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Organic matter and exogenous hypothesis

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Abstract

The idea of an exogenous origin of prebiotic species taking part in the construction of living organisms relies on a delivery of these species by meteorites and comets in-falls on the Earth. On another side real complex prebiotic molecules are not detected in the interstellar medium (ISM). Here we consider three fundamental points: i) the possible detection of small peptides, ii) the role of environmental conditions on amino acids, iii) the possible survival of these species to the radiation field.

1. Introduction

The fact that ~90% of the simple molecules identified [1] are the most stable isomers of their respective families is consistent with what is called the minimum energy principle (MEP) [2]. Using MEP as a pragmatic tool, we look for new candidates in the peptide family that is known to be a precursor of the more complex proteins and metabolites like urea. Using the same tool we look at amino acids Glycine (Gly) and Alanine (Ala) and find that they are not the most stable compounds in neutral form but are the most stable as protonated or zwitterions [3]. Here we consider whether the relative abundances of isomers could help in the characterization of the environment in which they are formed. The most primitive meteorites provide a window on organic matter in the solar system. In this geo-mineralogical context parent bodies appear as spatial laboratories in which aqueous alteration may have created the conditions of a rich catalytic chemistry in presence of metallic elements. After completion of a cooling process (solidification of the ice ~ 150K), the organic matter, embedded in the matrix of the carbonaceous chondrites, may be delivered to the Earth. In this scenario the role of these meteorites would be limited to that of means of communication.

2. Peptide models

A first study shows that the peptide bonding -CO-N- is most probably more common than originally thought. Formamide H-CO-NH_2 is the lowest energy isomer of the generic formula CH3NO. Up to now, it is the only isomer detected (1971) in the ISM [1]. After detection (2006) of CH_3CONH_2 [1], the next member of the amide series CH_3NHCHO [1] has been identified (2017) in agreement with MEP. The stability of the -[N-CO]- arrangement has been confirmed by the detection of Urea, and Thiourea should also be identified [4].

3. Amino acids and environment

According to the environment the most stable isomer is not the same. Neutral or protonated in gas phase, protonated or zwitterionic as a result of an aqueous alteration: the relative abundances appear as tracers of the geochemical structure of the parent bodies at the origin of the carbonaceous chondrites.

Table 1: Relative energy of amino acids isomers

C2H5NO2	ΔE	C2H7NO2	ΔE
Neutral isomers			
$CH_3NHCOOH$	0.0	$CH_3CH_2NHCOOH$	0.0
$CH_3OC(NH_2)O$	4.7	$CH_3CH_2OC(NH_2)O$	3.3
NH_2CH_2COOH	10.3	$(CH_3)_2NCOOH$	7.0
$HOCH_2C(NH_2)O$	10.6	$HOCH(CH_3)CONH_2$	10.3
$HOCH_2NHCHO$	17.0	CH_3-OOC-NH-CH_3	10.6
		$NH_2CH(CH_3)COOH$	10.8
		$NH_2CH_2CH_2COOH$	11.5
Protonated isomers			
NH_3^+-CH_2COOH	0.0	$NH_3^+CH_2CH_2COOH$	0.0
CH_3-NH-$C(OH)_2^+$	2.2	$NH_3^+CH(CH_3)COOH$	5.8
CH_3-$OC(OH^+)NH_2$	4.7	$HOCH_2CH_2C(OH^+)NH_2$	6.5
HO-$CH_2C(OH^+)NH_2$	6.0	$CH_3CH_2OC(OH^+)NH_2$	9.5
NH_3^+-CH_2O—CHO	15.4	$CH_3CH_2NHC(OH)_2^+$	9.6
Zwitterion isomers(*)			
NH_3^+-CH_2COO^-	0.0	$NH_3^+CH(CH_3)COO^-$	0.0
CH_3-NH_2^+-COO^-	2.6	$NH_2CH_2CH_2COO^-$	0.5
		CH_3CH_2-NH_2^+-COO^-	3.7

Technical note: Density functional theory (DFT), within the B3LYP/6-311G** formalism was used throughout, except for zwitterions(*) where dispersion effects are introduced at the MP2 level. All structures, fully optimized, were verified to be stationary points by vibrational analysis. ΔE(kcal/mol.)

Based on MEP, the quantum simulations show that Gly, α- and β-Ala isomers are the most stable species in only two conditions, namely in protonated or in zwitterionic forms. However, it is remarkable that the stability order for Ala is not the same in both cases. In a protic environment, β-alanine is more stable than the biological α isomer and for that reason should be more abundant. It is what is found in the most extensively parent-body altered chondrites Orgueil, Ivuna and Essebi. In a neutral water environment, that favors the zwitterionic structures, α-alanine is more stable than the β-isomer and for the same energetic reason should be more abundant. It is precisely what is found in meteorites that have experienced terrestrial weathering.

4. Survival of amino acids

It has been shown that several amino acids can be formed in the laboratory by UV irradiation of interstellar ice analogues containing H_2O, CH_3OH, NH_3, CO, and CO_2 [5]. The survival of these amino acids embedded in the ice along their journey to the Earth is still an open question.

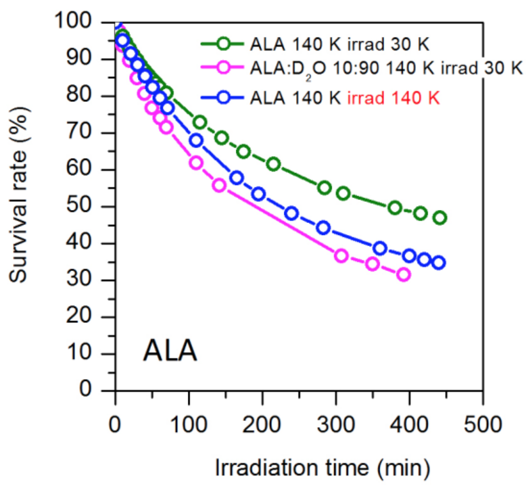

Figure 1: Ala survival followed by ν CO frequency.

Irradiation in ultra high vacuum (30K) on the TEMPO beam line (SOLEIL synchrotron), simultaneously with near-edge X-ray absorption spectroscopy was carried out. The experiments show that Ala, like Gly [6] is only partially destroyed. Its abundance is found to stay at a level of ~ 30-40% of the initial concentration, for an irradiation dose equivalent to three years of solar radiation (at a distance of one astronomical unit).

This result supports the hypothesis that, if trapped in icy environments and/or in the interior of interplanetary particles and meteorites, amino acids may partly resist the radiation field to which they are submitted and survive the journey to the Earth.

5. Summary and Conclusions

Using MEP as a pragmatic tool, we show that the peptide link -CO-NH- is the most stable arrangement leading to amides and to urea and by extension to peptides. These simulations, which agree with observations and experiments can be extended to new targets to search for in the ISM. Looking at amino acids Glycine and Alanine we find that they are not the most stable compounds in neutral form but are the most stable as protonated or zwitterions. The relative abundances of isomers differ with the nature (protonated or zwitterions) and represent a possible tracer of the environment in the parent bodies where they are formed. Partial survival of these acids when embedded in the ice has been demonstrated.

However, one critical question remains unsettled, i.e. whether homochirality is preserved in these transfer conditions. It is currently under investigation.

Acknowledgements

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