT) is an efficient tool to explore the chemical parameters of a species. We explicitly use DFT formalism to calculate the different chemical parameters for the synthesis of interstellar pre-biotic molecules. The computations were performed using the B3LYP functional with the 6-31G** basis set available in the Gaussian 03W package. Total energies, zero point vibrational energy and electronic energies of all the species which are formed during the synthesis of different interstellar pre-biotic molecules were calculated. Armed with these important chemical parameters, the desired rate coefficients for any reaction at 30 K have been calculated by using a semi-empirical

Table 1 Estimated rate coefficients for the formation of various pre-biotic molecules in the gas phase based on B3LYP/6-31G** calculations and the semi-empirical formula of Bates (1983).

Species	Neutral-neutral reaction pathways	Magnitude of association energies (eV)/ Rate coefficients ($\text{cm}^3 \text{s}^{-1}$)	Radical-radical/ radical-molecular reaction pathways	Magnitude of association energies (eV)/ Rate coefficients ($\text{cm}^3 \text{s}^{-1}$)
Adenine	(A) $\text{HCN}+\text{HCN}\rightarrow\text{CH}(\text{NH})\text{CN}$	0.14 / 8.38×10^{-20}	(a) $\text{HCCN}+\text{HCN}\rightarrow\text{Molecule 1}$	0.6443 / 2.13×10^{-17}
	(B) $\text{CH}(\text{NH})\text{CN}+\text{HCN}\rightarrow\text{NH}_2\text{CH}(\text{CN})_2$	2.13 / 3.43×10^{-12}	(b) $\text{Molecule 1} + \text{H} \rightarrow \text{Molecule 2}$	4.2362 / 7.96×10^{-9}
	(C) $\text{NH}_2\text{CH}(\text{CN})_2+\text{HCN}\rightarrow\text{NH}_2(\text{CN})\text{C}=\text{C}(\text{CN})\text{NH}_2$	1.12 / 3.30×10^{-15}	(c) $\text{Molecule 2}+\text{NH}_2\text{CN} \rightarrow \text{Molecule 3}$	1.9019 / 6.24×10^{-12}
	(D) $\text{NH}_2(\text{CN})\text{C}=\text{C}(\text{CN})\text{NH}_2+\text{HCN}\rightarrow\text{C}_5\text{H}_5\text{N}_5$	2.31 / 3.99×10^{-10}	(d) $\text{Molecule 3}+\text{CN} \rightarrow \text{Molecule 4}$	3.6300 / 1.80×10^{-9}
			(e) $\text{Molecule 4}+\text{H} \rightarrow \text{Molecule 5}$	3.0380 / 8.71×10^{-9}
Glycine	(A) $\text{H}_2\text{CO}+\text{HCN}\rightarrow\text{C}_2\text{H}_3\text{ON}$	2.40 / 1.23×10^{-12}	(a) $\text{HCN}+\text{H}\rightarrow\text{HCNH}$	0.64 / 5.56×10^{-18}
	(B) $\text{C}_2\text{H}_3\text{ON}+\text{H}_2\text{O}\rightarrow\text{C}_2\text{H}_5\text{NO}_2$	1.11 / 2.68×10^{-15}	(b) $\text{HCNH}+\text{H}\rightarrow\text{CH}_2\text{NH}$	4.50 / 1.63×10^{-12}
			(c) $\text{CH}_2\text{NH}+\text{H}\rightarrow\text{CH}_2\text{NH}_2$	1.70 / 1.17×10^{-14}
			(d) $\text{CO}+\text{OH}\rightarrow\text{COOH}$	0.78 / 1.13×10^{-17}
			(e) $\text{CH}_2\text{NH}_2+\text{COOH}\rightarrow\text{C}_2\text{H}_5\text{NO}_2$	3.06 / 1.82×10^{-9}
Alanine	(A) $\text{CH}_3\text{CHO}+\text{HCN}\rightarrow\text{C}_3\text{H}_5\text{ON}$	3.58 / 1.84×10^{-9}	(a) $\text{C}_2\text{H}_5\text{NO}_2\rightarrow\text{NH}_2\text{CHCOOH}+\text{H}$	13.55 / 7.22×10^{-10}
	(B) $\text{C}_3\text{H}_5\text{ON}+\text{H}_2\text{O}\rightarrow\text{C}_3\text{H}_7\text{NO}_2$	1.33 / 3.09×10^{-14}	(b) $\text{NH}_2\text{CHCOOH}+\text{CH}_3\rightarrow\text{C}_3\text{H}_7\text{NO}_2$	2.06 / 2.30×10^{-11}
Glycolic Acid	(A) $\text{C}_2\text{H}_5\text{NO}_2+\text{H}_2\text{O}\rightarrow\text{C}_2\text{H}_4\text{O}_3 + \text{NH}_3$	1.22 / 9.51×10^{-15}	–	–
Lactic Acid	(A) $\text{C}_3\text{H}_7\text{NO}_2+\text{H}_2\text{O}\rightarrow\text{C}_3\text{H}_6\text{O}_3 + \text{NH}_3$	2.56 / 2.31×10^{-9}	–	–

relationship developed by Bates (1983), i.e.,

$$K = 1 \times 10^{-21} A_r (6E_0 + N - 2)^{(3N-7)} / (3N - 7)! \text{ cm}^3 \text{ s}^{-1}, \quad (1)$$

where E_0 is the magnitude of association energy in eV, A_r is the transition probability (in s^{-1}) of the stabilizing transition (the numerical value of which may be taken to be 100 unless better information is available) and N is the number of nuclei in the complex.

If the calculated rate coefficients from Equation (1) exceed the limit set by the following equation (Eq. (2)), then this limiting value should be adopted

$$K = 7.41 \times 10^{-10} \alpha^{1/2} (10/\mu)^{1/2} \text{ cm}^3 \text{ s}^{-1}, \quad (2)$$

where α is the polarizability in \AA^3 and μ is the reduced mass of the reactants on the ^{12}C amu scale as suggested by Bates (1983). Though the rate expression reported by Bates (1983) is not a modern robust rate theory as it depends only on the association energy and not on the reaction barrier height or other relevant features of the reaction surface, we are still considering this expression in order to get an estimation of the rate coefficient for the formation of different interstellar pre-biotic molecules around the low temperature region of molecular clouds. Here, we have used different thermodynamical variables from Das et al. (2008a), which are assumed to be at 10 K. Thus we are also implementing Bates (1983)'s relation at 10 K.

2.2 Hydro-chemical Model

Since the chemical evolution around the star forming region strongly depends on the physical properties of the ISM, it is necessary to have a realistic description of the collapsing cloud to generate accurate abundances of various interstellar species. In the present paper, for the sake of simplicity, we assume a density distribution as described in Das et al. (2008a) and Das et al. (2010). A spherically symmetric self-gravitating interstellar cloud was considered in order to mimic the physical

behavior during star formation. We assume that the outer boundary of the cloud is located at one parsec and the inner boundary is located at 10^{-4} parsec. Matter entering through the inner boundary is assumed to be added to the core mass. In Das et al. (2008a), the entire cloud was divided into 100 logarithmically equally spaced grids in the radial direction. For the sake of simplicity in averaging, we assume 10 radial shells, so that one shell consists of 10 radial grids. We took the volume average of the number densities for each of the 10 grids to assign the number density of any particular shell.

We developed a large gas-grain chemical network to explore the chemical evolution of a collapsing cloud. For the gas-phase chemical network, we follow the UMIST 2006 database. Formation of different pre-biotic molecules are included in this gas phase chemical network. However, the rate coefficients for the formation of several pre-biotic molecules are currently unknown. We calculate all these rate coefficients and include them in our gas phase network. For the grain surface reaction network, we follow Hasegawa et al. (1992), Cuppen & Herbst (2007), Das et al. (2010) and Das & Chakrabarti (2011). Our surface network consists of all the updated interaction barrier energies as mentioned in Das & Chakrabarti (2011) and references therein. A detailed discussion about our gas-grain chemical model has already been presented in Das et al. (2012). Following the hydrodynamical model as discussed in Das et al. (2008a) and Das et al. (2010), we consider the density distribution of a collapsing cloud as an input parameter of our code describing the chemicals in gas and grains.

3 RESULTS AND DISCUSSION

3.1 Reaction Pathways and Rate Coefficients

There are several pathways by which a complex molecule can be formed. But since we are focusing on the formation of these species around a star forming region, we need to consider the most energetically economical route in which these species can be synthesized. Chemical abundances of those species, which are identified as the precursor for the formation of pre-biotic molecules such as HCN (Ziurys 2006), HCCN (Guelin & Cernicharo 1991), NH_2CN (Turner et al. 1975), CN (Fuente et al. 2005), C_2H_5 , H_2CO , CH_3CHO (Woodall et al. 2007) etc. dictate the reaction pathways for the formation of the interstellar pre-biotic molecules. So it is essential to consider the energy budget of any reaction along with the abundance of the reactive species. There are several neutral-neutral as well as radical-radical/radical-molecular pathways for the formation of these pre-biotic molecules. However, we consider only the most feasible pathways under interstellar conditions. We mainly concentrate on the formation of adenine, glycine, alanine, lactic acid and glycolic acid in the gas phase. The formation of these molecules via neutral-neutral and radical-radical/radical-molecular pathways with their rate coefficients and association energies (energy difference in eV, with zero point corrected values) are listed in Table 1. Formations of other pre-biotic molecules, such as glycolic acid and lactic acid via only neutral-neutral reaction pathways (there is no evidence for the synthesis of these species by the radical-radical/radical-molecular reaction pathways), are also written with their rate coefficients along with the association energies. Details of the formation routes towards the formation of interstellar pre-biotic molecules considered in the present paper are as follows.

3.1.1 Formation of adenine

Adenine is an important constituent of the DNA molecule and significant production of it may provide an important clue into the problem of the origin of life on a planet like ours. This is why it is essential to carry out careful analysis on the reaction rates during the formation of adenine. Here we used the formation of adenine via neutral-neutral and other variant reaction types by density functional calculations. In the neutral-neutral reaction pathways, the rate coefficient for the gas phase reaction $\text{HCN} + \text{HCN} \rightarrow \text{CH}(\text{NH})\text{CN}$ is calculated to be $8.38 \times 10^{-20} \text{ cm}^3 \text{ s}^{-1}$. This rate is very small since two neutral HCN molecules combine together by radiative association. In the next step, $\text{CH}(\text{NH})\text{CN}$ combines with HCN to form $\text{NH}_2\text{CH}(\text{CN})_2$ and the cal-

culated rate coefficient is $3.43 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$. Similarly, $\text{NH}_2\text{CH}(\text{CN})_2$ combines with HCN to form $\text{NH}_2(\text{CN})\text{C}=\text{C}(\text{CN})\text{NH}_2$ and the rate coefficient is $3.30 \times 10^{-15} \text{ cm}^3 \text{ s}^{-1}$ and finally $\text{NH}_2(\text{CN})\text{C}=\text{C}(\text{CN})\text{NH}_2$ combines with HCN to form adenine ($\text{C}_5\text{H}_5\text{N}_5$) and the rate coefficient is $3.99 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$.

Through the radical-radical/radical-molecular reaction pathways, adenine is formed in interstellar space through a barrierless exothermic reaction between hydrogen cyanide (HCN) and cyanocarbene (HCCN) (Gupta et al. 2011). HCN is highly abundant around the star forming region and the existence of HCCN in the ISM was reported by Guélin & Cernicharo (1991). Formation of HCCN on the surface of grains was already considered by Hasegawa et al. (1992). In our gas phase chemical network, we have considered this reaction between H and C_2N and the rate for the formation of HCCN ($2.67 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$) has been calculated following Bates (1983). Following Park & Lee (2002), we have considered the association reaction between HC and CN for the production of HCCN, which is barrierless and very exothermic in nature. According to them, this reaction might be considered as an efficient means for the production of HCCN in interstellar space. Here, the rate of formation has been calculated using the method of Bates (1983). Following Cherchneff et al. (1993), we have incorporated all possible destruction reaction pathways for the gas phase of HCCN. According to them, the gas phase HCCN could be destroyed very efficiently by the photodissociation reaction, with an estimated rate coefficient of $1.7 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$.

HCCN and HCN are both highly reactive carbene structures. The reaction between them leads to the formation of 1, 2 dihydro imidazole (Molecule 1) with a rate coefficient of $2.13 \times 10^{-17} \text{ cm}^3 \text{ s}^{-1}$. In an exothermic addition reaction 1, 2 dihydro imidazole combines with a hydrogen atom to form a 2, 3 dihydro-1H-imidazole radical (Molecule 2) with a rate coefficient $7.96 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$. CN is a very common interstellar species and was the first to be detected in the interstellar clouds (McKellar 1940). Existence of NH_2CN and CN radicals in interstellar clouds was first reported by Fuente et al. (2005). Till then, these species have also been observed in both diffuse clouds and dense clouds (Liszt & Lucas 2001). The reaction between the 2, 3 dihydro-1H-imidazole radical and NH_2CN leads to the formation of the 4 carboximidine-1H-imidazole (Molecule 3) radical with a rate coefficient $6.24 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$. The cyanide radical is very abundant in interstellar space (Fuente et al. 2005). The addition of the CN radical with the 4 carboximidine-1H-imidazole radical leads to the formation of 2, 4 dihydro-3H-purine-6 amine (Molecule 4) with a rate coefficient of $1.80 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$. In the next step, 2, 4 dihydro-3H-purine-6 amine combines with a hydrogen atom to form 6 amino-3H-purine (Molecule 5) with the rate coefficient $8.71 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$. At the end, the reaction between the cyanide radical and Molecule 5 leads to the formation of adenine with the release of one HNC/HCN. The calculated rate coefficient of this reaction is $1.89 \times 10^{-9}/1.91 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$. On the basis of results of the quantum chemical calculations presented above, it is evident that the formations of adenine by the radical-radical/radical-molecular reactions are more favorable than the neutral-neutral reactions in terms of the rate coefficients. It would be of great interest to learn whether any significant adenine is formed during the collapsing phase or not and to compare between the different pathways for its formation. It is possible that some of these reactions may also take place on the icy grains, but that is outside the scope of the present paper.

3.1.2 Formation of glycine

Glycine ($\text{C}_2\text{H}_5\text{NO}_2$) is the smallest among the 20 amino acids commonly found in proteins and also the only pre-biotic molecule which was claimed to be observed in the ISM (Kuan et al. 2003), though there were a number of unsuccessful attempts to confirm this observation (Snyder et al. 2005). Guélin et al. (2008) derived a 3σ upper limit on the column density of glycine of $1 \times 10^{15} \text{ cm}^{-2}$ per $2'' \times 3''$ beam in the Orion Hot Core and Compact Ridge. Here we consider the formation of glycine via neutral-neutral as well as radical-radical/radical-molecular pathways. Neutral-neutral pathways are taken from CC00ab and radical-radical/radical-molecular pathways are taken from

Woon (2002). Woon (2002) studied the formation of these molecules on UV irradiated ices. Here in our present study, we assume that these reactions are also feasible in the gas phase. In the case of the neutral-neutral pathways, H_2CO combines with the HCN to form $\text{C}_2\text{H}_3\text{ON}$ with a rate coefficient of $1.23 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ and the produced $\text{C}_2\text{H}_3\text{ON}$ combines with H_2O to form interstellar glycine with a rate of $2.68 \times 10^{-15} \text{ cm}^3 \text{ s}^{-1}$. In the case of radical-radical/radical-molecular pathways, reactions between CH_2NH_2 and the HCN lead to the formation of glycine. According to Woon (2002), CH_2NH_2 is produced via sequential hydrogenation of HCN and COOH originates from the reaction between CO and OH with a rate coefficient $1.13 \times 10^{-17} \text{ cm}^3 \text{ s}^{-1}$, where OH can be produced mainly through the photolysis of H_2O . COOH then recombines with CH_2NH_2 to form interstellar glycine with a rate coefficient $1.82 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$. According to Woon (2002), glycine formation by radical-radical/radical-molecular pathways most likely happens in such kind of interstellar ices, which could have experienced thermal shocks or could have formed in comets that could have passed through warmer regions of the solar system. In our model, we have assumed that these reactions are also feasible in the dense and cold gas as well, provided the cloud would have gone through the thermal shock regions. But if the cloud is dense enough and interstellar radiation field is not able to penetrate deep inside, in that case we could disregard the radical-radical/radical-molecular pathways.

3.1.3 Formation of alanine

Alanine is an α -amino acid with the chemical formula $\text{CH}_3\text{CH}(\text{NH}_2)\text{COOH}$ ($\text{C}_3\text{H}_7\text{NO}_2$). The α -carbon atom of alanine is bound with a methyl group ($-\text{CH}_3$), making it one of the simplest α -amino acids. This group of alanine is non-reactive so it is never directly involved in the function of proteins. Here we find out the rate coefficients for the formation of alanine via neutral-neutral (CC00ab) and radical-radical/radical-molecular (Woon 2002) reactions. For the neutral-neutral reactions, CH_3CHO , HCN and water molecules are involved. All species are reasonably abundant in the ISM. In the first step, HCN and CH_3CHO react together to form $\text{C}_3\text{H}_5\text{ON}$ with a rate coefficient of $1.84 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ (obtained from Eq. (2), by using polarizability 41.82 Bohr^3) and finally, $\text{C}_3\text{H}_5\text{ON}$ combines with the water molecule to form alanine ($\text{C}_3\text{H}_7\text{NO}_2$) with a rate coefficient of $3.09 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$. In the radical-radical/radical-molecular reaction pathways, NH_2CHCOOH and H are formed due to the fragmentation reaction of glycine ($\text{NH}_2\text{CH}_2\text{COOH}$). As glycine is formed with enough internal energy by a recombination reaction of CH_2NH_2 and COOH, the fragmentation energy of the above reaction is readily supplied during the formation of glycine. The rate coefficient of this reaction is $7.22 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$. Finally, NH_2CHCOOH combines with CH_3 to form alanine ($\text{C}_3\text{H}_7\text{NO}_2$) with a rate coefficient of $2.30 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$. As in the formation of glycine, Woon (2002) discussed the production of alanine in UV irradiated ice, which is much warmer. So this pathway might not be useful for a dense cloud. The neutral-neutral pathways as described by CC00a could be very useful in this context, since these two reactions are exothermic in nature.

3.1.4 Formation of glycolic and lactic acids

Glycolic acid is the smallest α -hydroxy acid, but lactic acid is a carboxylic acid. Both of them are classified as pre-biotic molecules. Due to the lack of any references on radical-radical/radical-molecular reaction pathways for the formation of these important pre-biotic molecules, we only consider the neutral-neutral pathways as used by CC00a, though these are endothermic reactions. The rate coefficient for the formation of lactic acid is calculated to be $2.31 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ (obtained from Eq. (2), by using polarizability 98.22 Bohr^3) and for glycolic acid it is $9.510 \times 10^{-15} \text{ cm}^3 \text{ s}^{-1}$.

3.2 Chemical Evolution of Pre-biotic Molecules

We consider a large network of gas phase and grain phase species to study the chemical evolution of the biologically important interstellar species. A separate hydrodynamic simulation was performed to obtain the physical parameters of a collapsing cloud. Our simulation was carried out for a spherically symmetric isothermal ($T = 10$ K) interstellar cloud collapsing for more than 4 million years. This is the typical lifetime of a molecular cloud (Das et al. 2010, 2012). Though the calculated rate coefficients, which are calculated by using the semi-empirical relation developed by Bates (1983), are applied for 30 K, we assume that implementation of these rate coefficients into our present 10 K model would be within the error bar.

In Figure 1, the time evolution of the number densities around different shells are shown. As expected, deep inside the cloud the density reaches its maximum value. We took the density distribution of the collapsing cloud as the input parameter of our chemical model to explore the ISM. In Figure 2, the variation of the final abundances of the interstellar pre-biotic molecules are shown with the associated depth of the cloud. On the 'Y' axis, n_X denotes the number of bio-species and n_H denotes the total number of hydrogen nuclei in all forms. It is evident from Figure 2 that the abundances are peaking inside the region around the 4th to 5th shell (in the case of glycine, it is peaking around the 1st shell). In the case of glycine, we also plot the peak abundance along with the final abundance. Glycine is decreasing due to the formation of $C_2H_4O_3$ ($C_2H_5NO_2 + H_2O \rightarrow C_2H_4O_3 + NH_3$) by the neutral-neutral reaction and formation of $C_2H_4NO_3$ by the fragmentation reaction ($C_2H_5NO_2 \rightarrow C_2H_4NO_2 + H$). Peak abundance obtained during the timescales of the simulation are 4.43×10^{-25} , 5.83×10^{-16} , 1.57×10^{-18} , 2.14×10^{-15} and 1.89×10^{-22} for interstellar adenine, alanine, glycine, lactic acid and glycolic acid respectively. If we exclude the radical-radical/radical-molecular pathways for the production of glycine and alanine due to the reason mentioned in the context of glycine and alanine, peak abundance obtained during the simulation time scales are 4.43×10^{-25} , 8.85×10^{-18} , 1.96×10^{-17} , 2.35×10^{-16} and 1.36×10^{-21} for the interstellar adenine, alanine, glycine, lactic acid and glycolic acid respectively around the region in the 4th to 5th shell. Abundance of adenine remains unchanged since excluded pathways do not influence its production at all. Abundance of glycine and glycolic acid experiences a huge jump due to this exclusion. In the pathways of Woon (2002), glycine readily dissociates into $NH_2CHCOOH$ and H, but now glycine is only channelized to form glycolic acid by reacting with a water molecule.

Since the abundances of most of the pre-biotic molecules are peaking at intermediate shells, in Figure 3, the time evolution of the pre-biotic molecules are only shown for the 5th shell. We started our simulation by assuming the initial elemental abundances are the same as mentioned in Woodall et al. (2007). We assumed that all the hydrogen was initially in the atomic stage. As time evolves, all the species start to become complex enough to initiate the formation of some pre-biotic molecules. In Figure 3, we plot the 'X' axis on a linear scale, whereas the 'Y' axis is shown on a log scale. This is because, in the beginning, formations of pre-biotic molecules are strongly hindered due to not having enough abundance for their required precursor species. Once the complex species that are required in the chemical network process start to form, the abundance of the pre-biotic molecules also starts to grow. During the timescale of the simulation, a near-steady state is attained by the stable complex molecules. The cause of the decrease in glycine abundance has been mentioned in the context of Figure 2 above. The first attempt to quantify the interstellar adenine was made by CC00a who proposed HCN addition reactions for its production. The rate coefficient for the successive HCN addition reactions was assumed to be $10^{-10} \text{ cm}^3 \text{ s}^{-1}$. Implementing the outcome of the quantum chemical calculation into our hydro-chemical model, it is verified that the radical-radical/radical-molecular interaction was found to be more suitable for the production of adenine in the ISM. In CC00b, the rate coefficients were parameterized by assuming that as the HCN addition reaction continues, the size of the molecule increases and thus the rate coefficient also increases

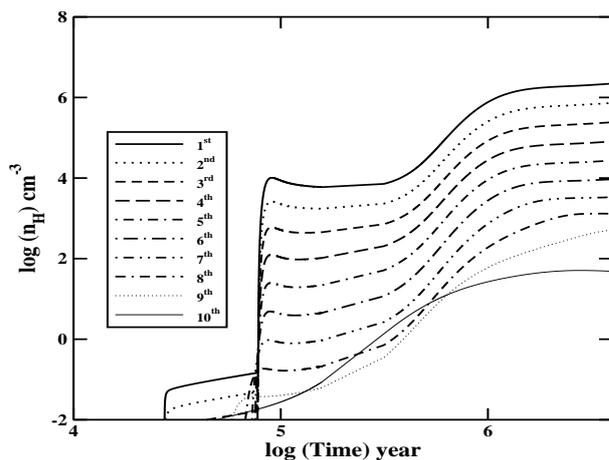


Fig. 1 Time evolution of the number density is shown for different regions of the collapsing cloud.

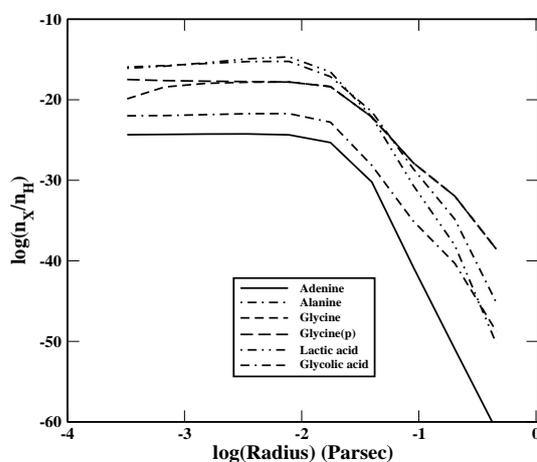


Fig. 2 Final abundances of several pre-biotic molecules along different radial distances in the collapsing cloud.

proportionally to the area in each of the intermediate steps of the adenine formation reaction. They assumed that the reaction rate constant varies as

$$\alpha_i = f^{i-1} \alpha_{Ad}, \quad (3)$$

where i is the number of steps involved (in CC00ab, adenine formation requires four steps); α_{Ad} and f were used to parameterize the reaction rates. By parameterizing the reaction rate constant, they ran seven models, namely: Model A ($\alpha_{Ad} = 10^{-16}$ and $f = 1$), Model B ($\alpha_{Ad} = 10^{-14}$ and $f = 1$), Model C ($\alpha_{Ad} = 10^{-12}$ and $f = 1$), Model D ($\alpha_{Ad} = 10^{-10}$ and $f = 1$, same as CC00a), Model

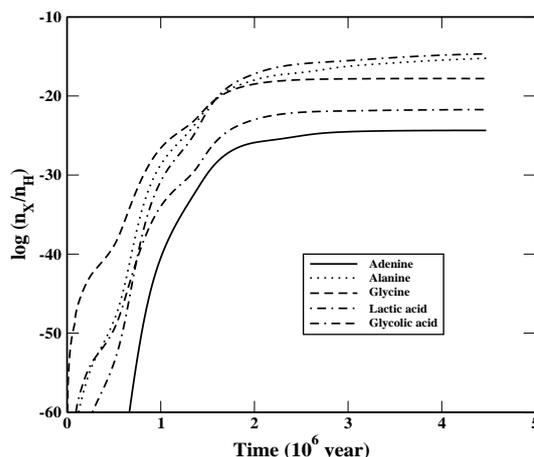


Fig. 3 Time evolution of the interstellar pre-biotic molecules around an intermediate shell of a collapsing cloud.

E ($\alpha_{Ad} = 10^{-16}$ and $f = 100$), Model F ($\alpha_{Ad} = 10^{-14}$ and $f = 10$), and Model G ($\alpha_{Ad} = 10^{-12}$ and $f = 5$).

According to CC00a (i.e., Model D of CC00b), the abundance of adenine was predicted to be 6.35×10^{-11} when the effective rate, $10^{-10} \text{ cm}^3 \text{ s}^{-1}$, was used. In the present simulation, even with the same rate constant as in CC00a, we find that the abundance is much lower at 9.84×10^{-15} . In CC00b, the adenine abundance was calculated to be 1.36×10^{-34} , 1.2×10^{-22} and 1.8×10^{-14} for Models A, E and G respectively. However, for the same models and assuming the same rate coefficients, our model calculates the adenine abundances 1.1×10^{-38} , 1.1×10^{-26} , and 1.65×10^{-18} respectively. These numbers are several magnitudes lower. There are mainly two reasons for this difference. First, we assume a different density distribution which directly comes from a numerical simulation. More importantly, we thoroughly consider the simultaneous interactions between gas and grains. We use a larger network of grain interactions along with a larger network of gas. Due to the presence of grains in our code, the gas phase HCN accretes onto the grain and as a result, the amount of HCN in the gas phase decreases. This in turn decreases the production of adenine by a few orders of magnitude. Production of adenine by assuming values from our present quantum chemical calculations is also plotted in Figure 4(a) (4.43×10^{-25}). As a passing remark, we note that the reaction rate coefficients considered in Model E of CC00b appear to be quite close to the actual adenine abundances reported in Figure 4(a). In Figure 4(b) and (c), a comparison by assuming the parameters given by CC00a and our present work has been carried out for the alanine and glycine respectively. As most of the pre-biotic molecules have a peak around the intermediate region, here we also use the density distribution according to only the 5th shell (Fig. 1). From Table 1, it is clear that for some of the reactions, estimated rate coefficients in CC00a are a few orders of magnitude higher in the case of neutral-neutral reaction pathways and since neutral species are very abundant in comparison to the radicals for the formation of alanine/glycine, abundances obtained by CC00a are much higher compared to those obtained by us. It should be noted that throughout the lifetime of the collapsing cloud considered here, the production of adenine is dominated by the radical-radical/radical-molecular reaction. This is because the reaction rates involved in the 1st step of the radical-radical/radical-molecular pathways are three orders of magnitude higher than the 1st step of the neutral-neutral pathways.

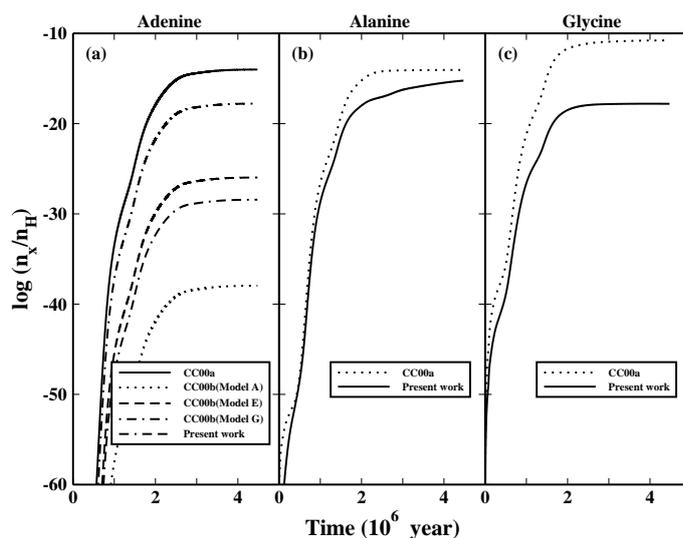


Fig. 4 Comparison of the calculated abundances of (a) adenine, (b) alanine and (c) glycine using various prescriptions.

In the case of adenine, $\text{NH}_2(\text{CN})\text{C}=\text{C}(\text{CN})\text{NH}_2$ (peak gas phase abundance 2.68×10^{-28}) and HCN (peak gas phase abundance 1.87×10^{-9}) recombine to form $\text{C}_5\text{H}_5\text{N}_5$ with a reaction rate of $3.99 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ in the last step of the neutral-neutral reaction network. Its formation via the radical-radical/radical-molecular reaction requires 6 amino 3H-purine (Molecule 5) (having a peak gas phase abundance of 2.63×10^{-26}) and CN (having a peak gas phase abundance of 7.23×10^{-9}) with a rate coefficient of $1.89 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$, when HCN is produced as an immediate product and $1.91 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ in case HNC is an immediate product. In the case of glycine production, CH_2NH_2 , having peak gas phase abundance of 7.09×10^{-11} and COOH , having peak gas phase abundance of 3.53×10^{-13} , are involved in the radical-radical/radical-molecular pathways with a reaction rate coefficient of $1.82 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$. Neutral-neutral pathways require $\text{C}_2\text{H}_3\text{ON}$, having a peak gas phase abundance of 7.29×10^{-13} and H_2O , having a peak abundance of 3.74×10^{-8} with a rate coefficient of $2.68 \times 10^{-15} \text{ cm}^3 \text{ s}^{-1}$. Though the neutral species for the formation of interstellar glycine are very abundant in the gas phase, the formation route via radical-radical/radical-molecular pathways contributes $\sim 100\%$ of the production. The reason is that a comparatively high rate coefficient is involved during the formation of glycine via radical-radical/radical-molecular pathways.

Interstellar alanine production by the neutral-neutral pathways requires $\text{C}_3\text{H}_5\text{ON}$ which has a peak gas phase abundance of 5.24×10^{-13} and a high abundance of the gas phase of H_2O with a rate coefficient of $3.09 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$. Radical-radical pathways require NH_2CHCOOH , having a peak gas phase abundance of 7.49×10^{-14} and CH_3 , having a peak gas phase abundance of 1.84×10^{-9} with a rate coefficient of $2.3 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$. An interesting trend is noted for production of alanine in the ISM. Throughout the process, a competition is going on between the two formation pathways. Sometimes the neutral-neutral pathway dominates over the radical-radical/radical-molecular pathway and sometimes the other way around. This depends on the abundances of the reactive species involved at that instant.

4 CONCLUDING REMARKS

In this paper, we explored the possibility of formation of various pre-biotic molecules during the collapse phase of a proto-star. Our main goal was to compute the abundances with realistic reaction rates and with the associated grain chemistry taken into account. We observed that not only the reaction rates were important, but the presence or absence of the grains also made a difference of several orders of magnitude in the final abundances of most of the pre-biotic molecules. Despite the high abundances of the neutral species, it is noted that in most cases, the radical-radical/radical-molecular reactions dominate over the neutral-neutral reaction pathways. The reason behind this is that the neutral-neutral reactions very often possess high activation barrier energies, whereas most of the radical-radical and radical-radical/radical-molecular reactions are found to be barrierless. In the case of adenine formation, it appears that the radical-radical/radical-molecular reaction is dominant (Smith et al. 2001), though the abundances of the neutral species are much higher. In CC00b, the reaction cross-sections for the neutral-neutral reaction of adenine was computed by assuming empirically that the reaction cross-sections increase with the size of the reactants and indeed, the final abundances of Model E of CC00b predict more or less similar results to what we have found here, though present rates are more accurate. In the case of adenine, throughout the time evolution, the production is dominated by the radical-radical/radical-molecular pathways. If the reaction pathways adopted from Woon (2002) for the production of alanine and glycine are assumed to be feasible in a cold dense cloud, then in the case of glycine, we find that the radical-radical/radical-molecular interaction plays the major role and in the case of alanine, both pathways significantly contribute.

In the last decade, the subject of computing abundances of pre-biotic molecules has considerably improved. The work presented in Das et al. (2008a) represents significant improvements over earlier works in describing grain chemistry in a collapsing cloud. This, along with improvements of the hydro-code to include the self-gravitating cloud, gives a more realistic understanding of the evolution of the chemical processes. In the future, we will reexamine these results by including rotation in the collapsing cloud, which includes shocks and outflows.

The earth is a generic planet around a generic star, and the processes to form pre-biotic molecules we described in the present paper are also generic. Thus, it is likely that every collapsing cloud would produce these molecules during the collapse phase. It is possible that during the stage of planet formation, the temperature increased sufficiently to destroy these molecules. As was speculated in CC00a, the residuals of a planetary disk, such as comets, could have preserved these molecules and showered the planet much latter with these molecules, providing the seeds of life in planets inside the so-called habitable zone. These are realistic speculations and works are under way to quantify them.

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