

Synthesis of further biological compounds in interstellar-like conditions

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Abstract – A graphite target is bombarded at very low pressures with molecular beams of dihydrogen and dinitrogen, in the presence of low-pressure dioxygen. The large variety of complex organic molecules thus produced have been characterized by their mass spectra (molecular and fragmentation peaks) and identified by comparison of these spectra with authentic samples. This extends the variety of complex biological substances obtained in these ‘interstellar-like’ conditions. **To cite this article:** *F.M. Devienne et al., C. R. Chimie 5 (2002) 651–653* © 2002 Académie des sciences / Éditions scientifiques et médicales Elsevier SAS

molecular beams / mass spectrometry / fragmentations / syntheses / biomolecules

Résumé – Synthèse de nouveaux composés biologiques dans des conditions quasi interstellaires. Par bombardement d’une cible de graphite par des jets moléculaires de dihydrogène et de diazote, en présence de dioxygène à basse pression, on obtient une grande variété de produits organiques complexes : acides aminés, bases azotées nucléiques, sucres, acides organiques, etc. Ces produits ont été identifiés par leur masse moléculaire et leurs spectres de dissociation, par comparaison avec les spectres obtenus à partir d’échantillons authentiques dans les mêmes conditions de spectrométrie de masse. Ceci vient notablement enrichir le catalogue de substances organiques complexes d’importance biologique, dont nous avons déjà montré qu’elles peuvent être obtenues dans ces conditions « quasi interstellaires ». Contrairement aux résultats précédemment décrits, qui avaient été confirmés par l’utilisation de cibles en graphite ¹³C et d’un jet de ²H₂, les nouvelles identifications découlent uniquement de la masse moléculaire et des masses des fragments obtenus dans une chambre de collisions, comparées au spectre de fragmentation d’échantillons authentiques. Nous commentons la signification de ces synthèses, dont nous pensons qu’elles démontrent, comme d’ailleurs celles, classiques, de Miller et d’autres, plus récentes, la facilité d’obtention des « briques de la vie » à partir des éléments, si on porte ceux-ci à des niveaux énergétiques élevés et si on réalise ensuite une « trempe ». **Pour citer cet article :** *F.M. Devienne et al., C. R. Chimie 5 (2002) 651–653* © 2002 Académie des sciences / Éditions scientifiques et médicales Elsevier SAS

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1. Introduction

In a previous publication [1], we have described the synthesis of a series of amino acids and of nucleic bases by bombardment of a graphite target with high-energy molecular beams of hydrogen and nitrogen, in a low-pressure atmosphere of oxygen. The substances formed under these ‘quasi-interstellar conditions’ were

identified by combining several criteria: peaks were selected at the expected mass in the primary spectrum and passed through a collision box (argon) to give a fragmentation spectrum of secondary ions. This secondary spectrum was compared and identified with published fragmentation spectra found in various databases, and with the spectra obtained in similar conditions from a reference sample of the postulated sub-

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stance. Furthermore, replacement of the ^{12}C graphite target by one of ^{13}C , and/or replacement of the $^1\text{H}_2$ beam by a $^2\text{H}_2$ beam, gave independent and confirmatory evidence both for the mass of the parent molecule, and for that of the fragments. We consider that the convergence of this series of indications is tantamount to a strict proof of the formation of the molecular species then reported.

However, in these experiments, the primary spectrum shows many more peaks than the few we had identified, which points to the formation of a still richer variety of products. We wish now to list those which we have identified, admittedly less rigorously than those of the first series in so far as we have *not* run in these cases the important – some would say decisive – isotopic replacement experiments. We rely therefore in these new cases *only* on the coincidence of the mass fragmentation spectra with those of reference materials, tested by us on the same mass spectrometer or an equivalent one.

2. Materials and methods

The experimental set-up and the experimental procedures were identical with those previously described [1, 2]. However, in the present case, we have limited the study to a ^{12}C target, using, as we had done previously, a high-energy jet of $^1\text{H}_2$ and $^{14}\text{N}_2$ and a low-pressure atmosphere of $^{16}\text{O}_2$.

The primary spectrum shows peaks easily separated into unit peaks without pushing the resolving power of the instrument to its limit. There are primary peaks at all unit masses (some have been assigned with a better accuracy, 0.2 m.u.), but of course having quite different intensities. From these, as in our previous study, we have arbitrarily selected some, either on the basis of their relatively higher intensity, or because their molecular formula corresponded to ‘interesting’ potential products. We present here only those cases that have led to clear conclusions by comparison with authentic materials tested by us in similar conditions. These authentic materials were all of the best commercial quality available (usually from Fluka AG).

In a few cases, the same mass (at unit resolution) corresponded to several primary products for which we obtained authentic samples. We have proposed identifications when the fragmentation spectrum observed for the corresponding primary unit peak contained all the fragments observed by us in the fragmentation spectra of both postulated components; these cases will be mentioned explicitly in the text.

3. Results

3.1. Amino acids

To those already identified (glycine, alanine, leucine or isoleucine), we now add *asparagine* (132), *aspartic acid* (133), *glutamic acid* (147), *histidine* (155), *phenylalanine* (165), *arginine* (174), *tyrosine* (181), and the dipeptide *glycylalanine* (162). A peak at 146 could correspond to *lysine* (146.19) or to *glutamine* (146.15), or to both (the identity of the fragmentation observed for authentic samples of these substances made it impossible to distinguish between them).

3.2. Nucleic and other nitrogenous bases

To adenine and uracil, can now be added: *creatinine* (113), *purine* (120), *nicotinamide* (122), *nicotinic acid* (123), *thymine* (126), *creatine* (131), *guanine* (151) and *orotic acid* (156).

3.3. Sugars

The peaks at 134, 150, 180, gave the same fragmentation patterns as authentic *deoxyribose*, *ribose* and *glucose*, respectively, but we have *not* checked the fragmentation spectra of the stereoisomers of these sugars, from which they can most probably not be distinguished. For a peak at 120, the fragmentation pattern (17, 28, 29, 31, 57, 60, 86, 89, 91, 103, 119) was identical with those of the undifferentiated C_4 -sugars *erythrose* or *erythrulose* (120).

3.4. Diacids

We have identified *fumaric* or *maleic* (116), *succinic* (118), *oxaloacetic* (132), *malic* (134) and *citric* (192) acids.

3.5. Aromatic hydrocarbons

We have identified *toluene* (92), *xylene* (106), *cumene* (120) and *naphthalene* (128).

3.6. Various products

A peak at 172 gave all the 12 fragmentation peaks observed for *vitamin K₃*. When the graphite target had been sprinkled with sulphur before bombardment, we could detect peaks at 121 and 149, which gave all the fragmentation peaks of *cysteine* and *methionine* respectively. In this case, a primary peak at $m/e = 135$ might correspond either to *S-methylcysteine* or to its isomer *homocysteine*. Its dissociation gave fragments at 14, 17, 33, 40, 43, 44, 45, 46, 47, 57, 60, 73, 74, 88, 90, 102, 118, 134. Dissociation of authentic *S-methylcysteine* and of authentic *homocysteine* gave the following fragments.

S-methylcysteine: 14, 17, 43, 44, 45, 46, 47, 60, 74, 75, 88, 90, 118, 134.

Homocysteine: 17, 33, 40, 45, 57, 73, 90, 102, 134.

We therefore conclude that both isomers are present in the products of bombardment.

4. Discussion

Of course, the molecular identifications described earlier, supported by isotopic replacements, are more reliable, and we have even mentioned here a few cases where we cannot distinguish between isomers. At any rate, the results described in our previous publication [1] and here reveal the bewildering variety of substances formed under quite brutal conditions similar to those that may occur on interstellar dust grains and which might have ‘seeded’ the Earth. Most of the products we have identified are of biological importance, but this is due only to an intentional bias: we have focussed our search on those, and our results, therefore, seem to suggest that the products we have identified are the major products of these brutal experiments. The identification of toluene and

other aromatic hydrocarbons shows, in fact, that molecules without any biochemical significance are also formed; we had also already shown in an earlier study that graphite, under bombardment by high energy molecular beams of dinitrogen and dihydrogen, gave a series of acetylenic nitriles, culminating at HC₉N [3]. These nitriles are interesting as they have been found by astrophysicists in interstellar matter, but are certainly of no biochemical significance.

We would like to conclude with a remark applying to all the ‘prebiotic’ syntheses described so far [4, 5]. We feel that all these syntheses show is that the ‘bricks of life’ are easy to obtain under harsh conditions, provided of course the right atoms are present. All that is required is that enough energy be injected, in whatever manner, and that the system be appropriately quenched. This would imply that any discussion of the significance of any of these results to validate conditions having prevailed on the primitive Earth at the time of the origin of Life is irrelevant, whether it relates to the nature of the primordial atmosphere (reducing or not), or to the concept of seeding of the Earth by organic matter synthesized in interstellar space (despite the title of the present article!), or to that of photochemical prebiotic syntheses [5], all of which may have played a concurrent role.

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