Bioastrophysical Aspects of Low Energy Ion Irradiation of Frozen Anthracene Containing Water

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The origin of life on Earth remains a fascinating mystery in spite of many theories existing on this subject. However, it seems that simple prebiotic molecules could play an essential role in the formation of more complex organisms. In our experiment, we synthesized a class of these molecules (quinones) bombarding frozen anthracene containing water with low energy hydrogen ions. This experiment roughly simulated the astrophysical conditions which one can find in the solar system. Thus, we can hypothesize that prebiotic molecules could be created by interaction of the solar wind with interplanetary dust grains. The delivery of these molecules to early Earth may have contributed to the generation of life on our planet.

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It is widely accepted that polycyclic aromatic hydrocarbons (PAHs) are present both in interstellar space (interstellar dust grains) and in the solar system (comets, meteorites, and interplanetary dust grains) [1–3]. These bodies are irradiated by energetic charged particles (cosmic rays, solar wind, and flares) and ultraviolet radiation. The main source of PAH molecules is late-type giant stars. In the dense interstellar clouds, these molecules are accreted on refractory grain cores forming with frozen species (water—the most abundant of all, carbon monoxide, carbon dioxide, methane, ammonia, methanol, and others) icy grain mantles [4]. Such types of grains are constituents of comets, meteorites, and interplanetary dust. However, the composition of grains depends on environmental conditions such as ultraviolet and charged-particle irradiation, temperature, and concentration of free molecules. These factors lead to compositional changes of grains due to photolysis and sputtering effects, evaporation of volatile species, thermal processing and production of new molecules, radicals, and molecular fragments. The above phenomena were investigated in laboratory experiments simulating various astrophysical conditions using ices of simple gases, water, methanol and their mixtures, benzene, and others [5–14]. Also, the interaction of UV photons with PAHs in water ice was examined [1,15]. In some of these experiments, complex organic molecules having a biogenic nature were synthesized [1,10,16]. We investigated the possibility of generation of such molecules using frozen anthracene containing water irradiated by low energy protons.

A thin layer of anthracene ($C_{14}H_{10}$) was deposited on a gold coated copper substrate from a solution of anthracene in benzene and then cooled to a temperature of 150 K in a vacuum chamber. The sample was irradiated with a 3.5 keV hydrogen ions (H_2^+) flux of 2.6×10^{14} ions $cm^{-2}\,s^{-1}$ to a dose of the order of 10^{17} ions cm^{-2}. Simultaneously, a stream of water vapor from a tube connected to a water reservoir via a needle valve was directed onto the anthracene layer. The flux of condensing water molecules could be roughly estimated at 10^{15} molecules $cm^{-2}\,s^{-1}$. This experimental procedure avoids sample production by an anthracene evaporation process, which can be a source of enhanced contamination due to preferential condensation of more volatile hydrocarbon impurities. After irradiation, the sample was warmed to room temperature and removed from the vacuum chamber. A solid residue on the substrate showed the color change from white, typical of anthracene, to yellow-brown. The color became darker as the ion dose increased.

The bombardment products were analyzed using the electrospray ionization mass spectrometry (ESI MS) technique characterized, among others, by the soft (nondestructive) ionization of the molecules and high sensitivity. Generally, this technique comprises sample dissolution, the transfer of sample ions from solution to the gas phase, and mass analysis [17,18]. The measurements were conducted with the Finnigan LCQ instrument. A solution of soluble parts of the residue in a mixture of 50% methanol and 0.5% acetic acid was introduced using the syringe pump into the electrospray chamber through a fused-silica capillary placed inside a metal needle with a flow rate of 3 μl/min. A voltage of 4.2 kV was applied to the needle and thereby charged aerosol droplets containing sample ions were formed. In order to help in the nebulization and evaporation of the sample solution, the sheath gas (the inner coaxial nitrogen gas) with a flow rate of 0.9 l/min and the auxiliary gas (the outer coaxial nitrogen gas) with a flow rate of 3 l/min were used. The droplets evaporate during flight and their surface charge density increases to a value at which the electrostatic repulsion exceeds the surface tension, and the droplets begin to divide into smaller ones. At a certain moment, the droplets become so small that their electric field reaches a level high enough to desorb sample ions into the gas phase. These ions enter the

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mass spectrometer and can be analyzed. Mass spectra in the positive ion mode (the needle is positively polarized) were measured.

The normalized mass spectrum of the bombardment products is shown in Fig. 1. This is the difference between the residual spectrum and a reference one obtained for anthracene subjected to the same experimental procedure as during the production of residue but without ion bombardment. The intensities of particular peaks in the reference spectrum were below 1% of the corresponding peak intensities in the residual one. According to the nature of the ESI MS technique and the applied experimental conditions, the labeled main peaks can be identified with the single charged quasimolecular $(M + H)^+$ ions, where M and H are the nominal molecular weights of particular constituents of the analyzed material and hydrogen, respectively. The lower mass peaks can result from the presence of the ^{13}C isotope and other unidentified synthesized species such as radicals, molecules, and molecular fragments bonded to various atoms or atomic groups. The base peak at mass equal to 239 amu corresponds to a (hydroxymethyl)anthraquinone molecule. The peaks at 195, 211, 227, 225, 241, and 257 amu correspond to hydroxy-, dihydroxy-, trihydroxyanthracene and hydroxy-, dihydroxy-, trihydroxyanthraquinone, respectively. The masses of 193 and 223 are attributed to methylanthracene and methylanthraquinone, respectively. The next masses are assigned as follows: 207—ethylanthracene and/or dimethylanthracene, 237—ethylanthraquinone and/or dimethylanthraquinone, 209—(hydroxymethyl)anthracene and/or anthraquinone, 255—dihydroxymethylanthraquinone. The peaks denoted H can be connected with the hydrogenation of the above species. The peak assignments show the presence of the following groups: OH, CH_3, CH_2OH, and CH_2CH_3, which are attached to anthracene or anthraquinone with the simultaneous loss of an appropriate number of hydrogen atoms from an aromatic ring. Such an interpretation of the mass spectrum is supported by the results obtained for PAHs in water ice exposed to ultraviolet radiation [1] and frozen benzene irradiated by hydrogen and helium ions [13,14]. The creation process of new molecules is shown schematically in Fig. 2. Using a method of external standards [19], we estimated that five quinones which have the highest abundances in the mass spectrum are present in the amount of 8×10^{-9} g. This quantity was obtained for a dose of 3.2×10^{17} protons cm^{-2} (a proton dose is 2 times higher than a $H_2{}^+$ dose because of dissociation of $H_2{}^+$ ions at the first collision with the sample surface [6]). For a dose of 1.3×10^{18} protons cm^{-2}, we obtained a mass of quinones about 4 times smaller than before, but still at the level of 10^{-9} g.

The discussion of the present results will concern the physicochemical interactions of impinging ions with a frozen material and its bioastrophysical implications. The energetic ions cause sputtering, movement, and rearrangement of target atoms due to breaking of chemical bonds. Also, incident ions can be implanted in the target. These effects can induce formation of new kinds of molecules. In the present experiment, the energy of protons is deposited into the target via nuclear and electronic stopping processes, with the first predominant, and it is enough to decompose some frozen anthracene and water molecules whose enthalpies of atomization were estimated at 120 and 9.7 eV/molecule, respectively [20]. The energy transferred to particular anthracene molecules fluctuates in value due to the stochastic character of the collision process. This fact causes varied decomposition of anthracene from the loss of a number of hydrogen atoms (dehydrogenation) to the destruction of the aromatic ring. Similarly, water ice molecules are decomposed to hydrogen atoms and hydroxyl groups or hydrogen and oxygen atoms. The above species can recombine creating molecules of substituted and/or hydrogenated anthracene and anthraquinone and others. Also, the bombarding ions slowing down in the target may participate in hydrogenation of molecules.

The experimental formation of the complex organic molecules gives an opportunity to consider the question from the astrophysical point of view of how and where

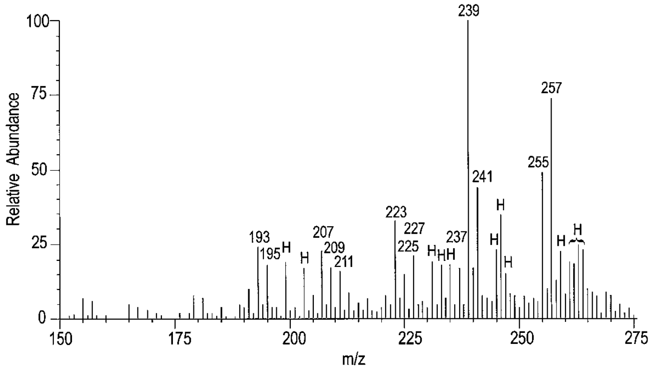

FIG. 1. The mass spectrum of products resulting from bombardment by hydrogen ions ($H_2{}^+$) of a water-containing frozen anthracene sample, for a total dose of 1.6×10^{17} ions cm^{-2}.

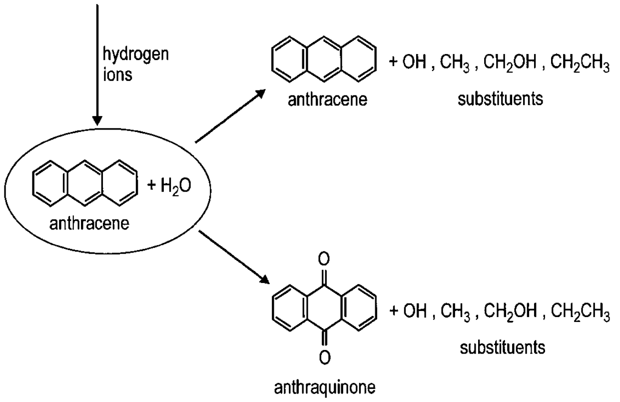

FIG. 2. Schematic illustration of new molecule formation.

in space these molecules can be produced. The present choices of proton energy and of the sample temperature are adequate to simulate the astrophysical conditions which one can find in the solar system. However, this is only an approximate simulation because such types of terrestrial experiments do not reproduce fully cosmic conditions as discussed in Ref. [21]. Thus, we can assume that protons of the solar wind interacting with icy bodies (comets, interplanetary dust grains) can create such types of molecules. The range of the solar wind protons in an icy material (about 0.1–0.5 μm) [22] is too small, relative to the dimensions of cometary nuclei of the order of kilometers, to expect any significant compositional changes of comet surfaces. Moreover, the nuclei are protected from attack by the solar wind which is deflected by the cometary atmosphere formed during the closer approach of comets to the Sun. Contrary to the massive part of comets, the submicron grains interact effectively with the solar wind due to their large surface/volume ratio. So, one can suppose that the collision process between the solar wind and grains is relatively dominant in the production of new molecules. It is widely accepted that interplanetary grains, being mainly cometary debris, are micrometer-sized fluffy conglomerates of submicron core-mantle-type grains. These interplanetary grains released by comets move first in an elliptical orbit which slowly changes into a quasicircular one due to the Poynting-Robertson effect. The grains spend about 10^4–10^5 years in the solar system before being collected in the upper atmosphere of Earth [23]. During this time, their composition is changed due to the action of solar particles and photons. For an exposure of about 10^4 years at 1 AU and under present solar activity conditions, the solar wind dose received by grains can be estimated to be $\approx 10^{19}$ ions cm^{-2} [23]. At this distance from the Sun, the temperature of water-ice grains with a typical radius of a few tens of μm is about 150 K [24], i.e., the same as in our irradiations. The presence of PAHs in the grains may decrease water evaporation because of possible trapping of water molecules by various chemical structures which form PAH molecules. These are clusters, graphitelike structures or their randomly oriented mixture, bounded by van der Waals forces or various bridging chemical groups [2]. In order to approach the problem of creation of organic molecules quantitatively, let us assume that an idealized model of an interplanetary fluffy grain consists of small submicron spheres of radius of 0.1 μm and density of 1 g cm^{-3} [21]. The grains move in the interplanetary space, and in a given moment various surface parts of spheres (maximal hemispheres) dependent on the grain orientation in relation to the direction of solar wind are bombarded by solar wind protons. This means that spheres can receive a dose of $\approx 5 \times 10^{18}$ ions cm^{-2} or lower. In our experiment, we produce the mass of quinones of the order of 10^{-9} g using doses approximately meeting this requirement. Extrapolating the obtained results to the dimension and mass of submicron grain, one can estimate that about 10^{-3}–10^{-4} of the grain mass may be composed of quinones. Thus, we can hypothesize that in the interplanetary medium PAH molecules may be converted to other organic molecules. This fact involves a biological implication which we will consider below.

The formation of terrestrial life is still an open question in spite of many theories existing on this subject [1,16,25–32]. However, it is believed that the abiotic creation of simple biogenic molecules and their later chemical and physical transformation could lead to generation of cells and then contemporary organisms. It is noticeable that some of the molecules synthesized in our experiment have such a biologically active nature. For example, quinones are present in most living organisms on Earth. They play an important role as electron carriers in the synthesis processes of adenosine triphosphate which occur in mitochondria (oxidative phosphorylation) and in chloroplasts (photosynthesis) [33]. Also, anthraquinones substituted by hydroxyl and methyl groups (anthraquinones dyes) were found in various plants, fungi, and insects. These biogenic molecules can fall on Earth as constituents of an interplanetary dust with a flux reaching the contemporary Earth of about 3.2×10^6 kg yr^{-1} [29]. The dust grains are small enough to be sufficiently gently decelerated during entry to Earth's atmosphere [16,29]. This causes at least some forms of organic material (for example, PAHs) to remain intact after atmosphere entry [16]. It is known that hydroquinones due to hydrogen bonds can form clathrate structures [20]. One can suppose that more fragile organic species may be located inside such structures and survive atmospheric passage. The other interesting feature of quinones is their ability to absorb ultraviolet radiation. We can speculate that, in grains consisting of the catalytic surface of inorganic core, an organic material and water molecules covered by quinones absorbing UV radiation may undergo more complex chemical processes. The organic material could be delivered to Earth also by comets. However, such material in the form of dust has a better chance to reach Earth's surface intact [16]. The terrestrial organic carbon mass influx from interplanetary dust is found to be higher than that from comet impacts [29]. In summary, we can say that an exogenous transportation of biogenic molecules to early Earth could have contributed to formation of life on our planet.

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