

Chapter 10

Photochemistry and Photoreactions of Organic Molecules in Space



Avinash Vicholous Dass, Hervé Cottin, and André Brack

Abstract The primary aim of exobiology research is to recognize the routes leading to the initiation of life on Earth and its plausibility elsewhere in the universe. How would we recognize life if we encounter it or its remnants on an extraterrestrial body? This is the critical question of biosignature research to which astrochemical studies can contribute. Our understanding of preserved fossils and contemporary terrestrial life serves as a guide in the search for biosignatures in the universe. Of the various life-detection techniques available, carbon chemistry is particularly pertinent and perhaps the most significant biosignature (Summons et al., *Astrobiology* 11 (2):157–181; 2011). ‘Life’ as we know it is based on C, H, N, O, P, S chemistry and the organic matter derived from its remains is ubiquitous on Earth, constituting an extensive chemical and isotopic record of past life that surpasses by a huge margin what is recorded by visible (and microscopic) fossils. Biosignatures are highly subjective to the geological conditions in which they form and the subsequent diagenetic and metamorphic events that reprocess them (Sleep, *Cold Spring Harb Perspect Biol.* 2(6): a002527; 2010) and thus need careful assessing before coming to concrete conclusions concerning biogenicity. However, chemistry alone is inadequate to detect life and collaborative efforts from all of the relevant investigations, combined with considerations of geological and environmental factors, will likely provide the best evidence for the presence or absence of life, in localities of interest.

A. V. Dass (✉) · A. Brack
Centre de Biophysique Moléculaire, CNRS, Orléans, France
e-mail: avinash.dass@cnrs-orleans.fr; brack@cnrs-orleans.fr

H. Cottin
Laboratoire Interuniversitaire des Systèmes Atmosphériques (LISA), UMR CNRS 7583,
Université Paris Est Créteil et Université Paris Diderot, Institut Pierre Simon Laplace, Paris,
France
e-mail: herve.cottin@lisa.u-pec.fr

10.1 Why Are We Interested in Radiation Chemistry for Biosignatures?

Radiation is an important factor that influences organic molecules (Swallow 1960) and the antagonistic nature of radiation over a long period of time makes direct detection of biosignatures difficult, as the search for organic signatures on Mars has amply documented (e.g. Freissinet et al. 2015).

Spectroscopic studies have revealed an abundance of small molecules, such as CH_3OH , $\text{CH}_3\text{CH}_2\text{OH}$, HCHO , HCOOH and HCN , in the interstellar medium and the role these molecules play in the formation of organic polymers or complex organic material on exposure to UV radiation and/or thermal activation (Tielens and Charnley 1997). Moreover, the major source of organic molecules on the early Earth is credited to extraterrestrial matter, impact shocks and UV or electrical discharges (Chyba and Sagan 1992). Radiation can lead to molecular synthesis, as well as destruction and thus, the understanding of radiation-molecule interactions becomes pertinent to biosignature investigations.

10.2 Modes of Production and Delivery of Organic Material

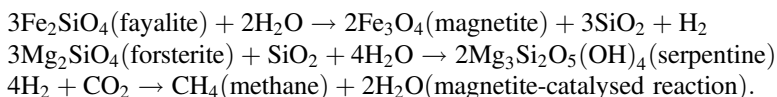
10.2.1 *Endogenous Delivery*

The present understanding is that atmospheric conditions on our primitive Earth were very different to the conditions simulated in the Miller–Urey experiment (Miller and Urey 1959), the atmosphere being rather neutral to mildly reducing (e.g. Kasting et al. 1993). The Miller–Urey experiment demonstrated the ease of production of several amino acids and other prebiotically relevant organic compounds from small molecules, like water (H_2O), methane (CH_4), ammonia (NH_3) and hydrogen (H_2). Recent studies also reveal that more than 40 amino acids and other amines were synthesized with similar experiments by conditions that simulated volcanic eruptions and lighting on the primitive Earth environment (Bada 2013).

Organic molecules in the subsurface of present Earth are mainly found in the zones influenced by hydrothermal activity. Central to origins of life hypotheses focused on hydrothermal vents are their associated reactions and products, such as minerals in vent walls and small molecules including CO_2 , CH_4 and H_2 (Shock and Schulte 1998), formed by Fischer Tropsch-type (FTT) synthesis. FTT synthesis involves the interaction of hot hydrothermal fluids with (ultra) mafic rocks, i.e., rocks rich in Fe and Mg minerals (olivines, pyroxenes), a process termed serpentinisation. Fischer Tropsch-type synthesis on hydrothermally formed alloys has been demonstrated to catalyse the formation of alkanes (C1–C3) in alkaline hydrothermal conditions (Sherwood Lollar et al. 1993; Horita and Berndt 1999). The formation of C2 and C3 alkanes apparently depends on the presence of metallic catalysts, such as Cr, an

element common in peridotite rocks associated with oceanic crusts (Foustoukos and Seyfried 2004).

Common serpentinisation reactions include:



Although the fact that these kinds of molecules could be produced by and in hydrothermal processes initially suggested that the subsurface could be a potentially substantial source of organics for prebiotic reactions, McCollom and Seewald (2001, 2003) estimated that the potential for abiogenic methanogenesis, for instance, on the early Earth may have been minimal. Furthermore, a recent observation suggests that methane (CH_4) and higher hydrocarbons are, in fact, derived from fluid inclusions trapped in plutonic rocks, which are liberated upon cooling at the seawater-hydrothermal fluid interface, thus generating hydrocarbon-rich fluids (McDermott et al. 2015), rather than being formed by subsurface Fischer Tropsch synthesis. In each of these scenarios, however, the subsurface is an endogenous source of organic molecules.

10.2.2 Exogenous Delivery

10.2.2.1 Extraterrestrial Delivery

There is abundant evidence for the presence of organic molecules in comets, asteroids, interplanetary dust particles, meteorites (specifically carbonaceous chondrites, which contain up to 4% C and micrometeorites. The wide variety of organic compounds, including macromolecular carbon, amino acids and monocarboxylic acids among many others, in these extraterrestrial bodies is well-documented and beyond the scope of this chapter, although we direct readers to comprehensive reviews by Sephton (2002, 2005), and references therein. During its life time, and especially in the early formative ~600 million years, the Earth has been bombarded by a large variety of impactors ranging from the huge Mars-sized impactor (Theia) that created the Moon to cosmic dust less than 1 μm in size (Peucker-Ehrenbrink and Schmitz 2012). This impact phenomenon continues even to this day but the flux of impactors is no longer as high as it was during the Hadean and Early Archaean eras. Some of the carbon in meteorites is so primitive that it is speculated to have a pre-solar origin (Martins et al. 2015).

Estimates of the flux of extraterrestrial material to the present-day Earth are highly variable, ranging from 30,000–60,000 tonnes per year ($\pm 15,000$ tonnes); (Bland et al. 1996), the error being related to poor understanding of the complete size range of incoming materials, for instance the mass of incoming micrometeorites (Maurette 2006).

The value of $\sim 0.1 \text{ kg/km}^2/\text{year}$ (Dass et al. 2016) for the modern Earth impactor flux is modelled to have been 1000 times greater during the hypothesized Late Heavy Bombardment (LHB), $\sim 3.9\text{--}3.8 \text{ Ga}$ (Frey 1980; Ryder et al. 2000; Ryder 2002), therefore roughly $100 \text{ kg/km}^2/\text{year}$. This flux represents the absolute maximum for extraterrestrial input to Earth at any point during its history, perhaps equaled solely in the initial stages of planetary accretion (Koeberl 2006). A rough estimation for the amount of extraterrestrial flux during the Hadean between 4.5 and 4.0 Ga indicates that it averaged $< 11.76 \text{ kg/km}^2/\text{year}$ over that time period (from the lunar cratering record, cf. Koeberl 2006). Note, however, that the LHB has since been re-assessed and appears to have been an artefact of the original lunar sampling programme, rather than an actual event (Zellner 2017).

Laboratory studies to simulate the formation of organic molecules under interstellar conditions were conducted extensively (Briggs et al. 1992; Kobayashi et al. 1998) and the experimental results revealed the formation of amino acids when ice mixtures containing CO , CH_4 , CH_3OH , NH_3 , H_2O were irradiated (see also Bernstein et al. 2002). Moreover, recently, synthesis of ribose and other sugar was achieved after photolysis of an icy mixture of H_2O , CH_3OH and NH_3 (Meinert et al. 2016). In order to test these results in realistic space conditions and to understand the cumulative effects of vacuum, high-energy particles, near-weightlessness and extreme low temperatures on organic molecules, space as an astrobiology tool became pertinent (Hashimoto et al. 2002).

10.3 Radiation Studies on Earth *versus* Space

Limited access to space (Martins et al. 2017) poses one of the major challenges in studying the realistic space radiation effects on molecules. Photochemical studies in laboratories are useful but the challenge arises in mimicking the complete range of solar radiation using a typical lamp source. Table 10.1, provides an overview of the types of lamp sources that have been used in laboratories to attain a specific range of UV wavelength (see Cottin et al. (2017) for a detailed review of artificial light sources).

Table 10.1 Sources of UV lamps used to generate specific ranges of UV wavelengths

UV source	λ in nm	References
H_2/He	122	Cottin et al. (2000, 2008), Es-sebbar et al. (2015)
Kr	145	Kuzicheva and Gontareva (2003)
Xe	147	Cottin et al. (2000, 2008)
CH_4/He	193	Cottin et al. (2000, 2008)
H_2	122–160	Ten Kate et al. (2005)
D_2 or Xe	190–400	Ten Kate et al. (2005), Stalport et al. (2009)
Synchrotron	25–300, varied wavelength	Schwell et al. (2006, 2008), Nahon et al. (2012)

However, even this comes at a price and the synchrotron facilities have their own shortcomings as pointed out by Cottin et al. (2017). For example; the integrated solar UV flux for a range of 100 and 300 nm is of the order of 2×10^{13} ph cm⁻² s⁻¹ (Thuillier et al. 2004) while, in the same range of wavelengths, the flux generated by the DESIRS synchrotron source can reach 10^{15} ph cm⁻² s⁻¹, i.e. about 50 times more intense than from the Sun.

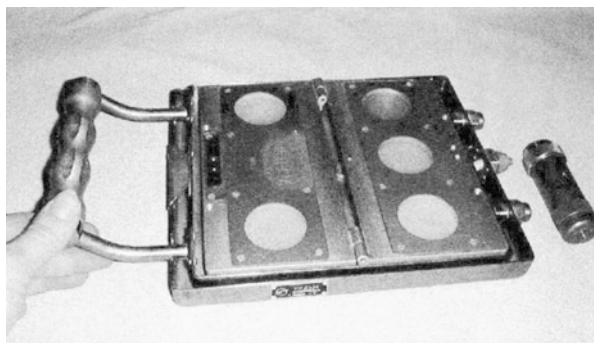
10.4 Space Experiments Relevant to Exposure of Organics

In this chapter, we will restrict our discussions to the space expose experiments that were carried out with organic molecules and, if the reader is interested to explore various other space-expose experiments (e.g. Biological experiments), we refer you to (Horneck 2007; Horneck et al. 2010; Cottin et al. 2017) and the references therein.

During the 1970s, onboard the Salut-6 orbital mission, for the first time, the formation of adenosine, deoxyadenosine, and thymidine nucleosides was demonstrated (Kuzicheva and Gontareva 2003). This, in turn, stirred a series of follow up investigations resulting in a cascade of explorations in space-related chemistry experiments. Two follow-up experiments on board the Salut-7 space craft were carried out for the durations of 13 and 16 months respectively (Kuzicheva and Gontareva 2003). A specially designed cassette-like device called “Menduzza” fitted with quartz glasses with a UV cut-off at 220 nm (see Fig. 10.1) was used for the two missions. The in-flight temperature on this device varied between -50 °C and 65 °C.

Similar flight missions called Bion-9 (Cosmos-2044/Kosmos-2044) and Bion-11 with flight durations of 14 days were carried out using devices similar to the Menduzza, called “outside container” (OC). The OC resembles a circular suitcase with an overhead lid and a base plate. The base plate could be fitted with quartz windows and the overhead lid locks onto the base plate with automatic unlocking on deployment in orbit. The OC of Bion-9 experienced a range of temperatures from -13 °C to $+67$ °C and the Bion-11 OC experienced temperatures between -30 °C and 100 °C. In order to substantiate the results obtained during the Salyut-7 missions,

Fig. 10.1 Cassette-like device called ‘Menduzza’ used onboard Salut-7. Source: Modified from Kuzicheva and Gontareva (2003)



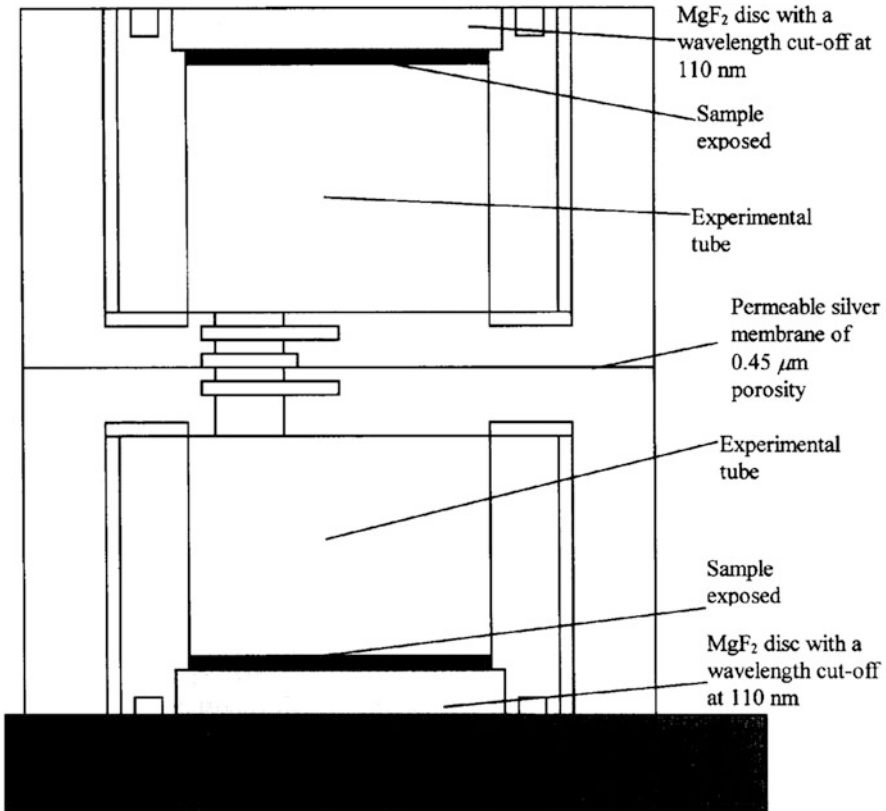


Fig. 10.2 A general scheme of the cell holder during the “Perseus Exobiology mission”, where the top stage was exposed to radiation, and the lower stage served as the in-flight control. Source: Reprinted with permission from Kuzicheva and Gontareva (2001)

a new experiment called “Perseus exobiology” onboard the Mir space station was carried out. The Perseus experiment was also used for simultaneous studies on amino acids and peptides (Kuzicheva and Gontareva 2001, 2003; Boillot et al. 2002). For this flight, a specially designed, two-stage monoblock device was designed in France.

During the experiment, the top stage was exposed to the UV radiation of space, whereas the lower stage was used as flight-control. The monoblock consisted of 66 cell holders. Each holder (see Fig. 10.2) had two stages, with a temperature sensor each. The samples were deposited on MgF₂ windows with a UV cut-off at 120 nm, which was an improvement from the Salyut-7 missions. During the course of the mission, the monoblock experienced a high temperature of 41 °C.

For each of the missions following the Salyut-6 mission, the aim was to photosynthesize nucleotides (e.g. adenosine nucleotide, Fig. 10.3) by reaction of nucleosides (sugar like ribose + bases like adenine) with orthophosphates (like KH₂PO₄). Adenosine, deoxyadenosine, cytidine, uridine, thymidine and deoxythymidine

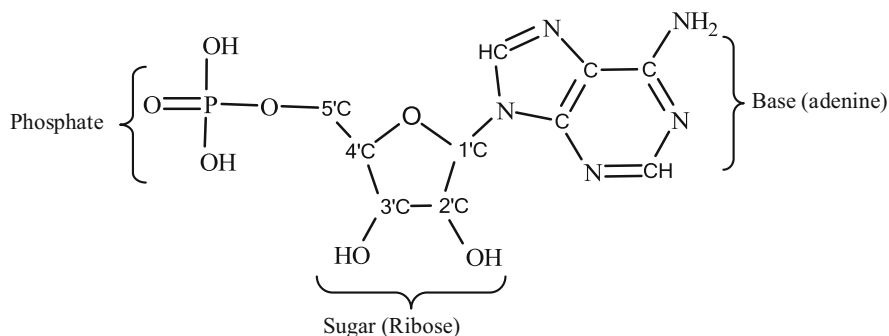


Fig. 10.3 Adenosine nucleotide with 5' phosphate (i.e. phosphate on carbon 5'), the other possible sites for phosphorylation are 2' and 3' carbons. Source: A V Dass

nucleosides were homogenized in solution with orthophosphates and evaporated as thin films on MgF₂ (Perseus) or quartz windows (Salyut 7, Bion-9, 11).

The results of the missions demonstrated that, due to a favourable spatial orientation, 5' nucleotide was the predominant product in comparison to 2', 3' nucleotides. They also observed that purine nucleotides (with bicyclic bases) were less prone to degradation, possibly due to an extended conjugation (double bond) system, in comparison to pyrimidine nucleotides. Additionally, it was observed that, in all the experiments, the rate of degradation of adenosine nucleotides was lowest in comparison to uridine and cytidine nucleotides (this could also be due to bicyclic system influence). Interestingly, 5' ATP was also detected at trace levels (Kuzicheva and Gontareva 2003) after the Perseus mission. This was attributed to the ambient temperatures recorded on the Perseus monoblock device (~41 °C), thus reducing the extent of hydrolysis of 5'ATP (highly energetic molecule).

Parallel experiments carried out on ground, aided better understanding of the conditions of photoreactions and it was concluded during that, Vacuum UV and elevated temperatures (~160 °C) were more effective in the synthesis of nucleotides in comparison to γ -radiations (highly energetic). Although, this could be a result of simultaneous destruction of the formed nucleotides in the presence of high-energy γ -radiations. This conclusion could be derived from the reported results of effective synthesis 5'AMP with reduced flux of γ -radiation (~3 times lower flux to VUV). This reinforces the importance of the thermodynamic stability of 5'AMP to 5'ATP in surviving hydrolysis. The researchers also observed that shorter flight times (like Bion-9, 11) resulted in greater molecular survival quantitatively. This was accredited to the fact that, during prolonged exposure times, the rate of formation of the products was far exceeded by the rate of degradation. The other conclusion of the study was that infrared energy was the most effective in the synthesis of nucleotides (canonical), followed by VUV of 145 nm wavelength in comparison to 254 nm radiation. It was pointed out that lower yields of nucleotides are due to the fact that 254 nm radiation is mainly absorbed by nucleobases, whereas at 145 nm, the sugar

and the phosphates are photochemically excited, thus resulting in nucleotide synthesis and hence higher yields.

As mentioned above, during the Perseus mission, amino acids and peptides were also exposed and studied. The experiment was carried out for 97 days in protected (with clay, basalt and meteoritic powder) and unprotected mode (pure molecules). Two amino acids *L*-leucine, α -methyl *L*-leucine, one cyclic dipeptide, *L*-leucine diketopiperazine (DKP) and one activated tripeptide, and tri-*L*-leucine thioethylester were used for the experiment (Boillot et al. 2002). The samples were mainly composed of leucine and its derivatives since this molecule occurs in the Murchison meteorite. Methyl leucine was chosen in order to compare the relative stabilities of substituted (alkyl group on the α -carbon) and unsubstituted amino acid (only hydrogen on the α -carbon) to radiation. The dipeptides were used to study the stability of peptide bonds and thioethylester of the tripeptide was used due to its activated state in order to study oligomerisation and the prebiotic relevance of thioesters (Wächtershäuser 2000, 2006). After the conclusion of the experiment, the results revealed that the cyclic peptide (DKP) was relatively inert towards space radiation as a whole. It is important to note that cyclic peptides are not composed of a carboxyl terminal and thus are not prone to the decarboxylation; the most common photoreaction is observed in solid-state samples under the effect of UV radiation. During sample analysis, it was observed that there was no diversity of chemical photoproducts for peptides and yet loss of starting material, which led to the interpretation that peptides were more susceptible to sublimation under high vacuum space-conditions (Boillot et al. 2002). In the case of the thioethylester tripeptide, the loss of starting material was attributed to the additive effects of sublimation and degradation at mildly elevated temperature (40 °C) over the period of the Perseus experiment. Moreover, the peptide bond decomposition process is considered to hinder the oligomerization of thioethylester peptide. The authors concluded that, in the case of rest of the samples, decarboxylation and decarbonylation were the most common photoreactions. This conclusion was supported by the laboratory studies involving solid-state samples irradiated with UV radiation. For the samples using mineral surfaces to mimic a natural protection mechanism, it was determined that the threshold for efficient protection against radiation was about 5 μm . This information was used to buttress the idea that a 50–100 μm micrometeorite fraction could deliver organic compounds to Earth like bodies.

In 1982, ESA's Directorate of Manned Spaceflight and Microgravity offered an interesting opportunity to study the response of microorganisms to outer space with the exobiology radiation assembly (ERA) on board the European Retrieval Carrier (EURECA). Hereafter, ESA developed the BIOPAN facility in 1994, a multi-purpose space exposure system devoted to research in space biology. BIOPAN was installed on the external surface of the FOTON descent capsule protruding from the thermal blanket that envelops the satellite. It was a large circular container with a deployable lid, which is opened in orbit upon command and remained closed and sealed during launch and re-entry (Fig. 10.4). BIOPAN-1 was fixed outside the Russian FOTON-9 satellite (for a review, refer to Horneck 2007). Three chemistry experiments were carried out on the BIOPAN facility.

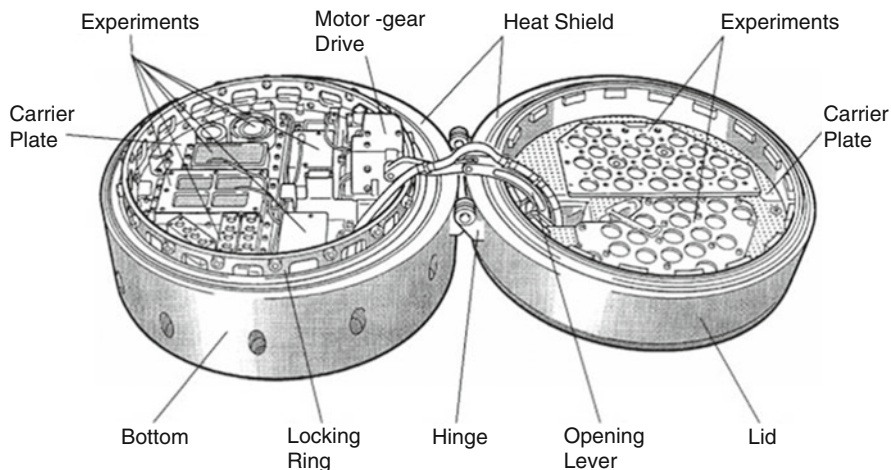


Fig. 10.4 A scheme of the BIOPAN facility. Source: Reprinted with permission from Demets et al. (2005)

The Biopan-1 and Biopan-2 experiments were carried out as templates to test molecules and hardware for future long-duration experiments outside space stations. Each chemistry-related experiment was named with respect to the platform used during a specific mission. For example, Dust-1 was the name given to the chemistry segment carried out on the Biopan facility during the Biopan-1 mission.

For Biopan-1 (Dust-1), L-forms of Gly, Ala, Leu, Val, Asp, Glu, all of which were reported in Murchison meteorite, were used to study the potential racemisation and stability of amino acids in space conditions (Barbier et al. 1998). In order to study possible photochemical oligomerisation and due to its photosensitivity, L-tyrosine was also chosen, although this molecule was not detected in Murchison samples. A dipeptide L-alanyl-L-alanine was also selected to test the stability of the peptide bond. After the conclusion of the experiment, there was no analytical evidence that pointed to inversion of configuration (i.e. no racemisation). Post-flight analysis of the amino acids showed that L-Asp and L-Glu had undergone partial decomposition (10–15%). Not so surprisingly, when shielded in a 5–7 μm thick layer of mineral matrix (montmorillonite and kaolinite), the same amino acids survived the duration of the space exposure experiment. The other amino acids samples remained unaffected by the flight, especially L-Gly, an achiral molecule, which remained virtually unaffected, and L-Ala, L-Leu, L-Val, the aliphatic amino acids, which also showed excellent stability. L-tyrosine displayed no oligomerisation and the dipeptide L-Alanyl-L-Alanine showed greater stability (Barbier et al. 1998). Surprisingly, there were no reports of loss of the peptide samples to space vacuum, indicating the difference between linear peptides and cyclic peptides as reported in the Perseus mission (Boillot et al. 2002). This might be due to the ability of linear chains to remain in zwitterionic form and therefore more stable in comparison to their cyclic counterparts. Alternatively, the authors suggested that the overall stability of the samples during the mission was

due to shorter exposure times, non-synchronous orbitals and absence of sun-pointing device and thus milder degradation and therefore recommended longer exposure times (Barbier et al. 1998).

Biopan-2 (Dust-2) with an exposure time of 10 days and exposing Gly, Glu, Asp and Tyr was carried out to confirm the results of the Biopan-1. Additionally a new set of compounds, including various esters of glutamic acid and leucine, such as nitrobenzyl (–ONb), benzyl (–OBzl), thioethyl (–SEt) and methyl (–OMe), were exposed in order to examine the possibility of amino acid oligomerization under solar UV radiation. Thioethyl esters are known to activate amino acids and thus were chosen to study the nature of oligomerisation in activated compared to inactivated esters. A tripeptide (Glu)₃ was selected to study the peptide linkage stability and (Leu)₃–ONb was selected to study the possibility of peptide condensation. Tripeptides were selected over dipeptides to prevent the formation of diketopiperazines, as cyclic dipeptides are generally considered as relatively inert in oligomerisation processes. The thickness of the films was maintained at 0.5 microns to be able to irradiate most of the exposed molecules. The molecules were also exposed in clay, shielded environment, with a 50 microns thick film, representing a micrometeorite-like protection.

The analytical results confirmed the absence of racemization of the exposed molecules and also the high sensitivity of acidic amino acids towards UV radiation already observed in the DUST 1 experiment. Surprisingly, the degradation of glycine was observed to be enhanced when protected in montmorillonite. This behaviour was attributed to photoionization of residual water molecules in the clay sheets, although this effect was observed only in the case of glycine. Laboratory studies confirmed that loss of glycine was not due to sublimation and thus the cause remained unexplained. Oligomerisation was observed with the esters of amino acids, although it was noted that, in the case of the benzyl ester of Leucine, the unexposed samples showed the presence of cyclic peptides indicating that space vacuum had a major role in the formation of such products. Additionally, it was observed that esters of the amino acids (since they lack the zwitterionic state) were lost due to sublimation in space vacuum. The results with the tripeptides also confirmed that photolysis reactions were the main cause of the loss of CO₂ and CO and not peptide bond hydrolysis, even when embedded in a mineral matrix. Overall, peptides showed greater stability in comparison to amino acids.

The ORGANICS experiment was flown on Biopan-5 in 2005 (Ehrenfreund et al. 2007). Polycyclic aromatic hydrocarbons (PAHs) and fullerenes (C₆₀) (see Fig. 10.5) were exposed to a total fluence of 602.45 kJ m⁻² (for photons in the range 170–280 nm). The experiment was a precursor hardware test-flight for the long-term exposure experiment (Survival of organics in space) on the EXPOSE facility on the International Space Station (ISS). Thin films of the selected organic molecules were used for expose studies lasting 16 days in the LEO.

The space exposure experiments were compared to the laboratory studies carried out using a hydrogen discharge lamp with photon wavelengths ranging between 150–195 nm. In space, the most widespread form of carbon is found in the form of PAH's and fullerenes. They form the bulk of the organic matter found in meteorites and micrometeorites (Maurette 2006). Post-flight analysis on the samples revealed

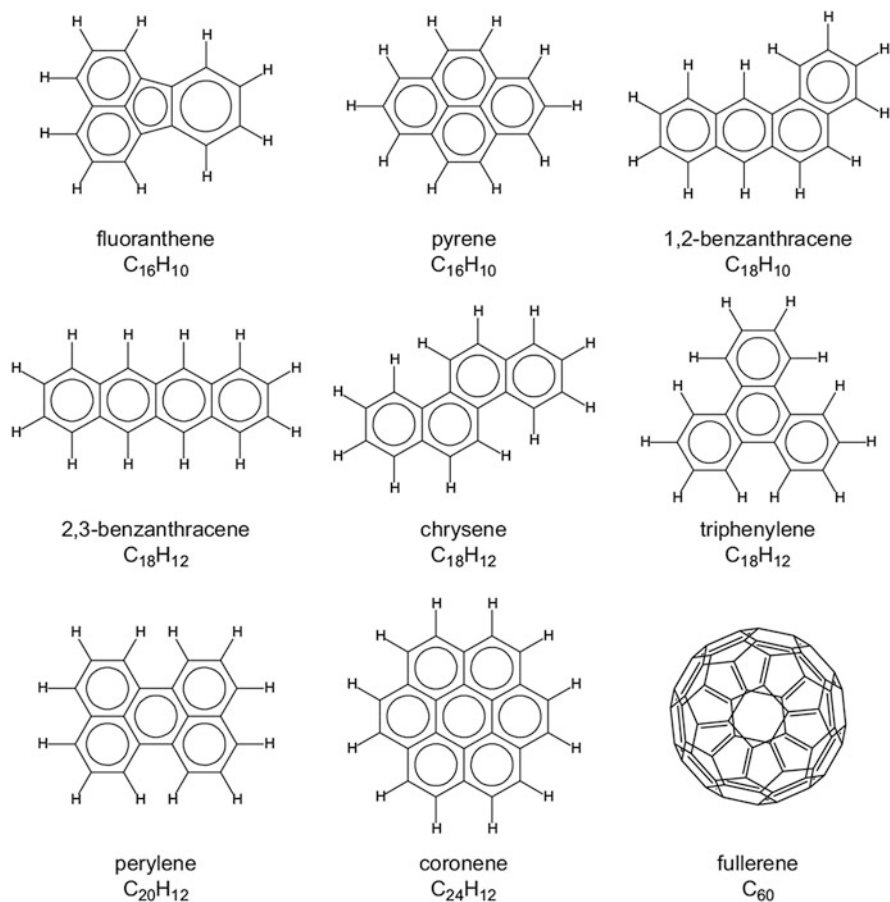


Fig. 10.5 Showing the polycyclic aromatic hydrocarbons and Fullerene (C_{60}) selected for flight on Biopan-5. Source: Reprinted with permission from Ehrenfreund et al. (2007)

no dehydrogenation reaction, even though the selected molecules had a gas-phase ionizing potential of up to 7 eV. The results revealed that there was a difference of only 1% loss of starting material between the flight-exposed and flight control samples, which falls within the measure of an analytical error bar.

The results show that the type of photon fluence (order of 10^{17}) observed during Biopan-5 was insufficient to cause effective photolysis of the samples over the 16 days period. It was predicted that a photon fluence of the order of $>10^{20}$ with an effective energy greater than 10 eV would be necessary to initiate a photochemical response with this set of molecules. The laboratory studies confirmed these observations and were in agreement with the results of Biopan-5.

At this point, the reader is familiar with the diverse categories of molecules studied under space conditions (sugars, amino acids and PAH's) and the following experiments involved a detailed study of specific molecules within these categories

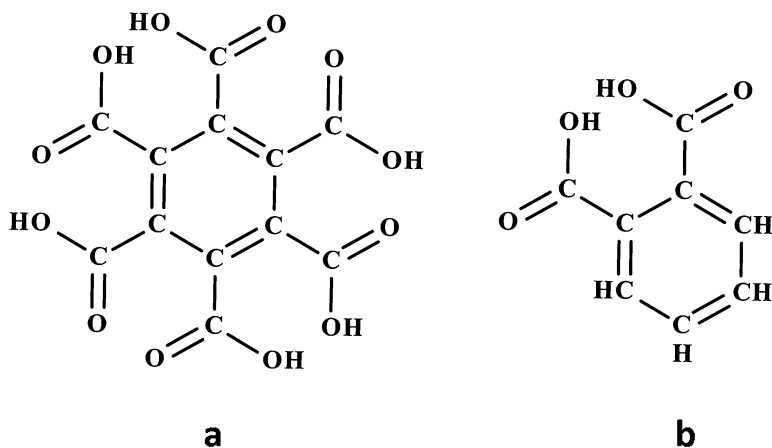


Fig. 10.6 Some molecules selected for UVloution experiment (a) Mellitic acid and (b) Phthalic acid. Source: A V Dass

in order to understand individual types of molecules. Therefore, in the following, we will concentrate only on the important discussions and conclusions.

In 2007, the UVolution experiment was carried on the Biopan-6 mission over an orbital period of (Stalport et al. 2010). The main aim of this experiment was to study the behaviour of molecules in Mars-like conditions, since Mars is amongst the prime locations for astrobiology exploration. The surface layers of Mars are intermixed with oxidizing agents (e.g. peroxides) and, thus, any organic molecules could be potentially destroyed even if present. It was hypothesised that metastable molecules (Fig. 10.6) could potentially be part of the organic inventory on the Martian surface or in its subsurface. Most of the acids used had a carboxylic acid substitution at different positions on the benzene ring. α -aminoisobutyric acid (AIB) was also selected as it is also present in both meteoritic and micrometeoritic material.

Stalport et al. (2010) concluded that the exposed molecules were less photostable as they were partially destroyed in a short period of time. In particular, the behaviour of mellitic acid showed a greater difference in comparison to laboratory simulation experiments (Stalport et al. 2009, 2010) as it was almost completely decomposed with no byproducts reported. Gauging from the previous chemistry expose experiments, and given the abundance of the carboxylic acid functionality of the selected molecules, decarboxylation could be the predominant reaction. However, it is important to study the sublimation pattern of these molecules more rigorously before arriving at concrete conclusions. The greater photolysis of the selected molecules in the presence of analogous martian soil led to the authors to conclude that a search for such molecules on the martial surface could be potentially futile. Nevertheless, it would be interesting to know the byproducts of some of these molecules, since the residual products might be of interest for biosignature studies on Mars.

The next generation of long-term expose experiments was carried out on the EXPOSE facility of the International Space Station (ISS). The EXPOSE facility is located on an external platform secured to the outer hull of the Zvezda Service Module of the ISS in the Russian segment. Three experiments have been carried out successfully on this facility, including the most recent one called the PSS (photochemistry on the space station). Depending on the type of molecules to be exposed, cells of different configuration are used. Traditional open cells and semi-hermetic cells are used routinely, but for gaseous samples, special cells named “CNES closed cells” have been employed. For comprehensive information on the hardware, please refer to (Cottin et al. 2017).

The first experiment was emplaced as a part of the EXPOSE payload in 2008 and lasted almost 1.5 years. The experiment was carried out to study the chemical behaviour of amino acids and dileucine, exposed unprotected and embedded in meteorite powder, to irradiation. It was concluded that both types of samples (with or without meteorite powder) were affected chemically to varying degrees when exposed to solar radiation. This study also included the quantification of organic degradation (Bertrand et al. 2012). The results revealed that resistance to irradiation depended on (1) the chemical nature (structure and composition) of the exposed molecules, (2) the emission spectrum of the UV source (laboratory lamp source versus solar radiation), and (3) the shielding effect of the meteorite powder. Moreover, it was observed that amino acids with two-acid group functionality (e.g. aspartic acid) was more sensitive to UV radiation than amino acids with alkyl side-chains (e.g. valine). The dipeptide with an amide bond was almost completely degraded when unprotected by a mineral coating. Additionally, amino acids with a substituted chain, such as valine, were more stable than those with a linear chain, as in the case of aminobutyric acid. As part of the PROCESS experiment mission on board the space station, a study was performed on the degradation of organics under filtered electromagnetic radiation that mimics Mars-like surface UV radiation. The mission served as a test-bed for further understanding of the nature of certain PAH's and to confirm the results of UVolution experiment on a long duration flight. Glycine, serine, phthalic acid, mellitic acid were amongst the molecules selected for the experiment and the researchers concluded that most of these molecules underwent extensive photodegradation (Noblet et al. 2012). The presence of a martian soil did not prevent the degradation of these molecules. The results do not follow the usual trend of PAH's which display greater levels of photostability under extreme UV conditions. There appear to be inconsistencies with exposure regime (as glycine was recovered well preserved post-flight) and interference of the cell material during this mission that might have contributed to non-uniform observations.

The ORGANIC and AMINO experiments were exposed on the EXPOSE facility in 2009. The objectives of the ORGANIC experiment on EXPOSE-R were (1) to study the photostability of selected PAH's and fullerene-type molecules in an interplanetary environment to allow a comparison with space data; and (2) to allow a quantitative estimation of dissociation regimes for organic molecules that could be extrapolated to different space environments (interstellar medium, interplanetary, Earth atmosphere, etc.) (Bryson et al. 2011). The ORGANIC

experiment on EXPOSE-R spent 682 days outside the ISS and the fourteen samples (11 polycyclic aromatic hydrocarbons (PAHs) and three fullerenes) received an irradiation dose of the order of $14,000 \text{ MJ m}^{-2}$ over 2900 h of unshadowed solar illumination (Bryson et al. 2015). Analyses on the returned samples and ground control measurements showed limited spectral changes in most cases, pointing to the stability of PAHs and fullerenes under space exposure conditions. However, some molecules were strongly depleted and the experiments confirm the known trend in the stability of PAH species according to molecular structure: compact PAHs are more stable than non-compact PAHs and the least stable are PAHs containing heteroatoms (Bryson et al. 2015).

AMINO was the second experiment carried out on the EXPOSE platform in 2009. For the experiment, the amino acids glycine, D-alanine, D-valine, D-aspartic acid, amino isobutyric acid, 2-amino butyric acid and the dipeptide dileucine were exposed to space conditions in the free form (i.e. non protected by meteorite powder) and embedded in meteorite powder (Bertrand et al. 2015; Cottin et al. 2017). This experiment was mainly carried out to confirm the previous results obtained from the PROCESS experiment, showing indeed that amino acids with two-acid functional groups (e.g. aspartic acid) are more sensitive to UV radiation than amino acids with a hydrocarbon chain (e.g. aspartic acid). It was also confirmed that the dileucine amide bond had a high susceptibility to degradation, only surviving when protected by a mineral matrix of ground meteorite. High resolution mass spectrometry analyses demonstrated, for the first time, that some degradation is due to decarbonylation and decarboxylation caused by exposure to UV radiation. The new compounds formed by losing their carboxylic group were then more resistant to UV radiation (Bertrand et al. 2015). The conclusion of the experiment was that it would be necessary to investigate additional samples in the laboratory and in low Earth orbit (LEO) in order to obtain better understanding of the effects of photochemistry in UV radiation and to establish the link between organic matter synthesized in space and the first living organisms on Earth. Thus, it was decided that a new set of organic molecules with different structural configurations and chemical compositions would be used for the next mission.

The most recent experiment to be carried out on the EXPOSE platform was the PSS (Photochemistry on the Space Station). The updated platform can accommodate 75 samples thus allowing for gathering numerically higher analytical data with more diverse molecules. At the time of compilation of this chapter, the exposed samples are being analysed. The PSS experiment was a long-term experiment lasting almost 531 days. For this mission, several types of molecules including peptides and nucleobases have been exposed.

10.5 Conclusions and Perspectives

This chapter has provided a brief overview of experiments concerning the photoreactivity of organic molecules of general interest to the origins of life—and this from the point of view of the exogenous delivery of organic molecules to Earth during the Hadean. We have seen that, while it is impossible to recreate the full range of Vacuum UV conditions of space in a laboratory setting, ground-based simulations are generally useful for providing a preliminary indication of what could happen in space (and in the environmental conditions of another planet, such as Mars), as well as for testing experimental procedures and protocols. The space environment, however, is invaluable for photochemical experiments and the long series of experiments undertaken on the various types of support—the Photon capsules, the MIR and ISS stations—have provided a wealth of information on what affects the photoreactivity and stability of various molecules found in carbonaceous meteorites and micrometeorites: these include, for example, the structural conformation and types of bonding exhibited by the original molecules, for example peptides being more stable than amino acids. The processes of alteration of the molecules could also be determined, with decarboxylation and decarbonylation reactions as the major contributors to the degradation of molecules. Finally, a number of expose experiments have clearly demonstrated the protective power of even a thin coating of mineral matrix, thus confirming that extraterrestrial organic molecules can be delivered (not considering atmospheric entry), some of them unscathed, to Earth and that they would have been an important contribution to the organic inventory that was available for prebiotic reactions leading to the emergence of life on Earth in the Hadean Era.

The experiments described have shown that the space environment is an excellent vehicle for simulating conditions at the surface of Mars, where the lack of a significant atmosphere and, especially, the lack of an ozone layer, allows UV radiation to reach the surface of the planet with subsequent deleterious effects on the organic molecules. These kinds of experiments are essential for preparing for what kinds of organic molecules could potentially be preserved in the martian surface materials, and this in view of the on-going Mars Science Laboratory mission to Gale Crater and also the future missions, the European/Russian ExoMars 2020 and the international Mars Sample Return missions.

In terms of perspectives, there are a number of aspects of space experimentation that could be improved and new scientific paths to be followed. As the reader might have noticed, all of the aforementioned missions have only two points of realistic analytical data; one before flight and another after flight. A wide range of chemical dynamics data is unaccounted for during the actual flight, thus a need for real time data gathering on chemical transformations of exposed molecules arises. In order to do so, a more futuristic and much needed piece of technology has been conceived which resembles a nanosatellite, capable of in-situ analysis on a concentric conveyer belt-like system fitted with a step motor. The cells used in this instrument can contain their own microenvironment, independent of that of the neighbouring cells. UV-Vis spectroscopy is the mode of analysis on the miniaturized system. For hardware design

and technical information of the subject, the reader is directed to (Ehrenfreund et al. 2014; Cottin et al. 2017). A NASA cubesat Organism/Organic Exposure to Orbital Stresses (O/OREOS) was launched in November 19, 2010 on a 6-month mission as a cost-effective technology demonstration flight. This technology will be utilized in a more recent project called OREOcube (Elsaesser et al. 2014).

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