Tracing the Glycine from Quantum Chemical Simulations

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Glycine (Gly), NH2CH2COOH, is the simplest amino acid. Although it has not been directly detected in the interstellar gas-phase medium, it has been identified in comets and meteorites, and its synthesis in these environments has been simulated in terrestrial laboratory experiments. Likewise, condensation of Gly to form peptides in scenarios resembling those present in a primordial Earth has been demonstrated experimentally. Thus, Gly is a paradigmatic system for biomolecular building blocks to investigate how they can be synthesized in astrophysical environments, transported and delivered by fragments of asteroids (meteorites, once they land on Earth) and comets (interplanetary dust particles that land on Earth) to the primitive Earth, and there react to form biopolymers as a step towards the emergence of life.

Keywords: astrochemistry ; prebiotic chemistry ; interstellar grains ; primitive Earth ; computational chemistry ; surface modelling

1. Introduction

There is clear evidence that the Universe contains a rich chemical diversity and complexity. Since the detection of the first interstellar polyatomic molecule, i.e., NH_{3} , in 1968 ^[1], astrochemistry has experienced vertiginous growth, and it is, at present, a mature field of astrophysics.

Spectroscopic and photometric observations show that the space between stars is not empty but filled with diffuse matter, the interstellar medium (ISM). The ISM consists of gas and submicron-sized grain particles mixed together, which are not evenly distributed in the galaxy but are aggregated in clouds of gas, dust and ice ^{[2][3][4]}. Radio to near-infrared observations of the gaseous component have allowed the detection of more than 250 gas-phase molecules in the millimeter and submillimeter spectral regions ^[5]. Mid-infrared absorption has been used to probe the existence, composition and structural state of the interstellar grains. In diffuse clouds (with temperature 50–100 K and gas density $10-10^2$ cm⁻³), grains consist of amorphous silicates or carbonaceous materials ^{[6][7]}, while in dense cold clouds (with temperature 5–10 K and gas density 10^4 – 10^5 cm⁻³) these refractory materials are covered by ice mantles, mainly made of H₂O, and less abundant species, such as CO, CO₂, NH₃ and CH₃OH ^[8].

The chemistry involved during the formation of a solar-type planetary system from a primordial interstellar cloud is of great significance. Indeed, astronomical observations show that the physical evolution of a nascent solar-type system goes hand-in-hand with its chemical evolution ^[9], in which, at each step, more complex molecules form. In turn, the chemical evolution during the first phases of a solar-type planetary system formation could ultimately be connected with the origin of life ^{[10][11]}. The increase in molecular complexity can be summarized in three major steps: (i) formation of simple molecules, such as H₂ (the simplest ever molecule), H₂O, NH₃ or CH₃OH, during the prestellar phase; (ii) synthesis of interstellar complex organic molecules (iCOMs ^[12]), which are made up of 6–13 atoms where at least one is C, such as CH₃CHO or NH₂CHO, during the protostellar phase; and (iii) enhancement of the chemical complexity, with the production of some molecules with biological relevance, such as amino acids, nucleobases and sugars, during the final planet formation phase ^[9]. Remarkably, the chemical richness observed in solar-type planetary systems is not limited to local galactic star formation. Indeed, clouds in external galaxies are also made up of gas enriched with molecules (a remarkable fraction, ca. 33%, of the known interstellar molecules have also been detected towards external galaxies ^[5]) and grains (also consisting of silicates, carbonaceous grains and ice mantles ^{[13][14]}). Therefore, the same reactions responsible for the chemical richness of the galaxy also take place in external galaxies, demonstrating that chemistry, which is ultimately at the base of terrestrial life, is universal, as indicated by the Nobel prize C. De Duve ^[15].

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evolution during the first phases of a solar-type planetary system formation could ultimately be connected with the origin of life [10][11]. The increase in molecular complexity can be summarized in three major steps: (i) formation of simple molecules, such as H₂ (the simplest ever molecule), H₂O, NH₃ or CH₃OH, during the prestellar phase; (ii) synthesis of interstellar complex organic molecules (iCOMs [12]), which are made up of 6–13 atoms where at least one is C, such as CH₃CHO or NH₂CHO, during the protostellar phase; and (iii) enhancement of the chemical complexity, with the production of some molecules with biological relevance, such as amino acids, nucleobases and sugars, during the final planet formation phase ^[9]. Remarkably, the chemical richness observed in solar-type planetary systems is not limited to local galactic star formation. Indeed, clouds in external galaxies are also made up of gas enriched with molecules (a remarkable fraction, ca. 33%, of the known interstellar molecules have also been detected towards external galaxies ^[5] and grains (also consisting of silicates, carbonaceous grains and ice mantles ^{[13][14]}). Therefore, the same reactions responsible for the chemical richness of our galaxy also take place in external galaxies, demonstrating that chemistry, which is ultimately at the base of terrestrial life, is universal, as indicated by the Nobel prize C. De Duve ^[15].

Simple molecules and iCOMs have been detected in different astrophysical environments in the early stages of star formation (i.e., prestellar cores, protostellar envelopes and protoplanetary disks). Reaction chains taking place in the gas phase can explain the formation of some of these compounds but not all of them. Indeed, grains, besides their role in absorbing the interstellar UV photons and protecting molecules from photolysis, can also act as helpers in the formation of key species that cannot be efficiently synthesized by gas-phase reactions. Examples of species that are synthesized by surface reactions (evidenced by experimental and theoretical investigations) are H_2 [16][17][18][19][20], H_2O [21][22][23][24][25][26], CO_2 [27][28] and CH_3OH [27][28][29][30] as simple molecules, and some iCOMs such as CH_3CH_2OH [31] and, perhaps, NH_2CHO and CH_3OOCH [32][33][34][35][36][37][38][39]. Molecules of more enhanced complexity than iCOMs are hitherto exclusively identified in some comets and meteorites [40][41].

Two reasons could explain this exclusivity. On the one hand, the detection of large molecules in the ISM, which is only possible via the identification of radio to microwave rovibrational spectral lines, is hampered by the lower abundance and the larger number of transitions in species of increasing complexity. The result is that increasingly complex molecules have weaker and weaker lines, and, ultimately, their lines form a grass in the observed spectra, where it is impossible to uniquely identify a complex molecule. On the other hand, meteorites are fragments of asteroids that, when they fall on Earth, can be studied in terrestrial laboratories. Similarly, in situ (space mission) observations of comets allows people to identify rather complex molecules. In addition, alteration processes occurring in asteroids probably form complex species [42]. Indeed, hydrothermal processes can give rise to a net increase in molecular complexity because the asteroidal material, called "parent material", undergoes a variety of organic reactions in solution, yielding the formation of a new generation of more complex organic molecules ^{[43][44][45]}. Moreover, the inorganic solid components of these bodies (i.e., minerals, rocks and ices) have also been advocated to act as catalysts in the formation of these compounds ^{[46][47][48]}.

Some comets are remnant planetesimals that did not end up on planets and were scattered in and from the cold outer regions of the solar system. Space- and Earth-based investigations show that comets contain organic entities ^[49], which can be refractory in nature (and hence the suspicion that they are macromolecular organic polymers ^[50]), or volatile compounds ^{[51][52][53]}, like small aliphatic hydrocarbons (e.g., CH₄, C₂H₆ and C₂H₂) and simple aldehydes (e.g., H₂CO, CH₃CHO, NH₂CHO), alcohols (CH₃OH), carboxylic acids (HCOOH) and nitriles (CH₃CN). Among the meteorites, the carbonaceous chondrites (CCs) are the most pristine, less altered ones and are considered similar to the materials forming the original planetesimals. CCs contain large fractions of organic components ^{[41][54]}, which can be insoluble organic compounds, which can be as wide and diverse as amines, amides, alcohols, aldehydes, ketones, carboxylic and hydroxycarboxylic acids, sulphonic and phosphonic acids, aliphatic and aromatic hydrocarbons, and heterocyclic compounds. These organic compounds are important in terrestrial biochemistry as they could have been exogenously delivered to the early Earth, hence contributing to the emergence of the first prebiotic building blocks of life.

Among the different extraterrestrial organic compounds with biological relevance, the amino acid glycine (Gly) enjoys a central position. All the α -amino acids have a general formula of NH₂CHRCOOH, in which NH₂CHCOOH is the backbone chain (common for all the α -amino acids) and R is the lateral chain (allowing one amino acid to be differentiated from the others). Gly is the simplest amino acid because R=H, and its presence has been confirmed both in the Stardust's Wild 2 ^{[52][53]} and Rosetta's 67P ^[51] comets as well as in several CC meteorites ^{[41][54][55]}. Because of its chemical "simplicity" and its biological significance, Gly is a paradigmatic case to trace the sequential path of "formation \rightarrow transportation \rightarrow exogenous delivery to a primordial Earth" of essential biomolecular building blocks that could have played a crucial role in the emergence and evolution of biochemical systems in a prebiotic era. For the particular case of Gly (as well as for the other amino acids), condensation reactions between them lead to the formation of peptides and, ultimately, proteins.

The first step, the Gly formation, could take place in the early phases of the solar-type planetary system formation. In principle, Gly can be synthesised in the gas phase and/or on the surfaces of the dust grains ^[56]. Despite various propositions of gas-phase routes of Gly formation, none have so far been found to be efficient. The studied neutral-neutral and ion-neutral reactions have large activation barriers ^{[57][58]}. Thus, the alternative is its formation on the grain surfaces. In terrestrial laboratories, Gly has been successfully synthesized in experiments based on the energetic processing of ices ^{[59][60][61][62][63][64]}, whose composition is presumably similar to the interstellar ices. These experiments often use UV or proton/electron irradiation to simulate the stellar UV field and the cosmic rays that permeate the galaxy, although in quantities several orders of magnitude larger in order to have detections. As an alternative to these energetic processes, the non-energetic addition of atoms and radicals to ice mantle analogues also results in the formation of Gly ^{[65][66]}. However, one should bear in mind that, despite these positive results, interstellar Gly has not been detected yet, in spite of the numerous attempts ^{[67][68][69][70]}. A possible reason for the non-detection, in addition to the intrinsic difficulty to detect weak lines from such large and low-abundance species (see above), is that, if formed on the grain surfaces, the mechanism which would then liberate Gly into the gas phase could destroy it, as Gly is a fragile molecule ^[71].

Astrochemistry investigations have been traditionally based on a multidisciplinary approach, in which astronomical observations are combined with astrochemical modelling and laboratory experiments. However, this approach holds several limitations, especially when grain surface chemistry is concerned. Indeed, spectroscopic astronomical observations detect molecules and their quantity, but they do not tell us how they are formed, whether in the gas phase or on the grain surfaces, and, in the latter case, whether the presence of grains would be mandatory. Astrochemical models are used to reproduce and rationalize the observations; however, the uncertainties associated with the various parameters (reaction rate coefficients, species diffusion on the surfaces, etc.) used as input data cause the predictions to also be uncertain ^[72]. Laboratory experiments have been used to characterize the nature of the formed products, but the details of the reaction mechanisms and the exact role played by the grains cannot be elucidated ^[73], causing controversies in the proposed mechanisms. Such limitations can partly be alleviated by using a fourth pillar of investigation: quantum chemical simulations (QCs), as they can provide unique, quantitative information on processes of astrochemical (and prebiotic as well) relevance ^{[35][74][75]}, such as molecular mechanistic steps and the associated structure and energetics at an atomic scale.

2. Computational Framework

2.1. Quantum Chemical Methods and Basis Sets

Accurate calculations for reactivity (i.e., dealing with bond formation and/or breaking) require the use of quantum chemistry methods. Most of the time scholars are dealing with conditions and molecular entities in which the solution of the time-independent, non-relativistic electronic Schrödinger equation within the Born–Oppenheimer approximation is good enough (these calculations are often called electronic structure calculations). Quantum chemical methods can be classified into two major groups, based respectively on: (i) the wave function (WF) and (ii) the electron density through the density functional theory (DFT). WF methods are based on the resolution of the electronic Schrödinger equation for an N-electrons wave function. DFT methods, instead, focus on the Kohn–Sham rigorous theorem ^[76], establishing a one-by-one relationship between the energy of the non-degenerate electronic ground state and its corresponding electron density p(r) through an unknown (but formally proved to exist) functional F[p(r)] of the density itself.

The simplest WF-based method is the Hartree–Fock (HF) method, in which the WF is represented by the best set of mono-electronic spin-orbitals within a single Slater determinant representation of an N-electron system. This relatively simple description of the WF allows the HF equations to be solved in a highly efficient way by modern computer programs, at the price of the limited accuracy of the physicochemical predictions. The reasons for the limited accuracy lay in the instantaneous electron-electron correlation, lost within the HF mean-field approximation. This leads, among many other drawbacks, to a bad description of radical species, H-bond and charge transfer processes; besides, London dispersion interactions are also entirely missing within the HF approach.

2.2. Potential Energy Surfaces (PESs) and Thermochemical Corrections

The energy features of a chemical reaction (i.e., reaction energies, energy barriers, and, when occurring on surfaces, adsorption/desorption energies) can be characterized by its PES. Thus, PESs describe the evolution along a specific reaction coordinate of the energy of a reaction as a function of the geometries of the reacting species at each point of the reaction coordinate (energy profile). The most relevant points of the PESs (computed by means of any of the quantum chemical methods explained above) are the stationary points, i.e., points in which the gradient of the energy is zero. Stationary points have a physical meaning: minima are stable species and correspond to reactants, products, and

intermediates, while first-order saddle points correspond to transition state (TS) structures. A TS is the highest energy structure connecting two minima (e.g., between reactants and products), thus representing the minimum energy path to go from one minimum to the other.

The nature of the stationary points is characterized by the eigenvalues of the Hessian matrix, the second derivatives of the potential energy with respect to the atomic positions. Hessians with all positive eigenvalues characterize minima of the PES while one imaginary eigenvalue defines a TS, the associated eigenvector providing the direct line connecting the two minima.

2.3. Molecular Dynamics and Metadynamics

PESs are built from the electronic structure calculation of the different stationary points, which are structures in which atoms are considered stationary (besides the ZPE motion, vide supra). Thus, in these calculations, dynamic effects inferred by the temperature are not considered, and hence they are called static calculations.

Molecular dynamics simulations (MDs) must be employed to account for dynamical effects. They are also based on the Born-Oppenheimer approximation (separation of the electrons and nuclei degrees of freedom), in which the nuclei equations of motion are propagated classically following Newton's equation, in which the nuclei velocities are a function of the macroscopic temperature of the system. The forces acting on the nuclei are the opposite of the first derivative of the potential energy E, computed at the DFT level at each time step of the system evolution. To ensure proper energy conservation (in the case of the microcanonical system simulation), the integration time step should be less than 1 fs. These kinds of simulations are referred to as ab initio molecular dynamics simulations (AIMDs) [77]. As AIMDs are based on a DFT energy PES, they envisage the formation and breaking of chemical bonds. However, simulations of chemical reactions with standard AIMDs are hampered by the limitation of practical simulation timescales. That is, a chemical reaction is a rare event (due to the need of surmounting one or more energy barriers) that take place in much longer timescales than those provided by AIMDs (on the order of picoseconds). This drawback can be alleviated by adopting metadynamics [78][79]. It is a powerful computational technique that allows the sampling of free energy surfaces on selected degrees of freedom that govern the chemical reaction, which are called collective variables (CVs). The sampling is facilitated by the introduction of an external bias potential acting on the CVs. This external potential is a sum of Gaussian functions deposited along the system trajectory in the space of the CVs. The resulting deformed PES has reduced (up to zero) kinetic barriers, which can be easily overcome during the simulation time. Hence, metadynamics are informally described as "filling the free energy wells with computational sand".

2.4. Surface Modeling

Modelling surfaces requires the adoption of a model representative of the real surface. To this end, two strategies can be adopted: the periodic approach and the cluster approach ^{[74][75][80][81]}. In the periodic approach, a slab of finite thickness is cut out from the bulk (along specific Miller indexes) of the system under study. The resulting unit cell containing the most relevant surface features (normally adsorptive/catalytic sites) is repeated to an infinite 2D slab model. Convergence of the results (surface energy, structures, surface electrostatic potential, etc.) should be checked against the slab thickness. In contrast, the cluster approach consists of using a finite block of atoms cut out from the 2D slab model properly saturated at the frontiers of the block, arriving at a molecular system.

3. Gly Formation in the ISM

As for iCOMs, the formation of Gly in the ISM can occur through two routes: in the gas phases and on the grain surfaces. The first one advocates that the reactants are species in the gas phase, while in the second one, reactants are adsorbed and diffuse on the icy mantles. Several theoretical works have simulated Gly formation following these two major routes.

3.1. Gas-Phase Routes

One of the main reaction types to form Gly in the gas phase invokes the coupling of two radical species. These reactions are particularly appealing in astrochemistry because they are energetically very favorable; that is, they are barrierless, and the reaction energies are negative and very large, a crucial aspect due to the very low temperatures of the ISM. By means of these reactions, Woon ^[82] and Pilling ^[83] suggested that Gly could form by the coupling of the COOH and NH₂CH₂ radicals, and Sato et al. ^[84] suggested that Gly could form by the coupling of the H/NHCH₂COOH, NH₂/CH₂COOH and NH₂CH₂CO/OH radical pairs. Shivani et al. ^[85] also suggested similar processes for a plausible route to form serine, a more complex α -amino acid with R=CH₂OH. For all the cases, the authors also investigated the formation of the reactive radicals, which were based on reactions between a simpler radical and a closed-shell species

(the so-called radical-neutral reactions in the astrochemistry community). For instance, in the work of Woon ^[82], the formation of COOH takes place via a reaction involving OH and CO and NH_2CH_2 by successive reactions of H + HCN \rightarrow CH₂N, CH₂N + H \rightarrow CH₂NH and CH₂NH + H \rightarrow CH₂NH₂. It is worth mentioning that the precursor radical-neutral reactions, although having very favorable reaction energies, present high energy barriers so that these previous processes can inhibit Gly formation by radical-radical couplings. The same has been seen for the reaction of CH₃COOH with NH and NH₂OH ^[83]. Additionally, the efficiency of the radical-radical coupling in the gas phase is limited since Gly can dissociate back to reactants because it is not stabilized by three-body reactions.

3.2. Grain Surface Routes

Because of the watery nature of the ices, a reasonable path towards interstellar Gly is that occurring in water solution, namely, the Strecker synthesis. Strecker reactions comprise the synthesis of amino acids under acidic conditions by the reactivity of aldehydes/ketones with ammonia and hydrogen cyanide. For the particular case of Gly, the reaction involves three steps:

(i) $H_2C=O + NH_3 \rightarrow NH_2CH_2OH \rightarrow NH=CH_2 + H_2O;$

(ii) NH=CH₂ + HCN \rightarrow NH₂CH₂CN;

(iii) $NH_2CH_2CN + 2H_2O \rightarrow NH_2CH_2COOH + NH_3$.

This reaction is particularly attractive from an interstellar perspective because the reactants (i.e., H₂C=O, NH₃ and HCN) are compounds usually identified as minor species in the ice mantles, and the NH=CH₂ and NH₂CH₂CN intermediates are compounds observationally detected in different interstellar environments. Because of that, different works have simulated the Strecker synthesis (partly, totally or modifications of it) for the formation of Gly in the presence of water molecules mimicking the watery ice mantles.

4. Gly Transportation and Delivery to Primitive Earth

Irrespective of the way through which Gly forms in space, the next step to evolve into a more biochemically complex form in terrestrial environments is its transportation and delivery to the primitive Earth. A feasible way was that Gly, once synthesized, was adsorbed and entrapped on asteroidal dust grains (either of cometary, meteoritic or any other origin) and then released to the early Earth's surface. Although the chances of Gly delivery were highly likely during the epoch of intense meteoritic bombardments, it is worth mentioning that even today, great amounts of these dust grains continuously penetrate the atmosphere, enriching the planet with organic matter ^[86].

Theoretical simulations are useful tools to assess the validity of this "transportation and delivery" process since they can provide quantitative adsorption energies of organic compounds (here for Gly) on the grains. The critical point is what sort of solid materials one has to consider in this Gly adsorption. The rocky components of comets, meteorites and other asteroidal bodies are highly complex and heterogeneous (for instance, in meteorites, more than 275 class of minerals have been identified ^[87]. However, the most usual and recurrent families are: (i) silica, silicates, and aluminosilicates, (ii) metal oxides and (iii) metal sulphides. As a final comment, it is worth mentioning that these materials are usually in an amorphous structural state. However, due to the difficulty to model theoretically amorphous materials (see above), in most of the reported results, the solid-state substrates are in a crystalline form, in which the interaction occurs on extended surfaces (usually the most stable one) of their crystal morphology. Although this is not the actual situation, results provide useful insights into the Gly/surface interactions, as they are essentially driven by the presence of local surface defects (e.g., unsaturated sites, vacancies, dangling bonds), which are available in both crystalline and amorphous states.

4.1. Gly Interaction with Silica, Silicates and Aluminosilicates

These materials are abundant not only in the nuclei of comets, meteorites and interstellar grains but also in the Earth's crust. Pure silica (SiO_2) consists of $[SiO_4]$ tetrahedral units, whose different possible arrangements define a wide variety of polymorphs and structures. Silica surfaces are featured by siloxane (Si-O-Si) and silanol (SiOH) groups, the relative abundance of which dictates their adsorbent properties. Silicates are SiO_2 -based materials in which the negative charges of the $[SiO_4]^{4-}$ units are compensated by divalent cations (usually Mg²⁺ and Fe²⁺). Olivines are one of the most important silicate families, with the general formula Mg_{2x}Fe_(2-2x)SiO₄ (x = 0–1), whose Mg-pure member is forsterite (Mg₂SiO₄). Aluminosilicates are silicates in which Si atoms have been morphologically substituted by Al atoms. They usually contain additional alkali and alkaline earth cations and are a major component of clay minerals, such as montmorillonite.

4.2. Gly Interaction with Metal Oxides and Sulphides

Among metal oxides identified in presolar grains (i.e., solid matter that originated before the Sun was formed, including interstellar stardust, cometary and meteoritic dust, and interplanetary dust particles), the most usually identified ones are Al_2O_3 , $MgAl_2O_4$, $CaAl_{12}O_{19}$ and TiO_2 [88][89][90][91]. Interestingly, TiO_2 has been invoked as, in addition to silicate, a likely candidate to first form under the astrophysical conditions at which interstellar dust nucleated and condensated [92][93]. In relation to metal sulphides, FeS has been identified in protoplanetary disk grains ^[94] and is common in the mineralogy of meteorites ^[95]. Moreover, its presence indicates a low degree of water alteration since magnetite (Fe₃O₄) is the associated Fe-containing mineral for water-altered meteorites ^[42]. In comets, the usual way to identify iron sulphides is due to the presence of GEMS, i.e., glass with embedded metal and sulphides ^{[96][97]}. Investigations on the mineralogical nature of the 81P/Wild 2 and 67P comets indicate that the metal sulphide content is in the form of FeS and Fe-Ni sulphides ^{[98][99][100][101][102]}.

5. Gly Polymerization in the Primitive Earth

The polymerization of Gly leading to the formation of peptides takes place by the condensation reaction between two Gly molecules, i.e., $2NH_2CH_2COOH \rightarrow NH_2CH_2CH(=O)NHCH_2COOH + H_2O$ (see **Figure 1** for its intrinsic reaction mechanism in the gas phase). The chemical link between the two Gly (and, by extension, between two amino acids) is the peptide bond CH(=O)-NH. This reaction is associated with the release of one water molecule. This water release, however, renders the reaction to be thermodynamically disfavoured in an aqueous solution due to Le Chatelier's principle. Additionally, the intrinsic gas-phase reaction presents a high free energy barrier (~190 kJ mol⁻¹ in normal conditions, computed at B3LYP-D3) due to the highly strained 4th-membered ring present in the transition state structure (see **Figure 1**), and it is nearly isoergonic. Several postulates overcoming such thermodynamic and kinetic problems have been investigated, including the role of mineral surfaces, the presence of iron sulphides in extreme oceanic conditions, and the interaction of metal cations in aqueous environments as promoters of the reaction. These three plausible scenarios are briefly explained in the following subsections jointly with investigations carried out with quantum chemical simulations supporting them.



Figure 1. Reaction mechanism of the peptide bond formation between two Gly molecules. TS is the transition state connecting Gly with Gly Gly. Values in brackets refer to the energetics of the process in kJ mol⁻¹.

5.1. In the Presence of Mineral Surfaces

The formation of peptides in the presence of mineral surfaces was first suggested in the middle of the last century by the British biophysicist J. D. Bernal. He proposed the possibility that minerals can concentrate amino acids and activate them to polymerize and protect the formed peptides from external actions such as hydrolysis ^[103]. This seminal postulation has been subsequently strengthened and improved by a great number of experimental investigations ^{[104][105][106][107][108][109]} ^{[110][111][112][113][114][115][116][117][118][119][120]}, not only for peptide formation but also for the formation of other relevant biochemical systems such as polynucleotides ^{[121][122]}. The key point of this "polymerization on the rocks" ^{[123][124]} is that minerals can thermodynamically and kinetically favour the condensation of the biomolecular building blocks because, in essence, (i) mineral surfaces can act as dehydrating agents retaining the released water on their surfaces (thus overcoming the thermodynamic problem) and (ii) the interaction of the reactants with the mineral surfaces can activate them and reduce the energy barriers (thus overcoming the kinetic problem).

5.2. In the Presence of Iron Sulphides under Oceanic Extreme Conditions

Iron sulphides have also been invoked as relevant materials in the evolution of the primordial chemistry, in this case in the framework of the chemoautotrophy theory developed by Wächtershäuer ^[125] and Russell ^[126]. This theory proposes that the catalytic properties of iron sulphides driven by their redox chemistry could have promoted C fixation reactions from, e.g., simple CO or CO₂ that allowed the formation of organic compounds of biological relevance. These bioorganic compounds, on the iron sulphide surfaces, could have served as catalytic centres where primordial metabolic processes might operate, giving rise to the so-called autocatalytic surface metabolism. Hydrothermal vents present on the seabed, including their extreme conditions (i.e., high temperatures and pressures), have been shown to be plausible environments in which this surface metabolism can work ^[127]. A fundamental aspect of this theory is that the redox energy released in the oxidation of FeS to FeS₂ at the expenses of the reduction of H₂S into H₂ (Δ G = -38.6 kJ mol⁻¹) could have promoted the C fixation reactions. This has been validated by experimental evidence, e.g., formation of carboxylic acids from the reaction between CH₃SH and CO on (Fe,Ni)S surfaces ^[128](129], the formation of amino acids by the reaction of CO with cyano and methylthio ligands bound to (Fe,Ni)S surfaces ^[130], and the formation of peptides by activation of amino acids with CO in the presence of H₂S/CH₃SH on (Fe,Ni)S surfaces ^[131](132].

5.3. In the Presence of Metal Cations in Aqueous Solution

The experimental evidence that systems containing amino acids evolve into peptides in an aqueous solution in the presence of relatively concentrated NaCl and a small amount of $CuCl_2$ at T \approx 80 °C ^[133] formed the basis of the "salt-induced peptide formation" (SIPF) theory. Under these conditions, it was postulated that (i) the sodium ions are not fully hydrated so that they can act as strong dehydrating agents, and (ii) the interaction of the reactive amino acids with Cu^{2+} brings the two partners in close proximity and activates them, hence reducing the activation energies ^{[134][135]}. The SIPF reaction has also been combined in the presence of clay minerals, improving the yields of the peptide formation ^{[136][137]}. Despite these findings, the SIPF reaction has never been fully simulated with quantum chemical calculations.

6. Conclusions

Relative to the Gly synthesis in space, works based on processes occurring in the gas phase and on the icy grain mantles have been summarised. The works provided molecular insights into the proposed synthetic pathways and the related energetics, which in some cases were complemented with kinetic calculations. Although most of the routes were found to be promising, they required additional inputs for proper progress, such as the need for some temperature (100–200 K) to activate the reactions, the presence of third bodies that dissipate the large nascent energies, the occurrence of quantum tunnelling, or the presence of water ice defects caused by UV/cosmic-ray incidence.

According to the abovementioned sequence, the next step is the transportation of Gly to the primitive Earth by fragments of asteroids (found in meteorites) or comets (found in interplanetary dust particles), which could well have occurred during the very first phases of the solar system formation ^[138]. On that, theoretical works mostly address the interaction of Gly with different minerals present in comets and meteorites, particularly silica, silicates, aluminosilicates, metal oxides, and metal sulphides. The interaction of Gly with these inorganic materials is actually very strong, demonstrating their capability to capture and retain Gly up to an eventual release on Earth. Moreover, in some works, such a release process was demonstrated to be carried out by water, e.g., of the primitive Earth's oceans.

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