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Computer simulation and experimental self-assembly of irradiated glycine amino acid under magnetic fields: Its possible significance in prebiotic chemistry

Alejandro Heredia[a,*], María Colín-García[b], Teresa Pi i Puig[b], Leticia Alba-Aldave[b], Adriana Meléndez[a,c], Jorge A. Cruz-Castañeda[a,c], Vladimir A. Basiuk[a], Sergio Ramos-Bernal[a], Alicia Negrón Mendoza[a]

[a] Instituto de Ciencias Nucleares, Universidad Nacional Autónoma de México, Ciudad Universitaria, Circuito Exterior S/N, Coyoacán, C.P. 04510 Ciudad de México, D.F, Mexico
[b] Instituto de Geología, Universidad Nacional Autónoma de México, Instituto de Geología, Ciudad Universitaria, Circuito Exterior S/N, Coyoacán, C.P. 04510 Ciudad de México, D.F, Mexico
[c] Posgrado en Ciencias Químicas, Universidad Nacional Autónoma de México, Mexico

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ABSTRACT

Ionizing radiation may have played a relevant role in chemical reactions for prebiotic biomolecule formation on ancient Earth. Environmental conditions such as the presence of water and magnetic fields were possibly relevant in the formation of organic compounds such as amino acids. ATR-FTIR, Raman, EPR and X-ray spectroscopies provide valuable information about molecular organization of different glycine polymorphs under static magnetic fields. γ-glycine polymorph formation increases in irradiated samples interacting with static magnetic fields. The increase in γ-glycine polymorph agrees with the computer simulations. The *AM1 semi-empirical* simulations show a change in the catalyst behavior and dipole moment values in α and γ-glycine interaction with the static magnetic field. The simulated crystal lattice energy in α-glycine is also affected by the free radicals under the magnetic field, which decreases its stability. Therefore, solid α and γ-glycine containing free radicals under static magnetic fields might have affected the prebiotic scenario on ancient Earth by causing the oligomerization of glycine in prebiotic reactions.

1. Introduction

Glycine (amino acetic acid) is the smallest biological amino acid; this important peptide-forming molecule is also found in the interstellar medium (Elsila et al., 2009). Glycine formation in space has been suggested to be a product of ultraviolet photolysis(Lee et al., 2009) or high-pressure reaction from cometary impact (Goldman et al., 2010; Singh et al., 2013), although other possible mechanisms of formation are proposed (Elsila et al., 2007, 2009). This molecule is readily formed in prebiotic experiments and is important in chemical evolution (Goldman et al., 2010). In prebiotic chemistry, the interactions of amino acids and inorganic solids are relevant (Colin-Garcia et al., 2014; de la Cruz-López et al., 2016) because of the possibility of minerals adsorbing the different organic monomers to further catalyze some reactions or to promote polymerization processes (Fig. 1). In prebiotic chemistry, the condensation of glycine on silica, its thermal stability (Basiuk et al., n.d.), its process of oligomerization, and self-assembly are among the particularly important properties of glycine and glycine derivatives (Basiuk et al., n.d., n.d.; Basiuk and Bassiouk, 2011; Basiuk and Montiel, 2005; Meggy, 1956; Shanker et al., 2012).

At the molecular level, glycine shows singularities; differences in its crystalline features create diverse polymorphs α (space group $P2_1/n$, a = 5.102 b = 11.970 c = 5.457 β = 111°), β (space group, $P2_1$ a = 5.077 b = 6.267 c = 5.397 β = 113°) and γ (space group $P3_2$, a = b = 7.008 Å, c = 5.460 Å, α = 120°) (Iitaka, 1961). The γ-polymorph has potentially useful technological (Heredia et al., 2012) and possibly medical properties (Markel et al., 2010, 2011), which makes the crystalline structure relevant for effective action on the biological level. Glycine crystals have peculiar features, depending on molecular assembly and packing (Heredia et al., 2012). This makes this molecule a high-performance candidate for prebiotic chem-

* Corresponding author.
E-mail address: aheredia@nucleares.unam.mx (A. Heredia).

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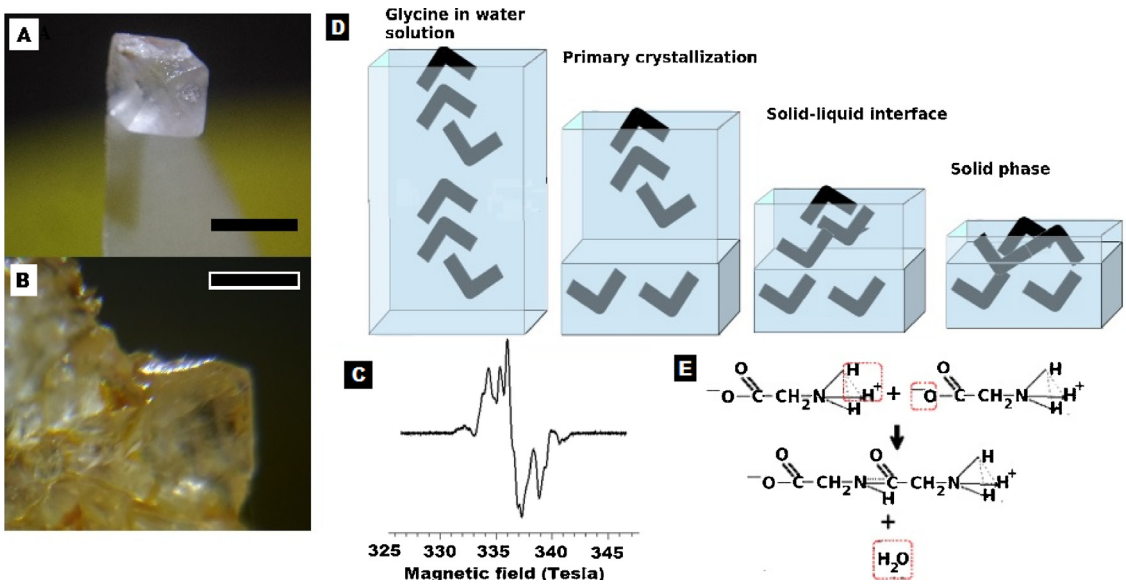

Fig. 1. A) A single glycine crystal grows under controlled conditions and B) irradiated glycine solid for water solutions (scale bars = 500 μm). C) EPR characterization shows the prevalence of free radicals in the glycine before its dissolution in water (EPR after present crystals' self-assembly showed no signal. Not shown). D) Schematic representation of progressive dehydration of glycine in the water solution. The solution with glycine dehydrates up to the point where saturation occurs. The last steps might promote peptide bond formation (E).

istry studies (Thomas et al., 2006). An important emerging property of the α-glycine is that when assembled in the presence of a magnetic field, the *c* axis is self-oriented at about 45° with the direction of the magnetic field (Sueda et al., 2006). Under the control of a magnetic field, this property potentially opens the way for a distinctive pre-designed molecular assembly or a possible low molecular weight magnetic signal transducer, relevant for both prebiotic and biological phenomena (Mitra-Delmotte and Mitra, 2010).

The different molecular organizations of glycine molecules (polymorphs) may contribute important additional information to the self-assembly of organics and help to further understand the behavior of molecules when exposed to magnetic fields, including surfaces of magnetic minerals. This could have taken place both on primitive Earth and on other bodies like comets or meteorites that contain magnetic solids such as magnetite. Since peptide bond formation is common during the hydration-dehydration process (Fox, 1957; Georgelin et al., 2013; Melius and Yon-Ping Sheng, 1975; Rodriguez-Garcia et al., 2015) (Fig. 1) it might be thermodynamically affected if a specific glycine-type polymorph forms as a template in advance. Peptide bond formation studies are fundamental in prebiotic chemistry (Jarvo and Miller, 2002; Ruiz-Mirazo et al., 2014). Some metabolic pathways use amino acid dehydration to covalently lengthen and form peptides (Garg et al., 2013).

Along with the fact that the molecular orientation of glycine changes with the surface interactions (de la Cruz-López et al., 2016) and magnetic fields (Hill et al., 2007; Sueda et al., 2006), the magnetic field also affects polymerization rates depending on molecular size, suggesting no clear effect of magnetism on monomers at 0.1 T (Rintoul and Wandrey, 2008). Furthermore, living forms are also sensitive to magnetic fields o (Acosta-Avalos et al., 1999; Ahmad et al., 2007; de Oliveira et al., 2010).

The effect of gamma ionizing radiation on glycine was studied as early as 1959 (Aydin and Osmangolu, 2011; Ghosh and Whiffen, 1959) and may be a driving force for the formation of new organic compounds (Negrón-Mendoza et al., 1983, 2001) through free radical formation (Fig. 1C). Glycine free radical $\left({}^{+}NH_3 - \dot{C}HCOO^{-}\right)$ might be an asset triggering electric signals and be a structural "guidance" under a magnetic field (De Bie and Braams, 1969).

Therefore, if free radicals can be affected by magnetic fields and the formation of alpha glycine polymorph is favored under such conditions, we are interested in determining what kind of glycine crystal polymorphs are subsequently formed under the effect of ionizing radiation and static magnetic fields. This study aims to understand the possible magnetic-induced formation of α-glycine and its transformation in γ- glycine crystals. We approached this challenge analyzing samples with attenuated total reflectance FTIR and Raman spectroscopy since both techniques can offer valuable information about changes at the molecular scale. Furthermore, to understand the potential catalytic preference of glycine polymorphs in promoting the dimerization of glycine single molecules, a theoretical study was performed finding the energetic differences of the polymorphs by the so-called AM1 semi-empirical simulations. We paid special attention to energies and dipole moments in the presence of magnetic fields. All this information is relevant considering small differences at the molecular scale can limit or favor the formation of supra-molecular crystalline structures (Jarvo and Miller, 2002) or can switch catalytic potentiality storage of the glycine crystal. At the molecular scale, glycine crystals are of relevance in prebiotic chemistry since those polymorphs promote the formation of peptide bonds (Rodriguez-Garcia et al., 2015).

2. Experimental

2.1. Sample preparation

All samples were prepared from water solutions (triple distilled water) of glycine (Sigma-Aldrich, 98.5% purity, USA) 1.5 M. All glassware used was previously washed with distilled water, rinsed out with ethanol, then dried at *ca.* 70 °C for 3 h. Pyrex glass Petri dishes (diameter 10 cm) were filled with 2.5 ml aliquots of the amino acid solution. Slow crystallization experiments were carried out at room temperature (23 °C) in the glass Petri dishes. Two sets of experiments were designed: 1) without a magnetic field and 2) in contact with 1, 5 and 10 magnets (6.0×10^{-2} T each; No. 372, DAISO, Japan) where duplicates were performed.

For the irradiated samples, glycine powder was exposed to gamma rays for 181 h (70 kGy) in a cobalt-60 Gammabeam 651PT facility at Instituto de Ciencias Nucleares, UNAM. Water solutions were prepared with the irradiated glycine. Crystallization experiments were carried out as described elsewhere (Heredia et al.,