

In silico study of the interstellar prebiotic formation and delivery of glycine

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Abstract Reactions of simple molecules occurring at the surface of interstellar icy-based particles to give glycine, its capture on defects at a silica matrix simulating a meteoritic grain and its delivery to primordial Earth have been dealt with entirely via a molecular modeling approach based on rigorous quantum mechanical methods.

Keywords Quantum mechanical calculations · Strecker synthesis · Icy-particles · Amorphous silica · D2 defects · B3LYP

1 Introduction

In the early 1950s, the first computer simulation was carried out to study the equation of state of a simple two-dimensional fluid (Metropolis et al. 1953). A computer simulation is based on a model composed of equations that represent the functional relationships within the real system, and it is coded as a computer program. Since then, the field of computer simulation has grown enormously as the empirical Moore's law, which predicted that the number of transistors in a chip would double every 2 years, has been obeyed until the present time, ensuring enough computing power to solve, with good accuracy, the Schrödinger equation for both molecules and crystals. Computer simulations have advantages over real experiments in being able to study chemical processes occurring in particularly harsh conditions or in rather exotic environments which can be difficult or impossible to deal within a laboratory. Moreover, hypothetical chemical processes

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(what if...?) can be screened out quickly and cheaply by simulation before planning costly and difficult experiments. This last point is particularly relevant in the field of prebiotic chemistry, where it is indeed very hard to simulate in laboratory the conditions occurring at interstellar grain particles, or to decide which minerals may act as catalysts with respect to a given reaction (of the many possible) occurring in the primordial Earth. In the present work, we review some selected work from our group to show the usefulness of computer simulation based on quantum mechanical methods to establish the atomistic steps towards: (1) the formation of glycine (the simplest amino acid) from NH_3 , H_2O , $\text{HC}\equiv\text{N}$ and $\text{H}_2\text{C}=\text{O}$, as occurring on icy particles of the interstellar medium (Bernstein et al. 2002; Muñoz-Caro et al. 2002; Nuevo et al. 2008); (2) its trapping on strained silica surfaces present as one of the constituents of meteorites (Pizzarello 2006) and its release in the primordial Earth ocean.

2 Computational framework

The kind of chemical processes we address here concern reactions occurring in gas-phase and at the surface of either icy particles or minerals, these latter acting as effective catalysts. Furthermore, a large and diverse pool of reactive mechanisms may occur, involving proton/electron transfer, nucleophilic/electrophilic attacks and so on. Within the quantum mechanical context, approaches based on the refinement of the wave function such as Møller-Plesset (MP2) and coupled cluster [e.g., CCSD(T)] methods are adopted when high accuracy is needed (Sherrill 2010). Applicability of these methods is, however, hampered by the size of the system to model. Alternatively, since the late 1990s, approaches based on electron density (DFT) rather than on the wave function have become computationally cheaper alternatives to MP2 and CCSD(T), while achieving acceptable accuracy by means of well-designed electron density functionals (Sousa et al. 2007). When dealing with adsorption at the surfaces, either of icy-particles or of minerals, periodic boundary conditions (PBC), with the unit cell containing the potentially catalytic sites, are the natural methods of choice. Alternatively, it is possible to adopt a finite set of atoms cut out from the crystalline model but still containing the catalytic sites. Powerful computer codes have been developed over the years to solve the PBC problem for infinite systems; however, due to the infinite nature of the crystals, they can only be studied at the DFT level of theory. Furthermore, the search and characterization of transition state structures is far less developed compared to molecular codes. On the contrary, a large variety of quantum molecular programs can deal with the “finite cluster” approach (Sauer et al. 1994), in which complex chemical reactions can be studied by fully characterizing both minima and transition states, and the level of theory can be pushed up to CCSD(T), depending on the cluster size. This approach is plagued by the need to “heal” the dangling bonds resulting from cutting covalent/ionic bonds from the extended system and by the size of the cluster, which should be large enough to include the chemical features of the catalytic sites contained in the original infinite system. For that, the size of the cluster may become prohibitively large, reducing the aforementioned advantages when adopting a molecular computer code. A possible way out is to rely on an embedding techniques like the ONIOM method, proposed by Morokuma and co-workers (Morokuma 2003), in which only the region of main interest, e.g., the region close to a catalytic center, is treated at high level of theory [MP2, CCSD(T)], whereas the surrounding region is treated at a lower level (DFT, semi-empirical or even molecular mechanics). This last approach has been the method of choice adopted for many of the calculations reviewed here.

3 Synthesis of glycine from simple molecules as catalyzed by icy grains

Several experiments simulating the conditions of the circumstellar medium (ICM) in Earth laboratories resulted in the successful synthesis of amino acids (Bernstein et al. 2002; Muñoz-Caro et al. 2002; Nuevo et al. 2008), in which the catalytic role played by icy dust grain particles is evidenced. In this sense, theoretical works focused on thermally activated astrochemical reactions show the strong catalytic effect of the ice water (H_2O –ice) due to the proton mobility at the ice surface itself (Koch et al. 2008), in a similar manner to that observed for heterogeneous reactions occurring on stratospheric ices (Abbatt 2003).

One of the possible routes to form amino acids is the Strecker synthesis (Shibasaki et al. 2008; Strecker 1850), which has been postulated to occur in ICM, since the needed NH_3 , $\text{H}_2\text{C}=\text{O}$, H_2O and $\text{HC}\equiv\text{N}$ molecules are available in relative abundance. The detailed four-step Strecker-type scheme is shown in Fig. 1.

The potential energy surface (PES) for the four gas-phase steps shown in Fig. 1 was fully characterized at B3LYP/6-31+G(d,p) (Rimola et al. 2010). The role of a water icy particle was then modeled using a cluster of water molecules cut out from the (010) surface of XI bulk ice, a proton-ordered phase, analogous to ice Ih phase, which is stable at the conditions occurring in deep space. This is at variance with previous calculations (Koch et al. 2008) in which water was not organized in any definite crystal structure. To enforce the constraints due to the real surface on the finite cluster, the geometry of the water molecules (shown as balls and sticks in Fig. 2) was allowed to relax, whereas the external water molecules (shown as sticks) were kept fixed at their positions in the crystal.

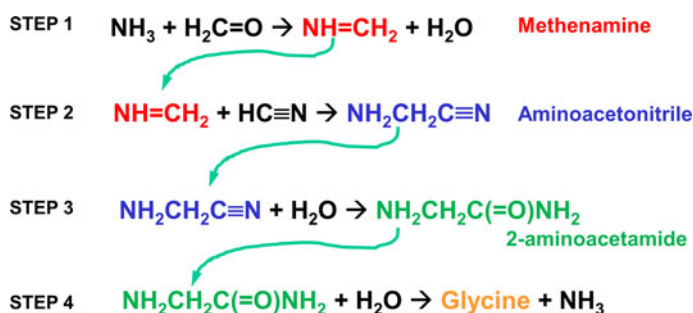


Fig. 1 The four steps of the Strecker synthesis of glycine

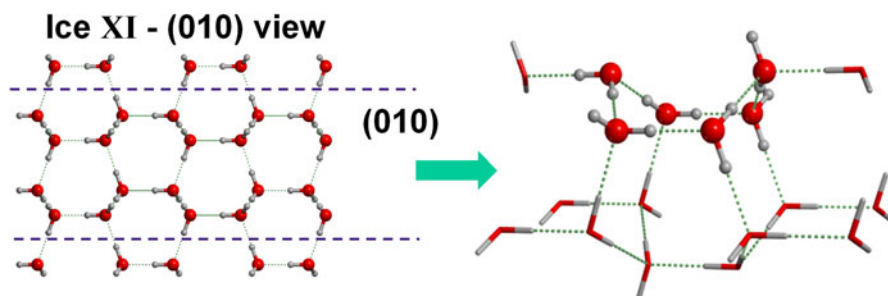


Fig. 2 Crystal portion of the water proton ordered ice XI. The cluster has been cut out from the (010) crystalline surface. Those H_2O shown as ball-and-stick models are free to optimize; the stick-only H_2O are kept at the same position as found in the crystal

In our simulation, we have excluded any effect due to the intense radiation and high-energy particles occurring in the ICM as our purpose was only to assess a potential catalytic role of the ice particle. The PES for the first step (S1) is shown in Fig. 3.

The ice particle has a dramatic catalytic role as the actual PES shows energy barriers which are reduced from 32 to 10 and from 44 to 15 kcal/mol, respectively, compared to the gas-phase reactions. The ice also stabilizes the methenamine product compared to the gas-phase. Analysis of the transition state structures reveals that the catalytic effect is due to the proton relay mechanism, i.e., the ice greatly helps the proton transfer within the reactants by synchronous proton displacements within the icy particle due to cooperative H-bond interaction. For the PES of the second step (S2, Fig. 3), a critical assumption was made, i.e., that the reactant $\text{HC}\equiv\text{N}$ can diffuse either from the gas phase or from a next neighbor site at the ice surface (a process hampered by the very low temperature of deep space) towards the trapped methenamine to initiate the reaction. The intermediate $\text{C}\equiv\text{N}^-/\text{CH}_2\text{NH}_2^+$ is formed, about 16 kcal/mol higher in energy with respect to the reactants, showing an ionic character. This adduct will not be formed in gas-phase, as charge separated complexes are very unstable, but it can survive adsorbed on the icy-particle due to the stabilization effect provided by H-bonds and polarization with and by the ice surface. The same reasons can be invoked to explain the large reduction of the last energy barrier compared with the gas-phase value. The reduction of the energy barriers due to the ice surface, compared to the gas-phase reaction, also resulted for step S3 (from 54 to 38 and from 27 to 5 kcal/mol, not shown in Fig. 3 for brevity). In the last step (S4, Fig. 3), the exchange of the NH_2 group of the amide with the OH group of the incoming H_2O has a rather high energetic cost which is not reduced enough by the presence of ice (from 49 to 39 kcal/mol), seriously hindering the formation of glycine. The main conclusions on the role of the ice particle are: (1) in all cases, reactions on the icy particle are thermodynamically favored; (2) the “proton relay” mechanism significantly lowers the reaction barrier compared to gas-phase reactions; (3) the reaction barriers are too high for the reaction to occur at the very low temperatures of deep space and aminoacetonitrile will accumulate [and indeed this intermediate has been detected in the ICM (Belloche et al. 2008)]; (4) a radical–radical mechanism (Woon 2002) and UV photons and high energy particles are expected to play an important role.

In conclusion, it is then conceivable that a reservoir of aminoacetonitrile (as a glycine precursor) could have accumulated in ICM, carried on cometary and interplanetary dust particles, and seeded on the early Earth by micro-asteroidal bombardment, behaving as a potential source for glycine formation.

4 Trapping and delivery of glycine at IDP

The main body of interplanetary dust particles (IDPs), besides organic fractions and ice, mainly contains inorganic silicates. Because of the several energy inputs in deep space, one can find phyllosilicates and anhydrous silicates, both in amorphous and crystalline phases, the latter only possible by high-temperature annealing of the former (e.g., when orbiting close to stars, $T > 1,000^\circ\text{C}$). The surface of silica IDPs shows silanol Si-OH groups which may undergo condensation processes such as $\text{Si-OH} + \text{Si-OH} \rightarrow \text{Si-O-Si} + \text{H}_2\text{O}$ due to the exposure to high T , which may lead to some strained surface defects. Among these, the $(\text{SiO})_2$ defective surface rings (so-called D2) are of particular interest because they are extremely reactive towards molecules (Bolis et al. 1991; Morrow et al. 1976; Rimola and

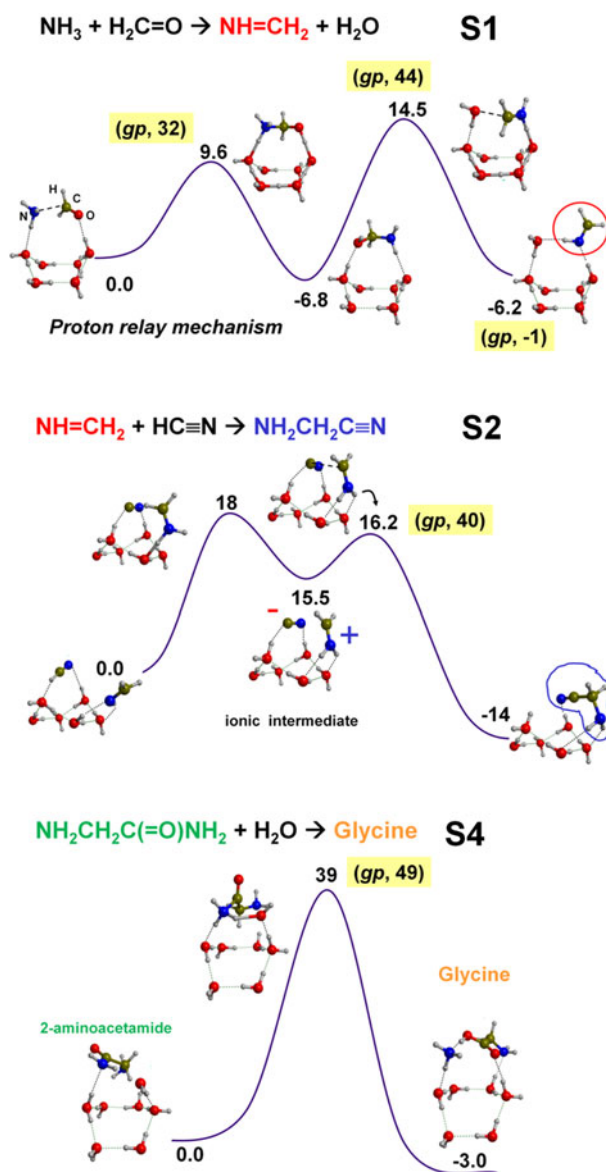


Fig. 3 B3LYP/6-31+G(d,p) PES of the first step (S1), second step (S2) and last step (S4) of the Strecker synthesis of glycine. For clarity of representation only the H_2O molecules of the ice particle free to relax are shown. Gas-phase values for the energy barrier are shown in *parentheses* and labeled as *gp*. All data are in units of kcal/mol

Ugliengo 2008) but seem to exhibit great stability in space due to the very low pressures and gas densities (see Fig. 4).

We have recently studied whether the D2 defects can play some role in capturing and transporting glycine from deep space to our planet. Quantum chemical calculations for the reaction between glycine and the D2 cluster model (shown in Fig. 4) were carried out

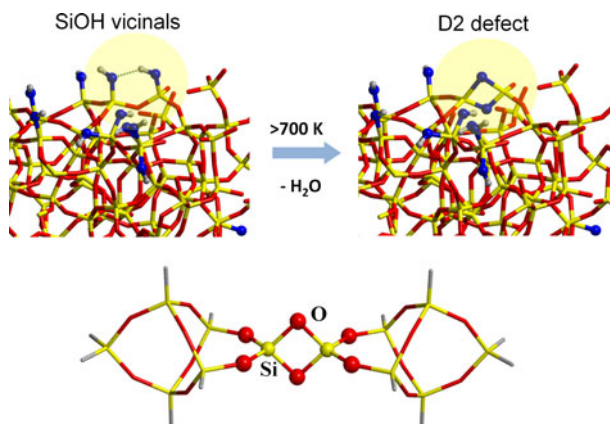


Fig. 4 Model of an amorphous silica grain and its surface features showing silanol groups (SiOH) which condense to give defective D2 rings when exposed to high T. At the *bottom* is the cluster model adopted for the D2 defect. Spheres/sticks treated at B3LYP/6-31+G(d,p)/MNDO levels with ONIOM2 approach

(Rimola et al. 2009b) to check the feasibility of the reaction. Calculations have been carried out optimizing the structures at the ONIOM2[B3LYP/6-31+G(d,p):MNDO] level and performing full B3LYP/6-31+G(d,p) single-point energy calculations onto the ONIOM2 geometries to improve the accuracy.

The energy profile for the reaction between Gly and D2 is shown in Fig. 5a.

The nucleophilic attack of the CO group towards the Si atom with a simultaneous proton transfer from the acidic OH group to the O atom of the Si–O–Si bond yields a very favorable opening of the D2 ring via a barrier-less process (transition state TS2-CO in Fig. 5a), showing the feasibility of the process at the cryogenic temperatures found in IDP. The P-CO product shows glycine chemically bound to the silica through a surface mixed anhydride $\text{Si}_{\text{surf}}\text{--O--C(=O)}$ bond, in agreement with experimental measurements (Basiuk et al. 1990). We also showed (Rimola and Ugliengo 2009) the chemical stability of P-CO against aggressive external agents (i.e., single molecules, UV radiation and cosmic rays) present in ICM, suggesting that its population in the IDPs might have been large enough to seed the early Earth by means of micro-meteoritic entries. Indeed, glycine was recently detected in samples returned from the NASA's Stardust spacecraft mission close to 81P/Wild comet (Elsila et al. 2009). We have also addressed the fate of P-CO once IDPs have landed in the primordial ocean. Computer modeling (see Fig. 5b) revealed that micro-solvating the P-CO (with 4 H_2O molecules) resulted in a free energy barrier and reaction energy ($T = 298\text{ K}$) of 21 and -14 kcal/mol , respectively, thus rendering the release of glycine a plausible process in normal ocean conditions.

According to these results, it seems that D2 defects are suitable for reaction, transport and release of glycine. However, D2 is just one possible defect among many others. Other surface silica defects, for instance, D3 rings, Si=O bonds and $\text{O}\equiv\text{Si}_3$ centers, may also be stable in the anhydrous conditions of space, and accordingly, a variety of organic molecules might have undergone similar reactions to those showed to occur with D2. A significant role of silica surface defects in capturing and delivering prebiotic organic molecules onto the primitive Earth is thus suggested.

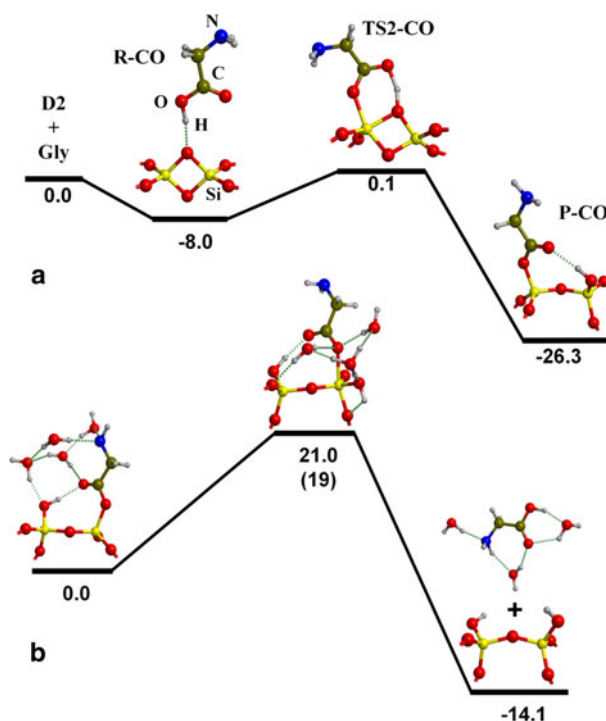


Fig. 5 **a** ZPE-corrected B3LYP//ONIOM2 potential energy profile for the reaction of the D2 defect with Gly. **b** B3LYP//ONIOM2 free energy profile ($T = 298$ K) for the hydrolysis of the surface mixed anhydride $\text{Si}_{\text{surf}}\text{-O-C(=O)-CH}_2\text{NH}_2$ by four water molecules. In *parentheses* is the value computed using the CPCM solvation model. Relative energies in kcal/mol

5 Conclusions

Overall, this short review shows that quantum chemical calculations on well-designed models can provide a fundamental understanding on the mechanistic aspects involved in chemical evolution (for further examples see Rimola et al. 2007, 2009a, 2010). It should be noted, however, that interpretation of theoretical results based on simplified models should be made with caution and that further improvements to describe these complex systems, including better surface models, role of the environment and dynamical effects (Schreiner et al. 2008), are major goals to be achieved in the coming years.

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